

Sol–gel nanocoating on commercial TiO₂ nanopowder using ultrasound

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Abstract The surface of commercial titania particles was coated by a layer of silica by a two-step process which involved a power ultrasound initiated sol–gel reaction. In the first step of this solution process, aminosilane, i.e. organosilane with amino functional group, was used to modify the surface of pristine nanoparticles. Subsequent silica nanocoating was initiated and sustained under power ultrasound agitation in a mixture of surface modified particles and epoxysilane. As a result, a homogenous coverage of silica on the nanoparticles' surface, with thickness controllable from one to several nanometers, was obtained. Fourier transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and particle surface zeta potential measurements were employed to follow steps in the process and to confirm the reaction mechanism.

Keywords Nanopowder · Nanocoating · Nanoparticle · Organosilane · Ultrasound · Sol–gel · Silica

1 Introduction

Recently, research on nanocoating has attracted increasing attention [1, 2]. Here nanocoating refers to the act of covering a material with a layer on the nanometer scale or

to cover a nanoscaled entity. Nanocoating forms a nanocomposite that comprises a combination of two or more different substances of nanometer size, thereby producing a material that generally has enhanced or specific targeted properties due to the combined properties and/or structuring effects of the components.

Different approaches have been explored to fabricate such structures including: vapor deposition, chemical reduction, pulsed laser deposition, mechanical milling, and electrochemical deposition [3] etc. Among these processes, the sol–gel process, being able to be carried out in solution, is attractive [4]. Sol–gel nanocoating in solution is generally performed using either precursor molecules or preformed particles to form the layer. The sol–gel process involves inorganic precursors (a metal salt or organometallic molecule) that undergo various chemical reactions resulting in the formation of a three-dimensional molecular network. One of the most common routes is via hydrolysis and condensation reactions of metal alkoxides to form larger metal oxide molecules that polymerize into a coating entity. The sol–gel procedure allows coating of substrates with complex shapes on the micrometer to nanometer scale, which some commonly used coating procedures cannot achieve. Such substrate entities include: colloidal particles, organic/inorganic crystals, or even fibers and nanotubes. In terms of sol–gel processes per se, the Stober process, the seed polymerization process, and the microemulsion process are common approaches and their application as nanocoating processes has been reviewed [5]. Many successful examples of nanocoating of nanoparticles have been reported including silica coating on metal nanoparticles [6, 7], magnetic nanoparticles [8], semiconductors [9] and quantum dots [10].

However, so far most published methods are applicable only to particles which are stably dispersed throughout the

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coating process. A generic challenge often encountered in real nanoparticle applications is that it is generally very hard to keep dispersions of nanoparticles stable. Such problems are more severe in the case of commercially available nanopowders being re-dispersed in solutions for customer application since hard aggregates are generally formed during powder synthesis. Such hard aggregates require a high energy input to break down and to keep the nanoparticles dispersed. Techniques such as media milling and high shear homogenization have been used commercially for de-aggregation and emulsification, while power ultrasound has also been proven an ideal option for this purpose. Power ultrasound is a cheap method to generate cavitation for emulsification, and it is relatively easy to scale up. Under agitation of powerful ultrasonic waves, large particles or particle aggregates can be fragmented into smaller particles due to the combined effect of impact (jet) milling, attrition milling, knife milling and direct pressure milling brought about by generation and implosion of ultrasonic cavitations [11]. Such effects reduce the particle size and increase reactivity in solution [12].

Power ultrasound also promotes high energy chemical reaction through the formation, growth and implosive collapse of bubbles via the process of acoustic cavitation in liquids [13]. Since the early 1980s, sol–gel processes during which precursor–water mixtures are exposed to intense ultrasonic irradiation have been investigated, to establish practical consequences of this approach on reaction kinetics and on textural characteristics of the so-called sonogels [14] produced. During the sonogel process, hydrolysis proceeds by exposing the initial mixture, commonly alkoxide in acidified water, to ultrasonic waves in an open glass container. Energy input into the sonogel system is set by varying the output power of the ultrasound generator. The sonication time provides an additional parameter for controlling the sol and gel properties. We have previously reported a two-step sol–gel process involving ultrasound to trigger silica nanocoating on commercial ITO nanoparticles [15]. In the present research, the results from a modified process applied to commercial titania nanoparticles are reported.

2 Experimental section

2.1 Materials and facility

Titania nanopowder (Degussa P-25) was kindly provided by JJ-Degussa (Singapore) Ltd. 3-aminopropyltrimethoxysilane (APS) and 3-Glycidyloxypropyltrimethoxysilane (GPTS) were purchased from Degussa, GmbH, Germany. A Fisher branded (model 550) probe style sonicator was used as ultrasound source.

