Journal of Alloys and Compounds 508 (2010) L1–L4

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Investigation of photocatalytic activity and UV-shielding properties for silica coated titania nanoparticles by solvothermal coating

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ARTICLE INFO

Article history:
Received 20 May 2010
Received in revised form 5 August 2010
Accepted 6 August 2010
Available online 21 August 2010

Keywords:
Core–shell
Silica coating
Solvothermal
Photocatalytic activity
UV-shielding properties

ABSTRACT

Due to its excellent UV-rays shielding properties, titanium dioxide can be used in many sunscreen products. However, concerns have been raised about the possible photocatalytic decomposition of cosmetic formulation by titanium dioxide. Therefore, titania nanoparticles were encapsulated in silica shell by using solvothermal process. Both temperature and time parameters of the solvothermal process were optimized to produce silica shell with highest density (loss of micropores) and maximum shell thickness. The coated particles were characterized by X-ray diffraction (XRD), TEM, FTIR, XPS, zeta-potential, and porosity measurements. The photocatalytic activity of the coated samples was suppressed effectively by conducting solvothermal silica coating at 200 °C for 15 h where TEM observations revealed the gradual growth of silica shell around TiO_2 nanoparticles. On the other hand, UV-shielding properties were slightly reduced after silica coating which can be attributed to the loss of titania content.

1. Introduction

Since the intensity of reachable UV-rays increases due to the collapse of ozone layer in past 20 years, skin protection from UV-rays has been recently of a great concern [1]. Sunscreen agent is one of the important tools to protect the skin from UV irradiation that induces sunburn, sun-tanning, photo-aging, and skin cancer. Therefore, the development of effective sunscreen agent is essential in the future [2]. Inorganic UV-rays blockers such as TiO_2, zinc oxides [3] and cerium compounds [4,5] are materials that absorb, reflect or scatter the ultraviolet radiation. However, despite that TiO_2 showing a good UV-shielding property, but it also exhibits a strong photocatalytic behavior when absorbing UV-rays, which is harmful for the human skin and affect the photostability of the cosmetics matrices [6,7]. Egerton and Mattinson have suggested the possibility of the photoreduction of organic components in cosmetic formulation due to photocatalytic activity of titania [8] that in turn will reduce the sunscreen efficacy. Based on that, low photocatalytic activity is preferred when titania is used as UV-shielding material to avoid the degradation of cosmetic matrix [9]. To suppress TiO_2 photocatalytic activity while retaining its UV-shielding property, inert shells, which usually composed of silica [1,10–16] or silane [14,15], were coated onto TiO_2 cores. Various chemical methods have been used for silica coating, such as phase transfer reaction between organic chloroform and aqueous phases [11], Stöber process [10,12], seeded polymerization [13], microwave (MW) irradiation [1,14], flame spray pyrolysis [15–17], and post-heating of chemisorbed tetramethycyclotetrasiloxane [18,19]. Recently, Li et al. [20] attributed the exhibition of a certain photocatalytic activity of coated titania, even after coating with 25.19 wt% silica, to the porosity of silica shell. However, employing the solvothermal process as coating method could be a proper approach to suppress the photocatalytic activity via reducing the porosity of the grown silica shell. The solvothermal process has been regarded as one of the most convenient and practical techniques for nanoparticles synthesis, not only because it does not require special instruments, complicated processes and severe preparation conditions, but also because it provides a good control over homogeneity, phase and morphology of the resultant products [21–23]. Recently, various core–shell structured materials have been prepared by using solvothermal process [24–26]. However, to the best of our knowledge, there are no reports on the usage of solvothermal process in silica shell formation onto TiO_2 nanoparticles. In the present work, we are proposing silica coating for titania nanoparticles by solvothermal process to suppress its photocatalytic activity via formation of dense silica shell. Silica coated titania nanoparticles were characterized by TEM, FTIR,

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doi:10.1016/j.jallcom.2010.08.031

EDX, XPS, zeta-potential, and porosity measurements. The photocatalytic activity and UV-shielding properties were also evaluated for the silica coated titania nanoparticles.

