Synthesis and surface functionalization of titania nanocrystals for low temperature deposition on polymers

Thesis submitted to obtain the degree of Master of Science in Chemistry by

Wouter VAN GOMPEL

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Promotor: prof. dr. Isabel Van Driessche
Copromotor: dr. Petra Lommens
Supervisor: Jonathan Watté
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Wouter Van Gompel, May 2015
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Wouter Van Gompel, May 2015
Samenvatting

Titanium dioxide dunne films worden gebruikt als transparante zelfreinigende lagen omwille van hun fotokatalytische eigenschappen.¹ Onder invloed van UV-licht worden reactieve species (radicalen) gevormd, die voor de degradatie van organische pollucenten zorgen.² Zelfreinigende titania lagen werden al gecommercialiseerd op glas.³⁶ Het doel van deze thesis is het verkennen van een methode voor het bekomen van duurzame, fotokatalytisch actieve titania lagen op temperatuurgevoelige substraten zoals polymeren. Dit brengt enkele uitdagingen met zich mee: De warmtegevoeligheid van polymeren zorgt ervoor dat het niet mogelijk is om hoge temperatuur behandelingen te gebruiken voor het bekomen van kristallijn titanium dioxide. Daarom worden suspensies, die al kristallijne titania nanokristallen bevatten, gebruikt voor de depositie van dunne lagen op de PMMA substraten. De thermische nabehandeling van de lagen kon daardoor worden uitgevoerd bij de beperkte temperatuur van 180°C. Een bijkomend onderzoeksdoel is het verbeteren van de duurzaamheid van titania lagen op polymeer substraten. In deze thesis wordt het gebruik van chemische linkers tussen de titania nanokristallen en het polymeeroppervlak onderzocht. Hierbij doen silaan liganden op de nanokristallen dienst als chemische linkers. Door de nanokristallen covalent te binden aan het oppervlak van het polyemeersubstraat, verwachten we een verbeterde duurzaamheid van de coatings.

Het experimenteel werk voor deze thesis bestaat uit drie delen: (1) de synthese van titania nanokristallen, (2) de uitwisseling van de originele liganden met silanen en (3) het afzetten van lagen op oppervlakbehandelde PMMA substraten met bijhorende koppeling tussen de nanokristallen en het substraat.

Verschillende synthese routes voor titania nanokristallen werden geëvalueerd. Drie van deze routes leveren reproduceerbaar titania nanokristallen met een hoog percentage aan kristalliniteit, waarmee tevens heldere en stabiele suspensies kunnen gevormd worden. Een liganduitwisselingsprocedure voor het bekomen van APTES (3-aminopropyltriethoxysilaan) liganden op de nanokristallen werd onderzocht. Het succes van de liganduitwisseling werd geëvalueerd met zeta potentiaal metingen in functie van de pH, infrarood spectroscopie en NMR spectroscopie. Voor de nanokristallen verkregen uit één van de drie verder uitgewerkte synthese routes, werden de originele liganden uitgewisseld voor APTES. De resulterende suspensies van ladingestabiliseerde nanokristallen vertonen een pH afhankelijke stabiliteit. Bij een pH van 2 zijn deze suspensies stabiel voor meer dan 5 weken. Deze procedure voor het bekomen van heldere en stabiele waterige suspensies werd meer dan 10 keer gereproduceerd.
Om de APTES gefunctionaliseerde nanokristallen te koppelen aan het oppervlak van de PMMA substraten werd een amide binding tussen de amine functionaliteit van APTES en een carbonzuur op het polymeer substraat beoogd. Dit carbonzuur dient geactiveerd te worden voor de reactie met het amine. Deze activering zorgt voor een goede “leaving group” op de acyl koolstof van het carbonzuur. Hiervoor werd de combinatie van EDC (1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide) en NHS (N-Hydroxysuccinimide) gebruikt. Belangrijk bij deze koppeling is de pH waarbij de reactie doorgaat. Het amine dient gedeprotoneerd te zijn voor de aanval op het geactiveerde carbonzuur. De stabiliteit van de suspensies van ladingsgestabiliseerde nanokristallen is echter het beste in zuur milieu. De koppelingsreactie werd daarom uitgevoerd bij een pH van 4.75, bij deze pH kunnen heldere suspensie bekomen worden en werden EDC en NHS al gebruikt voor koppelingsreacties.\textsuperscript{7,8}

De lagen werden afgezet via dipcoaten, echter is de bevochtiging van onbehandelde PMMA substraten door de waterige suspensies ontoereikend voor het bekomen van homogene lagen. Om deze te verbeteren, werden onder meer een chemische behandeling, plasma modificatie en UV-irradiatie vergeleken. Naast het verbeteren van de bevochtiging dient deze oppervlakbehandeling ook voor het bekomen van carbonzuren aan het oppervlak van de PMMA substraten. Met UV-irradiatie werd de bevochtiging het meest verbeterd (de contacthoek verminderde van 79° zonder behandeling naar 21° na 2 uur UV-behandeling), met een duidelijke verbetering van de homogeniteit van de lagen tot gevolg. Het nadeel van deze procedure is de lichte geelbruine verkleuring van het substraat onder langdurige intense UV-irradiatie. Door toevoeging van 5 volume percent ethyleen glycol aan de suspensies werd de transparantie van de coatings verbeterd. De homogeniteit van de lagen dient nog verbeterd te worden.

De coatings werden geanalyseerd naar oppervlaktemorfologie, transparantie en fotokatalytische activiteit en preliminaire testen van de duurzaamheid van de coatings werden uitgevoerd. Infrarood en Raman spectroscopische metingen geven indicaties dat de koppeling van de nanokristallen aan het polymeeroppervlak succesvol was.

Een transparante fotokatalytisch actieve coating met een goede duurzaamheid werd bekomen gebruikmakend van een lage temperatuursmethode compatibel met de PMMA substraten.
A method to obtain transparent thin films of anatase nanocrystals on PMMA substrates was explored. Anatase nanocrystals were synthesized using a variety of nonaqueous synthesis routes. The obtained nanocrystals were characterized with regard to their crystallinity, size, dispersibility and stability of the resulting suspensions. The nanocrystals with the most promising characteristics were used for ligand exchange. The original ligands were exchanged for 3-aminopropyltriethoxysilane (APTES). The resulting aqueous suspensions of charge stabilized nanocrystals were adapted for use as coating suspensions for surface treated PMMA substrates. The goal was to obtain thin films containing anatase nanocrystals covalently coupled to the surface of the PMMA substrates. The formation of an amide bond between the silane ligands on the nanocrystals and carboxylic acid groups on the polymer substrate was envisioned. The surface morphology, transparency and photocatalytic activity of these coatings, obtained through dipcoating, were evaluated.

Key words: titanium dioxide, nanoparticles, ligand exchange, surface functionalization, PMMA substrate, photocatalytic film

Introduction

Titanium dioxide can be used to create transparent photocatalytically active self-cleaning and antibacterial coatings.(1) Under the influence of UV-light, electron-hole pairs are created. The electrons can reduce electron acceptors while the holes can oxidize electron donors. The resulting species (radicals) can subsequently degrade organic pollutants.(2)

Such coatings have already been commercialized on glass.(3–6) The transition to polymer substrates would open up a large and growing market for coatings on (touch)screens, signs, visors, sunglasses and noise barriers on highways.

In this thesis, a contribution was made to the development of durable transparent photocatalytically active coatings on polymer substrates.

This transition to polymer substrates poses some challenges. A first challenge is the thermal sensitivity of polymers. Hence, high temperature processes to obtain crystalline titanium dioxide coatings cannot be used. Therefore, suspensions already containing crystalline titania nanocrystals were used for coating. A second challenge is the limited wettability of the polymer substrates by the coating suspensions. In order to improve the wettability, different surface treatments were evaluated. A third challenge is the improvement of the durability of titania coatings on polymer substrates.(1,7,8)
In this work, the formation of a covalent bond between ligands on the titania nanocrystals and functional groups on the surface of the polymer substrate was explored as a method to obtain durable transparent titania coatings on PMMA substrates. 3-aminopropyltriethoxysilane ligands, obtained through exchange with the original ligands, were used as chemical linkers. The amine functionality of these silanes was used to form an amide bond with carboxylic acids on surface treated PMMA substrates. Aqueous suspensions of APTES functionalized nanocrystals were used to deposit coatings on PMMA substrates via dipcoating. These coatings were analyzed with regard to transparency, surface morphology and photocatalytic activity. Furthermore, preliminary tests of the durability of the coatings were conducted. Raman and FTIR spectroscopy were used to chemically characterize the coatings.

**Experimental**

**Materials**

- titanium tetraisopropoxide (TTIP, ≥97% - Sigma-Aldrich), oleic acid (OLAC, 90% - Sigma-Aldrich), triethylamine (Et₃N, ≥99% - Sigma-Aldrich), titanium tetrachloride (TiCl₄, 99.9% - Sigma-Aldrich), oleylalcohol (OLOH, 85% - Sigma-Aldrich), octadecene (ODE, 90% - Alfa Aesar), oleylamine (OLAM, 98% - Sigma-Aldrich), benzyl alcohol (anhydrous, 99.8% - Sigma-Aldrich), trimethylamine-N-oxide (TMAO, ≥98% - Alfa Aesar), dopamine hydrochloride (98% - Sigma-Aldrich), 3-aminopropyltriethoxysilane (APTES, > 98% - TCI), N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC, > 98% - TCI), N-hydroxysuccinimide (NHS, 98% - Sigma-Aldrich), ethylene glycol (EG, 99.8% - Sigma-Aldrich), 2-(N-morpholino)ethanesulfonic acid (MES, ≥ 99.5% - Sigma-Aldrich), were bought and used without any further purification.

---

**Figure 1** A schematic representation of the route followed to obtain thin films containing titania nanocrystals covalently coupled to the surface of PMMA substrates. (1) A precursor solution containing stabilizing ligands (oleic acid) and a titanium alkoxide (TTIP) is prepared. (2) The as-prepared reaction mixture is a sol containing crystalline nanocrystals, in-situ stabilized by ligands. (3) The original ligands are exchanged for APTES. (4-5) The nanocrystals are coupled to surface treated PMMA substrates via the formation of an amide bond between the amine group of APTES and carboxylic acid groups on the PMMA substrate. (6) The purpose of the ligand exchange and the subsequent formation of a film containing nanocrystals chemically linked to the polymer surface, is to contribute to increasing the durability of photocatalytically active anatase thin films on polymer substrates.
Synthesis of anatase nanorods

The synthesis was conducted as described in the article by Cozzoli et al. (9). In a three-neck flask, 124 mmol of OLAC was degassed at 120°C under vacuum for 1h. Next, the flask was allowed to cool down to 100°C and 3.33 mmol of TTIP was injected under an Ar atmosphere. After stirring for 10 min, either 5 ml of a 2 M TMAO aqueous solution or 10 mmol of Et₃N followed by 5 ml of MiliQ was injected. The mixture was left to stir under an Ar atmosphere for 6h at 100°C. In the subsequent work-up procedure, the nanocrystals were precipitated by adding methanol (in a ratio of 2:1) to the reaction mixture followed by centrifugation at 4000 RPM for 3 min. The resulting white precipitate was washed 5 times with methanol and was subsequently dispersed in toluene to produce optically clear colorless suspensions after sonication for 15 min.

Seeded-growth synthesis

In a three-neck flask, 30 mmol of OLOH, 32 mmol of ODE and 1.5 mmol of OLAC were combined and this mixture was stirred and degassed under vacuum at 120°C for 1h. Next, the mixture was put under an argon atmosphere before cooling down to 60°C. To prepare 10 ml of stock solution, 1.9 mmol TiCl₄ and 10 mmol of OLAC were mixed with 6.62 ml of ODE and stirred at room temperature to obtain a dark orange-brown solution. At 60°C, 1.5 ml of this stock solution was injected into the three-neck flask. Subsequently, the mixture was rapidly heated to 290°C, under refluxing. After 10 minutes of stirring at 290°C, 8 ml of the stock solution was manually injected at a rate of ~0.3 ml/min. The reaction mixture was cooled down to room temperature. The workup procedure was slightly adapted from the article (10) and was executed as follows. First, the reaction mixture was diluted using toluene (2:1) and the nanocrystals were separated by centrifugation at 5000 RPM for 5 min. The supernatant was discarded and the powder was washed three times using methanol. Subsequently, the nanocrystals were suspended in toluene and 50 µl of oleylamine was added per 5 ml of suspension. The suspension was sonicated for 15 min, after which the aggregated particles (those that could not be dispersed) were removed by centrifugation at 2000 RPM for 5 min. The supernatant was decanted into a separate centrifugation tube and the nanocrystals were precipitated from the supernatant using a mixture of 1:1 methanol:isopropanol in a 3:1 excess to the supernatant. This mixture was centrifuged at 5000 RPM for 5 min, after which the nanoparticles were resuspended in toluene. This procedure was repeated twice to obtain an optically clear and colorless dispersion.

Synthesis of dopamine functionalized nanoparticles

The synthesis was conducted as described in the article by Niederberger et al. (11) 160 mg of dopamine was added, under stirring, to 30 ml of benzyl alcohol at room temperature. Subsequently, the flask was flushed with argon gas and transferred to a glovebox in which 1.5 ml of TiCl₄ was added dropwise under intense stirring resulting in a deep red solution. This mixture was stirred under an Ar atmosphere for 3 days (72 h) at 80°C, producing a brown-red turbid suspension which was allowed to cool down to room temperature. Next, the suspension was centrifuged and the nanocrystals were washed five times with chloroform. Subsequently, the nanocrystals were suspended in MiliQ water. The pH was lowered to a pH of ~2 using diluted hydrochloric acid, producing optically clear yellow-brown suspensions after 15 min of sonication.

Ligand exchange

For the ligand exchange of oleic acid with APTES ((3-aminopropyl)triethoxysilane), a literature method for the ligand exchange of oleic acid with silanes on iron oxide nanoparticles (12) was adapted. The starting point for ligand exchange was an optically clear suspension of nanocrystals in toluene containing 100 mg of nano-powder. Subsequently, the amount of toluene was increased to a total of 25 ml and a certain amount of Et₃N was added (3.56 mol
Et$_3$N/mol TiO$_2$). Next, a small amount of MiliQ water (0.55 mol/mol TiO$_2$) was added to hydrolyze the silane alkoxy groups. The flask was flushed with Ar gas and APTES (0.43 mol/mol TiO$_2$) was injected. The mixture was left to stir at 50°C under an Ar atmosphere (for 5h). The suspension was centrifuged at 5000 RPM for 5 min, and the supernatant was discarded. The powder was washed three times with acetone to remove excess (unreacted) silane. Next, the powder was redispersed in MiliQ water. After sonication, a turbid suspension with a pH of 10.5 was obtained. The pH of this suspension was lowered using diluted hydrochloric acid to a pH of ~2, to obtain an optically clear dispersion.

**Surface treatments**

The substrates used were PMMA substrates cut from a PMMA plate using a milling machine, into substrates of 2x4 cm$^2$ or 2x2 cm$^2$ and 2 mm thick. First the PMMA substrates were rinsed with MiliQ water, next with isopropanol and then again with MiliQ water. Subsequently they were sonicated in a 50% (v/v) 2-propanol/MiliQ solution for 20 min. Next, the substrates were dried using a nitrogen flow.

For UV-treatment, the substrates were placed 1.5 cm below an intense UV lamp (Pen-Ray® Mercury Lamp, type 90-0012-01, 230V, $\lambda = 245$ nm, 4100 $\mu$W/cm$^2$) for 20 min up to 6h.

For H$_2$SO$_4$ treatment, the substrates were immersed in a 3M H$_2$SO$_4$ solution at 60°C for 20 min.

For oxygen plasma treatment, the substrates were transferred to a plasma chamber (a cylindrical dielectric discharge plasma reactor of the model Femto, ver. 3, Diener Electronic) that was filled with oxygen gas (O$_2$ pressure 0.8 mbar, power 100W). The substrates were subjected to the plasma for 2 min.

**Deposition of thin films**

20 ml of an aqueous suspension of APTES functionalised nanorods in 0.1 M of MES buffer (a non-amine, non-carboxylate buffer) at a pH of 4.75 was prepared. Subsequently, a 10 times molar excess of EDC with respect to surface COOH groups on the PMMA substrate was added and the mixture was allowed to stir for 5 min. Next, a 25 times molar excess of NHS with respect to surface COOH groups was added, followed by another 5 min of stirring. Afterwards, the surface treated substrates were immersed in this coating suspension using the dip-coater apparatus and were left immersed in this suspension for 2 min, after which the substrates were removed from the suspension at a controlled speed (e.g. 50 mm/min).

Next, the coated substrates were dried, either at 60°C for 1h in a drying furnace or alternatively using an IR lamp or a hotplate immediately after dip-coating. This was followed by a thermal treatment in a muffle furnace, consisting of heating up from room temperature to 180°C in 30 min, followed by 1h at 180°C and subsequently immediately removing the coated substrate from the furnace.

**Analysis techniques**

A Perkin Elmer FTIR spectrometer spectrum 1000 with HATR module was used for infrared spectroscopy. For Raman spectroscopy, a dispersive Raman RXN1 from Kaiser optical systems with a laser at 542 nm was used. XRD diffractograms were collected on a Thermo ARL X’tra diffractometer (CuK$\alpha = 1.5405$ Å) using a 0.02° step size and a 1 s step counting time. Topas Academic V4.1 software was used for Rietveld refinement. A JEOL JEM-2200FS was used for TEM measurements. The photocatalytic activity of the films was determined according to ISO 10678:2010(E). To measure the transparency of the coated substrates, a Perkin Elmer Lambda 900 Spectrometer was used.
Results and discussion

Synthesis of titania nanocrystals

The synthesis by Cozzoli et al. results in nanorods with a length of ~20 nm and a diameter of ~2.5 nm (Figure 2a). XRD measurements show that the nanorods predominantly belong to the anatase phase (Figure 2d) (with a small fraction of brookite that might be present). A percentage crystallinity of 45.5% anatase (corrected for organic material using TGA) was obtained using Rietveld refinement and the yield of the synthesis was calculated to be 74%. Infrared spectroscopy shows that the nanorods are functionalised with oleate ligands (Figure 3a and TABLE 1). The nano-crystals form clear suspensions in toluene, these suspensions remain stable for more than three months.

The seeded-growth synthesis by Murray et al. results in tetragonal bipyramidal anatase nanocrystals of ~25 nm along the longest axis (Figure 2b). The nanocrystals belong to the anatase phase (Figure 2e). A percentage crystallinity of 73.5% (corrected using TGA) was obtained using Rietveld refinement and the yield of the synthesis was calculated to be 58%. This relatively low yield is thought to be the result of the workup procedure, where the non-dispersible part of the nanocrystals is discarded. Suspensions of nanocrystals in toluene remain stable for more than a month.
The synthesis of dopamine functionalized nanoparticles by the group of Niederberger, results in semi-spherical nanoparticles of 5-7 nm in diameter (Figure 2c) belonging to the anatase crystal phase (Figure 2e). A percentage crystallinity of 83.2% (corrected using TGA) was obtained. The yield of the synthesis was calculated to be 81%. The powder obtained from the synthesis has a characteristic brown-red color indicative of a charge transfer between dopamine ligands bound to the nanoparticles and the titanium atoms at the surface of the nanoparticles.

Infrared spectroscopic measurements (Figure 3b and TABLE II) confirm the presence of dopamine on the nanoparticles. The stability of aqueous suspensions of these nanoparticles is pH dependent. The stability is optimal at a pH of ~2, with an average zeta potential of +35.8 mV. At this pH, the suspensions are clear and visually stable (i.e. no turbidity nor precipitation can be noticed) for more than 1 month. At pH values above 3.5, turbid suspensions are obtained.

The synthesis of dopamine functionalized nanoparticles by the group of Niederberger, results in semi-spherical nanoparticles of 5-7 nm in diameter (Figure 2c) belonging to the anatase crystal phase (Figure 2e). A percentage crystallinity of 83.2% (corrected using TGA) was obtained. The yield of the synthesis was calculated to be 81%. The powder obtained from the synthesis has a characteristic brown-red color indicative of a charge transfer between dopamine ligands bound to the nanoparticles and the titanium atoms at the surface of the nanoparticles.

