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Multi-Step Coating of Monodisperse Silica Spheres by Titania Nanoparticles Base on Electrostatic Attraction Strategy

M. Zarrin Khame Forosh[1], V. Tajer-Kajinebaf[2] and H. Sarpoolaky [*3]

[1.] M. Sc. Student, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, P. O. Box: 16846-13114, Tehran, Iran.

[2.] Assistant Professor, Department of Materials Engineering, Takestan Branch, Islamic Azad University, P. O. Box: 34815-1515, Takestan, Iran.

[3.] Associate Professor, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, P. O. Box: 16846-13114, Tehran, Iran.

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ABSTRACT

TiO_2-SiO_2 core-shell particles with monodisperse silica core and nanostructured titania shell were synthesized by a multi-step coating process. The monodisperse silica spheres were prepared by Stöber method and titania shell obtained from a colloidal sol prepared by a hydrolysis–condensation reaction. The titania sol was deposited on monodisperse silica spheres by a multi-step coating method based on electrostatic attraction. Characterization was performed by DLS, SEM, DTA-TG, FT-IR and XRD. Also, the photoactivity of the core-shell particles was evaluated using methyl orange degradation by UV–visible spectrophotometer. The mean particle size of the colloidal titania sol was determined about 20 nm. The particle size of TiO_2-SiO_2 core-shell was about 500 nm. The deposit of titania nanoparticles on silica spheres was caused to delay anatase-rutile transformation. The core-shell particles calcined at 650°C showed a higher photocatalytic activity than that of pure titania. Prog. Color Colorants Coat. 7(2014), 259-268 © Institute for Color Science and Technology.

1. Introduction

Titania has received significant attention because of its numerous applications, such as white pigments [1,2], photocatalytic film [3-7], catalytic membrane [8-10], mesoporous material [11] and battery electrodes [12]. Titania nanoparticles are not thermally stable and also undergo phase transformation and crystallite growth at high temperatures leading to reduction in the effective surface area [13]. Also, it was found that fine particles, such as nano-TiO_2 may have adverse effects on health [14] and, moreover, recovery of particles in nano-size range is a problem. A solution of this problem is the adsorption of such fine particles on larger particles to form a thin layer with high porosity and high surface area [15,16]. Deposition of titania on a suitable support

*Corresponding author: hsarpoolaky@iust.ac.ir

such as silica due to its stability and low expense in the form of core-shell particles can be an appropriate method. In this condition, the core and shell will be composed of the monodisperse silica spheres and a nanostructured titania coating, respectively [16-18].

TiO_2-SiO_2 core-shell particle as an interesting photonic band-gap material has many applications. Also, low refractive index of silica (1.48) and high refractive index of titania (2.5) produces substantial modulation of dielectric medium when organized as a two- or three-dimensional crystal [18]. Moreover, SiO_2–TiO_2 composite materials are used due to their unique photocatalytic properties [19, 20].

However, for the catalytic applications, it is imperative that a proper thickness of TiO_2 film with well-defined textural morphology be developed in order to effect the desired reactions. The proper thickness of titania film may be achieved by increasing the concentration of the titania precursor solution or applying a multi-step titania coating during the synthesis process [13].

On the basis of our knowledge, few researches have been done on the photocatalytic properties of titania-silica core shell particles. In the present work, TiO_2-SiO_2 core–shell composite particles composed of monodisperse silica spheres and titania nanoparticles were prepared base on electrostatic attraction strategy by a multi-step coating. The core-shell particles calcined at 650°C showed a higher photocatalytic activity than that of pure titania for decomposition of methyl orange solution.

2. Experimental

2. 1. Materials

Tetraethyl orthosilicate (TEOS, Merck 800658), Ethanol (EtOH, Merck 100983), ammonia (25%, Merck 105432) and deionized water were used as raw materials for the synthesis of silica microspheres. Also, titanium tetraisopropoxide (TTIP, Merck 821895), isopropanol (IPA, Merck 109634), nitric acid (65% solution, Merck 100317) and deionized water were used as raw materials for the preparation of colloidal titania sol.