2. Experimental

2.1. Synthesis

In our synthetic approach, titania powder (Degussa p25 (99.5%), Nippon Aerosil Co. Ltd., Tokyo, Japan) was coated with 20 wt% silica by a solvothermal process as follows: the molar ratios of tetraethoxysilane (TEOS), ethanol, water, and ammonia were 1, 100, 400, and 20, respectively [13,27]. First, 0.693 g TEOS was dissolved in 15.3 g ethanol, then 1 g titania was dispersed in the TEOS/ethanol solution. Thereafter, 24 and 2.3 g of water and aqueous ammonia were added, respectively. Finally, the mixture was transferred into a Teflon-lined, sealed stainless vessel of internal volume of 50 cm^3, then it was heated to 120–240 °C at a rotation speed of 200 rpm and maintained for 6–15 h. After that, the slurry was filtered, washed, and dried. To investigate the impact of solvothermal process on pure titania, the TEOS free mixture was heated to 200 °C for 15 h.

2.2. Characterization

The average silica shell thickness was roughly estimated for 50 nanoparticles of silica coated titania using TEM (JEOL, JEM-2000EX II, Tokyo, Japan). The standard deviation calculated for each sample is shown in Table S1, where it can be seen that it varied from 0.078 to 0.117. These values indicate that the deviation of silica shell thickness from its average value was acceptable. FTIR spectroscopy measurements were conducted using FTS 7000 series (DIGILIB, Biorad Digilab Series 7000 FTIR Spectrometer, CA). The amount of precipitated silica was evaluated by energy dispersive X-ray spectroscopy (EDX) (Rayny EDX-800HS, Shimadzu, Tokyo, Japan). Barrett–Joyner–Halenda (BJH) pore parameters for the silica shell of the coated samples were determined by nitrogen adsorption–desorption isotherm measurements at 77 K (Quantachrome NOVA 1000-TS, Quantachrome Instruments, FL). The ζ potential–pH curve of silica coated TiO_2 nanoparticles are obtained by NanoZS (Malvern Instruments, UK). The UV-shielding ability of non-coated and silica coated samples was evaluated by measuring the transmittance spectra of thin film containing uniformly dispersed sample powder with UV–vis spectrophotometer (Shimadzu, UV-2550), as described previously [28]. To test the quality of silica coating, the photocatalytic activity was evaluated by measuring the degree of decomposition of phenol by UV–vis spectroscopy (Shimadzu, UV-2450) at different time intervals with the irradiation of 100-W high-pressure mercury arc ($\lambda > 290$ nm) to 0.5 mM phenol solution containing 0.25 g of the sample powder at 60 °C while bubbling 250 $cm^3\ min^{-1}$ of air (see Supplementary materials).

3. Results and discussion

The X-ray diffraction (XRD) patterns in Fig. S1 (see Supplementary materials) represent silica coated TiO_2 samples at solvothermal temperatures of 200 °C for reaction times of 6 and 9 h. All the samples exhibit anatase phase with (1 0 1), (0 0 4), (2 0 0), and (2 1 1) peaks (powder diffraction file no. 86-1157, ICCD), together with slight proportion of rutile phase. Solvothermal treatment of titania samples did not result in any phase transformation of titania nanoparticles since the peak position hardly changed. On the other hand, the decrease of diffraction peaks intensity while varying the solvothermal temperature and time, can be attributed to the silica shell that has shielded the detection of the X-rays [29].

Fig. 1 shows the FTIR spectra of non-coated and silica coated TiO_2 nanoparticles at different solvothermal temperature and time. There is a weak peak at 960 cm^{-1} corresponding to Si—OH bond [30] together with strong ones at 1100 and 1220 cm^{-1} corresponding to the asymmetric Si—O—Si vibration and asymmetric Si—O—Si stretching vibration, respectively [31]. The gradual increase of peak intensity at 1100 and 1220 cm^{-1} with varying solvothermal time and temperature indicates the formation of a network between silica nuclei in the silica shell through symmetric Si—O—Si vibration, and asymmetric Si—O—Si stretching vibrations. On the other hand, the Si—OH poor intensity as compared to the asymmetric Si—O—Si vibration and asymmetric Si—O—Si stretching vibration, suggested that the contribution of Si—OH within the silica shell was much lower than the networked Si—O—Si bonding which in turn points to the dense character of silica shell. In addition, FTIR results seem to be constituent with silica shell textural analysis in Table S1, which shows the impact of the solvothermal parameters on the silica shell characteristics, i.e. silica content, shell thickness, and shell porosity (pore volume for pore <1 nm). It can be noticed that the silica content and shell thickness was grown with increasing solvothermal temperature and time, while the porosity was diminished. Moreover, although at 120 and 160 °C a great portion of TEOS was hydrolyzed to produce silica nuclei, still the silica shell did not grown accordingly (Table S1). While at 200 and 240 °C, the silica shell was grown together with the increase of silica content. This means below 200 °C, the solvothermal temperature enhanced hydrolysis step rather than condensation one to form more secondary silica nuclei. On the other hand, above 200 °C, both hydrolysis and condensation are promoted where primary silica shell around titania surface is grown accordingly. Furthermore, solvothermal reaction time possessed a significant impact on shells dense character. At 15 h reaction time, silica shell thickness and silica content are increased to their maximum, along with the suppression of the shell porosity which indicates that the silica nuclei were being densely packed in the shell through asymmetric Si—O—Si and asymmetric Si—O—Si stretching vibrations. In other words, a prolonged reaction time at high solvothermal temperature induces more condensation of silica nuclei in the primary silica shell around titania surface.