### TABLE I. Assignment of peaks in the FTIR spectrum of powder obtained from the fast hydrolysis synthesis

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Peak position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3200 (br)</td>
<td>$\nu$(O-H)</td>
</tr>
<tr>
<td>2</td>
<td>3004</td>
<td>$\nu$(C=C-H)</td>
</tr>
<tr>
<td>3</td>
<td>2918</td>
<td>$\nu_{as}$(CH$_3$)</td>
</tr>
<tr>
<td>4</td>
<td>2850</td>
<td>$\nu$(CH$_2$)</td>
</tr>
<tr>
<td>5</td>
<td>2360</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>6</td>
<td>1712</td>
<td>residual oleic acid C=O</td>
</tr>
<tr>
<td>7</td>
<td>1628</td>
<td>$\nu$(as) COO’ free oleate</td>
</tr>
<tr>
<td>8</td>
<td>1520</td>
<td>$\nu$(as) COO’ bound oleate</td>
</tr>
<tr>
<td>9</td>
<td>1430</td>
<td>$\nu$(s) COO’ bound oleate</td>
</tr>
<tr>
<td>10</td>
<td>1310</td>
<td>$\nu$(s) COO’ free oleate</td>
</tr>
<tr>
<td>11</td>
<td>1088</td>
<td>$\nu$(C=O) of COO</td>
</tr>
<tr>
<td>12</td>
<td>908</td>
<td>$\delta_r$(CH) alkene</td>
</tr>
<tr>
<td>13</td>
<td>726</td>
<td>$\delta_{lr}$(CH$_2$)</td>
</tr>
<tr>
<td>14</td>
<td>628</td>
<td>OH rock</td>
</tr>
</tbody>
</table>

### TABLE II. Assignment of peaks in the FTIR spectrum of dopamine functionalized nanoparticles

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Peak position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3250 (br)</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>2</td>
<td>3062</td>
<td>C-H stretch aromatic</td>
</tr>
<tr>
<td>3</td>
<td>2360</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>4</td>
<td>1618</td>
<td>$\beta$(NH$_3^+$)</td>
</tr>
<tr>
<td>5</td>
<td>1492</td>
<td>aromatic C=C stretch</td>
</tr>
<tr>
<td>6</td>
<td>1430</td>
<td>symmetric N—H mode of NH$_3^+$</td>
</tr>
<tr>
<td>7</td>
<td>1272</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>8</td>
<td>1212</td>
<td>C-N stretch</td>
</tr>
<tr>
<td>9</td>
<td>1200-1000</td>
<td>in plane bending phenolic and CH/CH$_2$ groups</td>
</tr>
<tr>
<td>10</td>
<td>908</td>
<td>NH$_3^+$ rocking</td>
</tr>
<tr>
<td>11</td>
<td>746</td>
<td>aromatic C-H bending</td>
</tr>
</tbody>
</table>
Ligand exchange

Suspensions of oleic acid functionalized nanorods in toluene were used in a ligand exchange procedure to obtain APTES functionalised nanorods. The powder obtained from this procedure could be dispersed in aqueous solutions, with a pH dependent stability. This indicates that the nanorods are charge stabilized in water. The zeta potential of the nanorods in the aqueous suspensions was measured as a function of the pH (Figure 4). An isoelectric point between 10.5 and 11 was obtained, this is close to the isoelectric point of 10.4 reported for CoFe$_2$O$_4$ nanoparticles functionalised with APTES. The suspensions are most stable at a pH ~2, with an average zeta potential of +30.9 mV. At this pH, the suspensions remain stable for more than 5 weeks.

![Figure 4](image.png)

Figure 4 Zeta potential of suspensions of APTES bound nanorods as a function of pH (pH adapted using diluted HCl and diluted NaOH), the data points are averages over 3 measurements at each pH value. The suspensions were obtained from a ligand exchange procedure using 100 mg of OLAC functionalised nanopowder, 1.07 mmol of APTES, 8.9 mmol of Et$_3$N and 1.39 mmol of H$_2$O in 25 ml of toluene.

An infrared spectrum of powder obtained from the ligand exchange procedure, contains peaks that can be assigned to vibrations of APTES bound to the nanorods (Figure 5 and TABLE III). The most important peak in this spectrum, is the peak with a maximum at 910 cm$^{-1}$. This peak has been assigned in literature to the characteristic stretching vibration of Ti-O-Si bonds. (14–17)

![Figure 5](image.png)

Figure 5 FTIR spectrum of powder obtained from the ligand exchange of OLAC with APTES. The powder was obtained from a suspension of a ligand exchange procedure using 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et$_3$N and 0.69 mmol of H$_2$O in 25 ml of toluene.

TABLE III. Assignment of peaks in the FTIR spectrum of powder obtained from the ligand exchange of OLAC by APTES.

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Peak position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1562+1484</td>
<td>NH$_2$ deformation modes</td>
</tr>
<tr>
<td>2</td>
<td>1432</td>
<td>$\delta_{\beta\delta}$(CH$_2$) next to NH$_2$</td>
</tr>
<tr>
<td>3</td>
<td>1300</td>
<td>CH$_3$ wagging</td>
</tr>
<tr>
<td>4</td>
<td>1120</td>
<td>Symmetric Si-O + C-N</td>
</tr>
<tr>
<td>5</td>
<td>1040</td>
<td>Antisymmetric Si-O-Si</td>
</tr>
<tr>
<td>6</td>
<td>910</td>
<td>Ti-O-Si + (Si-OH)</td>
</tr>
<tr>
<td>7</td>
<td>764</td>
<td>CH$_3$ rock in Si-CH$_2$</td>
</tr>
</tbody>
</table>

Deposition of thin films

A first step to obtain a titania thin film on polymer substrates, is the surface treatment of the polymer substrates. This surface treatment should activate the polymer surface (i.e. induce the presence of carboxylic acids with which the primary amine group of APTES can react), as well as improve the wettability of the substrate by the coating solution. In this regard, three different surface treatments were evaluated. The treatment using H$_2$SO$_4$ did not significantly improve the wettability of the substrates (the contact angle decreased from 79.0° ± 3.4° to 76.3° ± 1.4°). Oxygen plasma treatment had a more significant effect on the wettability, the contact angle decreased to 47.5° ± 0.8°.
UV-treatment had the most significant effect on the wettability of the PMMA substrates (Figure 6). A downside to this surface modification procedure, is the slight discoloration (yellowing) caused by prolonged intense UV irradiation of the PMMA substrates. This has been linked to the formation of double bonds due to side-chain scission.(18)

Figure 6 Contact angle of a droplet of the coating suspension with a PMMA substrate subjected to UV irradiation.

In order to couple the nanocrystals to the PMMA substrates, the carboxylic acid groups that were formed during surface treatment need to be activated for the nucleophilic attack by the amine group of the APTES ligands. This activation involves the formation of a good leaving group on the acyl carbon of the acids. A combination of EDC and NHS was chosen for this purpose.(19–21) A difficulty in this procedure for our case, is the fact that the nanoparticles are stabilized in water by the presence of the positively charged protonated amine groups of the ligands \((\text{NH}_3^+)\). Therefore, the pH could not be increased above a pH of 5, otherwise turbid and unstable suspensions were obtained. A pH of 4.75 was chosen for the coupling reaction, since this is the lowest pH used for coupling between an amine and an EDC and NHS activated carboxylic acid in literature (21,22) and the coating suspensions are clear at this pH value.

Coatings deposited on substrates that were exposed to UV-irradiation for 2h showed good macroscopic homogeneity, but the transparency of the coatings could still be improved. The addition of 5 volume% of ethylene glycol significantly improved the transparency of the coatings. It is thought that this is linked to the slower evaporation of liquid from the thin films after deposition. Coatings with a transmittance of ~87%-84% between 500 nm and 800 nm and 79% at 400 nm could be obtained (as compared to ~93% for clean PMMA between 400 nm and 800 nm) (Figure 7).

Figure 7 (a) 50 mm/min, 5 v% EG, 150°C IR drying, 180°C furnace (b) 50 mm/min, 5 v% EG, 150°C IR drying, 180°C furnace (reproduced) (c) 100 mm/min, 5 v% EG, 150°C IR drying, 180°C furnace (d) 50 mm/min, 5 v% EG, 100°C IR drying, 180°C furnace.

Raman measurements point to the presence of anatase on the surface of the coated substrates whilst FTIR measurements show that silanes are present in the coatings. Together, these measurements indicate that the coupling of the nanocrystals to the surface of the PMMA substrates was successful.

The photocatalytic activity of a model coated substrate was evaluated according to an ISO certified test (ISO 10678:2010(E)) based on the photocatalytic degradation of the well-known dye methylene blue. This degradation process is generally accepted to follow pseudo-first order kinetics (23), as described by:

\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]
With $C$ the concentration of methylene blue after a UV-irradiation time $t$, $C_0$ the initial methylene blue concentration and $k$ the rate constant of the reaction. This equation can be represented graphically (Figure 8).

![Logarithmic plot of the decomposition of methylene blue as a function of UV exposure time for a blank sample and a coated PMMA sample. The sample is a substrate coated with a suspension containing 5 v% of EG using a dip-coating speed of 50 mm/min, dried at 150°C under an IR lamp for 30s and subjected to thermal treatment at 180°C.](image)

The initial steep drop for the curve of the coated sample might be attributed to adsorption of methylene blue on the sample. Therefore, datapoints collected before 1h into the test are not taken into account for calculations. The specific degradation rate of the coated sample was calculated to be $1.45 \times 10^{-5}$ mol/m²h. This is a relatively low value, values up to $3.8 \times 10^{-5}$ mol/m²h have been obtained using aqueous suspensions on glass substrates.(24) The relatively low activity of the coating could be ascribed to the presence of APTES around the nanorods. It has been shown that the presence of APTES molecules around anatase nanoparticles can significantly suppress their photocatalytic activity, with a decrease of up to 75% compared to bare nanoparticles for high ligand densities (6.2 nm$^3$). (25)

Conclusions
Anatase nanocrystals with good crystallinity that can be used to obtain clear and stable suspensions were reproducibly synthesized. The nanorods synthesized through the fast hydrolysis procedure were used in a ligand exchange procedure to obtain APTES capped nanorods dispersible in aqueous solutions. The stability of the resulting suspensions is pH dependent and at a pH of ~2, clear suspensions can be obtained that remain stable for more than a month. These aqueous suspensions were subsequently used to coat PMMA substrates. In order to improve the wettability of the substrates, different surface treatments were explored. UV-irradiation proved the most effective surface treatment, resulting in more homogeneous coatings. The addition of ethylene glycol to the suspensions further improved the transparency of the coatings. Coatings with only a slightly reduced transparency as compared to uncoated PMMA substrates were obtained, these coatings were moreover found to be durable through the use of preliminary durability tests. Raman and infrared spectroscopy measurements provide indications that the coupling of the nanocrystals to the PMMA substrate was successful. A transparent photocatalytically active coating with good durability was obtained through the use of a low temperature procedure compatible with the thermal sensitivity of the PMMA substrates.

Acknowledgments
The author would like to thank prof. dr. Isabel Van Driessche for her advice and the opportunity to work in the SCRiPTS group and dr. Petra Lommens for her expertise and guidance. My thanks also goes out to Jonathan Watté for his guidance. Koen Vandaele, Glenn Pollefeyt and Olivier Janssens are greatly acknowledged for XRD analysis, Glenn Pollefeyt and Katrien De Keukeleere for TEM measurements, Jonathan Watté for photo-catalytic tests and Veerle Boterberg for oxygen plasma treatment.
References

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1. Goal

It takes time, energy and money to keep surfaces clean and it generally involves the use of superfluous amounts of water and detergents. Clearly, it would be beneficial from an economical and an environmental point of view if surfaces were able to stay clean longer without needing maintenance. This can be achieved using a self-cleaning coating.

Self-cleaning coatings can mitigate staining, fogging and the odour and deterioration caused by dirt. Furthermore, some of these coatings have anti-bacterial properties. Self-cleaning coatings are an important topic in research, and are highly commercially relevant with worldwide revenues for self-cleaning appliances totaling approximately US$ 764.2 million in 2010, which is expected to increase to US$ 2117.75 million by the end of 2015 (partly due to a projected increased use of self-cleaning coatings for solar panels).

In this regard, a thin film of crystalline titanium dioxide (TiO$_2$) applied as a coating is a versatile system due to its properties of being transparent and colorless, chemically stable, non-toxic and relatively cheap, but most important its ability to become photocatalytically active and superhydrophilic under UV-irradiation. Organic pollutants will eventually be degraded to CO$_2$, H$_2$O and inorganic ions. Titania photocatalysts find use not only in self-cleaning coatings, but also in wastewater treatment and the reduction of air pollution (e.g. the degradation of NO$_x$ and VOCs).

TiO$_2$ coatings are already commercialized on glass by companies such as Pilkington, PPG Industries, Cardinal Ig Company and Saint-Gobain Vitrage, using deposition techniques such as chemical vapour deposition and magnetron sputtering. In this thesis, we want to contribute into extending the use of these coatings to polymers, since this opens up a large market of coatings for applications such as (touch)-screens, sunglasses, visors, light-domes and noise barriers on highways.

This transition to polymer substrates, however, poses some challenges.

A first challenge is the thermal sensitivity of polymers. It is imperative for the photocatalytic properties that the TiO$_2$ thin film is crystalline (or contains crystalline nanoparticles), preferably of the anatase crystal phase. In order to induce crystallinity to a film deposited from a precursor solution, however, these films need to be subjected to elevated temperatures (>400°C). This is incompatible with the use of polymers as substrates, since these high temperatures will cause deformation and/or deterioration of the polymer substrate.

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a 1012 articles on Web Of Science with self-cleaning or easy-clean as topic of which 319 published in 2013-2014. (as per 28/10/2014)
1. Goal

In order to circumvent this issue, films are deposited on the substrates from colloidal suspensions that already contain anatase nanocrystals, such that, ideally, a drying step should be sufficient to obtain the titania coating.

A second challenge is the wettability of the polymer surface by the coating suspension. To improve this, there are a variety of possible treatments for polymer surfaces, such as UV-irradiation, chemical treatments and plasma modification, which could enhance the wettability.\textsuperscript{14-16}

A third and very important challenge is the durability of the coating, especially since most applications entail outdoor use.\textsuperscript{1,17,18} In this thesis, the use of chemical linkers to durably bind titania nanocrystals to the surface of a polymer substrate is explored. Silanes were chosen as chemical linkers because of their established use as linkers at organic-inorganic interfaces\textsuperscript{19} and their proven compatibility with titania\textsuperscript{20-23} as well as polymer surfaces\textsuperscript{19,24}. This covalent linking of the nanocrystals to the surface of the polymer substrate is envisioned to improve the durability of the final titania coating.

A fourth challenge is the possibility that the polymer surface and/or (part of) the chemical linker is degraded because of the photocatalytic properties of the TiO\textsubscript{2} film.\textsuperscript{25} In this respect, the thin layer of titania nanocrystals functionalized with silanes may also serve as a buffer layer between the rest of the titania film and the polymer surface (in analogy to a silica buffer layer). It has indeed been shown that surface modification of (commercial) titania nanoparticles with silanes can significantly suppress their photocatalytic activity.\textsuperscript{26} Upon this “buffer/coupling layer” of silane functionalised titania nanocrystals, bare (ligand-stripped) nanocrystals can be deposited in a next step such that highly photocatalytically active films might be obtained.
1. Goal

The concepts of this thesis are summarized in Figure 1.

1. A precursor solution generally containing stabilizing ligands and a titanium halide (TiX₃) or a titanium alkoxide (TiOR₃), as a titanium precursor, is prepared.
2. The as-prepared reaction mixture is a sol containing crystalline nanoparticles, *in-situ* stabilized by ligands (e.g. oleic acid, oleyl alcohol or dopamine).
3. If the original ligands used in the synthesis are not suitable to link the nanoparticles to the surface of a polymer substrate, these ligands are exchanged with more suitable ligands (i.e. silanes).
4-5. Through a chemical reaction, the nanocrystals are coupled to the (surface treated) polymer surface via the ligands that act as chemical linkers. This should result in a thin film containing titania nanocrystals that are covalently linked to the polymer surface. On this film, a layer of ‘bare’ titania nanocrystals can be deposited in a next step.
6. The purpose of the ligand exchange and the subsequent formation of a film containing nanocrystals chemically linked to the polymer surface, is to contribute to increasing the durability of photocatalytically active anatase thin films on polymer substrates.

![Figure 1](image-url) A schematic representation of the concepts of this thesis. (Adapted from De Palma et al.²⁷ and Malik et al.²⁸)
1. Goal

This thesis has three main goals:

- To find a reproducible synthesis for titania nanocrystals of the anatase phase with a size between 5 nm and 50 nm and a percentage crystallinity higher than 13%, that produces nanocrystals that can be used to form clear and stable suspensions.
- To obtain anatase nanocrystals capped with ligands that are suitable as linkers between these nanocrystals and the surface of a polymer substrate, by exchanging the original ligands.
- To couple the anatase nanocrystals to a polymer substrate *via* the ligands that act as chemical linkers.

Nonaqueous syntheses were preferred over syntheses in an aqueous environment because syntheses in an nonaqueous environment are often more controlled, lead to better-defined nanocrystals in terms of size and shape\(^{29}\) and can produce nanocrystals with a higher percentage crystallinity.\(^ {30}\)

Nanocrystals with a size between 5 nm and 50 nm were envisioned, because nanoparticles in this size range were successfully used previously within the SCRiPTS group to form dense titania layers from aqueous suspensions on glass substrates.\(^ {31}\) A percentage crystallinity of the nanocrystals of more than 13% was set as a goal, as the syntheses in aqueous environment that were used previously within the SCRiPTS group lead to nanoparticles with a percentage crystallinity between 10% and 13%.\(^ {31}\) It must be noted that the percentage crystallinity of titania nanocrystals obtained through a certain synthesis procedure is rarely reported in literature, although this parameter is crucial for use of the nanocrystals in many applications, including self-cleaning.\(^ b\) Moreover, not all literature synthesis procedures for titania nanocrystals proved to be reproducible.

The ultimate goal of this line of research is to obtain durable photocatalytically active titania layers on thermally sensitive substrates such as polymers.

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\(^b\) Mostly, XRD patterns and/or (HR)TEM images are used in literature to prove that the nanocrystals are crystalline and belong to a certain crystal phase, however an XRD spectrum only proves that at least a fraction of the nanocrystals are crystalline and TEM analysis is often used in a way that is not statistically representative of the entire sample. Using Rietveld refinement, the percentage crystallinity of the nanocrystals obtained through the main synthesis procedures used in this thesis will be provided.
2. Introduction

2.1. Titania (nano-)materials

2.1.1. Crystal structures of naturally occurring titania polymorphs

The most common polymorphs of titania are anatase, rutile and brookite. Anatase and rutile have a tetragonal structure, brookite has an orthorhombic structure.\(^9\) The elementary repeating unit of anatase, rutile and brookite is a (distorted) \(\text{TiO}_6\)-octahedron, but the pattern by which these octahedra are interconnected is different. In anatase the octahedra are connected by their vertices, in rutile the edges are connected and in brookite both the vertices and the edges are connected.\(^9\)

![Figure 2](image_url)

**Figure 2** Crystal structures of anatase (a), rutile (b) and brookite (c).\(^9\)

For bulk titania, rutile is the thermodynamically most stable phase at all temperatures for pressures up to 60 kbar. That said, there is only a small difference in Gibbs free energy between bulk anatase, rutile and brookite. Bulk anatase and brookite are metastable at room temperature and atmospheric pressure. It is important to note that, in the nano-regime, the relative phase stabilities are also highly dependent on the size of the titania particles. In this size regime, the surface energy of the particles is of a similar magnitude as the differences in the ‘bulk’ free energy contribution between the phases.\(^2,9\) For equally sized particles with a size below 11 nm, anatase is the most stable, between 11 and 35 nm brookite is the most stable, and rutile is most stable at sizes greater than 35 nm (this was derived in literature using theoretical values for the surface enthalpy of these polymorphs).\(^32\) An experimental example of this effect comes from the synthesis of titania nanorods by Buonsanti et al. Nanorods with length lower than 20 nm crystallized in the anatase polymorph, hybrid anatase-brookite nanorods were identified in the 20-30 nm length regime, whilst nanorods with dimensions above 25-30 nm crystallized in the brookite polymorph. The authors suggest that the formation of brookite nanorods is due to a solid-state conversion of initially formed anatase nanorods into brookite nanorods.\(^33\)
2. Introduction

2.1.2. Comparison of rutile-, anatase-, brookite- and mixed phase nanoparticles with regard to photocatalytic properties

For most photocatalytic reactions, the anatase polymorph shows an increased activity as compared to rutile and brookite.\(^2\) The higher activity of the anatase polymorph has been attributed to a lower rate of recombination of holes and electrons as compared to rutile (holes and electrons that recombine do not contribute to the photocatalytic degradation of species in the vicinity of the nanocrystals).\(^3\) In a recent study, the increased activity of anatase as compared to rutile has been linked to the generation of mobile, free hydroxyl radicals on the surface of anatase, whilst these radicals would only appear as surface bound species on rutile. Therefore, the photocatalytic oxidation on rutile would be limited to adsorbed species whereas that on anatase is more extended owing to the presence of the mobile hydroxyl radicals.\(^5\) Brookite is the least studied as a photocatalyst out of these polymorphs, partly due to the difficulty to obtain it as a pure phase.\(^6\)

It has been stated that a combination of anatase and rutile in certain ratios is more active than either anatase or rutile seperately.\(^7\) An example is the commercial titania catalyst Degussa P25, containing 80% anatase and 20% rutile.\(^8\) This increased activity has been linked to the smaller bandgap of rutile, extending the useful range of light into the visible region, combined with charge transfer from rutile to anatase such that the recombination of charge carriers is reduced.\(^9\) For our research, it was opted to focus on nanocrystals of the anatase polymorph.

2.2. Self-cleaning applications

The self-cleaning properties of a crystalline TiO\(_2\) layer can be explained through a combination of UV-induced superhydrophilicity and photocatalytic activity. When the surface is exposed to UV-light, dirt is broken down photocatalytically. When the surface becomes wet, because of the superhydrophilicity of the surface, water enters below the (hydrophobic) dirt/dust particles and lifts them off the surface. This combination reduces the dust and dirt on the surface under the influence of both light and (rain)water.\(^1\) The self-cleaning properties of TiO\(_2\) are illustrated in Figure 3.\(^1\) The photocatalytic- and superhydrophilic effects will be explained in more detail in the next two sections.