2.2. Synthesis of colloidal titania sol

Colloidal titania sol was prepared by a complete hydrolysis of titanium tetraisopropoxide via the addition of an excess H_2O ($[H_2O]/[Ti] > 4$). A solution of titanium tetraisopropoxide and isopropanol was added dropwise to a solution of water and isopropanol while stirring at high speed. Then the alcohol was removed from the solution and the product was dispersed in water to achieve a certain concentration. The molar ratio for TTIP:IPA:H_2O of the resultant mixture was 0.45:1:4.5, respectively. The mixture was peptized with acid by adjusted pH to 1.5 and was refluxed at about 75°C for 20 hr. Finally, a stable colloidal sol was obtained.

2. 3. Synthesis of monodisperse silica spheres

Monodisperse silica spheres as a support were synthesized by sol-precipitation using the Stöber method [21]. In a typical preparation, ammonia was dissolved in a solution of ethanol and water. Then, tetraethoxysilane was added dropwise to the above solution at about 25°C. The molar ratio for TEOS:H_2O:NH_4OH was 0.5:5:1, respectively. The solution was stirred for 3h, and then the white precipitate was filtrated. The products were repeatedly washed with water for three times, and then were dried at 80°C for 4h in an oven in order to remove water.

2. 4. Coating process

TiO_2–SiO_2 core–shell particles were prepared via heterogenic coagulation method. For this purpose, 0.25 gr of silica microspheres were dispersed in 25 mL of deionized water and the pH of SiO_2 suspension solution was adjusted to 1.25 then 2 mL of TiO_2 sol was added to the above solution. After stirring for 30 min, the pH of the mixed solution was adjusted again to 4.0 by NH_3 and then the precipitate was centrifugally separated. The obtained product was washed with water for three times to ensure complete removal of alcohol. The resultant powder was dried at 80°C to remove water, and then coating process was repeated for multi-step by the colloidal sol. Finally, the obtained dried composite particles were calcined at 650°C for 1 h in a muffle furnace.

2. 5. Characterization

Particle size distribution of the colloidal titania sol was determined by dynamic light scattering technique (DLS, Malvern, UK, ZS3600). The microstructure and morphology of samples were characterized by scanning electron microscope with an accelerating voltage of 30 kV (SEM WEGA\\TESCAN). Thermal properties of

samples were investigated by thermogravimetric analysis (DTA-TG PERKINELMER) with a nitrogen atmosphere at the rate of 7.5°C/min. Infrared measurements were performed using an FT-IR spectrometer (Tensor27 Bruker) at room temperature on sample wafers consisting of 100 mg of dry KBr and about 1 mg of sample. The phase composition of titania was determined by X-ray diffraction technique with Cu K_α wavelength at 30 mA and 40 kV (XRD, Jeol JDX-8030). In the last stage, the photocatalytic activity of the prepared samples was measured by the photocatalytic degradation of methyl orange (MO) in an aqueous solution by UV-Vis spectophotometer (Cecil Aquarius, CE 7200). In this study, 0.5 g of the TiO_2-SiO_2 core-shell particles was used to photodegrade MO solution with concentration of 20 mg/L in a 1.2 L reaction vessel. The catalyzed MO reaction was photo-excited by exposing the catalyst particles in the solution under UV irradiation source (24 W/cm^2, 254 nm).

3. Results and discussion

3.1. Particle size distribution of titania sol

Particle size distribution of the colloidal titania sol is shown in Figure 1. Results show particle size of the colloidal titania sol is in the range of 10-50 nm and the mean particle size is about 20 nm. So, the particle size of the colloidal titania sol is in nano-size range with narrow distribution.

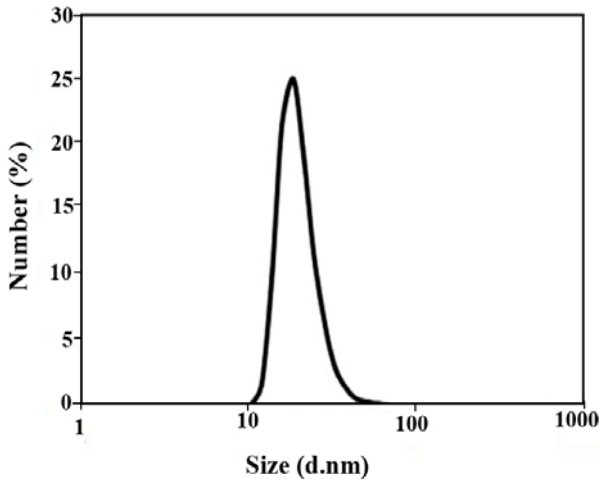

Figure 1: The particle size distribution of the colloidal titania sol determined by the dynamic light scattering technique.