2.2 Chemical process

2.2.1 Aminosilane surface treatment

In a typical treatment process, 1.0 g of as-received titania powder was added into 20 mL of deionized water acidified by acetic acid, whilst stirring vigorously. Then 1.0 mL of APS was slowly added to the dispersion whilst stirring. This mixture was refluxed for 20 h. Upon completion of the treatment, nanoparticles were separated using a centrifuge and were washed three times each with water and ethanol separately. Bath sonication was employed to help re-dispersal of the particles during the washing process.

2.2.2 Silica coating under ultrasound irradiation

In a typical process, 10 mL GPTS was mixed slowly with 20 mL of water acidified by hydrochloric acid (HCl) (pH value was adjusted to 1.5). 1.0 g of the aforesaid aminosilane treated particles was then added to the mixture, contained in a 100 mL glass bottle. The bottle was then placed under the probe of the sonicator for continuous ultrasound irradiation with an output power of 60 W or above. The sol–gel reaction was initiated after approximately 2–3 min ultrasound irradiation, upon which white foam was generated, due to the release of alcohol upon extensive hydrolysis of GPTS. A thermometer attached to the sonicator was plunged into the dispersion to monitor temperature. Throughout the process, the temperature of the dispersion increased to close to 60 °C within 6–8 min then dropped down and remained stable at between 50–55 °C due to heat convection. The dispersion was sonicated between 20 min and 1 h then kept stirring for several hours to allow it to cool down. Once the reaction was completed, particles were gathered by centrifuging, were washed repeatedly with water and ethanol then either dried for characterization or kept in dispersion in either water or organic solvents.

Particle samples gathered at different stages of the process were named as: AR-TiO₂ (as-received particle), A-TiO₂ (aminosilane treated), and AG-TiO₂ (aminosilane treated powder with silica coating by the sonogel process).

2.3 Sample characterization

Fourier transform infrared spectra (FTIR) of nanoparticle samples in KBr pellet form were recorded using a Bio-RAD Excalibur Series IR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried using an ESCALAB 250 manufactured by Thermo VG Scientific. The scan conditions for each energy range was saved and applied to all other samples for consistency. Powder samples were observed by a Philips CM300 high resolution Transmission

electron microscope (HRTEM) operated at 300 kV. Zeta potential measurement was carried out using a Marvin Zetasizer (Nano Series) connected with a MPT2 multipurpose titrator. 0.1 N HCl and 0.02 N, 0.1 N NaOH were used as titrants.

3 Results and discussion

FTIR spectra of samples at different stages of the process are shown in Fig. 1. In spectrum AR-TiO₂ (as-received powder), the mainly saturated peak below 700 cm⁻¹ is assigned to Ti–O and Ti–O–Ti bonding of titania. The small peak at 1640 cm⁻¹ and the large hump between 3000 and 3600 cm⁻¹ are attributed to stretching of –OH groups present in the powder. After surface modification by aminosilane, as presented in spectrum A-TiO₂, a small shoulder appears around 1560 cm⁻¹, which corresponds to bending of –NH₂ at the functional amino group. A shoulder at about 950 cm⁻¹, though not clear in the figure, suggests bonds of the type Ti–O–Si as a result of surface modification. A small peak at around 2920 cm⁻¹ indicates the existence of –CH₂– on the modified surface. Significant change can be found after silica nanocoating is applied on the particle surface. As shown by spectrum AG-TiO₂, an obvious new peak appears between 1000 and 1100 cm⁻¹, which clearly indicates the formation of an Si–O and Si–O–Si network as a result of silica coating. Peaks below 3000 cm⁻¹ are much more clearly defined as a result of increased organic species present on the surface that came from the reaction product of GPTS.

XPS was used to verify elements present on the particles' surface and their bonding states. XPS spectra of N (1s), O (1s) and Si (2p) in all samples are displayed in Fig. 2a–c. As shown in Fig. 2a there is no N (1s) found in

AR-TiO₂ while the appearance of a peak at 397 eV for the A-TiO₂ sample is attributed to nitrogen in the amino groups of APS. The presence of this peak proves the grafted amino groups after particles are modified by aminosilane. No peak around 103 eV can be found in the AR-TiO₂ sample (in Fig. 2b), confirming the absence of silica on the as-received particles. A significant increase in silicon is observed for AG-TiO₂ as a result of silica coated