It must be noted that it is not correct to state that self-cleaning surfaces will never become dirty, since the self-cleaning process is dependent on parameters such as the amount of rainfall and sunlight and on the accumulation rate of dirt. That said, such a self-cleaning coating will slow down the rate of contamination and therefore save time and cost for cleaning maintenance.\(^9\)
2. Introduction

**Figure 3** Schematic diagram of the decontamination process occurring on a superhydrophilic self-cleaning surface such as an anatase coating.¹ (left) Adsorbed organic dirt is decomposed by the photocatalytic properties of TiO₂, while organic contaminants and dust can be washed off by rainwater because of the superhydrophilicity of the surface (right).

2.2.1. **Photocatalytic activity**

The basis of the photocatalytic properties of TiO₂ is the formation of electron-hole pairs upon absorbing light with an energy higher than or equal to the bandgap of the titania semiconductor (3.2 eV for bulk anatase)² and the subsequent formation of radicals through reaction of the generated electrons and holes with species adsorbed onto the surface of the particles.

**Figure 4** Simplified scheme of the processes taking place in and around an anatase photocatalyst leading up to the degradation of adsorbed pollutants.⁴⁰
2. Introduction

The processes leading up to the degradation of contaminants (e.g. organic species) adsorbed on the particle, can be understood by the following sequence of reactions\textsuperscript{2,39,41} (summarized in Figure 4):

Generation of charge carriers (the generation of an exciton):

\[ TiO_2 + h\nu \rightarrow e^- + h^+ \] (1)

Trapping of charge carriers at the surface:

\[ e^- + Ti(IV)O - H \rightarrow Ti(III)O - H \] (2)
\[ h^+ + Ti(IV)O - H \rightarrow Ti(IV)O^- - H^+ \] (3)

Transfer of charge carriers on the titania surface to adsorbed species (either a reductant or an oxidant):

\[ Ti(III)O - H + Ox \rightarrow Ti(IV)O - H + Ox^- \] (4)
\[ Ti(IV)O^- - H^+ + Red \rightarrow Ti(IV)O - H + Red^+ \] (5)

for example:

\[ e^- + O_{2,absorbed} \rightarrow O_2^- \] (6)
\[ h^+ + OH_{absorbed}^- \rightarrow \cdot OH \] (7)
\[ h^+ + H_2O_{absorbed} \rightarrow H^+ + \cdot OH \] (8)

Recombination processes:

\[ h^+ + Ti(III)O - H \rightarrow Ti(IV)O - H \] (9)
\[ e^- + Ti(IV)O^- - H^+ \rightarrow Ti(IV)O - H \] (10)
\[ O_{2,adsorbed} + Ti(IV)O^- - H^+ \rightarrow Ti(IV)O - H + O_{2,adsorbed} \] (11)

There are many secondary reactions\textsuperscript{42} of the radicals generated at the surface, whereby other reactive species such as the potent oxidants hydrogen peroxide and the hydroperoxyl radical can be formed:

\[ H^+ + O_2^- \rightarrow HO_2^- \] (12)
\[ HO_2^- + e^- \rightarrow HO_2\cdot^- \] (13)
\[ HO_2\cdot^- + H^+ \rightarrow H_2O_2 \] (14)
\[ 2HO\cdot \rightarrow H_2O_2 \] (15)

Reactions such as (6), (7), (8) and (12) generate reactive radicals that can in turn react with adsorbed contaminants. Recombination processes such as (9)-(11) limit the efficiency of the photocatalyst. In summary, charge carriers are generated under the influence of UV-light, these charge carriers can be trapped at the surface of the nanoparticle until they react with adsorbed species to form radicals. These radicals can in turn react with species in the surroundings of the nanoparticles, which are thereby degraded.
2. Introduction

2.2.2. Superhydrophilicity

Superhydrophilicity is defined as the property of a surface to have a water contact-angle $<5^\circ$ (for a TiO$_2$ coating of good quality, under UV-irradiation, the water contact angle can approach $0^\circ$). The mechanism of superhydrophilicity is often related to an increased amount of surface hydroxyl groups appearing under UV-irradiation. Following band gap excitation of TiO$_2$, electron-hole pairs are created. Part of the created electrons and holes diffuse to the surface and are trapped there, others recombine (either at the surface or in the bulk of the nanoparticle). The holes can be trapped at lattice oxygen sites on the surface. A hole trapped at a lattice oxygen site weakens the bond between this lattice oxygen and the titanium atom to which it is bound. This weakened bond can be broken through reaction with water molecules (e.g. moisture from the air or from rainfall), forming new hydroxyl groups. Thus, one hydroxyl group doubly coordinated to two neighboring titanium atoms converts, through the reaction with water, to two hydroxyl groups singly bonded to these titanium atoms. This mechanism is shown schematically in Figure 5.39

Another effect that can contribute to the UV-induced superhydrophilicity is the removal of adsorbed organic layers (which are generally hydrophobic) through photo-oxidation.44

![Figure 5](image_url)

**Figure 5** Surface reconstruction on TiO$_2$ during reversible hydrophilic changes under the influence of UV-light.39
2. Introduction

2.3. State of the art

2.3.1. Summary of the literature on the deposition of TiO$_2$ on polymers

Coatings of TiO$_2$ are already deposited on unmodified polymer surfaces$^{45-47}$, on polymers surface-coated with a buffer layer$^{43,48}$ (e.g. silica), on surface treated polymer surfaces$^{49}$ and on polymer surfaces grafted with organic species such as sulfonic acid$^{50}$, sulfonate$^{51}$ and silanes$^{52}$. TiO$_2$ coatings are already deposited on: polyethylene terephthalate$^{52}$, polycarbonate$^{43,45}$, polymethylmethacrylate$^{48}$, polystyrene$^{47,50}$, polyimide$^{49,51}$ and Acrylonitrile Butadiene Styrene (ABS)$^{46}$. A variety of deposition-techniques were used, such as radio frequency magnetron sputtering$^{45}$, chemical vapour deposition$^{48}$, spray-coating$^{47}$, spin-coating$^{49}$ and dip-coating$^{43,46,50-52}$.

To our knowledge, the use of ligands on anatase nanocrystals to act as chemical linkers between these nanocrystals and the surface of a polymer substrate has not been described in literature. The formation of covalent bonds between the nanocrystals and the surface of the polymer is envisioned to enhance the durability of the titania coating on the substrate.

For our research, PMMA was chosen as a substrate because it is transparent and its surface functional groups (the methyl ester units) can be converted into carboxylic acid groups$^{14}$, such that nanoparticles functionalised with ligands that possess an amine functionality can be coupled to the surface via the formation of an amide bond. Next to these practical reasons, PMMA was also chosen because it is relatively cheap and because a (durable) titania coating on this polymer would be highly relevant from a commercial point of view. It is used as a glass substitute (i.e. Plexiglas$^{50}$) and its major applications include (automotive) glazing, lighting fixtures, signs and displays and construction.$^{53}$

Despite the importance, few researchers have investigated the (long-term) durability of their titania coating on the polymer substrate. Loddo et al.$^{47}$ tested the durability of their coating by subjecting it to ultrasound treatment in water. Hashizume et al. tested the durability of their newly prepared coatings by using the Scotch$^\text{C}$ tape test$^{49}$.

The main purpose of this research is to enhance the durability of titania coatings on polymer substrates. The method that is proposed does however lead to an increase in the amount of steps used to obtain the coating (nanocrystal synthesis, ligand exchange, coupling to the polymer surface, a drying step, deposition of ‘bare’ nanocrystals and finally another drying step) which increases the cost of the entire process. The cost of the separate steps should be relatively low, however, since no expensive deposition techniques (e.g. magnetron sputtering or CVD) are used. Moreover, if the durability of the coating is sufficiently enhanced, the potential extra cost of the process can be justifiable.
2. Introduction

2.3.2. Synthesis of titania nanocrystals

2.3.2.1. Seeded-growth synthesis of tetragonal bipyramidal nanocrystals

A seeded-growth synthesis was used to produce tetragonal bipyramidal anatase nanocrystals (a tetragonal bipyramidal shape is the thermodynamically most stable form of the anatase polymorph). A first step in such a seeded-growth synthesis is the formation of seed particles, which act as nucleation centres for further nucleation and growth. Seed formation is achieved by injecting a small volume of stock solution (containing TiCl$_4$, oleic acid and 1-octadecene) into the reaction mixture (containing oleylalcohol, oleic acid and 1-octadecene) at a low temperature (60°C) and subsequently heating up quickly to a higher temperature (290°C). After waiting for the seeds to form, a larger volume of stock solution is slowly injected. This slow continuous addition of stock solution results in the slow growth of the seeds to produce nanocrystals of good size and shape-uniformity.

The choice of different co-surfactants next to the ‘main’ surfactant oleic acid, oleylamine (OLAM) vs 1-octadecanol (1-ODOL) or equivalently oleylalcohol (OLOH), and different titanium precursors (TiCl$_4$ vs. TiF$_4$) can be used to tune the shape of the nanocrystals, as shown in Figure 6. The co-surfactants and the absence or presence of F$^-$ influence the truncation of the tetragonal bipyramidal nanoparticles (the relative amount of {001} and {101} facets). In case TiCl$_4$ is used as a titanium-precursor and oleic acid (OLAC) and 1-ODOL (or OLOH) as surfactants, anatase tetragonal bipyramidal crystals are produced. Next to the shape, the size of the nanocrystals can also be tuned by changing the volume of the second injection of stock solution and concomitantly adjusting the reaction time (a larger volume injected at the same injection rate automatically results in a longer reaction time). The suggested reaction mechanism for this synthesis is shown in Figure 7.

![Figure 6](image)

*Figure 6* TEM images of TiO$_2$ NCs synthesized using the precursor TiF$_4$ (a,d), a mixed precursor of TiF$_4$ and TiCl$_4$ (b,e), and TiCl$_4$ (c,f). Those depicted in a–c and d–f are synthesized in the presence of OLAM and 1-ODOL, respectively. $^{54}$
2. Introduction

\[ TiX_4 + \text{OLAC} + \text{OLOH} \rightarrow X_3Ti-O-R_1 + HX + \text{polymerisation} \]

**Figure 7** Mechanism for the formation of TiO$_2$ nanoparticles out of TiX$_4$, OLAC and OLOH with R$_1$ \((\text{CH}_2)_{12}\text{CH=CH(CH}_2)_{8}\) and \(\text{R}_2\) \((\text{CH}_2)_{8}\text{CH=CH(CH}_2)_{8}\).\(^5\)

2.3.2.2. Synthesis of anatase nanorods

A synthesis procedure by Cozzoli et al. was used to produce anatase nanorods.\(^5\) This synthesis has the advantage of being a low temperature synthesis (100°C), furthermore the resulting nanoparticles are easily dispersed in apolar solvents. The synthesis is based on the hydrolysis of a titanium alkoxide (titanium tetraisopropoxide, TTIP) in the presence of a base (tertiary amines or quaternary ammonium hydroxides) as a catalyst for the polycondensation of the Ti-O-Ti network, with oleic acid acting as both the solvent as well as a ligand for the growing NCs. The article by Cozzoli et al. discusses two nanoparticle syntheses, called the slow hydrolysis and the fast hydrolysis, where the slow hydrolysis produces spherical nanoparticles whilst the fast hydrolysis produces nanorods. As the names suggest, the fast hydrolysis method is based on the fast hydrolysis of the alkoxide through the injection of a relatively large amount of aqueous base solution (83 mol H$_2$O/mol Ti), as opposed to slow hydrolysis by the in-situ release of water through the esterification of oleic acid (OLAC) by ethylene glycol (EG).

The anisotropic growth (the formation of rods instead of spheres) for the fast hydrolysis was attributed to the selective binding of OLAC to the nanoparticle surface (inhibiting the growth rate along certain crystallographic directions) and to the supply rate of water. For the fast hydrolysis, water is injected at the beginning of the synthesis. This results in a very high solute concentration, which puts the reaction into ‘kinetic overdrive’.

---

5. Cozzoli et al. (2010).
2. Introduction

In the opposite regime, thermodynamic control, i.e. in slow growth conditions, nanocrystals with low aspect ratios are formed because this minimizes the surface area. However, the growth rate of a crystal facet depends exponentially on the surface energy, so at high growth rates - under kinetic control - high-energy facets grow significantly quicker than low-energy facets. These fast growing (high energy) facets will eventually disappear during growth, resulting in a crystal terminated by the slower growing (lower energy) facets. The relative surface energy of different facets can be tuned by using ligands that selectively adhere to a particular type of facet; such ligands lower the surface energy and therefore slow down the growth rate of those facet relative to the others. Oleic acid binds preferentially to {001} facets, therefore these faces are preserved during growth and nanorods are formed. In the slow hydrolysis method water is released gradually through the esterification of OLAC by EG, this results in lower solute concentrations, under which thermodynamic control prevails, resulting in spherical particles. The mechanism for Ti-O-Ti network formation is given in the article, as follows:

\[
\begin{align*}
\text{Ti(OR)}_4 + x\text{H}_2\text{O} & \rightarrow \text{Ti(OH)}_x(\text{OR})_{4-x} + x\text{ROH} \\
(\text{OR})_{4-x}(\text{OH})_{x-1}\text{Ti} - \text{OH} + x\text{O} - \text{Ti(OH)}_x(\text{OR})_{3-x} & \rightarrow (\text{OR})_{4-x}(\text{OH})_{x-1}\text{Ti} - 0 - \text{Ti(OR)}_{3-x}(\text{OH})_x + x\text{OH}
\end{align*}
\]

First, the alkoxide (Ti(OR)_4) is hydrolysed to produce unstable hydroxyalkoxides (Ti(OH)_x(OR)_{4-x}), next these hydroxyalkoxides polycondensate via olation (elimination of water) or oxolation (elimination of alcohol) to form a Ti – O – Ti network. In the slow-hydrolysis method, the water molecules in (16) are generated through esterification of OLAC with EG. A competitive pathway for the formation of a Ti – O – Ti network is substitution of an alkoxy group by an ester functional group followed by the condensation of the formed species:

\[
\begin{align*}
\text{Ti(OR)}_4 + x\text{R'CO}_2\text{H} & \rightarrow \text{Ti(OR)}_{4-x}(\text{R'CO}_2)_x + x\text{ROH} \\
n\text{Ti(OR)}_{4-x}(\text{R'CO}_2)_x & \rightarrow \frac{n}{2} [(\text{OR})_{3-x}\text{Ti} - 0 - \text{Ti(}\text{R'CO}_2)_{x-1}] + \text{R'CO}_2\text{R}
\end{align*}
\]
2.3.2.3. Synthesis of dopamine functionalised nanoparticles

A synthesis by the group of Niederberger was used to obtain nanoparticles functionalised \textit{in-situ} with dopamine (\textbf{Figure 8}).\textsuperscript{58} The synthesis produces small (5-7 nm) spherical anatase nanoparticles functionalized with dopamine that can be dispersed in acidic aqueous solutions. The dopamine molecule and the silane APTES that was used for ligand exchange (see section 3.2) both possess a primary amine function such that a similar procedure might be used to link nanocrystals functionalized with these ligands to the surface of the polymer substrate. This synthesis is based on the reaction of TiCl\textsubscript{4} with benzyl alcohol, the mechanism\textsuperscript{59,60} for this reaction is shown in \textbf{Figure 9}.

\textbf{Figure 8} The structure of dopamine.

\textbf{Figure 9} Proposed reaction mechanism (alkyl halide elimination) for the formation of TiO\textsubscript{2} out of benzyl alcohol and TiCl\textsubscript{4}.\textsuperscript{59,60}
2. Introduction

2.3.3. Organosilanes as ligands for metal oxides

Organosilanes, with a general formula of $Y$-(CH$_2$)$_n$-Si-X$_m$ where X is a leaving group such as a halide or an alkoxy group and m generally ranges from 1-3, can have a large variety of different headgroups (Y), including but not limited to NH$_2$ (e.g. 3-aminopropyltriethoxysilane or APTES), C=O, COOR, N=C=O, SH and C≡N. They have been used to surface-modify metal oxides such as silicon dioxide, aluminium oxide, zinc oxide, iron oxide and titanium dioxide.

Binding of the silanes to (flat) metal oxide surfaces can be described as self-assembled monolayer (SAM) formation. The principle, for flat surfaces, is based on three main steps (see Figure 10). The first step is the hydrolysis of the organosilane by water that is adsorbed on the oxide surface, forming hydroxysilanes (e.g. $Y$-(CH$_2$)$_n$-Si(OH)$_3$). These hydroxysilanes are hydrogen-bonded to the oxide surface, but still mobile enough to move laterally across the surface. Due to attractive forces such as Van Der Waals interactions between the alkyl chains (London dispersion forces) and interactions between headgroups (e.g. dipole-dipole interactions), the silanes order themselves on the surface of the oxide. The final step is the condensation of the Si-OH groups with surface –OH groups (e.g. titanol groups) and with silanol groups of neighboring silane molecules (the extent of crosslinking depends on the structure of the silane).

![Figure 10](image)

The headgroups of the silane molecules can be used to form a covalent bond with organic species, such as polymers, and the silanol groups formed upon hydrolysis of the leaving group(s) can bind to metal oxide surfaces, therefore silanes can be used to link metal oxide nanoparticles to polymer surfaces. Organosilanes have been used to cap metal oxide nanoparticles, either through surface functionalization of ‘bare’ nanoparticles or through ligand-exchange with the original ligands. Metal oxide nanoparticles that have been capped with organosilanes include: Fe$_2$O$_3$ and Fe$_3$O$_4$, TiO$_2$, SiO$_2$, and Al$_2$O$_3$. Ligand exchange procedures for oleic acid on iron oxide nanoparticles have been reported. To our knowledge, silanes have not been used for ligand exchange on titania nanoparticles (they have been used to surface functionalize ‘bare’, commercial, titania nanoparticles, however).
3. Experimental

3.1. Synthesis of titania nanocrystals

3.1.1. Overview of titania nanocrystal syntheses

The first part of the experimental work for this thesis consisted of finding reproducible literature syntheses that result in well dispersible nanocrystals, of the anatase phase, with sufficient crystallinity. In this respect, a variety of literature syntheses was carried out, the procedures and results of which are summarized in Table A1, in the appendix. From these literature syntheses, three synthesis procedures were chosen for further research. The experimental procedures for these syntheses will be thoroughly discussed in the following sections. The chemicals used for these three synthesis procedures are listed in Table 1. For details on used apparatus, see section 7.3 in the appendix.

Table 1 Chemicals used, without any further purification, in the four synthesis procedures discussed in this chapter.

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seeded growth synthesis of tetragonal bipyramidal nanocrystals</td>
<td>titanium tetrachloride (TiCl₄) (Sigma-Aldrich, 99.9%)</td>
</tr>
<tr>
<td></td>
<td>oleic acid (OLAC) (Sigma-Aldrich, 90%)</td>
</tr>
<tr>
<td></td>
<td>oleylalcohol (OLOH) (Sigma-Aldrich, 85%)</td>
</tr>
<tr>
<td></td>
<td>octadecene (ODE) (Alfa Aesar, 90%)</td>
</tr>
<tr>
<td></td>
<td>oleylamine (Sigma-Aldrich, 98%)</td>
</tr>
<tr>
<td>Synthesis of anatase nanorods</td>
<td>titanium tetraisopropoxide (TTIP) (Sigma-Aldrich, ≥97%)</td>
</tr>
<tr>
<td></td>
<td>oleic acid (OLAC) (Sigma-Aldrich, 90%)</td>
</tr>
<tr>
<td></td>
<td>water (MilliQ)</td>
</tr>
<tr>
<td></td>
<td>trimethylamine-N-oxide (TMAO) (Alfa Aesar, 98%+) or triethylamine (Et₃N)</td>
</tr>
<tr>
<td></td>
<td>(Sigma- Aldrich, ≥99%)</td>
</tr>
<tr>
<td>Synthesis of dopamine functionalised nanoparticles</td>
<td>titanium tetrachloride (TiCl₄) (Sigma-Aldrich, 99.9%)</td>
</tr>
<tr>
<td></td>
<td>benzyl alcohol (BnOH) (Sigma-Aldrich, Anhydrous, 99.8%)</td>
</tr>
<tr>
<td></td>
<td>Dopamine.HCl (Sigma-Aldrich, 98%)</td>
</tr>
</tbody>
</table>
3. Experimental

3.1.2. Seeded-growth synthesis of tetragonal bipyramidal nanocrystals

In a three-neck flask, 30 mmol (9.487 ml) of OLOH (co-surfactant), 32 mmol (10.2 ml) of ODE (non-coordinating solvent) and 1.5 mmol (0.48 ml) of OLAC (surfactant) were combined and this clear colorless mixture was stirred and degassed under vacuum at 120°C for 1h (see Figure 11a). Next, the mixture was put under an argon atmosphere before cooling down to 60°C. To prepare 10 ml of stock solution, 1.9 mmol (0.22 ml) TiCl₄ (Ti-precursor) and 10 mmol of OLAC (3.16 ml) were mixed with 6.62 ml of ODE and stirred at room temperature to obtain a dark orange-brown solution. At 60°C, 1.5 ml of stock solution was injected into the three-neck flask (Figure 11b). Subsequently, the mixture was rapidly heated to 290°C, under refluxing. After 10 minutes of stirring at 290°C to let the seed crystals form, 8 ml of the stock solution was manually injected at a rate of ~0.3 ml/min (Figure 11c). A turbid white-brown suspension was obtained. The reaction mixture was allowed to cool down to room temperature. The workup procedure was slightly adapted from the article⁵⁴ and was executed as follows. First, the reaction mixture was diluted using toluene (2:1) and the nanocrystals were separated by centrifugation at 5000 RPM for 5 min. The supernatant was discarded and the powder was washed three times using methanol. Subsequently, the nanocrystals were suspended in toluene and 50 µl of oleylamine was added per 5 ml of suspension. The suspension was sonicated for 15 min, after which the aggregated particles (those that could not be dispersed) were removed by centrifugation at 2000 RPM for 5 min. The supernatant was decanted into a separate centrifugation tube and the nanocrystals were precipitated from the supernatant using a mixture of 1:1 methanol:isopropanol in a 3:1 excess to the supernatant. This mixture was centrifuged at 5000 RPM for 5 min, after which the nanoparticles were resuspended in toluene. This procedure was repeated twice to obtain an optically clear and colorless dispersion.