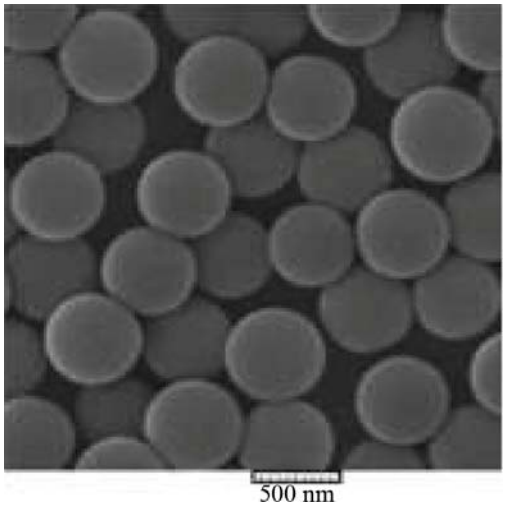

Figure 2: SEM micrograph of monodisperse silica microspheres.

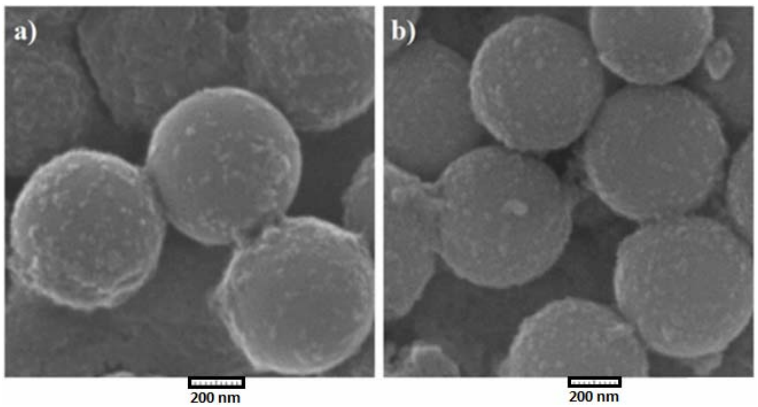

Figure 3: SEM micrographs of TiO_2-coated SiO_2 microspheres (a) before and (b) after calcination.