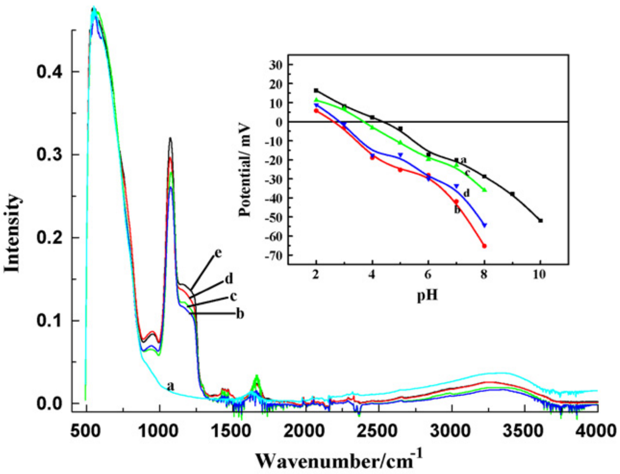

Fig. 1. FTIR spectra for (a) non-coated titania, 20 wt% silica coated sample (b) for 6 h at 120 °C, (c) for 6 h at 200 °C, (d) for 9 h at 200 °C and (e) for 15 h at 200 °C. Inset: *Z*-potential/pH curve for (a) non-coated titania, (b) silica, 20 wt% silica coated sample (c) for 6 h at 200 °C and (d) for 15 h at 200 °C.

In order to check the surface coating quality, the ζ potential–pH curves of silica, titania and silica coated titania nanoparticles were measured and shown in the inset of Fig. 1. The pH variation showed an isoelectric point (IEP) at 2.34 for silica nanoparticles and at 4.56 for titania nanoparticles. The behavior is similar to that in the literature [32,33]. The coated nanoparticles at 200 °C for 6 h with 18.3 wt% silica content have a zeta-potential that is different from pure titania nanoparticles, with an IEP of 4.02. Increasing the solvothermal coating time to 15 h brought a shift in zeta-potential to value similar to that of pure silica nanoparticles with IEP at 2.4. This suggested that titania nanoparticles are covered with complete, uniform silica shell.

To confirm the chemical state of the silica shell around titania surface, XPS measurements were conducted for non-coated and silica coated titania nanoparticles. O1s and Ti2p XPS spectra of pure and coated TiO_2 powder are shown in Figs. S2 and S3, respectively. The binding energy of O1s peaks for pure TiO_2 is 530.12 eV. For the silica coated TiO_2 powders at 15 h solvothermal time, two peaks at 533.50 and 530.87 eV were observed. The stronger peak at 533.50 eV is attributed to the binding energy of SiO_2 and the weaker