Figure 11 Procedure for the seeded-growth synthesis of tetragonal bipyramidal anatase nanocrystals. For (a), (b) and (c), see text above. In part (a), (1) is the temperature sensor, (2) is a septum and (3) is a connection to the Schlenk line.
3. Experimental

3.1.3. *Synthesis of anatase nanorods*

In a three-neck flask, 124 mmol (36 g) of OLAC (solvent and surfactant) was degassed at 120°C under vacuum for 1h. Next, the flask was allowed to cool down to 100°C and 3.33 mmol (1 ml) of TTIP (Ti-precursor) was injected under an Ar atmosphere to produce a clear light yellow solution. After stirring for 10 min, either 5 ml of a 2 M TMAO (base) aqueous solution or 10 mmol (1.395 ml) of (water insoluble) Et₃N (base) followed by 5 ml of MilliQ was injected, resulting in a slightly turbid yellow-white solution. The mixture was left to stir under an Ar atmosphere for 6h at 100°C. After ~60 min a clear increase in solution viscosity was apparent and the solution had become turbid white. After 6h, the reaction mixture was allowed to cool down to room temperature. Contrary to the article⁵⁵, it was not possible to obtain a clear reaction mixture upon removal of water under vacuum. In the subsequent work-up procedure, the nanocrystals were precipitated by adding methanol (in a ratio of 2:1) to the reaction mixture followed by centrifugation at 4000 RPM for 3 min. The resulting white precipitate was washed 5 times with methanol and subsequently dispersed in toluene to produce optically clear colorless suspensions after sonication for 15 min. Dispersions in apolar solvents (i.e. toluene and chloroform) remained stable for more than two months.

3.1.4. *Synthesis of dopamine functionalised nanoparticles*

160 mg of dopamine was added, under stirring, to 30 ml of benzyl alcohol at room temperature. Subsequently, the flask was flushed with argon gas and transferred to a glovebox where 1.5 ml of TiCl₄ was added dropwise under intense stirring resulting in a deep red solution. This mixture was stirred under an Ar atmosphere for 3 days (72 h) at 80°C, producing a brown-red turbid suspension which was allowed to cool down to room temperature. Next, the suspension was centrifuged and the nanocrystals were washed five times with chloroform. Subsequently, the nanocrystals were suspended in MilliQ water. The pH was lowered to a pH of ~2 using diluted hydrochloric acid, producing optically clear yellow-brown suspensions after 15 min of sonication (Figure 12).

![Figure 12](image.png)

*Figure 12* Picture of a suspension of dopamine functionalised nanoparticles in water at a pH of 2.
3. Experimental

3.2. Ligand exchange

For the ligand exchange of oleic acid with APTES ((3-aminopropyl)triethoxysilane) (TCI, >98%) (Figure 13), a literature method for the ligand exchange of oleic acid with silanes on iron oxide nanoparticles was adapted (the amounts between brackets correspond to the standard procedure, it is indicated in the results and discussion section for specific cases if different amounts were used). The starting point for ligand exchange was an optically clear suspension of nanocrystals in toluene containing 100 mg of nano-powder (Figure 14 (a)). Subsequently, the amount of toluene was increased to a total of 25 ml and a certain amount of triethylamine (Aldrich, ≥99%) was added (3.56 mol Et3N/mol TiO2). Next, a small amount of MilliQ water (0.55 mol/mol TiO2) was added to hydrolyze the silane alkoxy groups. The flask was flushed with Ar gas and APTES (0.43 mol/mol TiO2) was injected. The mixture was left to stir at 50°C under an Ar atmosphere (for 5h). After this period, the mixture had become very turbid (Figure 14 (b)) and precipitate settled down on the bottom of the flask after standing for ~10 min without stirring. The suspension was centrifuged at 5000 RPM for 5 min, and the supernatant was discarded. The powder was washed three times with acetone to remove excess (unreacted) silane. Next, the powder was redispersed in MilliQ water. After sonication, a turbid suspension with a pH of 10.5 was obtained (Figure 14 (c)). The pH of this suspension was lowered using diluted hydrochloric acid to a pH of ~2, to obtain an optically clear dispersion (Figure 14 (d)).

![Figure 13](image1.png)

**Figure 13** Structure of (3-aminopropyl)triethoxysilane (APTES)

![Figure 14](image2.png)

**Figure 14** Suspensions obtained in different steps of the ligand exchange procedure. (a) Suspension of nanorods with OLAC in toluene. (b) Suspension of nanorods functionalised with APTES, in toluene (ligand exchange mixture). (c) Suspension of nanorods functionalised with APTES transferred to water after workup, at the initial pH of 10.3. (d) Suspension of nanorods functionalised with APTES, in water with the pH altered to ~2.
3. Experimental

In a separate experiment, in order to improve the stability of the suspensions at higher pH values, (3-trihydroxysilyl)propyl methylphosphonate (THPMP)\textsuperscript{66,67} (Sigma-Aldrich, 50 wt% in H\textsubscript{2}O) (88%) was added to the ligand exchange mixture 10 min after the addition of APTES in a ratio of 4:1 in volume with respect to THPMP.\textsuperscript{66} All other subsequent steps were carried out the same as for the ligand exchange procedure using only APTES, as detailed above.

3.3. Deposition of thin films on polymers

3.3.1. Surface treatment of the polymer substrate

The substrates used were PMMA substrates cut from a PMMA plate using a milling machine, into substrates of 2x4 cm\textsuperscript{2} or 2x2 cm\textsuperscript{2} and 2 mm thick.

3.3.1.1. H\textsubscript{2}SO\textsubscript{4} treatment

The procedure according to Brown et al.\textsuperscript{14} was followed. First the PMMA substrates were rinsed with MilliQ water, next with isopropanol and then again with MilliQ water. Subsequently they were sonicated in a 50\% (v/v) 2-propanol/MilliQ solution for 20 min. The substrates were dried and transferred to a 3M H\textsubscript{2}SO\textsubscript{4} solution. The substrates were left in the solution at 60\(^\circ\)C for 20 min. Afterwards, the substrates were rinsed with MilliQ water and dried.

3.3.1.2. Oxygen plasma treatment

First the PMMA substrates were rinsed with MilliQ water, next with isopropanol and then again with MilliQ water. Subsequently they were sonicated in a 50\% (v/v) 2-propanol/MilliQ solution for 20 min. Next, the substrates were dried and transferred to a plasma chamber that was filled with oxygen gas (O\textsubscript{2} pressure 0.8 mbar, power 100W). The substrates were subjected to the plasma for 2 min.

3.3.1.3. UV treatment

First the PMMA substrates were rinsed with MilliQ water, next with isopropanol and then again with MilliQ water. Subsequently they were sonicated in a 50\% (v/v) 2-propanol/MilliQ solution for 20 min. Next, the substrates were dried and placed 1.5 cm below an intense UV lamp (type Pen-Ray\textsuperscript{®} Mercury Lamp, Mid-IR, most intense at 245 nm) for 20 min up to 6h.

3.3.1.4. Contact angle measurements

The contact angle of the aqueous coating suspension (3.3.3) with the surface treated PMMA substrate was measured using the sessile drop method (see 7.3.10 in the appendix).
3. Experimental

3.3.2. Determination of the carboxylic acids surface density

In order to determine the surface density of carboxylic acid groups present on the PMMA substrates after surface treatment, the treated PMMA substrates were put in a 10 mM aqueous solution of EDC for 2h, at room temperature. Next, the substrates were removed from the solution and the residual EDC concentration was determined using UV-VIS spectroscopy (Figure A 1, in the Appendix). In order to link the absorbance of these EDC solutions to concentrations, a calibration curve (Figure A2) was constructed by measuring the absorbance at peak maximum (~212 nm) of EDC solutions of different known concentrations. The difference between the concentration of the EDC solution before and after the immersion of the PMMA substrates was used to calculate the amount of carboxylic acid groups per cm² of substrate, assuming a 1:1 reaction stoichiometry for the reaction between an EDC molecule and a carboxylic acid group on the substrate. This was corrected for physical adsorption on the substrate using the concentration difference obtained with a PMMA substrate that was not subjected to the H₂SO₄ treatment.

3.3.3. Linking of the nanoparticles to the polymer substrates via an amide bond

The procedure used to couple the APTES functionalised nanoparticles to the surface of the PMMA substrate was adapted from literature methods to couple biomolecules to PMMA substrates or to couple biomolecules to nanoparticles functionalised with APTES. 8,68,69

20 ml of an aqueous suspension of APTES functionalised nanorods in 0.1 M of MES buffer (Sigma-Aldrich, ≥ 99.5%) (a non-amine, non-carboxylate buffer) at a pH of 4.75 was prepared. Subsequently, a 10 times molar excess of EDC (TCI, > 98%) with respect to surface COOH groups on the PMMA substrate was added and the mixture was allowed to stir for 5 min. Next, a 25 times molar excess of NHS (Sigma-Aldrich, 98%) with respect to surface COOH groups was added, followed by another 5 min of stirring. Afterwards, the surface treated substrates were immersed in this coating suspension using the dip-coater apparatus and were left immersed in this suspension for 2 min, after which the substrates were removed from the suspension at a controlled speed (e.g. 50 mm/min). Next, the coated substrates were dried, either at 60°C for 1h in a drying furnace or alternatively using an IR lamp or a hotplate immediately after dip-coating (different temperatures were tried; see results and discussion). This was followed by a thermal treatment in a muffle furnace, consisting of heating up from room temperature to 180°C in 30 min, followed by 1h at 180°C and subsequently immediately removing the coated substrate from the furnace.
4. Results and discussion

4.1. Synthesis of titania nanocrystals

4.1.1. Overview of titania nanocrystal syntheses

Initially, the focus of this thesis was on finding literature syntheses to obtain spherical nanoparticles of the anatase crystal phase that are well dispersible in apolar solvents. The slow hydrolysis synthesis by Cozzoli et al.\(^5\) seemed a good choice in this regard. The procedure as it is described in the article was performed multiple times but it produced nanoparticles of a predominantly amorphous nature (as detailed in Table A1 (in the appendix), at a constant reaction temperature of 100°C and a reaction time of 48h, both TMAO and Et\(_3\)N were tried as bases and reactant concentrations were varied). As shown in Figure A3, no crystal phases can be distinguished in the powder XRD pattern. However, in TEM images, some crystalline nanoparticles could be detected (Figure 15 left, the lattice fringes are clearly visible) and a selected area diffraction (Figure 15 right) shows that the nanoparticles predominantly belong to the anatase polymorph (some spots can be indexed to the rutile polymorph). Raman measurements on powders (Figure 16) also indicate the presence of the anatase polymorph.\(^7\)

![Figure 15](image.png)

*Figure 15* (left) TEM image of nanoparticles obtained from the slow hydrolysis procedure (right) selected area diffraction pattern. (From a synthesis for 48h at 100°C using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC).
4. Results and discussion

![Raman spectrum](image)

**Figure 16** Raman spectrum obtained from the slow hydrolysis synthesis with the Raman-active modes\(^70\) of anatase indicated. (From a synthesis for 48h at 100°C using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC).

From the results of these measurements, it is clear that the procedure as it is described in the article results in nanoparticles with only a very limited crystallinity.\(^6\) Therefore, a number of synthesis parameters were varied in order to obtain nanoparticles with enhanced crystallinity. The reaction time was increased from 48h to 72h at 100°C, which did not result in sufficiently crystalline nanoparticles either. The reaction temperature was increased from 100°C to 110°C and 120°C, for 48h. The result of the synthesis at 110°C did not deviate from the results at 100°C. When the synthesis was carried out at 120°C, however, some clear differences could be observed. The nanoparticles obtained at 120°C were sufficiently crystalline to result in anatase reflections in a powder XRD pattern. As shown in Figure 17, the reflections match those of the reference spectrum of the anatase crystal phase. A second difference, is in the appearance of the reaction mixtures. At 100°C and 110°C, clear yellow-orange suspensions were obtained, whereas at 120°C a turbid dark brown suspension was obtained. When the nanoparticles were separated using centrifugation, at 100°C and 110°C white-yellow powders were obtained whereas at 120°C a dark brown powder was obtained. Also, there was a clear difference in the dispersibility of the resulting powders. Whereas the powders obtained at 100°C and 110°C could be easily dispersed in apolar solvents such as toluene and chloroform, this was not the case for the powder obtained at 120°C. Multiple washing procedures with (combinations of) different solvents (acetone, methanol, ethanol, acetonitrile, diethylether, chloroform) and different (combinations of) ligands (OLAC, OLAM, TOPO) were tried but it was not possible to obtain a clear and stable suspension.

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\(^6\) Note that an XRD pattern of powder obtained from the slow hydrolysis procedure is not shown in the article by Cozzoli et al. (and there is also no supplementary information provided). It is merely stated in the article that this XRD pattern is similar to another XRD pattern (for the fast hydrolysis procedure, see further) that is provided in the article.
4. Results and discussion

Figure 17 XRD pattern collected for a TiO$_2$ powder obtained via the slow hydrolysis synthesis at 120°C. (from a synthesis for 48h at 120°C using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC).

The difficulty with dispersing the nanoparticles obtained using this procedure might be linked to the degradation of oleic acid at the more elevated temperature. It is noted in the article$^{55}$ that if the amount of oleic acid was decreased below a certain threshold (partially replaced by a non-coordinating solvent), aggregation between the particles occurred leading to insoluble precipitates. Judging from the difference in color and appearance of the reaction mixtures, this indeed seemed plausible. An infrared spectrum of the suspension was measured and compared to infrared spectra of suspensions obtained from a similar synthesis at 100°C (Figure 18). From the assignment (Table 2) of the peaks in the spectra of the suspensions, it is clear that no drastic changes, apart from ester and carboxylate formation, occurred to the (majority of) oleic acid molecules for both reaction temperatures. (Oleic acid, its ester and its carboxylate seem to be the main components in these suspensions; vibrations belonging to other possible components present in the suspensions cannot be distinguished). As evidenced from the vibration at 3004 cm$^{-1}$, that is present in both spectra, oleic acid nor its ester were cleaved at the double bond (at least for the majority of the molecules). Because of the presence of the CH$_2$ rocking vibration at 722 cm$^{-1}$ in both spectra, it can be concluded that these molecules possess at least 4 sequential CH$_2$ groups. Also, the peaks belonging to CH$_2$-group symmetric and asymmetric stretching are significantly more intense than those belonging to CH$_3$, indicating the presence of a significantly larger fraction of CH$_2$-groups than CH$_3$-groups (corresponding to e.g. the presence of a long alkyl chain, such as in oleic acid).
The most obvious difference between the two spectra is the intensity of the peak at 1738 cm$^{-1}$, corresponding to the C=O stretch vibration of ester molecules, relative to the intensity of the peak at 1714 cm$^{-1}$, corresponding the C=O stretch vibration of carboxylic acid molecules. The peak at 1738 cm$^{-1}$ is relatively more intense in the spectrum of the suspension from the synthesis at 120°C (other peaks that can be assigned to the ester molecules are also relatively more intense, see Table 2). This indicates that the increased temperature lead to a larger amount of oleic acid molecules being esterified by ethylene glycol during the same time period (48h). The asymmetric and symmetric stretch vibrations of the carboxylate group at 1548 cm$^{-1}$ and 1410 cm$^{-1}$, respectively, are also a little less intense (relative to the C=O stretch at 1714 cm$^{-1}$) in the spectrum of the suspension obtained at 120°C, which might indicate less bound ligands per nanoparticle. Another possibility is the presence of less and/or bigger nanoparticles in the suspension obtained from the synthesis at 120°C, such that there is less surface area for the oleate molecules to bind on. No TEM analysis was performed on this sample, however, because of the complete insolubility of the powder.

Also the spectra of the powders are very similar, except for the presence of a peak at 1646 cm$^{-1}$ in the spectrum of the powder obtained from the synthesis at 120°C that is absent in the spectrum of the powder obtained from the synthesis at 100°C. This peak could correspond to the H-O-H bending of water adsorbed on the nano-powder. If this is the case, however, one could ask why no such peak is observed in the spectrum of nano-powder synthesized at 100°C (since the powders did not receive different workup procedures). It could also correspond to the C=O stretch of a tertiary amide. This tertiary amide could have been formed by a reaction between trimethylamine (which could be present due to thermal degradation of trimethylamine-N-oxide) and oleic acid. If it does correspond to a tertiary amide, only a relatively small amount (relative to oleic acid) was formed since no peak around 1646 cm$^{-1}$ can be distinguished in the spectrum of the suspension.
4. Results and discussion

**Figure 18** (left) FTIR spectra of suspensions obtained from the slow hydrolysis synthesis (using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC) at 100°C (green) and 120°C (blue). (right) FTIR spectra of powders obtained from the same slow hydrolysis procedures at 100°C (green) and 120°C (blue) after washing 5 times with methanol.

**Table 2** Assignment of peaks in the FTIR spectra of suspensions (**Figure 18**, left) and powders (**Figure 18**, right) from the slow hydrolysis procedure (using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC) at 100°C and 120°C.

<table>
<thead>
<tr>
<th><strong>Suspensions</strong></th>
<th><strong>Number</strong></th>
<th>peak position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3004</td>
<td>$\nu$(C=C-H)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2954</td>
<td>$\nu_{as}$(CH$_3$)</td>
<td></td>
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<td>3</td>
<td>2920</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>2852</td>
<td>$\nu_{s}$(CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2360</td>
<td>CO$_2$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1738</td>
<td>$\nu$(C=O) ester</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1714</td>
<td>$\nu$(C=O) acid</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1550</td>
<td>$\nu_{as}$(COO$^-$)</td>
<td></td>
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<tr>
<td>9</td>
<td>1462</td>
<td>$\delta_{s}$(CH$_3$)</td>
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<tr>
<td>10</td>
<td>1410</td>
<td>$\nu_{s}$(COO$^-$)</td>
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<tr>
<td>11</td>
<td>1378</td>
<td>$\delta_{s}$(CH$_3$)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1278</td>
<td>C-C-O acid</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1174</td>
<td>$\delta$(C-O)</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1086</td>
<td>$\nu$(C-O)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>722</td>
<td>$\delta_{\beta r}$(CH$_2$)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Powders</strong></th>
<th><strong>Number</strong></th>
<th>peak position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3004</td>
<td>$\nu$(C=C-H)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2920</td>
<td>$\nu_{as}$(CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2852</td>
<td>$\nu_{s}$(CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1646</td>
<td>H-O-H bending/ $\nu$(C=O) tertiary amide</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1538</td>
<td>$\nu_{as}$(COO$^-$)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1442</td>
<td>$\nu_{s}$(COO$^-$)</td>
<td></td>
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<tr>
<td>7</td>
<td>1088</td>
<td>$\nu$(C-O)</td>
<td></td>
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<tr>
<td>8</td>
<td>904</td>
<td>$\delta_{\beta r}$(CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>788</td>
<td>C=C stretch</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>722</td>
<td>$\delta_{\beta r}$(CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>628</td>
<td>OH rock</td>
<td></td>
</tr>
</tbody>
</table>
Apart from changing the reaction temperature, the bases and the reagent concentrations, the original procedure was also carried out under water-free conditions. Since the principle of the slow hydrolysis method is the slow release of water through the esterification of oleic acid by ethylene glycol, it was thought that the presence of water in the reagents might make the synthesis uncontrolled (in the article it is not mentioned, however, that the reagents were made water-free). To this end, oleic acid and ethylene glycol were dried under vacuum, triethylamine was dried using molecular sieves in a glovebox and a new bottle of TTIP was opened in the glovebox. In addition, the mixing of the reagents was carried out in the glovebox. No difference in crystallinity (judging from the absence of reflections in a powder XRD pattern) was obtained using this water-free procedure (at 100°C).

Next to syntheses conducted using conventional heating, a microwave-based approach to the slow hydrolysis was also tested. Using this approach, similar results were obtained. The powders obtained at lower temperatures (<140°C) were of very low crystallinity and those obtained at higher temperatures were crystalline but could not be dispersed (see Table A1 for the reaction times and temperatures tested). A microwave post-treatment of suspensions obtained using conventional heating at 100°C for 48h using temperatures and reaction times below which non-dispersible nanoparticles were known to be formed, this did resulted in crystalline nanoparticles either.

Other literature synthesis procedures for spherical anatase nanoparticles were also carried out, the procedures and results of which are summarized in Table A1. Among the procedures tried for spherical nanocrystals, only a synthesis by the group of Niederberger resulted in dispersible crystalline spherical nanoparticles. Two other procedures, resulting in non-spherical nanocrystals, were also explored. The results of these three procedures are discussed in the following sections.