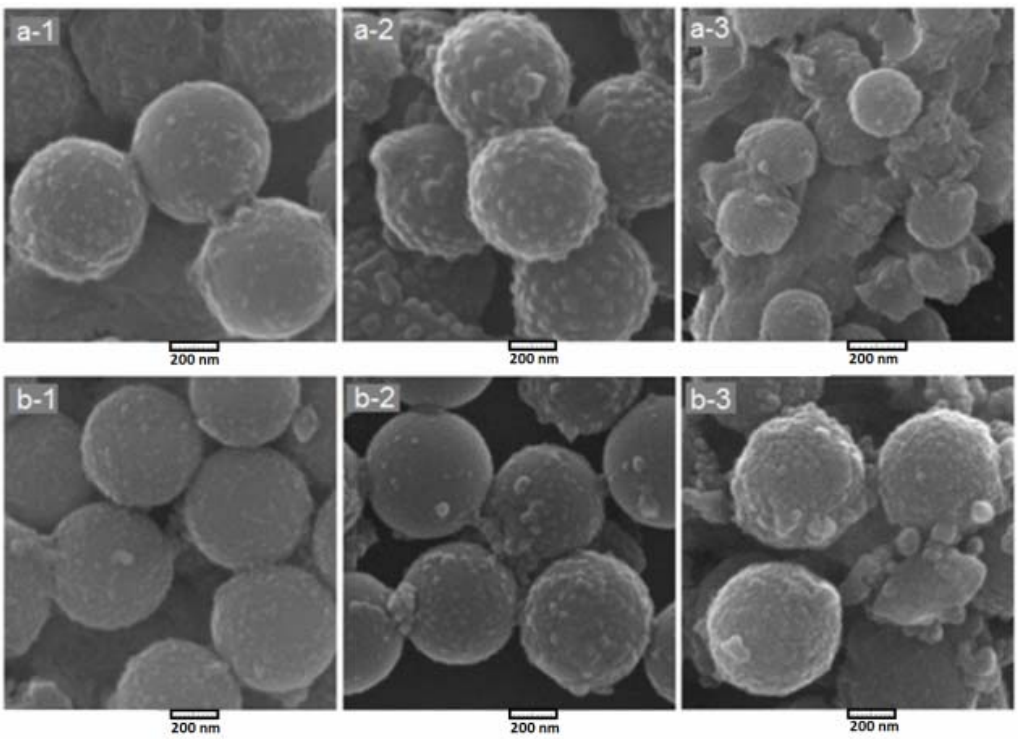

Figure 4: SEM micrographs of the core-shell particles upon multi-step coating (a) dried and (b) calcined at 650°C (1, 2 and 3 denote to the number of step coating).

3.2. Microstructure and morphology

SEM micrograph of the silica microspheres is shown in Figure 2. This image demonstrates monodisperse silica spheres obtained by the Stöber method have spherical shape and smooth surfaces with diameter about 500 nm.

Also, Figure 3 shows the SEM micrographs of the TiO_2-coated SiO_2 microspheres (TiO_2-SiO_2 composite core-shell particles) prepared at pH 4 before and after calcination. These images show the microspheres have rough and textured surfaces, which confirm the silica particles were coated by titania nanoparticles. The formation mechanisms of TiO_2-SiO_2 composite core-shell particles can be accounted by the pH of TiO_2

solution relative to the isoelectric points of TiO_2 and SiO_2. Isoelectric point of TiO_2 is reported in the interval 3.9-8.2 [22]. So at pH = 4, the colloidal titania particles have a positive surface charge density and expected to absorb to surfaces with a negative surface charge density. Reported values of the isoelectric point of SiO_2 are in the interval 1.7-3.5. This means that the SiO_2 surface would be negatively charged at pH = 4. Thus, the colloidal titania particles can be deposited on the surface of SiO_2 microspheres due to the electrostatic attraction.

The microstructure and morphology of TiO_2-SiO_2 core-shell particles with multi-step coating are shown in Figure 4. As shown in Figure 4, the size of core-shell particles increases with the number of coating steps. Although the titania layer in one-step coating before and after calcination (Figure 4(a), (b-1)) is not continuous, it has well covered the silica spheres in two-step coating process (Figure 4(a), (b-2)). However, three-step coating process increases the thickness of film and causes agglomeration between the particles (Figure 4(a), (b-3)). So, according to SEM images, it seems that two-step coating can be assumed as the optimum TiO_2-SiO_2 core-shell particles.

3.3. Thermal analysis

The T_g curves of the pure silica spheres and the optimum TiO_2-SiO_2 core–shell particles are shown in Figure 5. These curves are similar to the T_G curves of SiO_2/TiO_2 spherical core–shell particles synthesized by Lee *et al.* [13]. For the pure silica and titania-coated silica microspheres, total weight loss is about 14% and 18%, respectively. This is due to the higher amount of the organic ligands and water that titania-coated silica microspheres gained after deposition process. The weight loss originated mainly from desorption of physically absorbed water or solvents and surface dehydroxylation. T_G curves show that all the ligands are completely decomposed up to 1000°C.

3. 4. FT-IR spectroscopy

Figure 6 presents the IR spectra of pure titania and TiO_2-coated SiO_2 sphere particles calcined at 650°C in the wave number range from 4000 to 400 cm^{-1}. The broad peak at 2800-3800 cm^{-1} is assigned to O-H for absorbed water molecules [23]. Zhijie Li *et al.* claimed that Ti-O-Ti vibration appears in the range of 400-600 cm^{-1} as a result of condensation reaction [24].

Also, the 464 cm^{-1} peak is attributed to Si-O-Si bending modes, the 800 cm^{-1} peak is assigned for symmetric ν_s(Si-O-Si) stretching vibration, and the 1098 cm^{-1} peak can be attributed to asymmetric ν_{as}(Si-O-Si) stretching vibration [25], which reveals a dense silica network was formed. For TiO_2-SiO_2 core-shell particles, it is possible to distinguish two types of interaction between TiO_2 and SiO_2: physically mixed (weak Van der Waals forces) and chemically bonded (formation of Ti-O-Si linkages).