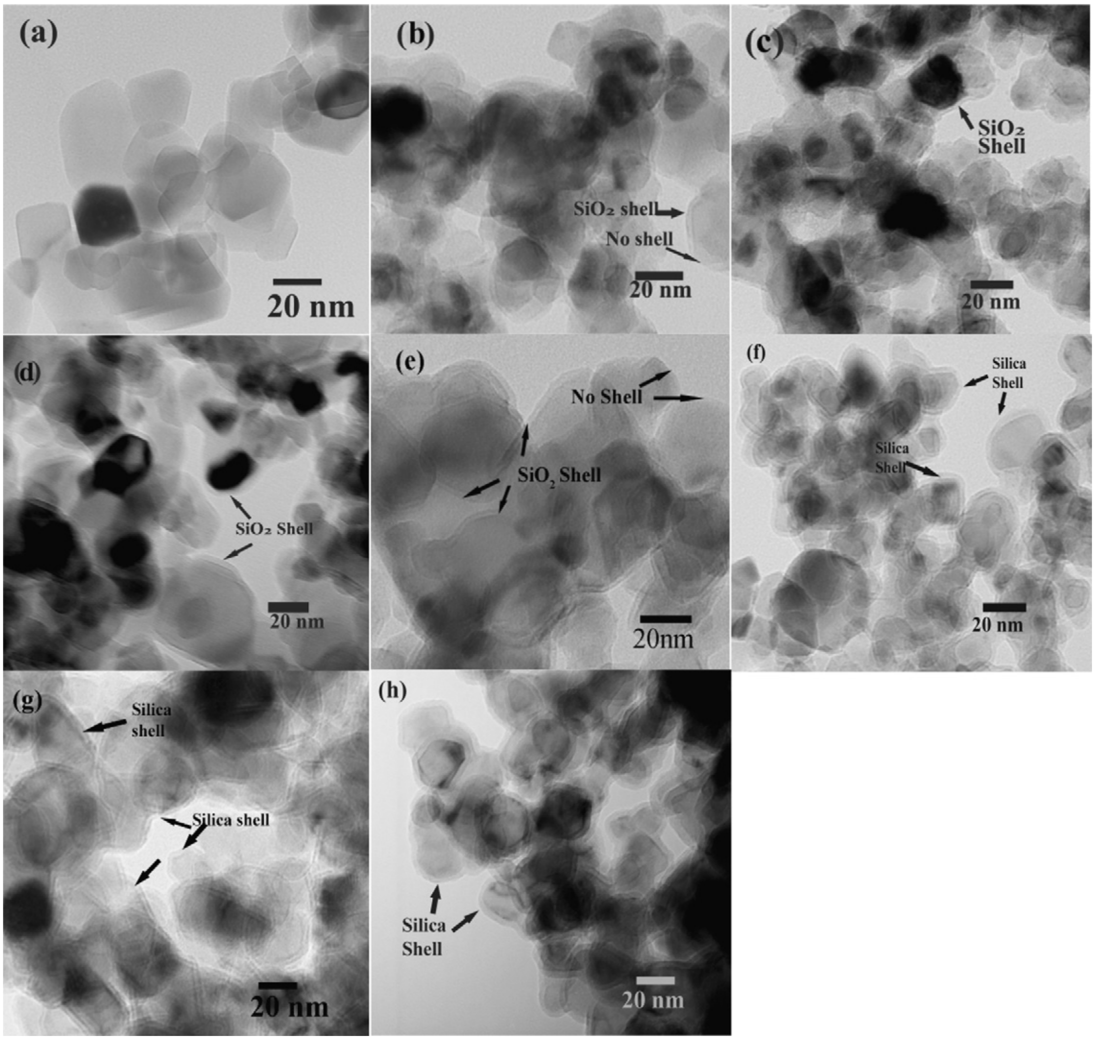

Fig. 2. TEM micrographs of (a) non-coated titania, 20 wt% silica coated sample for 6 h at (b) 120 °C, (c) 160 °C, (d) 200 °C, (e) 240 °C and 20 wt% silica coated sample at 200 °C for (f) 9 h, (g) 12 h and (h) 15 h.

one at 530.87 eV may be attributed to the coated TiO_2, which resulting from a chemical shift of 530.12 eV in pure TiO_2. In the coated TiO_2 sample, it is inferred that Si is combined onto the surface of TiO_2, forming a Ti—O—Si bond. Because the electronegativity of Si is greater than that of Ti, the shielding effect is weakened, and thus the binding energy is increased. Therefore, the O1s peak for TiO_2 has a chemical shift of +0.75 eV. The binding energies of O1s and Ti2p of pure and coated TiO_2 samples are summarized in Table S2.

Fig. 2 shows the TEM micrographs of TiO_2 nanoparticles coated with silica at different solvothermal temperatures and times. The TEM micrographs reveal that a uniform and continuous coating layer was formed around the surface of TiO_2 nanoparticles which gradually increased in thickness to about 3.8 nm at 200 °C for 15 h reaction time. In addition, the uniformity of the coating layer was significantly affected by the solvothermal temperature, i.e. below 200 °C a non-continuous shell can be observed around titania particles. In contrast, heating samples at 200 °C for lengthened reaction time, produced a distinct and continuous silica shell.