4.1.2. Seeded-growth synthesis of tetragonal bipyramidal nanocrystals

This seeded-growth synthesis produces tetragonal bipyramidal anatase nanocrystals of ~25 nm along the longest axis, as shown in Figure 19 left and Figure 20 left. In the XRD pattern (Figure 20 right), no crystalline phases other than the anatase crystal phase could be detected, the selected area diffraction pattern could be indexed for reflections belonging to anatase (Figure 19 right). The crystal phase of the nanocrystals can also be derived from the spacing of lattice fringes as visible in the HRTEM images (Figure A4 left). A lattice spacing of 0.35 nm is obtained, this matches with the spacing between (101) planes of the anatase crystal lattice (corresponding to the most intense peak in the XRD pattern).
4. Results and discussion

The percentage crystallinity was determined to be 73.5% using Rietveld refinement (corrected for the presence of organic material in the sample using TGA). The yield of the synthesis was calculated to be 58%. This relatively low yield is thought to be the result of the workup procedure, where the non-dispersible part of the nanocrystals is discarded. The suspensions of the nanocrystals in toluene remain stable for more than a month.

**Figure 19** (left) TEM image of titania nanoparticles obtained using the procedure by Murray et al. (right) Selected area diffraction pattern of the nanoparticles, indexed for the anatase crystal phase.

**Figure 20** (left) HRTEM image of a single nanocrystal (right) Powder XRD pattern of nanoparticles obtained using the procedure by Murray et al. (reflections not indexed to anatase belong to the Si sample holder).
4. Results and discussion

4.1.3. Synthesis of anatase nanorods

The fast hydrolysis synthesis by Cozzoli et al. produces nanorods of ~20 nm in length and ~2.5 nm in diameter (Figure 21). Raman (Figure 22 left) and XRD (Figure 22 right) measurements indicate that the nanorods belong to the anatase crystal phase.\(^d\) The results are given here for the procedure using TMAO, for an XRD pattern and a HRTEM image from the procedure using Et\(_3\)N as a base, see respectively Figure A5 and Figure A6. Using Rietveld refinement, a percentage crystallinity of 45.5%, corrected using TGA, was obtained. The yield of the synthesis was calculated to be 74%.

The fact that nanorods were obtained can also be derived from the diffractogram (Figure 22 right). It is clear that the 004 reflection is more intense relative to the 101 reflection than is the case for the reference pattern, pointing to the presence of nanorods with a preferred growth orientation along the c-axis of the anatase crystal lattice. The infrared spectrum of powder obtained from the fast hydrolysis after washing (Figure A7) is very similar to the infrared spectrum of powder from the slow hydrolysis procedure (Figure 18 right), apart from the absence of peaks corresponding to the ester of OLAC and ethylene glycol. This is as expected since ethylene glycol is not used in the fast hydrolysis procedure. All the peaks in this spectrum can be assigned to vibrations of oleic acid (Table A2). The suspensions of nanorods in toluene remain stable for more than three months.

![HRTEM image of nanorods obtained by the fast hydrolysis procedure. The yellow rectangle encompasses a single nanorod. From a synthesis for 6h at 100°C using 3.3 mmol TTIP, 10 mmol TMAO in 5 ml MilliQ (2 M) and 124 mmol OLAC.](image)

\(^d\) In the powder XRD pattern, reflections at ~30.5° and ~45° 2\(\theta\) might indicate the presence of a fraction of brookite. None of the other reflections of brookite in the measured range could be distinguished (possibly due to overlap with reflections belonging to anatase). Also, in the Raman spectrum, none of the characteristic vibrations of brookite can be distinguished.\(^d\)
4. Results and discussion

**Figure 22** (left) Raman spectrum with the Raman-active modes of anatase indicated and powder XRD pattern (right) of powder from the fast hydrolysis. (From a synthesis for 6h at 100°C using 3.3 mmol TTIP, 10 mmol TMAO in 5 ml MilliQ (2 M) and 124 mmol OLAC).

4.1.4. Synthesis of dopamine functionalised nanoparticles

This synthesis produces semi-spherical nanoparticles of 5-7 nm in diameter (**Figure 23**) of the anatase crystal phase (**Figure 24**). A percentage crystallinity of 83.2% was obtained using Rietveld refinement. The yield of the synthesis was calculated to be 81%. The powder obtained from this synthesis procedure has a characteristic brown-red color (that remains after the workup procedure, see **Figure A8**), which points to the presence of dopamine bound to the surface of the anatase nanoparticles. This color is the result of a ligand-to-metal charge transfer band located between 420 and 430 nm. The charge transfer is an excitation from a catechol π orbital to the Ti^{4+} (3d) levels at the bottom of the TiO₂ conduction band.

All the peaks in an FTIR spectrum (**Figure 25 left**) of powder obtained after the workup procedure can be assigned to dopamine bound to the anatase nanoparticles (**Table 3**). The spectrum of bound dopamine differs from that of free dopamine, in that the binding of dopamine to titania via the oxygen atoms of the two adjacent hydroxyl groups (**Figure 25 right**) affects the in-plane bending vibrations of the hydroxyl groups (δ_{C-OH}) present at 1320 cm⁻¹ in free dopamine, resulting in a decrease in intensity of this band. Indeed, this band cannot be distinguished in the FTIR spectrum of dopamine functionalised nanoparticles.
4. Results and discussion

**Figure 23** HRTEM image of dopamine functionalised nanoparticles (the yellow ellipses encompass single nanoparticles, the lattice fringes can be seen)

**Figure 24** (left) Powder XRD pattern and (right) selected area diffraction pattern of dopamine functionalised nanoparticles.
4. Results and discussion

Figure 25 (left) FTIR spectrum of powder obtained from the BnOH synthesis of dopamine functionalised nanoparticles after washing. (right) Possible binding structure of dopamine to the surface of a titania nanoparticle.

Table 3 Assignment of peaks in FTIR spectrum of dopamine functionalised nanorods

<table>
<thead>
<tr>
<th>Peak number</th>
<th>peak position (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3250</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>2</td>
<td>3062</td>
<td>C-H stretch aromatic</td>
</tr>
<tr>
<td>3</td>
<td>2360</td>
<td>CO(_2)</td>
</tr>
<tr>
<td>4</td>
<td>1618</td>
<td>(\beta(\text{NH}^3+))</td>
</tr>
<tr>
<td>5</td>
<td>1492</td>
<td>aromatic C=C stretch</td>
</tr>
<tr>
<td>6</td>
<td>1430</td>
<td>symmetric N—H mode of NH(^+)</td>
</tr>
<tr>
<td>7</td>
<td>1272</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>8</td>
<td>1212</td>
<td>C-N stretch</td>
</tr>
<tr>
<td>9</td>
<td>1200-1000</td>
<td>in plane bending phenolic and CH/CH(_2) groups</td>
</tr>
<tr>
<td>10</td>
<td>908</td>
<td>NH(^+_3) rocking</td>
</tr>
<tr>
<td>11</td>
<td>746</td>
<td>aromatic C-H bending</td>
</tr>
</tbody>
</table>

The stability of the suspensions as a function of the pH was determined visually. Below a pH of 3.5 the suspensions remained clear, between pH 4 and 5 the suspension became slightly turbid, from pH 5 to pH 11 agglomerates were present throughout the suspension, at pH 12 the agglomerates dissolved but the suspension remained slightly turbid. This pH dependent stability can be explained by the nature of the stabilization of the nanoparticles, namely charge stabilization. The primary amine functionality of the dopamine ligands is positively charged at low pH values (NH\(^+_3\)), such that the dopamine functionalised nanoparticles possess a positive surface charge. As a result, an electric double layer is formed around these nanoparticles in water. These double layers start to overlap when the nanoparticles approach each other, resulting in repulsion. Because the ionization of the amine groups is pH dependent, so is the surface charge on the nanoparticles. If the net charge on the surface of the nanoparticles approaches low values (at higher pH), the repulsion loses to attractive (Van Der Waals) forces and the nanoparticles agglomerate.
4. Results and discussion

In order to quantify the stability of charge stabilized suspensions, zeta potential measurements are often used. An absolute zeta potential of 30 mV is often taken as the lower limit for stability. At a pH of ~2, the average zeta potential of the nanoparticles in the suspension was determined to be +35.8 mV (Figure A9). DLS measurements at a pH of 2 indicate partial aggregation of the dopamine functionalised nanoparticles (Figure A10). The peak maximum of the size distribution (by volume) is found at 7.5 nm, which agrees well with TEM images where single nanoparticles with a size between 5 and 7 nm can be distinguished. Therefore, the peak at 7.5 nm in the DLS size distribution corresponds to the non-aggregated single nanoparticles, whilst the broader shoulder in the size distribution, towards higher sizes, corresponds to aggregates. Despite this aggregation, at a pH of 2, neither turbidity nor precipitation could be noticed visually. A DLS measurement was performed on the suspension after 1 month (Figure A11) and it is clear that the nanoparticles have further aggregated during this period. However, this partial aggregation did not result in turbidity nor the formation of a precipitate.

4.2. Ligand exchange

After the ligand exchange of OLAC by APTES on nanorods obtained from the fast hydrolysis synthesis, as described in the experimental section (3.2), the suspension of nanorods in toluene has become turbid and a precipitate forms upon standing. This is a first indication that ligand exchange was successful, such that the original OLAC ligands that provided steric stabilization to the nanorods were exchanged for the significantly shorter APTES ligands that do not provide sufficient steric stabilization for the nanorods to be stabilized in toluene. The resulting precipitate was washed and transferred to water. In water, a turbid suspension is obtained with an initial pH of 10.3. Upon lowering the pH using diluted hydrochloric acid, the suspension changes from turbid to clear. The optimal pH (on the basis of zeta potential measurements and visual observations; see further) was found to be ~2. This pH dependent dispersibility indicates that the nanorods are charge stabilized. Measurements of the zeta potential of the aqueous suspension as a function of the pH (Figure 26), show that the nanorods possess an isoelectric point (pI) between pH 10.5 and 11. This is close to the isoelectric point of 10.4 reported for CoFe$_2$O$_4$ nanoparticles functionalised with APTES. The pI of bare anatase nanoparticles (due to the presence of an equal amount of Ti-OH$_2^+$ and Ti-O$^-$ groups on the surface) is reported in literature to be in the range of 4.7-6.7 (For commercial the titania nanoparticles Degussa P25 it is reported as 6.4). Clearly, the measured pI does not correspond to that of bare anatase nanoparticles.
4. Results and discussion

**Figure 26** Zeta potential of suspensions of APTES bound nanorods as a function of pH (pH adapted using diluted HCl and diluted NaOH), the data points are averages over 3 measurements at each pH value. The suspensions were obtained from a ligand exchange procedure using 100 mg of OLAC functionalised nanopowder, 1.07 mmol of APTES, 8.9 mmol of Et$_3$N and 1.39 mmol of H$_2$O in 25 ml of toluene.

The stability of the suspensions as a function of the pH was also assessed visually; below a pH of ~5 the suspension was clear, between pH 5 and 8 the suspension immediately became turbid, between pH 8 and 10 the suspension became very turbid and between pH 10 and pH 12 agglomerates were visibly present throughout the suspension. Only at a pH of 2, the average zeta potential reaches a value >30 mV (+30.9 mV), indicating that long-term stability might only be obtained at this pH.

DLS measurements were performed on a suspension of nanorods with OLAC in toluene (Figure A 12) and on a suspension of nanorods with APTES in water at pH ~2 (Figure A 13). A first observation, is the broadness of the size distributions. This does not necessarily mean that the nanorods are very polydisperse, nor does it necessarily point to aggregation. One must take into account that nanorods feature both translational as well as rotational diffusion and that both motions are superimposed in the decay of the time correlation function from which the size of the nanorods is extracted. The algorithm that extracts the size distribution from the correlation function even showed two peaks for some measurements (as shown in Figure A 14). This was explained in literature for gold nanorods; the distribution at small sizes corresponds to the rotational diffusion of the nanorods and the size that is obtained corresponds to that of a (hypothetical) spherical nanoparticle with the same translational diffusion coefficient as the rotational diffusion coefficient of the nanorods. The distribution at bigger sizes corresponds to the translational diffusion coefficient of the nanorods and the size corresponds to that of an equivalent spherical particle with the same translational diffusion coefficient. For most measurements, the algorithm apparently ‘merges’ these peaks into one broad peak. Therefore, it is difficult to draw conclusions about the presence or absence of aggregation of the nanorods on the basis of DLS measurements.
4. Results and discussion

With these restrictions in mind, one can see that the distribution of the nanorods with APTES in water and the distribution of the nanorods with OLAC in toluene are similar. This indicates that at least there are no big differences in the degree of aggregation for nanorods with APTES in water as compared to those with OLAC in toluene. Aqueous suspensions at a pH of 2 remained visibly stable for more than five weeks (i.e. no turbidity or precipitation was noticed). After five weeks the zeta potential was measured to be +28.6 mV, the size distribution (Figure A 15) had shifted to slightly larger sizes (the Z-average size changed from 30 nm to 34 nm). This indicates that slight aggregation might have occurred. At a pH of ~5, the suspensions remain visibly stable for 1 day (24h) at room temperature; when put in a refrigerator at 7°C the suspensions remained stable for more than one week. When turbid suspensions were obtained by increasing the pH, these suspensions could be made clear once more by lowering the pH again to ~2. Hence, the nanorods can be precipitated and resuspended reversibly in water. It is important to note that APTES functionalised nanorods can form clear suspensions at higher pH values than is the case for the dopamine functionalised nanoparticles (section 4.1.4). The APTES functionalised nanorods form clear suspensions at pH values below 5, whereas the dopamine functionalised nanoparticles only form clear suspensions below a pH of 3.5.

Next to the visual and zeta potential trends as a function of the pH, also FTIR spectra indicate that the exchange of OLAC by APTES was successful. The peaks that have been assigned (Table 4) to OLAC (Figure A7) have disappeared and peaks that can be assigned (Table 5) to vibrations of (bound) APTES appear (Figure 27 left). For comparison, a reference sample was prepared (Figure 27 right). This reference sample was obtained using an identical ligand exchange procedure, but in the absence of the titania nanorods (i.e. all other reagents were mixed together in the same ratios and left to stir at the same temperature for the same amount of time).

Figure 27 (left) FTIR spectrum of powder obtained from the ligand exchange of OLAC with APTES. The powder was obtained from a suspension of a ligand exchange procedure using 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et₃N and 0.69 mmol of H₂O in 25 ml of toluene. (right) FTIR spectrum of powder obtained from a reference procedure using the same amounts of reagents but in the absence of nanopowder.
The powder obtained from this reference sample is thought to correspond to clusters of silane molecules formed through condensation of the APTES molecules with each other (Si-O-Si bond formation). As can be seen, the spectrum of silane clusters differs from that of APTES bound to the titania nanorods. The most important peak in the spectra of the APTES functionalised nanorods, is the peak with a maximum at 910 cm\(^{-1}\). This peak has been assigned in literature to the characteristic stretching vibration of Ti-O-Si bonds\(^ {20,82-84} \) and is indeed absent in the spectrum of the silane clusters obtained from the reference procedure. In this spectrum, there is a peak present at \( \sim 920 \text{ cm}^{-1} \), which could be assigned to silanol (Si-OH) asymmetric stretching\(^ {85} \). If silanol species are also still present in the mixture obtained from the ligand exchange procedure on the nanorods, the peak corresponding to the silanol asymmetric stretch will overlap with the peak belonging to Ti-O-Si. The peak assigned to Ti-O-Si stretching is indeed quite broad (860-945 cm\(^{-1}\)), but no shoulder belonging to Si-OH can be distinguished.

**Table 4** Assignment\(^ {20,64,85-92} \) of peaks in the FTIR spectrum of powder obtained from the ligand exchange of OLAC by APTES.

<table>
<thead>
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<th>Peak number</th>
<th>peak position (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1562+1484</td>
<td>NH(_2) deformation modes</td>
</tr>
<tr>
<td>2</td>
<td>1432</td>
<td>( \delta_{\text{RS}} \text{(CH})_{2} ) next to NH(_2)</td>
</tr>
<tr>
<td>3</td>
<td>1300</td>
<td>CH(_2) wagging</td>
</tr>
<tr>
<td>4</td>
<td>1120</td>
<td>Symmetric Si-O + C-N</td>
</tr>
<tr>
<td>5</td>
<td>1040</td>
<td>Antisymmetric Si-O-Si</td>
</tr>
<tr>
<td>6</td>
<td>910</td>
<td>Ti-O-Si + (Si-OH)</td>
</tr>
<tr>
<td>7</td>
<td>764</td>
<td>CH(_2) rock in Si-CH(_2)</td>
</tr>
</tbody>
</table>

**Table 5** Assignment of peaks\(^ {20,64,85-92} \) in FTIR spectrum of powder from an identical exchange procedure carried out in the absence of TiO\(_2\) nanorods.

<table>
<thead>
<tr>
<th>Peak number</th>
<th>peak position (cm(^{-1}))</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1562+1484</td>
<td>NH(_2) deformation modes</td>
</tr>
<tr>
<td>2</td>
<td>1406</td>
<td>CH(_2) bending in Si-CH(_2)</td>
</tr>
<tr>
<td>3</td>
<td>1308</td>
<td>CH(_2) wagging</td>
</tr>
<tr>
<td>4</td>
<td>1120</td>
<td>Symmetric Si-O + C-N</td>
</tr>
<tr>
<td>5</td>
<td>1020</td>
<td>Antisymmetric Si-O-Si</td>
</tr>
<tr>
<td>6</td>
<td>920</td>
<td>Si-OH</td>
</tr>
<tr>
<td>7</td>
<td>860</td>
<td>Si-O stretch of ( \equiv \text{Si} - \text{O} - \text{Si} \equiv ) bridges</td>
</tr>
<tr>
<td>8</td>
<td>762</td>
<td>CH(_2) rock in Si-CH(_2)</td>
</tr>
<tr>
<td>9</td>
<td>692</td>
<td>Si-C</td>
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</tbody>
</table>
It was observed that a larger amount of precipitate (certainly in volume, but also in weight: 183 mg) was present after the ligand-exchange procedure than the amount of OLAC functionalised nanorod-powder that was added at the beginning of this procedure (100 mg). This was hypothesized to be the result of condensation of the hydrolyzed silane molecules with each other, such that siloxane bonds (Si-O-Si) are formed between them, resulting in the formation of silane clusters (as was the case in the reference sample prepared for FTIR).

This hypothesis was tested using X-ray fluorescence (XRF) measurements. These measurements provide the molar percentage of titanium and silicon in the powders. The molar ratio of Si:Ti was measured to be 1:1.15 for the standard exchange procedure. Assuming that all the nanorods are anatase cylinders of 20 nm in length and 2.5 nm in diameter and assuming that all the APTES molecules (each containing only a single Si atom) are bound and that the ligands are distributed homogeneously over the nanorod, this would result in 20.5 APTES molecules per nm² of nanorod surface area. To evaluate if this value is reasonable for a monolayer of APTES around the nanorods, one has to have an idea of the ligand density of silanes expected for a monolayer. A ligand density for a monolayer of APTES is given as 4-5 silanes per nm² in literature.\(^93-95\) This value is much lower than the value that was calculated using the Si:Ti ratio obtained via XRF. In the article by De Palma et al., the ligand density of APTES on CoFe₂O₄ was estimated as 28.9 per nm², this (even higher) value was attributed to a cross-linked multilayer of APTES around the nanoparticles.\(^27\) An alternative explanation for this high value would be the presence of silane clusters. XRF, being an elemental analysis technique, cannot distinguish between a mixture of silane clusters with titania nanorods capped with a monolayer of silane molecules on the one hand and titania nanorods capped with a ‘thick’ layer of silane molecules (in the absence of clusters) on the other hand.

To distinguish between these possibilities, TEM, STEM and EDX measurements were performed. EDX measurements confirmed the presence of silicon and titanium, but in the STEM and TEM images the silanes around the nanorods could not be distinguished (Figure A 16 and Figure A 17). The APTES molecules are mostly organic (apart from the silicon atom), in order to distinguish these molecules around the nanorods one would certainly need to go to the highest resolution, but then the intense electron beam causes the organic material (APTES around the rods and possibly silane clusters) to burn up. An XRD pattern of powder obtained from the ligand exchange procedure was measured. As shown in Figure A18, the reflections correspond to the anatase crystal phase.
An NMR analysis of a suspension of nanorods in water after ligand exchange was performed (see section 7.3.5, in the appendix, for theoretical and technical details of the measurements). In the 1D $^1$H-spectrum (Figure 28 left) the resonances can be assigned to APTES molecules (0.6 ppm: $\text{H}_2\text{C-Si}$ in free APTES; 0.7 ppm $\text{H}_2\text{C-Si}$ in bound APTES; 1.7 ppm: $\text{Si-CH}_2\text{-CH}_2\text{-CH}_2$ in free and bound APTES; 2.9 ppm: $\text{H}_2\text{C-NH}_3^+$ in free and bound APTES; 3.2 ppm: $\text{H}_2\text{O}$; 2.1 ppm: acetone; the small resonances between 1 ppm and 1.5 ppm are related to unknown impurities that also seem to be bound). The resonances corresponding to bound APTES are clearly broadened when compared to the resonances of free APTES molecules, this is due to efficient transverse ($T_2$) relaxation of the protons in the bound ligands leading to broad signals. This is confirmed by the NOESY spectrum (Figure 28 right), where the broad resonances show negative cross peaks whilst the sharp resonances show positive cross peaks. For slowly tumbling molecules (such as ligands bound to the surface of a NP) negative cross-peaks are observed between dipolar coupled protons, whereas for fast tumbling molecules (free ligands) positive cross-peak are observed.