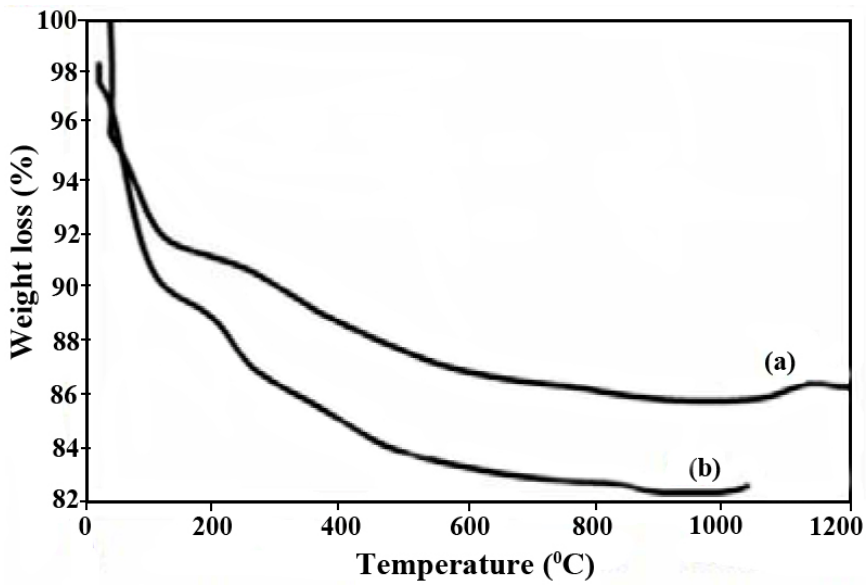

Figure 5: T_g curves of (a) pure silica spheres and (b) TiO_2-coated SiO_2 particles.

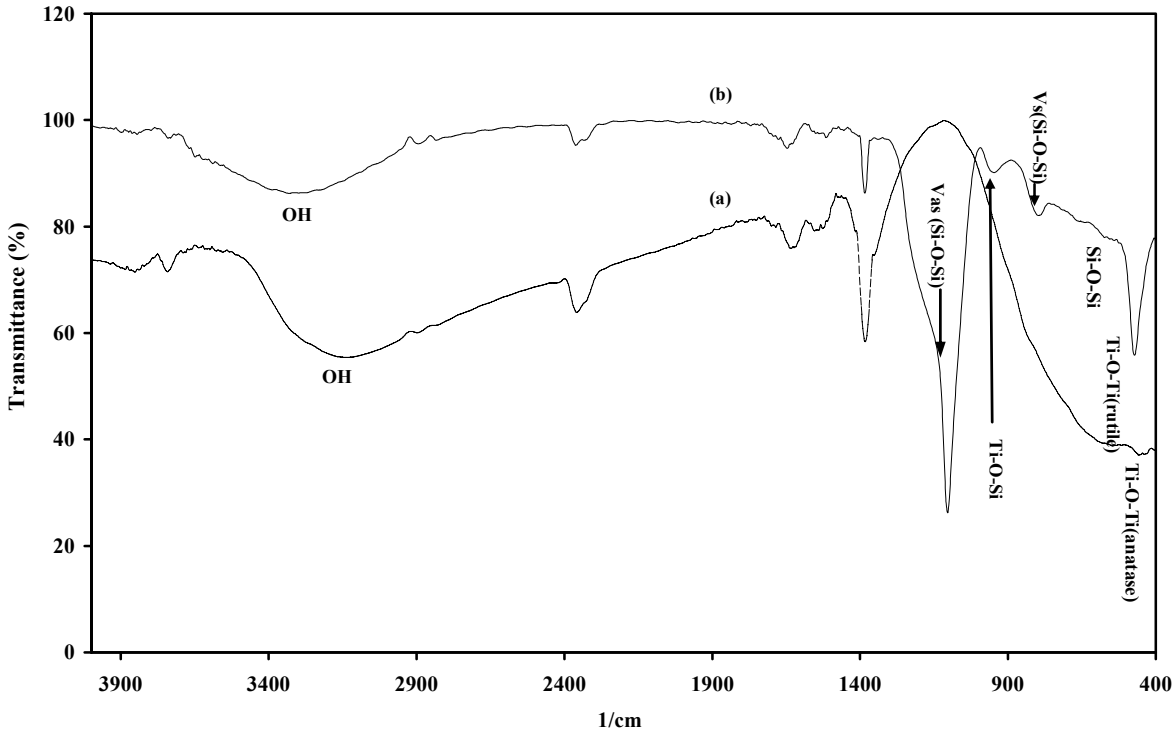

Figure 6: FT-IR absorption spectra of (a) pure TiO_2 and (b) TiO_2-coated SiO_2 particles calcined at 650°C.