For further evaluation of silica coating quality, the photocatalytic activity test for the phenol decomposition was conducted for silica coated samples at different solvothermal temperatures and times, as shown in Fig. 3. The non-coated titania nanoparticles (Degussa P25) decomposed phenol solution completely after 3 h as the remaining phenol concentration was 0.22%. However, solvothermal treatment of non-coated titania sample did not result

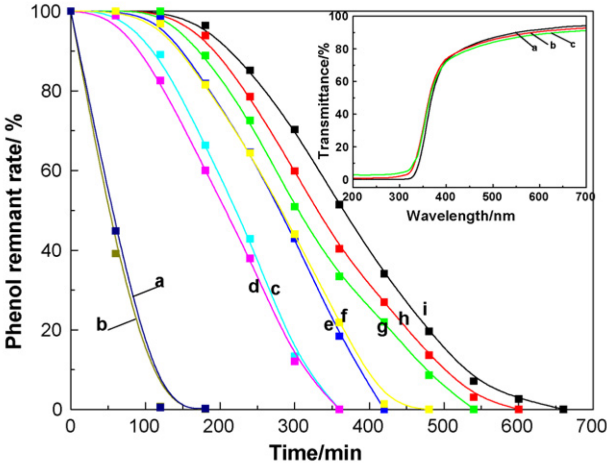

Fig. 3. Photocatalytic activity of (a) non-coated titania, (b) hydrothermal treated titania 20 wt% silica coated sample for 6 h at, (c) 120 °C, (d) 160 °C, (f) 200 °C, (e) 240 °C and 20 wt% silica coated sample at 200 °C for (g) 9 h, (h) 12 h, and (i) 15 h. Inset: UV–vis transmittance spectra of thin films of (a) non-coated titania, 20 wt% silica coated sample (b) for 6 h at 200 °C and (c) for 15 h at 200 °C.

in a significant change in its photocatalytic activity. The photocatalytic activity of coated titania nanoparticles decreased with increasing solvothermal temperature which can be attributed to the growth of shell thickness, as a result of enhancement of TEOS hydrolysis rate, together with the recession of shell porosity. Increasing the solvothermal coating time delayed the decomposition time of phenol up to 11 h. These results suggested that the quality of silica shell was improved by increasing coating time since the amount of precipitated silica did not change significantly as shown in Table S1. In other words, increasing coating time helped the growth of silica shell through transformation of secondary silica nuclei to primary silica shell through dissolution–precipitation reaction. Moreover, silica shell became denser by networking silica nuclei through asymmetric Si—O—Si vibration and asymmetric Si—O—Si stretching vibrations which could be confirmed from gradual loss of shell porosity.

To highlight the advantage of the solvothermal coating method over the other ones, a comparison was made for the impact of different coating methods (i.e. conventional sol–gel [20] and microwave methods [14] and this work data), over silica weight percent, shell thickness and photocatalytic activity as shown in Table S3. It is clear that solvothermal method was superior to microwave and sol–gel coating ones as both silica weight percent and shell thickness were promoted while photocatalytic remnant rate was significantly suppressed.

In order to evaluate UV-shielding ability of silica coated and non-coated titania, the UV–vis transmittance spectra of the samples were determined and the results are shown in the inset of Fig. 3. It can be seen that non-coated and silica coated titania samples at different solvothermal times had similar transparency in visible light region (700–400 nm). Transparency of the samples is crucial to allow penetration of the useful visible light radiation to the skin. However, at the UV-range of 400–340 nm, the entire three samples showed the gradual loss of transmittance. Furthermore, at UV-range of 340–200 nm, almost all UV-rays have been blocked out by either non-coated or silica coated sample since the UV–vis transmittances were almost approaching zero value. However, silica coated sample at 15 h solvothermal time showed a slight transmittance of UV-rays which can be attributed to the loss of titania content after silica coating process.

4. Conclusion

In conclusion, titania nanoparticles were coated with a dense silica shell via a solvothermal process. The optimization of solvothermal temperature and time resulted in complete (hermetic) coating of TiO_2 with a silica shell which was confirmed by the shift of IEP of the coated titania samples. Porosity and FTIR measurements suggested the dense character of silica shell which effectively suppressed the photocatalytic activity of titania nanoparticles. However, UV-shielding ability of coated titania was not significantly reduced by this dense coating.

Acknowledgements

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Scientific Research of Special Education and Research Expenses on “Post-Silicon Materials and Devices Research Alliance”, Japan.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.08.031.

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