Figure 28 (left) $^1$H-NMR spectrum of nanorods in $\text{D}_2\text{O}$ (right) 2D NOESY spectrum of nanorods in $\text{D}_2\text{O}$. The nanorods were synthesized using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et$_3$N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et$_3$N and 0.69 mmol of $\text{H}_2\text{O}$ in 25 ml of toluene.

From the 2D DOSY spectrum, it is found that the broad resonances correlate with a diffusion coefficient of $2.5 \times 10^{-10}$ m$^2$/s and the sharp resonances with a diffusion coefficient of $1.3 \times 10^{-9}$ m$^2$/s. The diffusion coefficient of $1.3 \times 10^{-9}$ m$^2$/s, corresponding to the sharp resonances, is linked to free APTES molecules. To extract size information from the diffusion coefficient of $2.5 \times 10^{-10}$ m$^2$/s, corresponding to the broad resonances, we need to take into account that the nanorods are non-spherical particles. Assuming a cylindrical shape, a formula that links the translational diffusion coefficient to the dimensions of the cylinder (analogous to the Stokes-Einstein equation for spheres) has been proposed. The diffusion coefficient depends on two characteristics of the cylinders, the length and the aspect ratio (length/diameter).
4. Results and discussion

From TEM measurements, an aspect ratio of 8 is obtained for the nanorods. Together with the experimental diffusion coefficient, a length of 4.8 nm is obtained through this formula. This does however not correspond to the dimensions of the nanorods as obtained from TEM measurements. The diffusion coefficient that would be expected for nanorods of 20 nm in length and 2.5 nm in diameter is calculated as \(6.0 \times 10^{-11} \text{ m}^2/\text{s}\), significantly smaller than the diffusion coefficient obtained from DOSY. Therefore, it is thought that the broad resonances correspond to silane clusters. If the Stokes-Einstein equation is used to calculate the diameter of these (presumably spherical) clusters, a diameter of 2.4 nm is obtained.

![2D DOSY of nanorods (with silane clusters) in D_2O. The nanorods were synthesized using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et3N and 0.69 mmol of H2O in 25 ml of toluene.](image)

The absence of resonances corresponding to APTES bound to the nanorods is thought to be linked to excessive line broadening of these resonances due to reduced mobility of the groups close to the surface of the nanorods. The linewidth of the resonances is known to increase significantly with increasing proximity to the surface of a nanoparticle and more so if the size of the nanoparticle to which the ligands are bound increases. It must be noted that APTES molecules on the surface of the silane clusters can be detected whilst APTES bound to the nanorods could not be detected. This can be explained by the dependence of the \(T_2\) relaxation time constant on the size of a molecule (and by extension on the size of the entire entity), it appears that the silane clusters are small enough such that the resonances are not too broadened to be detectable.
This effect was shown by Hostetler et al. for gold nanoparticles functionalized with dodecanethiol\textsuperscript{97}, where it was clearly seen that increasing the size of the nanoparticles from 0.65 nm to 2.8 nm has a significant effect on the broadness of the resonances closest to the surface. The APTES molecules are small and the nanorods are bigger than these gold nanoparticles, which makes it plausible that the resonances of the bound APTES molecules are broadened to an extent as to become invisible (i.e. broadened to an extent such that the signal to noise ratio becomes so low that the resonances disappear into the background).

A possible method that could be used to prove the presence of APTES on the nanorods, using NMR, would be to couple (e.g. via an amide bond) molecules with a long alkyl chain to the APTES molecules bound to the nanorods, such that the resonances belonging to the protons of the alkyl chain (further away from the surface of the nanorods) should be distinguishable.

It must be noted that the silane clusters could not be distinguished using DLS. It is possible that these small, mostly organic, clusters could not be detected using DLS because of their significantly lower scattering power as compared to the bigger anatase nanorods.

In summary, indications that the ligand exchange was successful are the pH dependent dispersibility of the nanorods in water after the ligand exchange procedure, the zeta potential as a function of pH (with a pI that closely matches the literature value) and FTIR measurements. Moreover, DLS measurements on aqueous suspensions and (S)TEM images obtained from these suspensions clearly show the presence of the dispersed nanorods.

The procedure to obtain the aqueous suspensions, from the synthesis of the nanorods to dispersing the nanorods in (acidic) water to obtain clear suspensions, was found to be very reproducible (it was reproduced more than 10 times).

An identical ligand exchange procedure was used starting from a suspension of tetragonal bipyramidal nanocrystals (from the synthesis by Murray), but no clear suspension in water could be obtained. An FTIR spectrum on powder obtained from the ligand exchange mixture (Figure A 19) is identical to the spectrum of APTES clusters obtained from the reference procedure which indicates that ligand exchange was not successful such that the APTES molecules could only react with each other and only silane clusters were formed. It is probable that oleylalcohol is present on the surface of these nanocrystals next to OLAC (since it is used as a co-surfactant in the synthesis). Possibly, these oleylalcohol ligands could not be exchanged for APTES.
4. Results and discussion

4.3. Deposition of thin films on polymers

A first step to obtain a titania thin film on a polymer substrate, is the surface treatment of the polymer substrate (section 4.3.1). This surface treatment should activate the polymer surface (i.e. induce the presence of carboxylic acids with which the primary amine group of APTES can react), as well as improve the wettability of the substrate. Next, the surface concentration of these groups needs to be determined (section 4.3.2) in order to select the amount of coupling reagents (EDC and NHS) to be used. The next step is the coupling of the nanoparticles to the activated surface of the polymer (section 4.3.4). Once a layer of covalently coupled nanoparticles is obtained, a second (thicker) layer containing ‘bare’ nanoparticles can be coated on top of the first layer in a next step (which therefore serves as a kind of buffer layer, next to a coupling layer). Schematically, these steps are illustrated in Figure 30.

Figure 30 Schematic representation of the steps to obtain a titania thin film on a PMMA substrate. The PMMA substrate (1) is surface modified to obtain carboxylic acid functionalities (2). The nanocrystals are coupled to the surface through a chemical reaction between the carboxylic acids and the ligands on the nanocrystals (3), such that a layer of coupled nanoparticles (4) is formed. A second thicker layer of ‘bare’ (ligand free) nanoparticles (c) can be deposited on the first layer (b), forming a titania thin film on the polymer substrate (a).
4. Results and discussion

4.3.1. Surface treatments

The surface treatment should serve two purposes; it should enhance the wettability of the substrate and it should induce the presence of carboxylic acid groups on the surface of the substrate. Given the polar nature of carboxylic acid groups, an increase in surface carboxylic acid groups should also result in an enhanced wettability with the aqueous suspensions.

The contact angle of the (aqueous) coating suspension on untreated PMMA (cleaned with MilliQ water and isopropanol) was measured to be 79.0°±3.4° (an average over 9 measurements spread over the substrate), a high value as expected for the hydrophobic PMMA surface. The contact angle with H2SO4 treated PMMA substrates was measured to be 76.3° ± 1.4°. This is only a slight improvement, in the article by Brown et al. the contact angle did likewise only decrease by a small amount (by 7°) after the H2SO4 treatment.

The wetting could be improved by adding ethanol to the coating suspension, but the volume percentage that could be used was limited by the stability of the suspensions, related to the lower polarity of ethanol as compared to water (the dielectric of the ethanol/water mixture is 24.3, whilst that of water is 78.5 at 25°C). A volume percentage up to 15% could be used without resulting in immediate turbidity. In this way, the contact angle on H2SO4 treated PMMA could be decreased to 49.9° ± 1.8°. This can be explained by the lower surface tension of the ethanol/water mixture (~47 mN/m at 25°C)100 as compared to water (~72 mN/m at 25°C)100, which in turn decreases the contact angle with the substrate.

Because of the importance of the wettability of the substrate to obtain more homogeneous coatings (see section 4.3.5.2), different surface treatments were evaluated. UV-treatment has been used in literature to improve the wettability of PMMA substrates.15 It was also used specifically to induce the presence of carboxylic acid groups on the surface of the substrate such that an amide bond could be formed with amine-modified oligonucleotides.101 Under UV radiation, radicals are formed due to bond breaking (photo-degradation). Polar groups, such as carboxylic acids, are formed on the surface of the substrate due to reaction with oxygen and/or water molecules from the air. The increase in the amount of polar surface groups decreases the contact angle with the aqueous coating suspension. UV-irradiation had a significant effect on the wettability of the surface of the substrate, as shown in Figure 31 and Figure 32, the contact angle decreased from 79.0° ± 3.4° for untreated PMMA to 25.2° ± 0.7° after 20 min, 20.8° ± 1.2 after 2h, 12.8° ± 0.99° after 3h and 6.3° ± 0.9° after 6h of irradiation.
4. Results and discussion

A downside to this surface modification procedure, is the slight discoloration (yellowing) caused by prolonged intense UV irradiation of the PMMA substrates. This has been linked to the formation of double bonds due to side-chain scission.\textsuperscript{102} For the majority of the substrates to be coated, a compromise was taken at 2h of irradiation.

![Figure 31](image)

**Figure 31** Pictures of a droplet of the coating suspension on a PMMA substrate not irradiated (left), irradiated for 20 min (middle) and 6h (right) using a UV lamp.

A PMMA substrate treated for 20 min under UV, was subjected afterwards to the H\textsubscript{2}SO\textsubscript{4} cleaning procedure as described in section 3.3.1.1. The contact angle was measured to be 68° ± 5.2°. The contact angle had thus significantly increased again as compared to the contact angle of ~25° obtained by UV treatment alone. This suggests that the thin surface layer that was most significantly modified by the UV irradiation was etched away by the H\textsubscript{2}SO\textsubscript{4} surface treatment leaving behind a layer that was only slightly UV modified (but still enough to decrease the contact angle from 79.0° for untreated PMMA to 68°). This indicates that indeed only the top layer of the substrates is significantly modified by the UV-treatment, as suggested in literature.\textsuperscript{103,104}

To test if the wettability of the UV treated substrates changes over time, the contact angle of a sample treated for 20 min under UV was measured again after being stored for 5h in a sealed petri-dish. The contact angle did not increase drastically (from 25.2° ± 0.7° to 28.4° ± 2.99°).

![Graph](image)

**Figure 32** Contact angle of a droplet of the coating suspension with a PMMA substrate subjected to UV irradiation.
4. Results and discussion

Next to UV treatment, oxygen plasma treatment has been used in literature to improve the wettability of PMMA substrates\(^1\) and also specifically to induce the presence of carboxylic acid groups.\(^4\) During the treatment, oxygen ions collide with the polymer surface which causes bond breaking and oxidation of the methyl or methyl-ester groups.\(^3\) After oxygen plasma treatment, a contact angle of 47.5° ± 0.8° with the standard coating suspension was obtained. The advantages of this method over the UV treatment are the absence of yellowing and the shorter duration of the treatment. Due to time constraints and the ease of use of the UV-treatment, the plasma treatment was not optimized.

4.3.2. Determination of the amount of carboxylic acid groups on the surface of the substrate

Using the method as described in the experimental section, the surface density of carboxylic acids on substrates treated using 3M of H\(_2\)SO\(_4\) was determined to be 188 nmol cm\(^{-2}\). In the article\(^1\) by Brown et al., the surface density was given as 240 ± 70 nmol cm\(^{-2}\). The value of 188 nmol cm\(^{-2}\) is within this range. In the previous section, it was seen that the contact angle only marginally improved using the H\(_2\)SO\(_4\) treatment. Given the polar nature of carboxylic acid groups, it must be concluded that this increase in the amount of carboxylic acid groups on the surface is not enough to reduce the contact angle significantly. Using UV-treatment, the contact angle drastically improves. This indicates that either a significantly larger surface concentration of carboxylic acid groups was obtained using this treatment and/or other polar species were formed during UV-irradiation.

4.3.3. Heat treatment of the coated polymer substrates

A temperature of 180°C was determined to be the highest temperature that could be used in order to avoid deformation of the PMMA substrate upon removal from the muffle furnace, at this temperature the maximum treatment time was likewise determined to be 1h (after heating up to 180°C in 30 min). It must be noted that this temperature treatment is not intended to induce crystallinity in the deposited thin film, since temperatures of ~400°C would be necessary to induce the formation of anatase. Indeed, since the suspension already contains crystalline nanocrystals this should not be necessary. The temperature treatment was used instead to remove volatiles and organic material.
4. Results and discussion

4.3.4. Formation of an amide bond between the substrate and the nanoparticles

When an amine and a carboxylic acid are mixed, an acid-base reaction occurs such that a salt is formed. This salt can react to result in the formation of an amide bond but the equilibrium lies strongly to the side of hydrolysis rather than amide bond formation (Figure 33). The direct condensation of the salt to an amide can only be achieved at high temperatures (160-180°C). Therefore, carboxylic acids are usually activated prior to reaction with the amine using coupling reagents that react with the carboxylic acid in such a way that a good leaving group is formed on the acyl carbon of the acid (see Figure 34).

\[
\text{RCOOH} + \text{R'NH}_2 \xrightarrow{\text{activating agent}} \text{RCOO}^- + \text{R'NH}_3^+ \xrightarrow{\text{aminalysis}} \text{RCONHR'} + \text{H}_2\text{O}
\]

pKa ~4-5 \hspace{1cm} pKa ~10-11

Figure 33 Reaction between a carboxylic acid and a primary amine to form a salt, followed by the condensation of the salt to form an amide.

Figure 34 Principle of an activating agent (e.g. EDC) to form an amide bond out of a carboxylic acid and a primary amine.

For our purposes, it was opted to use the combination of 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide (EDC) and N-hydroxysuccinimide (NHS). The reactions involved in this coupling are shown in Figure 35 (for the mechanism, see Figure A 20). Both of the reagents are water-soluble. The o-acylisourea ester that is formed through the reaction of EDC with the carboxylic acid is rather susceptible to hydrolysis (2-3 s\(^{-1}\) at pH 4.75)\(^{107}\), such that the activated carboxylic acid is deactivated fast and the amine has less chance to attack, and can moreover undergo cyclic electronic displacement (N→O displacement), giving the energetically more favored N-acylurea (Figure 36).\(^{108}\) This N-acylurea is not reactive towards primary amine groups.\(^{109}\)

To avoid this, NHS is used. NHS attacks the EDC activated carboxylic acid to form an NHS-ester that is more stable towards hydrolysis and the displacement reaction is hindered.\(^{109}\) The coupling reaction between EDC and carboxylic acids requires slightly acidic conditions and a pH of 4.75 can be used (e.g. using a MES buffer at this pH).\(^{69}\) For the formation of an amide bond, however, the pH should ideally be increased (to 7.2-7.5, e.g. through the addition of a phosphate buffer)\(^{69}\) to suppress ionization of the amine (since protonated amines are much less nucleophilic than deprotonated amines).
4. Results and discussion

A difficulty in this procedure for our case, is the fact that the nanoparticles are stabilized in water by the presence of the positively charged protonated amine groups of the ligands (NH$_3^+$). Therefore, the pH could not be increased above a pH of 5, otherwise turbid and unstable suspensions were obtained. At this pH, only a fraction of the amine groups of the ligands around the nanorods will be deprotonated and able to react with the activated carboxylic acid groups.

![Figure 35](image)

**Figure 35** Reaction scheme of the linking of the nanoparticles to the polymer substrates via an amide bond. EDC is added to a polymer substrate with carboxylic acid groups on the surface (1), forming a ε-acylisourea ester (2). This ester reacts with NHS to form a NHS-ester (3), which reacts with the primary amine function of APTES forming an amide bond (4).

![Figure 36](image)

**Figure 36** Formation of an N-acylurea from the O-acylourea formed upon reaction of EDC with a carboxylic acid.$^{110}$

In ref.$^{110}$ an amide bond is formed with an EDC activated carboxylic acid using APTES capped Fe$_3$O$_4$ nanoparticles. In their procedure, the nanoparticles are dispersed through sonication in THF in the presence of a base (N,N,N-diisopropylethylamine). It was tried to disperse the APTES capped nanorods in an identical manner. The nanorods immediately precipitated from this solution when sonication was ended, however. This is what would be expected, as the amine groups of APTES are deprotonated in this basic environment such that the nanorods are no longer charge stabilized, also THF is much less polar than water (dielectric constant of 7.52). In the article$^{110}$, the reaction is performed with molecules in solution instead of at the surface of a substrate such that the solution can be well stirred and the stability might be less critical.
4. Results and discussion

If the pH of an aqueous suspension would be chosen such that part of the amine groups of the APTES ligands on a particle are protonated whilst the rest are deprotonated, there might be sufficient stabilization as well as enough deprotonated amines that can react with the carboxylic acid groups on the polymer. Therefore, a balance needs to be sought between stability of the suspension on the one hand and the amount of deprotonated amine groups available for coupling on the other hand. A pH of 4.75 was chosen, since this is the lowest pH used for coupling between an amine and an EDC and NHS activated carboxylic acid in literature.\(^7,8\) and the coating suspensions are clear at this pH value.

A possible way to ameliorate this, is to use a second silane next to APTES such that this silane provides stabilization whilst APTES can be deprotonated to react. A silane that could be used for this purpose (and which should not take part in the coupling reaction) is 3-(trihydroxysilyl)-propylmethyphosphonate (THPMP).\(^66,67\) (Figure 37), this silane contains a phosphonate functional group which is negatively charged at pH>pKa (≈ 2). Therefore, the pH could then be increased in order to deprotonate a larger fraction of the amine groups of APTES whilst the THPMP provides charge stabilization to the suspension. THPMP was added to the reaction mixture 10 min after the addition of APTES. The reaction mixture became much more turbid immediately when compared to the procedure using APTES alone. The resulting powder was given the same workup procedure as for APTES modified nanorods. The pH dependent stability did not differ from the samples obtained using APTES alone (if the THPMP silane would also be present on the nanorods, one would expect that stable suspensions can be obtained at higher pH values, as was indeed the idea behind this method) and a zeta potential of +41 mV was measured at a pH of 2.5. These results indicate that THPMP is not present on the nanorods. Possibly this is related to the form in which THPMP is commercially available, namely as an aqueous salt solution, whereas APTES is available as an alkoxide. It is plausible that this difference in chemical form also influence the ligand exchange and the binding on the nanorods. Due to lack of time, it was not possible to work out an adapted ligand exchange procedure.

![Figure 37 Structure of THPMP.](image_url)
4. Results and discussion

4.3.5. Characterization of coated substrates

4.3.5.1. Transparency

For most of the self-cleaning applications, it is important that the coatings are transparent in the visible range. To evaluate this quantitatively, the transmittance of coated substrates in the visible range was measured using a UV-VIS spectrometer (Figure 38). The clean PMMA substrates had a transmittance of ~93% in the visible region. After UV-irradiation for 2 hours, the transmittance of the substrates decreased to ~91%-89% between 500 nm and 800 nm and more drastically in the range between 400 nm and 500 nm (the violet and blue region of the spectrum) with a transmittance of 82% at 400 nm. This is explained by the yellowing of the substrate, indeed a yellow-brown tinge can be noticed on the substrates. Substrates coated with a suspension containing 5 volume% of EG that were immediately dried under an IR lamp at 150°C for 30s (PMMA coated [1] and [2]) were the most transparent, with a transmittance of ~87%-84% between 500 nm and 800 nm and 79% at 400 nm. Thus this coating reduced the transparency of the substrates by only ~5% when compared to the UV-treated substrate. Substrates coated without the addition of EG to the coating suspensions were clearly less transparent (~80%-74% between 500 nm and 800 nm and ~69% at 400 nm). This can be explained by the white tinge of the coating due to scattering of visible light. Substrates treated with H₂SO₄ (without the use of UV irradiation) and without the addition of EG to the suspension were clearly less transparent.

Figure 38 UV-VIS spectrum (between 350 nm and 800 nm) of a clean PMMA substrate (black), a PMMA substrate subjected to UV irradiation for 2h (purple), (PMMA coated [1]) a substrate coated with a suspension containing 5 v% of EG using a dip-coating speed of 50 mm/min, dried at 150°C under an IR lamp for 30s and subjected to thermal treatment at 180°C (yellow), (PMMA coated [2]) a substrate coated using the same treatment as PMMA coated [1] (red), (PMMA coated [3]) A substrate coated using the same treatment as PMMA coated [1] using a suspension without EG, (PMMA coated [4]) A substrate treated with H₂SO₄ coated with a suspension without EG using a dip-coating speed of 50 mm/min, dried at 60°C in a drying furnace for 1h and subjected to thermal treatment at 180°C (blue). All the coated substrates except for PMMA coated [4] were subjected to 2h of UV treatment before coating.
4. Results and discussion

4.3.5.2. Surface morphology

Coatings obtained on substrates only treated with H$_2$SO$_4$ were not very homogeneous (Figure 39 left), this can be explained by the limited wettability of the substrate by the coating suspension which results in uncoated areas and areas with uneven thickness and edge effects. The addition of 15 v% of EtOH to the coating suspension (which lowered the contact angle with the H$_2$SO$_4$ treated substrates, as explained in the previous section) did not significantly improve the homogeneity of the coating (Figure 39 right).

Figure 39 (left) H$_2$SO$_4$ treated substrate coated with the standard coating suspension, dried at 60°C in a laboratory furnace, treated at 180°C in a muffle furnace. (right) H$_2$SO$_4$ treated substrate coated with a coating suspension containing 15 v% of EtOH at 50 mm/min, dried at 60°C in a laboratory furnace, treated at 180°C in a muffle furnace.

The homogeneity of the coatings improved if UV-treated substrates were used instead (Figure 40). This can be linked to the enhanced wettability of the substrates by the coating suspension. The coatings still showed a white color however, likely due to scattering linked to roughness of the coating (this can be most clearly seen for the substrate coated at 50 mm/min, because a thicker layer was formed). This was thought to be the result of the precipitation of the nanorods out of the liquid film after deposition, due to the fast evaporation of water out of the films upon drying.