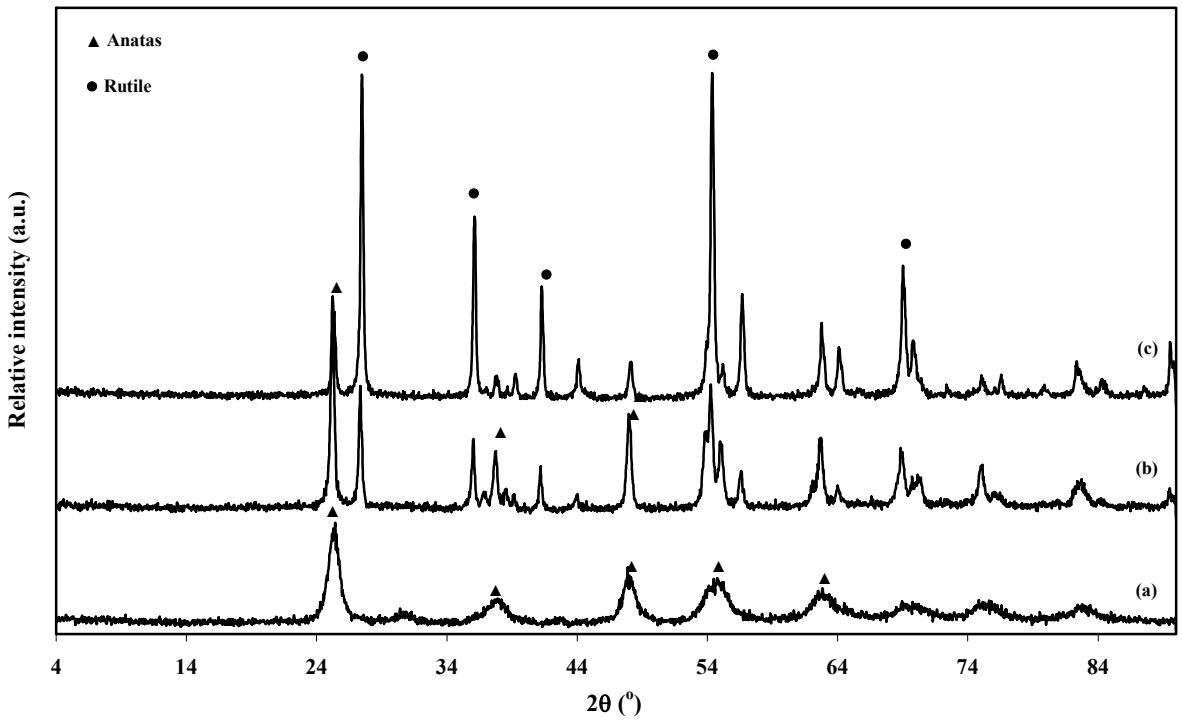

Figure 7: XRD patterns of the colloidal titania calcined at (a) 450°C, (b) 550°C and (c) 650°C.

The IR band at 910-960 cm^{-1} can be due to the stretching vibration band of Ti-O-Si bonds. So, the infrared band at 930 cm^{-1} in the spectra of the TiO_2-SiO_2 core-shell particles indicated the possibility of formation of bonds of Ti-O-Si [24].

Also, IR bands in the range of 433-438 cm^{-1} and 489-496 cm^{-1} were attributed to anatase and rutile, respectively [26]. So, it can be seen titania deposition on silica spheres changes Ti-O-Ti bending mode of rutile to anatase after calcination at 650°C according to curves in Figure 6.

3. 5. Phase analysis

XRD patterns of the colloidal titania calcined at different temperatures are shown in Figure 7. The strongest peaks of anatase and rutile phases are located at $2\theta = 25.3^{\circ}$ (101) and 27.4° (110), respectively [27]. These results indicate phase structure of the colloidal titania calcined at 450°C is anatase that with increasing temperature, these peaks are gradually resolved and rutile peaks are completed. It means that anatae phase is not stable at 650°C.