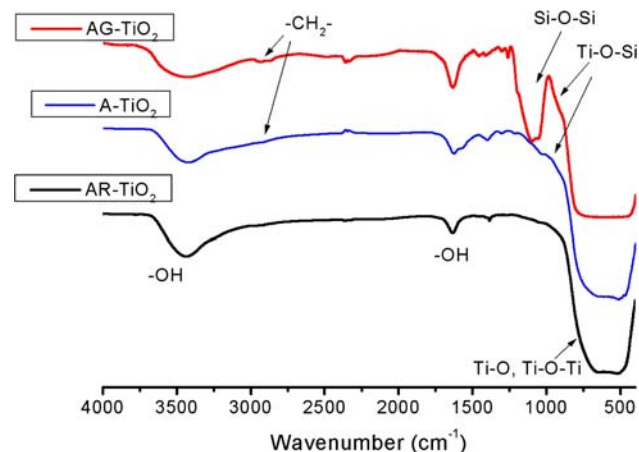


Fig. 1 FTIR spectra of titania nanoparticles at different stage of the process

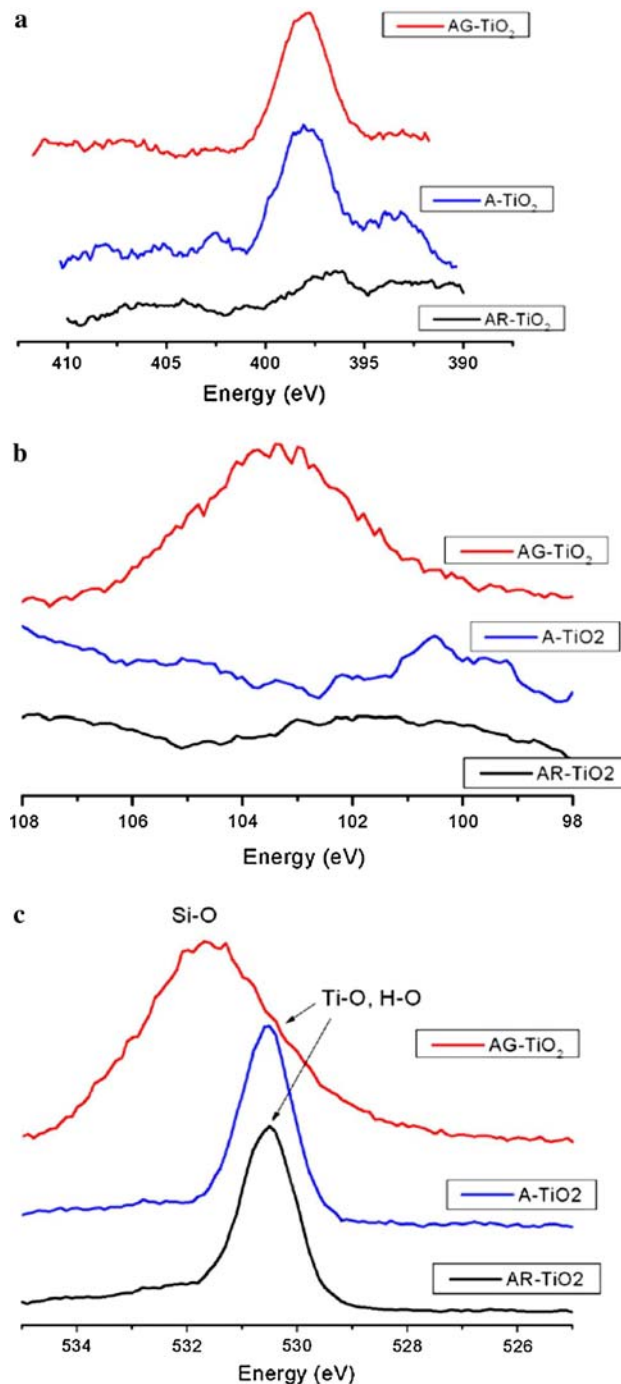


Fig. 2 XPS spectra of particle samples. **a** N 1s, **b** Si 2p, **c** O 1s

on the surface of nanoparticles after the two-step sonogel process. Figures 2 and 3 show the binding energy for O 1s for all three samples. Two significantly different sets of binding states can be found here, namely the peak at 530 eV corresponding to Ti–O, H–O in AR-TiO₂ and A-TiO₂, but in AG-TiO₂ this peak becomes broader and centered at higher energy. This change is due to the increase of silica (O–Si and Si–O–Si bonding) in the sample surface. Meanwhile another peak shift towards higher energy at just below 1000 eV was also found (not shown here). This can be assigned to the Auger line of oxygen KL₁L₂₃, KL₂₃L₂₃ and supports the existence of new oxidation states on the sample surface.