Figure 40 Substrates subjected to (a) 20 min of UV irradiation, (b) 30 min of UV irradiation, (c) 6 h of UV irradiation coated using the standard coating suspension at (a, b) 10 mm/min and (c) 50 mm/min. All substrates were dried at 60°C in a laboratory furnace and subjected to thermal treatment at 180°C.
4. Results and discussion

In order to reduce this effect, an additive with a higher boiling point than water was added such that the film evaporates more slowly. Ethylene glycol was chosen for this purpose. Addition of this substance to the suspension also increased the viscosity of the coating suspension (from 2.32 cP without EG to 2.82 cP with 5% EG; the viscosity of water is 0.89 cP at 25°C). As a test, 2 ml of suspension containing different volume percentages of ethylene glycol (0%, 1%, 5%, 10%) was pipetted in a petri dish and dried in a laboratory furnace at 60°C for 3h. The suspensions with 0% and 1% EG formed a hard translucent structure on the bottom of the petri dish whilst the suspension containing 5% EG formed a transparent “gel” and the suspension containing 10% of EG was still runny (Figure 41). It is thought that the formation of the gel-like substance is the result of the evaporation of water such that a residual highly viscous substance remains. Coatings formed using suspensions containing 5 v% of ethylene glycol were nearly macroscopically homogeneous and more transparent (Figure 42).

![Figure 41](image-url) 2 ml of coating suspension containing (a) 0 v% EG, (b) 1 v% EG, (c) 5 v% EG and (d) 10 v% EG, dried at 60°C for 3h.

![Figure 42](image-url) (a) 50 mm/min, 5 v% EG, 150°C IR drying, 180°C furnace (b) 50 mm/min, 5 v% EG, 150°C IR drying, 180°C furnace (reproduced) (c) 100 mm/min, 5 v% EG, 150°C IR drying, 180°C furnace (d) 50 mm/min, 5 v% EG, 100°C IR drying, 180°C furnace.
4. Results and discussion

In order to get a more detailed view of the homogeneity of the coatings, microscopy measurements were performed on the coated substrates. A substrate subjected to 2h of UV irradiation coated with a suspension not containing ethylene glycol was examined (Figure 43). It can be seen that the substrate was not coated homogeneously. Clear differences in thickness of the coating over the substrate are visible. A substrate subjected to 2h of UV irradiation coated with a suspension containing ethylene glycol was also examined (Figure 44), the homogeneity on a microscopic scale did not improve when compared to the substrate coated without 5 v% of ethylene glycol and uncoated areas can still be distinguished. Although coatings obtained using suspensions containing 5 v% of EG on UV-treated substrates appear nearly homogeneous on a macroscopic scale, the homogeneity of the coatings still needs to be improved.

**Figure 43** Microscopy images (10x magnification) of substrates coated using the standard coating solution without ethylene glycol (A substrate coated with a suspension without EG using a dip-coating speed of 50 mm/min, dried for 1h at 60°C and subjected to thermal treatment at 180°C) (left) image at the edge with the uncoated part of the substrate (right) image of the coating in the middle of the substrate.

**Figure 44** Microscopy images (10x magnification) of substrates coated using a coating solution containing 5 v% of ethylene glycol (A substrate coated with a suspension containing 5 v% of EG using a dip-coating speed of 50 mm/min, dried for 30s under a UV lamp and subjected to thermal treatment at 180°C. (left) image at the edge with the uncoated part of the substrate (right) image of the coating in the middle of the substrate.
4.3.5.3. Durability

The durability of the coatings was tested by submerging them in a solution of methylene blue (used for photocatalytic tests). If the adherence of the layer to the substrate is poor, it was known from previous experience (on glass substrates) that the layer dissolves in the solution (in principle, such layers would also dissolve in pure water). The coated substrates were submerged in this solution for 4h, afterwards the substrates were removed from the solution. Visibly, no deterioration of the layers could be noticed. The substrates were also subjected to sonication in water for 1h, again no deterioration could be noticed. Subsequently, the Scotch tape test was performed; Scotch tape was attached to the surface of the coated substrate and manually peeled off. The layer was still attached to the substrate after 3 times, but a small amount of residue could be distinguished on the tape. To test the durability of the coatings more thoroughly, a weatherometer could be used.

Figure 45 (left) Substrate subjected to 6 h of UV irradiation coated using the standard coating suspension at 50 mm/min, dried at 60°C in a laboratory furnace and subjected to thermal treatment at 180°C. (right) the same substrate after being submerged in a methylene blue solution for 4h.

4.3.5.4. Chemical characterization

A Raman spectrum of a coated PMMA substrate was measured and compared to the Raman spectrum of a clean PMMA substrate and the Raman spectrum of powder obtained from the fast hydrolysis (corresponding to the anatase crystal phase) (Figure 46). Most of the bands correspond to vibrations of the PMMA substrate (see Figure A 21 for the entire range), the only marked difference is a peak at 150 cm\(^{-1}\) in the spectrum of the coated substrate that is absent in the spectrum of the clean substrate. Comparing this to a spectrum of powder from the fast hydrolysis (corresponding to the anatase crystal phase), one sees that it coincides with the most intense characteristic vibration of anatase. The other characteristic vibrations of anatase are intrinsically much less intense and cannot therefore not be distinguished in the spectrum for the coated PMMA due to overlap with vibrations corresponding to the PMMA substrate. This peak is indicative for the presence of anatase in the coating on the substrate.
4. Results and discussion

![Raman spectra of coated PMMA](image)

**Figure 46** Raman spectra of coated PMMA (dried and heat treated) in blue, cleaned uncoated PMMA (in black) and powder from the fast hydrolysis (corresponding to anatase) in green. The coated substrate was a H$_2$SO$_4$ treated substrate coated with the standard coating suspension, dried at 60°C in a laboratory furnace, treated at 180°C in a muffle furnace.

An ATR-FTIR spectrum of a coated PMMA substrate was compared to a spectrum of a clean PMMA substrate. Peaks corresponding to vibrations of the PMMA substrate underneath the coating can be detected in the spectrum of the coated substrate but also some peaks unique to the spectrum of the coated substrate can be distinguished (**Figure 47**). These peaks can be assigned to vibrations related to APTES and silane networks (**Table 6**). (FTIR spectra of other coated substrates are very similar; see **Figure A 22**). Peaks that could be assigned to vibrations of amide bonds formed between the amine functionalities of APTES ligands with carboxylic acid groups on the substrate could not be distinguished. This does not necessarily mean that the coupling reaction was unsuccessful, however. The amide bonds, if present, form a molecular layer at the interface between two considerably thicker layers (the substrate and the coating) both of which possess infrared active components. It is plausible that the peaks belonging to vibrations of the amide bonds are not intense enough to be distinguished.
4. Results and discussion

Figure 47 Comparison of infrared spectra of coated (blue) and uncoated (black) PMMA substrates. The coated substrate was a H$_2$SO$_4$ treated substrate coated with the standard coating suspension, dried at 60°C in a laboratory furnace, treated at 180°C in a muffle furnace.

Table 6 Assignment of peaks $^{64,90-92}$ in the FTIR spectrum of a coated PMMA substrate

<table>
<thead>
<tr>
<th>Peak number</th>
<th>peak position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>630</td>
<td>OH rock</td>
</tr>
<tr>
<td>2</td>
<td>796</td>
<td>Si-O-Si bending</td>
</tr>
<tr>
<td>3</td>
<td>870</td>
<td>Si-O stretch of $\equiv$ Si – O – Si $\equiv$ bridges</td>
</tr>
<tr>
<td>4</td>
<td>1034</td>
<td>Antisymmetric stretch Si-O-Si</td>
</tr>
<tr>
<td>5</td>
<td>1120</td>
<td>Symmetric Si-O-Si + C-N</td>
</tr>
<tr>
<td>6</td>
<td>1168</td>
<td>Si-O</td>
</tr>
</tbody>
</table>

In summary, the combination of the Raman and the FTIR spectrum of the coated substrate indicate the presence of anatase (from the Raman spectrum) as well as silane components (from the ATR-FTIR spectrum). Although the presence of amide bonds could not be proven, these measurements indicate the successful deposition of the silane capped anatase nanorods on the PMMA substrate.
4. Results and discussion

4.3.5.5. Photocatalytic activity

The photocatalytic activity of a model coating was evaluated according to an ISO certified test (ISO 10678:2010(E))\textsuperscript{111} based on the photocatalytic degradation of the well-known dye methylene blue (see section 7.3.9 for details on the procedure). It is generally accepted that this photocatalytic degradation process follows pseudo-first order kinetics, as described by\textsuperscript{112}:

\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]

With \(C\) the concentration of methylene blue after a UV-irradiation time \(t\), \(C_0\) the initial methylene blue concentration and \(k\) the rate constant of the reaction. The equation can be represented graphically, because of the pseudo-first order nature of the degradation the curve should follow a straight line (Figure 48). The initial steep drop in the curve for the coated substrate and the drop for the blank sample might be attributed to adsorption of methylene blue, although the samples were conditioned before the measurements, as described in the ISO test (see section 7.3.9), in order to limit this effect. Such a steep initial decrease has also been observed in literature.\textsuperscript{112} The coated PMMA substrate clearly shows some photocatalytic activity. After 1h, the curve for the blank stabilizes (fluctuates) around -0.055 but the curve for the coated sample continues to drop further. This indicates that the decrease observed after 1h for the coated substrate is linked to actual photocatalytic degradation of methylene blue by the anatase nanocrystals in the coating.\textsuperscript{112}

![Figure 48](image-url) Logarithmic plot of the decomposition of methylene blue as a function of UV exposure time for a blank sample (not UV irradiated) and a coated PMMA sample. A least-squares linear fit of the data points after 1h is shown, the \(R^2\) value for this fit is determined to be 0.86. The sample is a substrate coated with a suspension containing 5 v\% of EG using a dip-coating speed of 50 mm/min, dried at 150°C under an IR lamp for 30s and subjected to thermal treatment at 180°C.
5. Conclusions

A specific degradation rate was calculated for this coated PMMA sample (as an average over the data-points after 1h of irradiation) as $1.45 \times 10^{-5}$ mol/m²h. This is a relatively low value, values up to $3.8 \times 10^{-5}$ mol/m²h have been obtained using aqueous suspensions on glass substrates.\textsuperscript{113} A possible explanation for this relatively low activity is the presence of APTES around the nanorods. It has been shown in literature that the presence of APTES ligands around anatase nanoparticles can significantly suppress their photocatalytic activity. For high ligand densities of APTES (6.2 nm\textsuperscript{2}), a decrease in activity of up to 75% compared to bare nanoparticles has been obtained.\textsuperscript{26} The possible presence of silane clusters in the coating next to the nanorods might further increase this effect. More photocatalytic tests on similarly coated substrates should be carried out in order assess whether similar activities are obtained.

5. Conclusions

The three main synthesis procedures that were explored for this thesis reproducibly result in nanocrystals with a size between 5 nm and 25 nm and a percentage crystallinity of $\geq 45.5\%$ which can be used to form clear suspensions that remain stable for more than a month.

The nanorods synthesized through the fast hydrolysis synthesis were used in a ligand exchange procedure to obtain APTES capped nanorods dispersible in aqueous solutions. The stability of the resulting suspensions is pH dependent and at a pH of ~2 clear suspensions can be obtained that remain stable for more than a month. The dispersibility of the nanorods in aqueous solutions, FTIR measurements and measurements of the zeta potential of the suspensions as a function of the pH indicate that the exchange of oleic acid with APTES was successful. The aqueous suspensions of APTES capped nanorods were subsequently used to coat PMMA substrates. For this purpose, the pH of the suspensions was adapted to a pH of 4.75, which reduces the stability to 24h at room temperature and 1 week when cooled at 7°C.

In order to improve the wettability of the PMMA substrates by the coating suspensions and concomitantly induce the presence of carboxylic acid groups on the surface, different surface treatments were examined. UV-treatment proved the most convenient and effective surface treatment, significantly improving the wettability of the substrate. The disadvantage of this treatment is the yellowing of the PMMA substrates caused by prolonged UV-irradiation. A combination of EDC and NHS was used to activate carboxylic acid groups on the surface of the substrates such that the nanocrystals could be covalently coupled to the surface through the formation of an amide bond.
6. Recommendations for further work

The transparency of the coatings was improved through the addition of ethylene glycol to the coating suspensions. The homogeneity of the coatings on a microscopic scale still needs to be improved. The coatings were found to be durable, based on the results of preliminary durability tests and Raman and infrared spectroscopy measurements provide indications that the coupling of the nanocrystals to the substrate was successful. The degradation of methylene blue indicates that a model coating shows photocatalytic activity.

A transparent photocatalytically active coating with good durability was obtained through the use of a low temperature procedure compatible with the thermal sensitivity of the PMMA substrate.

6. Recommendations for further work

In order to enhance the activity of the coatings, it is suggested that a second layer of bare (ligand-stripped) nanocrystals is deposited on the layers that were obtained. The relatively low activity of the first layers might reduce potential effects of photocatalytic degradation of the polymer substrate, such that this layer acts as a buffer layer between the more active second layer and the polymer substrate. The first layer then also acts as a coupling layer, such as to enhance the durability of the final coating. For ligand stripping, a literature procedure using NOBF₄ can be used.¹¹⁴ The nanocrystals from the seeded growth synthesis by Murray et al. are suitable candidates for this procedure.

Some improvements can also be made to certain steps of the developed method. The formation of silane clusters during the ligand exchange procedure should be avoided. A possible way to achieve this, is the use of a mono-alkoxy silane instead of a tri-alkoxy silane (like APTES), such that at most dimers instead of clusters can be formed. A candidate silane would be APDIPES (3-aminopropyl(diisopropylethoxysilane), this silane also possesses a primary amine functionality.²³ Although UV-treatment proved to be a surface treatment that sufficiently enhances the wettability of the substrates, the side effect of yellowing of the PMMA substrates is undesirable. Therefore, an alternative surface treatment should be found that improves the wettability to a similar extent but in the absence of yellowing. In this regard, plasma treatment could be further explored. The homogeneity of the coatings should also be further improved, in order to obtain fully coated substrates before a second layer is deposited. The durability of the coatings should be further evaluated using more rigorous tests, such as weathering tests in a weatherometer, in order to assess the long-term durability of the coatings for outdoor applications.
# Appendix

## 7.1. Overview of synthesis procedures

### Table A1 Overview of synthesis procedures

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>composition precursor solution</th>
<th>treatment</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>slow hydrolysis $^{55}$</td>
<td>10 mmol TTIP 10 mmol TMAO 100 mmol EG 124 mmol OLAC</td>
<td>48h, 100°C, Ar</td>
<td>Very weakly crystalline</td>
</tr>
<tr>
<td></td>
<td>10 mmol TTIP 10 mmol TMAO 100 mmol EG 124 mmol OLAC</td>
<td>48h, 120°C, Ar</td>
<td>crystalline; non-dispersible</td>
</tr>
<tr>
<td></td>
<td>3.333 mmol TTIP 10 mmol TMAO 100 mmol EG 124 mmol OLAC</td>
<td>48h, 100°C, Ar</td>
<td>not crystalline</td>
</tr>
<tr>
<td></td>
<td>10 mmol TTIP 10 mmol TMAO 100 mmol EG 124 mmol OLAC</td>
<td>48h, 110°C, Ar</td>
<td>not crystalline</td>
</tr>
<tr>
<td></td>
<td>10 mmol TTIP 10 mmol Et$_3$N 100 mmol EG 124 mmol OLAC</td>
<td>48h, 100°C, Ar</td>
<td>not crystalline</td>
</tr>
<tr>
<td></td>
<td>water free: 10 mmol TTIP (in glovebox) 10 mmol triethylamine (molsieves) 100 mmol EG (dried under vacuum) 124 mmol OLAC (dried under vacuum)</td>
<td>48h, 100°C, Ar</td>
<td>not crystalline</td>
</tr>
<tr>
<td>µwave slow hydrolysis</td>
<td>10 mmol TTIP 10 mmol TMAO 100 mmol EG 124 mmol OLAC</td>
<td>100°C, 3-12h</td>
<td>not crystalline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120°C; 130°C; 1-3h</td>
<td>not crystalline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140°C, 1h; 2h</td>
<td>not crystalline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140°C and 180°C; 3h</td>
<td>crystalline; non-dispersible</td>
</tr>
<tr>
<td>Appendix</td>
<td>3.333 mmol TTIP 10 mmol TMAO 100 mmol EG 124 mmol OLAC</td>
<td>100°C, 3h 120°C, 3h</td>
<td>not crystalline</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>2 mmol TTIP 2 mmol TMAO 20 mmol EG 124 mmol OLAC</td>
<td>130, 2h; 3h</td>
<td>not crystalline; crystalline non-dispersible</td>
</tr>
<tr>
<td>fast hydrolysis</td>
<td>3.333 mmol TTIP 10 mmol TMAO in 5 ml MilliQ (2 M) or 10 mmol Et$_3$N followed by 5 ml MilliQ 124 mmol OLAC</td>
<td>100°C, Ar, 6h</td>
<td>crystalline</td>
</tr>
<tr>
<td>Murray et al.</td>
<td>1.9 mmol TiCl$_4$ 11.5 mmol OLAC 30 mmol OLOH 52.6 mmol ODE</td>
<td>1.5 ml stock add at 60°C heat quickly to 290°C @290°C: 8 ml stock @ 0.3 ml/min</td>
<td>crystalline</td>
</tr>
<tr>
<td>Niederberger et al.</td>
<td>Benzyl alcohol TiCl$_4$ dopamine</td>
<td>80°C, 3 days (72 h)</td>
<td>crystalline</td>
</tr>
<tr>
<td>P. Wang et al.</td>
<td>0.3125 ml TTIP 5 ml EG 3 ml MilliQ</td>
<td>2 h, 150°C reflux</td>
<td>not crystalline</td>
</tr>
<tr>
<td>P. Wang et al.</td>
<td>0.1 ml TTIP 15 ml EG 5 ml MilliQ</td>
<td>150°C, 2h reflux</td>
<td>not crystalline</td>
</tr>
<tr>
<td>Pan et al. (example 6)</td>
<td>1 mmol TTIP 0.1 ml OLAC 10 ml toluene 2ml TBAH aqueous solution (5 mmol)</td>
<td>60°C, 4h</td>
<td>not crystalline</td>
</tr>
</tbody>
</table>
### 7. Appendix

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction Conditions</th>
<th>Temperature</th>
<th>Microwave</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlucci et al.</td>
<td>1 ml TTIP 97 mmol BA 26.9 mmol OLAC</td>
<td>210°C, 45 min; 90 min, µwave</td>
<td>not dispersible; weakly crystalline</td>
<td></td>
</tr>
<tr>
<td>Pan et al.¹¹⁸</td>
<td>1 mmol TTIP 0.1 ml OLAC 10 ml toluene 10 ml aqueous solution with 0.05 mmol TMAOH</td>
<td>180°C, 0.5 h, 3 h µwave</td>
<td>not crystalline</td>
<td></td>
</tr>
<tr>
<td>Li et al.¹¹⁹</td>
<td>0.25 g NH₄HCO₃ 6.325 ml OLAC 1.25 ml Et₃N 1.25 ml toluene 1 ml Ti(OBu)₄</td>
<td>150°C, 3 h, µwave</td>
<td>very little crystalline</td>
<td></td>
</tr>
<tr>
<td>Thomas et al.¹²⁰</td>
<td>0.75 ml TiCl₄ 5 ml toluene 15 ml tertbutanol</td>
<td>µwave 2x (1 min 80°C/85°C/90°C, 20 min 50°C) 2x (1 min 80°C, 40 min 50°C/60°C/70°C) 70°C/80°C, 30 min 2x (1 min 80°C, 30/40 min 50°C) 2x (1 min 85°C, 20/40 min 50°C)</td>
<td>not crystalline – weakly crystalline</td>
<td></td>
</tr>
<tr>
<td>Niederberger et al.¹²¹</td>
<td>Benzyl alcohol TiCl₄</td>
<td>220°C, 3 h, µwave</td>
<td>crystalline; non-dispersible</td>
<td></td>
</tr>
<tr>
<td>Koziej et al.¹²²</td>
<td>3-Mercaptopropyltrimethoxysilane (MPS) (0.105 ml) BA (15.08 ml) TTIP (4.31 ml)</td>
<td>190°C, 24 h, µwave</td>
<td>not crystalline</td>
<td></td>
</tr>
</tbody>
</table>
7. Appendix

7.2. Supporting Figures

**Figure A 1** UV absorption spectrum of EDC solutions. (red) 10 mM solution, (yellow) EDC solution (originally 10 mM) after 2h with an immersed untreated PMMA substrated, (blue) EDC solution (originally 10 mM) after 2h with an immersed H₂SO₄ treated PMMA substrate.

**Figure A 2** Calibration curve of the absorbance at 212 nm (peak maximum) of aqueous EDC solutions versus concentration. Background subtraction using MilliQ water, the absorbance at 400 nm was set to zero for all measurements and the absorbance value of the EDC 10 mM solution in Figure A1 was used as a reference.
7. Appendix

Figure A3: XRD pattern of powder from the slow hydrolysis procedure. 48h at 100°C under Ar atmosphere, 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG, 124 mmol OLAC.

Figure A4: (left) HRTEM image of a single nanocrystal obtained using the procedure by Murray et al. The yellow line shows the line along which the grey values in the plot to the right were obtained (right) Grey values of lattice fringes.