Also, XRD pattern of the monodisperse silica spheres coated with and without titania nanoparticles after calcination at 650°C are shown in Figure 8. Figure 8(a) shows partially amorphous structure of the monodisperse silica spheres after calcination at 650°C. Whilst the XRD patterns of TiO_2-coated SiO_2 spheres calcined in this temperature indicate dominant peaks at 2θ of about 25.2, 37.9, 47.8, 53.8, and 55.01 according to crystalline structure of anatase phase. It means that the coating of silica microspheres by titania nanoparticles causes to delay phase transition of anatase to rutile. In this condition, anatase phase would be stable at 650°C according to Figure 8 (b, c). So, the phase analysis results will be compatible with FT-IR ones (Figure 6).

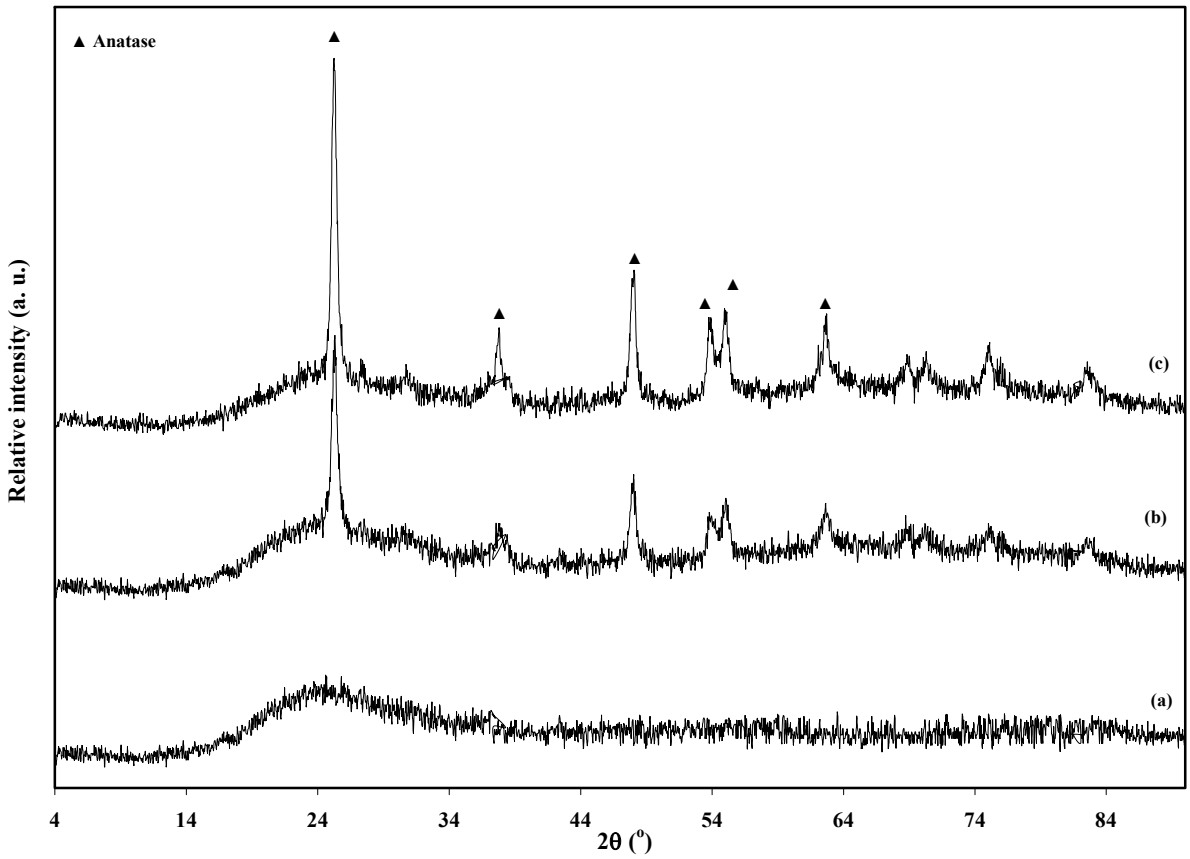

Figure 8: XRD patterns of the monodisperse silica spheres (a) without coating; (b) with one-step and (c) with two-step coating by titania after calcination at 650°C.