There is a concern that ultrasound agitation during the sonogel coating step may potentially remove or degrade amino functional groups grafted on the nanoparticle surface during the surface modification step, due to the harsh conditions that occur when cavitation collapse occurs at the particle surface. A separate experiment was conducted in which A-TiO₂ particles were sonicated in a simple

mixture of acidified water and ethanol under the same ultrasound conditions as used for the silica coating step, but without epoxysilane. XPS results from such particles indicated that nitrogen remained on the particle surface after sonication, thus confirming that the grafted amino groups were robust enough to react with epoxy silane in the subsequent sonogel process. This conclusion is in consistency with what we reported previously [15] where the sonogel coating process was applied to ITO nano particles.

Figure 3a–c shows representative TEM micrographs of titania samples. Figure 3a shows the particles of as-received P-25 powder that without any treatment. It is clear that all particles have a smooth surface. Figure 3b shows particles from a sample sonicated for 20 min with GPTS and Fig. 3c shows particles from a sample sonicated for 1 hour (note the particles in Fig. 3c locate on top of a cross point of lacy carbon). Uniform coatings, as indicated by a thin amorphous strip wrapping around the individual particles, can be clearly observed, confirming effectiveness of the surface coating process. For the 20 min sonication sample, the

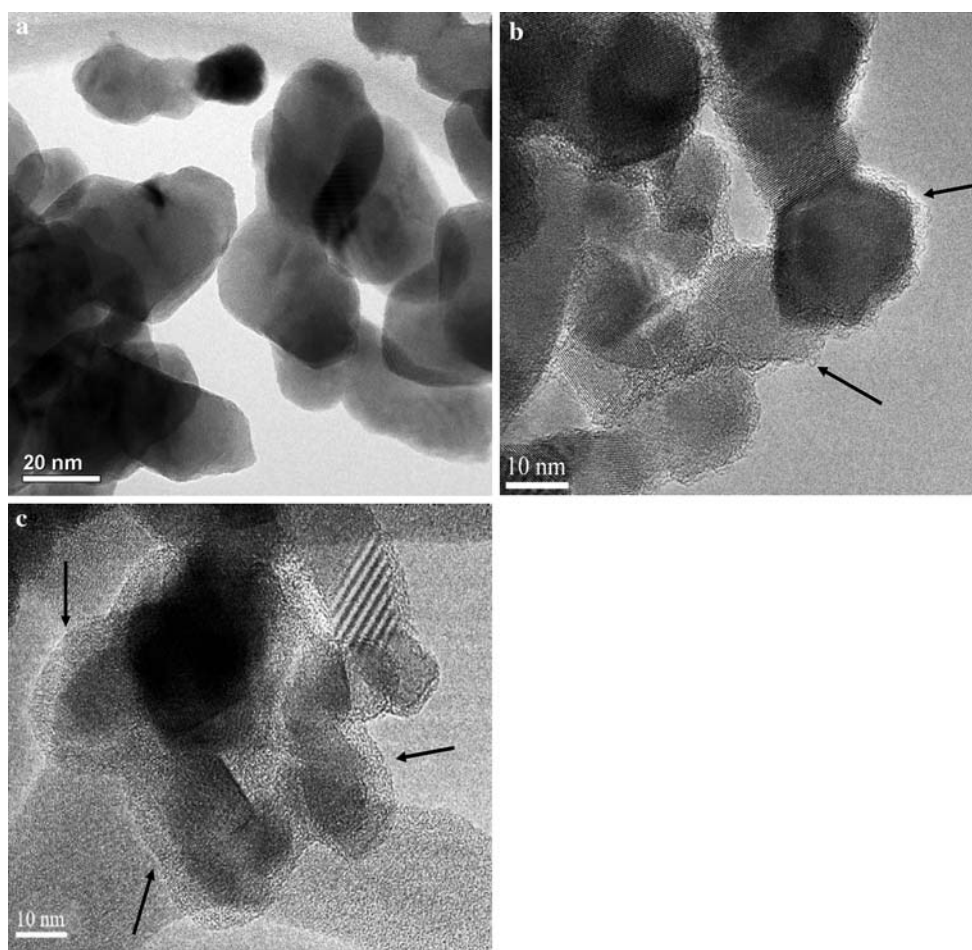


Fig. 3 Representative bright-field TEM images of titania nanoparticles. **a** as-received particles, **b** after 20 min of sonication, **c** after 1 h of sonication