Figure A5: Powder XRD pattern from powder obtained using the fast hydrolysis procedure with Et₃N as a base. (using 3.33 mmol TTIP, 10 mmol Et₃N, 5 ml MilliQ and 124 mmol OLAC).
7. Appendix

**Figure A6** HRTEM image of nanorods obtained using the fast hydrolysis procedure with Et$_3$N as a base. (using 3.33 mmol TTIP, 10 mmol Et$_3$N, 5 ml MilliQ and 124 mmol OLAC).

**Figure A7** FTIR spectra of powder obtained from the fast hydrolysis (black) (From a synthesis for 6h at 100°C using 3.3 mmol TTIP, 10 mmol TMAO in 5 ml MilliQ (2 M) and 124 mmol OLAC) and slow (blue) hydrolysis (From a synthesis for 48h at 100°C using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC)
Table A2 Assignment of peaks in the FTIR spectrum of powder obtained from the fast hydrolysis synthesis:\textsuperscript{55,71–73}

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Peak position (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3200 (br)</td>
<td>(\nu(O-H))</td>
</tr>
<tr>
<td>2</td>
<td>3004</td>
<td>(\nu(C=C-H))</td>
</tr>
<tr>
<td>3</td>
<td>2918</td>
<td>(\nu_{as}(CH_2))</td>
</tr>
<tr>
<td>4</td>
<td>2850</td>
<td>(\nu_{s}(CH_2))</td>
</tr>
<tr>
<td>5</td>
<td>2360</td>
<td>CO(_2)</td>
</tr>
<tr>
<td>6</td>
<td>1712</td>
<td>residual oleic acid C=O</td>
</tr>
<tr>
<td>7</td>
<td>1628</td>
<td>(\nu(as)) COO(^{-}) free oleate</td>
</tr>
<tr>
<td>8</td>
<td>1520</td>
<td>(\nu(as)) COO(^{-}) bound oleate</td>
</tr>
<tr>
<td>9</td>
<td>1430</td>
<td>(\nu(s)) COO(^{-}) bound oleate</td>
</tr>
<tr>
<td>10</td>
<td>1310</td>
<td>(\nu(s)) COO(^{-}) free oleate</td>
</tr>
<tr>
<td>11</td>
<td>1088</td>
<td>(\nu(C-O)) of COO</td>
</tr>
<tr>
<td>12</td>
<td>908</td>
<td>(\delta_{p}(CH)) alkene</td>
</tr>
<tr>
<td>13</td>
<td>726</td>
<td>(\delta_{sp}(CH_2))</td>
</tr>
<tr>
<td>14</td>
<td>628</td>
<td>OH rock</td>
</tr>
</tbody>
</table>

Figure A8 Picture of powder obtained from dopamine \textit{in-situ} functionalised nanoparticles after workup.
7. Appendix

Figure A9 Zeta potential distribution of an aqueous suspension of dopamine functionalised nanorods at a pH of 2.6.

<table>
<thead>
<tr>
<th>Z-Average (d.nm)</th>
<th>% Volume</th>
<th>St Dev (d.nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.45</td>
<td>99.9</td>
<td>12.60</td>
</tr>
<tr>
<td>PdI: 0.374</td>
<td>0.1</td>
<td>867.8</td>
</tr>
<tr>
<td>intercept: 0.948</td>
<td>0.0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Result quality: Good

Figure A10 Size distribution, obtained by DLS, of an aqueous suspension of dopamine functionalised nanoparticles at a pH of 2.
7. Appendix

Size distribution, obtained by DLS, of an aqueous suspension of dopamine functionalised nanoparticles at a pH of 2, one month after preparation.

![Graph](image1)

**Figure A 11** Size distribution, obtained by DLS, of an aqueous suspension of dopamine functionalised nanoparticles at a pH of 2 after 1 month.

Size Distribution by Volume

<table>
<thead>
<tr>
<th>Size (d.nm)</th>
<th>% Volume</th>
<th>St Dev (d.nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1:</td>
<td>10.10</td>
<td>1.347</td>
</tr>
<tr>
<td>Peak 2:</td>
<td>28.97</td>
<td>26.59</td>
</tr>
<tr>
<td>Peak 3:</td>
<td>49.15</td>
<td>879.5</td>
</tr>
</tbody>
</table>

Result quality: Good

---

DLS measurement of OLAC capped nanorods in toluene. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC).

![Graph](image2)

**Figure A 12** DLS measurement of OLAC capped nanorods in toluene. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC)

---

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7. Appendix

**Table A 1**

<table>
<thead>
<tr>
<th>Size (d.nm)</th>
<th>% Volume</th>
<th>St Dev (d.nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1: 17.73</td>
<td>100.0</td>
<td>9.431</td>
</tr>
<tr>
<td>Peak 2: 0.000</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>Peak 3: 0.000</td>
<td>0.0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Result quality: Good

**Figure A 13** DLS measurement of APTES functionalised nanorods in water at pH ~2. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et3N and 0.69 mmol of H2O in 25 ml of toluene.

**Figure A 14** DLS measurement of OLAC capped nanorods in toluene showing two size distributions. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC).
7. Appendix

**Figure A 15** DLS measurement of APTES functionalised nanorods in water at pH ~2 after 5 weeks. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et3N and 0.69 mmol of H2O in 25 ml of toluene.

**Figure A 16** TEM image of APTES functionalised nanorods. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et3N and 0.69 mmol of H2O in 25 ml of toluene.
7. Appendix

**Figure A17** Dark field STEM image of APTES functionalised nanorods. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et3N and 0.69 mmol of H2O in 25 ml of toluene.

**Figure A18** Powder XRD pattern of APTES functionalised nanorods. The nanorods were synthesised using the fast hydrolysis procedure (using 3.33 mmol TTIP, 10 mmol Et3N, 5 ml MilliQ and 124 mmol OLAC), the ligand exchange procedure used 100 mg of OLAC functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et3N and 0.69 mmol of H2O in 25 ml of toluene.
Figure A 19 FTIR spectra of APTES clusters obtained from a reference procedure (black) and from powder obtained from a ligand exchange procedure starting from a suspension in toluene obtained from the synthesis by Murray et al. (blue). (The ligand exchange procedure used 100 mg of OLAC/OLOH functionalised nanopowder, 0.53 mmol of APTES, 4.48 mmol of Et$_3$N and 0.69 mmol of H$_2$O in 25 ml of toluene).
Figure A 20 Mechanism of the formation of an amide bond between carboxylic acid and a primary amine using EDC and NHS. (1) Protonation of EDC. (2) Formation of a ω-acylisourea ester. (3) reaction with NHS and formation of the amide bond.\textsuperscript{123}
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Figure A 21 Comparison of Raman spectra of clean and coated PMMA in the range of 0 cm\(^{-1}\) - 4000 cm\(^{-1}\) (left) and 0 cm\(^{-1}\) - 2000 cm\(^{-1}\).

Figure A 22 FTIR spectra of coated PMMA substrates. (coated PMMA [1]) A substrate coated with a suspension containing 5 v% of EG using a dip-coating speed of 50 mm/min, dried at 180°C under an IR lamp for 30s and subjected to thermal treatment at 180°C. (coated PMMA [2]) A substrate coated with a suspension containing 5 v% of EG using a dip-coating speed of 50 mm/min, dried at 100°C under an IR lamp for 30s and subjected to thermal treatment at 180°C. (coated PMMA [3]) A substrate coated with a suspension containing 5 v% of EG using a dip-coating speed of 50 mm/min, dried at 60°C in a drying furnace for 1h and subjected to thermal treatment at 180°C.
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7.3. Used apparatus and analysis techniques

7.3.1. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

A Perkin Elmer FTIR spectrometer spectrum 1000 with HATR (Horizontal Attenuated Total Reflection) module was used.

7.3.2. Raman spectroscopy

A dispersive Raman RXN1 from Kaiser optical systems with a laser of 542 nm was used.

7.3.3. X-ray diffraction (XRD)

XRD diffractograms were collected on a Thermo ARL X’tra diffractometer (CuKa = 1.5405 Å) with a solid state Si-Li detector, using a 0.02° step size and a 1 s step counting time.

7.3.3.1. Rietveld refinement

Rietveld refinement is a method for crystal-structure refinement. The method is based on the use of model structures that are refined using a least-squares procedure to improve the agreement between the experimental diffraction pattern and the pattern calculated from the model structures. The Rietveld refinement method is used here for the determination of the percentage crystallinity of the sample. For this purpose, a known amount of the powder sample is mixed with a known amount of pure crystalline powder of another crystalline phase that serves as an internal standard. In our case, 10 wt% of zincite (ZnO) was mixed with the powder samples. A powder XRD pattern of this mixture (see Figure A 23 for an example) was collected and the percentage crystallinity was extracted from the analysis. The presence of organic matter left in the sample after workup of the nanoparticles (described in the experimental section) was corrected through the use of thermogravimetric analysis (TGA). Topas Academic V4.1 software was used for Rietveld refinement.
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Figure A 23 Powder XRD pattern of powder obtained from the fast hydrolysis synthesis (using 3.33 mmol of TTIP, 10 mmol of TMAO in 5 ml MilliQ (2 M) and 124 mmol OLAC) mixed with 10 wt% ZnO. (1)-(4) are reflections belonging to the anatase crystal phase; (a)-(e) are reflections belonging to zincite.

7.3.4. Transmission Electron Microscopy (TEM)

A JEOL JEM-2200FS TEM with Cs corrector was used. Specimens for TEM studies were prepared by depositing a drop of suspension on a 200 mesh holey carbon copper grid.

7.3.5. Nuclear Magnetic Resonance spectroscopy (NMR)

NMR or Nuclear Magnetic Resonance is ideally suited to study the surface chemistry of colloidal nanoparticles. For this purpose, a combination of NMR techniques including (quantitative) 1D $^1$H-NMR, NOESY and DOSY spectroscopy form what can be called a solution NMR toolbox. The combination of these techniques enables to distinguish bound from free ligands and to study ligand exchange dynamics.

7.3.5.1. 1D $^1$H-NMR

1D $^1$H-NMR can be used to assess whether a ligand is bound to the surface or free in solution. The resonances corresponding to bound ligands exhibit line broadening as compared to the resonances corresponding to free ligand. This is explained by efficient transverse ($T_2$) inter-proton dipolar relaxation of protons in the bound ligands, which experience restricted rotational mobility. Smaller values of the $T_2$ decay time constant (i.e. efficient or fast $T_2$-relaxation) lead to broader resonances ($\text{FWHM} \propto \frac{1}{\pi T_2}$).
The efficiency of $T_2$ relaxation depends on the distribution of frequencies with which magnetic field variations occur, this depends in turn on the frequency of the molecular motions. $T_2$-relaxation becomes more efficient when low frequency magnetic field variations become more prominent, which is the case for ligands bound to the surface of a nanoparticle. Next to line broadening, resonances corresponding to protons in bound ligands also show a (small) increase in chemical shift as compared to the free ligand resonances. If 1D $^1$H-NMR is executed under quantitative conditions and the nanocrystal concentration in the sample is known, the integration of bound ligand resonances gives access to the ligand density (i.e. the number of ligands bound to the surface per nm$^2$).

7.3.5.2. NOESY

NOESY or Nuclear Overhauser Effect Spectroscopy is an NMR technique that can also be used to distinguish bound ligands from free ligands. Two spins in close proximity to each other will couple through-space (dipolar coupling) and thereby transfer spin-polarization due to cross-relaxation, which results in a so-called NOE cross-peak in the 2D NOESY spectrum. The intensity and the sign of this cross-peak depend on the frequency of molecular motions. For slowly tumbling molecules (such as ligands bound to the surface of a NP) the rapid build-up of intense and negative (same colour as the diagonal) cross-peaks is observed between dipolar coupled protons, whereas for fast tumbling molecules (free ligands) the slow build-up of a weak and positive cross-peak is observed. In this way, bound ligands can be distinguished from free ligands.

7.3.5.3. DOSY

DOSY or Diffusion Ordered Spectroscopy can be seen as a virtual separation technique, where species in a mixture are virtually separated based on possessing a different diffusion coefficient in the solvent.

The diffusion coefficient of a spherical species in solution is given by the Stokes-Einstein equation:

$$D = \frac{k_B T}{3\pi \eta d_H}$$

With $\eta$ the solvent viscosity and $d_H$ the hydrodynamic diameter of the entity (for NPs this corresponds to the sum of the NP diameter and two times the thickness of the ligand shell). Bigger species possess a smaller diffusion coefficient (they diffuse more slowly). Therefore, ligands bound to the surface of a NP possess a smaller diffusion coefficient than free ligands of the same species.
The Stokes-Einstein equation can be rewritten for the hydrodynamic diameter; therefore, the diffusion coefficient together with knowledge of the NP diameter (from a separate technique such as TEM measurements) provides access to the ligand shell thickness.

Neglecting the effects of relaxation, the principle of a DOSY measurement can be explained as follows. A pulse with a Z-position dependent field strength (called a gradient pulse) is applied such that species present in the solution at different locations along the Z-axis (the length of the NMR tube) experience different local magnetic fields. After some time, a second gradient pulse is applied with an opposite strength, to refocus the magnetization of the species. During the time interval between the two gradient pulses, the species will diffuse. As shown schematically in Figure A 24, smaller species diffuse faster and will therefore have diffused further, on average, from their original positions along the Z-axis when compared to bigger species.

Because the species possess a different position along the Z-axis at the time of the second (opposite) gradient pulse, their magnetization will not be perfectly refocused. This results in a loss of signal intensity compared to the case where no diffusion would have taken place. This loss in signal intensity depends on the diffusion coefficient of a species and is larger for species that diffuse faster. Because of this dependence, the diffusion coefficient can be extracted from the analysis.\textsuperscript{124}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{dosy-principle.png}
\caption{Illustration of the principle of a DOSY measurement. Smaller species diffuse faster and therefore experience bigger differences in local field strength between the two gradient pulses (gradient pulse denoted by G).\textsuperscript{125}}
\end{figure}
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7.3.5.4. Technical details of the NMR measurements

Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance III Spectrometer operating at a $^1$H frequency of 500.13 MHz and equipped with a BBI-Z probe. The sample temperature was set to 298.2 K. One dimensional (1D) $^1$H and 2D NOESY (Nuclear Overhauser Effect Spectroscopy) spectra were acquired using standard pulse sequences from the Bruker library.

For quantitative 1D $^1$H measurements, 64k data points were sampled with the spectral width set to 16 ppm and a relaxation delay of 30 sec. NOESY mixing time was set to 300 ms and 2048 data points in the direct dimension for 512 data points in the indirect dimension were typically sampled, with the spectral width set to 11.5 ppm. Diffusion measurements (2D DOSY) were performed using a double stimulated echo sequence for convection compensation and with monopolar gradient pulses. 33 Smoothed rectangle gradient pulse shapes were used throughout. The gradient strength was varied linearly from 2-95% of the probe’s maximum value (calibrated at 50.2 G/cm) in 32 or 64 steps, with the gradient pulse duration and diffusion delay optimized to ensure a final attenuation of the signal in the final increment of less than 10% relative to the first increment. For 2D processing, the spectra were zero filled until a 4096×2048 real data matrix. Before Fourier transformation, the 2D spectra were multiplied with a squared cosine bell function in both dimensions, the 1D spectra were multiplied with an exponential window function.

For the suspension of APTES functionalised nanorods in water, the regular workup procedure was followed, but in the last washing step acetone was replaced by deuterated acetone ((CD$_3$)$_2$CO). The powder was dispersed in D$_2$O and the pH was adapted to a pH of 2 using DCI diluted with D$_2$O.

7.3.6. X-ray Fluorescence Spectroscopy (XRF)

A NEX CG energy dispersive XRF from Rigaku® was used. The molar percentages were calculated using the software through the fundamental parameter method.

7.3.7. Thermogravimetric analysis (TGA)

A NETZSCH STA 449F3 Jupiter was used, with a heating rate of 2°C/min, under O$_2$ flow.

7.3.8. Dynamic Light Scattering (DLS)

The DLS measurements were performed on a Nano ZS from Malvern®, with a laser at a wavelength of 633 nm. The scattered light is measured at an angle of 173°. The analyses were performed using the Zetasizer software.
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7.3.9. Photocatalytic tests

The photocatalytic activity of the films was determined using an International Organization for Standardization (ISO) certified test (ISO 10678:2010(E)).\textsuperscript{111} This test is based on the photocatalytic degradation of methylene blue, a well-known blue dye, in an aqueous solution using an UV-light source. Methylene blue is thereby reduced to the colorless leucomethyleneblue.

![Figure A 25](left) structure of methylene blue and (right) structure of the reduced form leucomethyleneblue.

The setup of this test is as follows. Before the actual photocatalytic test, the sample is prepared for the test. This comprises two steps, an ‘activation step’ and a ‘conditioning step’. The activation step entails illuminating the substrate for 48h using the UV lamp. The conditioning step entails submerging the substrate in a methylene blue solution with a concentration of 20 µmol/l for 12 h. This is done in order to avoid the influence of adsorption of methylene blue to the substrate during the actual test, since any possible adsorption should take place during this conditioning step.

For the actual measurement, the substrate is placed in a 10 µmol/l methylene blue solution in a double-walled glass cylinder. A volume of 33 ml of the 10 µmol/l solution is used. During the test, the solution is stirred using a magnetic stirrer and the temperature is kept constant at 23°C. The absorbance of the solution is measured at 664 nm at intervals of 10 or 20 min by sampling the solution and then returning the sampled solution to the test solution. The total time for the degradation should not exceed 3h and is ended when the solution has decolourised. A blank is measured in an analogous way without UV-irradiation. At a wavelength of 664 nm the molar extinction coefficient of the methylene blue solution is known to be 7402.8 m²/mol, therefore concentrations can be obtained using the law of Bouger-Lambert-Beer.

The specific degradation rate (mol/m²h) of a sample can be calculated as follows:

\[
R = \frac{\Delta A \lambda V}{\Delta t \cdot \varepsilon \cdot d \cdot A}
\]

With \(\Delta A \lambda\) the change in absorbance at a wavelength of 664 nm in a time interval \(\Delta t\) (h), \(V\) (m³) is the volume of the methylene blue solution used for the measurements (33 ml), \(\varepsilon\) is the molar extinction coefficient of the methylene blue solution, \(d\) is the path length of the cuvette (1 cm) and \(A\) is the surface area of the substrate.
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7.3.10. Contact angle measurements

The contact angle is a measure of the wettability of the surface by a solution (i.e. how effectively a liquid will spread over the surface). The contact angle was determined by using the so-called static sessile-drop method. In this method, a drop is deposited on the surface of the substrate and a microscope objective is used to view the contact angle. The contact angles were determined using an optical tensiometer (Kruss DSA30). Droplets with a volume of 5 µl were deposited on the surface using a syringe with a hub diameter of 4.717 mm and a needle with a diameter of 0.506 mm. The contact angle was determined using the drop shape analysis software delivered with the apparatus, using the Laplace-Young fitting method.

7.3.11. Microwave reactor

Microwave syntheses were performed using a CEM Discover SP with autosampler. The power was supplied using a 300 W Magnetron that works at a frequency of 2455 MHz. Pressures up to 34 bar and temperatures up to 300°C can be reached.

7.3.12. UV lamp

The UV lamp used was a Pen-Ray® Mercury Lamp type 90-0012-01 operating at 230V with a primary energy at 245 nm with an intensity of 4100 µW/cm². The substrates were placed 1.5 cm below the UV lamp.

7.3.13. Glovebox

A nitrogen filled glovebox from MBraun was used.

7.3.14. Oxygen plasma treatment

The apparatus used for oxygen plasma treatment was a cylindrical dielectric discharge plasma reactor of the model Femto, ver. 3 from Diener Electronic. AN O₂ pressure of 0.8 mbar, a power of 100W and a time of 30 s were used.

7.3.15. Dip coater

The substrates were dipcoated using a computer controlled dip-coating unit (KSV Instruments) in a clean room facility (class 100,000/1000)

7.3.16. IR lamp

An infrared lamp (230 V; 4600 W, mid-IR, highest intensity between 2000-3500 cm⁻¹) was used to dry coated substrates immediately after dipcoating.
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7.3.17. UV-VIS spectroscopy

For UV-VIS measurements of the EDC solutions, a Shimadzu UV-1800 spectrophotometer was used. To measure the transmittance of the coated substrates, a PerkinElmer Lambda 900 Spectrometer was used.

7.3.18. Viscometer

The viscosity of the suspensions was measured using a Brookfield DV-E viscometer with the suspension thermostated at 25°C.

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**List of Tables**

**Table 1** Chemicals used, without any further purification, in the four synthesis procedures discussed in this chapter.

**Table 2** Assignment of peaks in the FTIR spectra of suspensions (Figure 18, left) and powders (Figure 18, right) from the slow hydrolysis procedure (using 10 mmol TTIP, 10 mmol TMAO, 100 mmol EG and 124 mmol OLAC) at 100°C and 120°C.

**Table 3** Assignment of peaks in FTIR spectrum of dopamine functionalised nanorods.

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**Table 5** Assignment of peaks in the FTIR spectrum of powder from an identical exchange procedure carried out in the absence of TiO₂ nanorods.

**Table 6** Assignment of peaks in the FTIR spectrum of a coated PMMA substrate.

**List of Supporting Tables**

**Table A1** Overview of synthesis procedures.

**Table A2** Assignment of peaks in the FTIR spectrum of powder obtained from the fast hydrolysis synthesis.