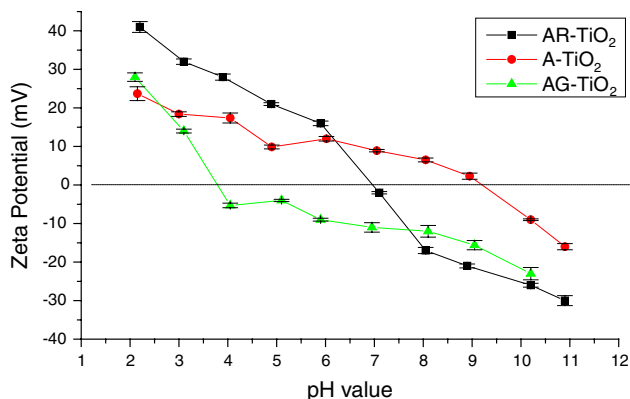


Fig. 4 pH dependent zeta potential of nanoparticle dispersions

silica layer is about 1 nanometer thick while on the 1 h sonication sample, the coating is 3–4 nm, which suggests a relationship between the length of sonication and the nano-coating thickness. Further investigation is in progress.

Solid oxides in aqueous suspension generally possess electrical charge due to the amphoteric dissociation of surface hydroxyl groups, the adsorption of H^+/OH^- ions, or metal hydroxo compounds due to hydrolysis of surface groups. The resultant surface charge is pH dependent. Zeta potentials of AR- TiO_2 , A- TiO_2 and AG- TiO_2 in the pH range from 2 to 11 are shown in Fig. 4. For AR- TiO_2 , the iso-electric point (IEP) is at pH 6.5–7.0. At pH values lower than the IEP, the zeta potential is positive, reaching 30–40 mV in the pH range of 2–4, while at a pH above the IEP, the zeta potential is negative, attaining a level of –30 mV at pH of 11. The IEP of A- TiO_2 is significantly shifted to a higher pH value after the aminosilane treatment step, or in other words, the surface charge of titania particles was rendered positive throughout a larger part of the pH range due to the presence of amino functional groups. Also it is noted that the zeta potential values are relative low. After the second sonogel coating step (AG- TiO_2), a more significant shift is observed as a result of a silica coating layer now fully covering the titania particles. The IEP was reduced to below pH 4, which is close to that of colloidal silica [16].

Based on the above evidence, a reaction mechanism for the sonogel coating step is proposed as shown in Fig. 5. In the first step, the particle surface is modified by a bifunctional organosilane molecule, containing NH_2 - and methoxy groups, to promote subsequent silica coverage. Hydrolysis of the methoxy groups produces silanols (Si–OH), which form covalent bonds with OH groups on the particles' surface, generating particles with NH_2 - terminated groups attached. Nanolayer coatings can subsequently be attached through the grafted NH_2 - groups. In the sonogel coating step, GPTS is first hydrolyzed under power ultrasound irradiation and acidic conditions. Large amounts

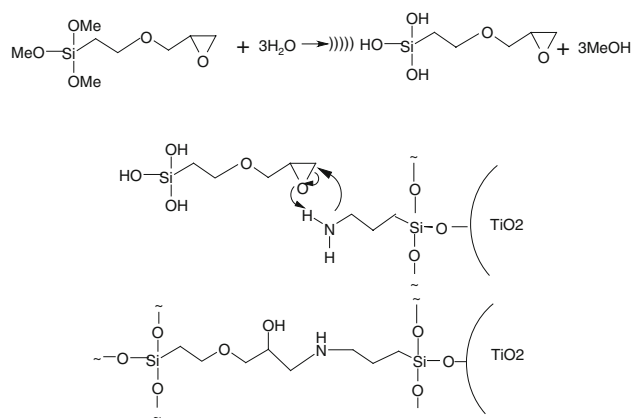


Fig. 5 Reaction mechanism for sonogel coating process

of silanol with an epoxy group attached are generated within a short time, while the lack of ethanol in the dispersion inhibits re-esterification of the silane. Epoxysilanol reacts with grafted aminosilanol on the particle surface by a ring opening and condensation reaction. Alcohol groups produced by this reaction can further react with epoxy groups to form ether groups, thus binding other hydrolyzed epoxysilanols near the particle surface. Furthermore, according to sonochemistry theory [12], the presence of particles in the dispersion enhances cavitation, since they act as nucleation sites. These two reasons render particles as “hot spots” to allow the silica coating to grow preferentially on the particle surface. Through this mechanism a layer of organo-modified silica assembles and eventually covers the particle surface.

4 Summary

In conclusion, we have demonstrated that this two-step sonogel process can be applied to commercial TiO_2 nanopowders to generate a thin layer of silica coated on the particle surface. Application of power ultrasound fulfils two functions, i.e. it initiates and sustains reactions leading to growth of silica, and it aids in dispersing the nanoparticles in solution. This process offers an alternative route for surface coating of commercial nanopowders used in various technological applications.

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