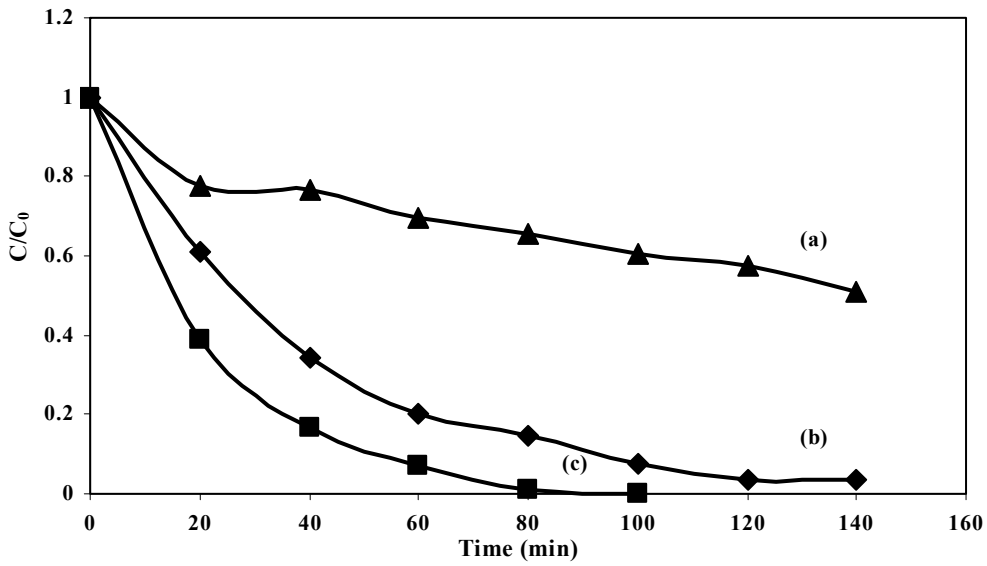

Figure 9: Concentration changes of MO in the presence of (a) pure titania, (b) one-step TiO_2-coated SiO_2 spheres and (c) two-step TiO_2-coated SiO_2 spheres calcined at 650°C.

It seems titania deposition on silica spheres has formed Ti-O-Si bond causing to postpone anatase-rutile transformation. According to the FT-IR results, the formation of Si-O-Ti cross-linking bonds and -OH radicals around the Ti-O network can delay the formation of phase from anatase to rutile. So, anatase phase would be stable at 650°C. Moreover comparing curves (b) and (c) (Figure 8) illustrates that increasing number of coating steps leads to amplifying anatase peak intensity.

3. 6. Photocatalytic activity

Figure 9 compares concentration changes of methyl orange aqueous solution in the presence of the pure titania and TiO_2-SiO_2 core-shell particles calcined at 650°C.

On the basis of results, TiO_2-SiO_2 core-shell particles calcined at 650°C show a higher photocatalytic activity than that of pure titania for decomposition of methyl orange aqueous solution. Also, the evolution of results indicates that the complete decomposition of MO occurs in less than 100 min in the presence of two-step TiO_2-coated SiO_2 spheres. In this condition, titania shell absorbs the UV irradiation to generate negatively and positively charged ions, the latter of which interacted with water to produce OH radicals that will degrade the MO.

In this process, the mechanism of photocatalytic degradation of MO is controlled by the silica core in a manner that, the electrons generated from the shell is immediately pulled towards the internal core, thereby effectively separating the different charges of ions and facilitating the production of the radicals [28].

4. Conclusion

In this work, TiO_2-SiO_2 composite core-shell particles including of monodisperse silica core and nanostructured titania shell were synthesized by a multi-step coating process. SEM images indicated the thickness of titania shell gradually increases by repeating of coating process. A mean diameter of TiO_2-SiO_2 composite core-shell particles was determined about 500 nm. Also FT-IR results confirmed the existence of Ti-O-Si bond at the interface between the titania shell and silica core. The deposit of titania nanoparticles on silica spheres was caused to delay anatase-rutile transformation. Also, the core-shell particles calcined at 650°C showed a higher photocatalytic activity than that of pure titania for decomposition of methyl orange.

5. References

1. J. Yu, L. Zhao, B. Cheng, Facile preparation of monodispersed SiO_2/TiO_2 composite microspheres with high surface area, *Mater. Chem. Phys.*, 96(2006), 311-316.
2. S. Farrokhpay, TiO_2 pigment suspension behaviour upon adsorption of polymeric dispersants, *Prog. Color Colorants Coat.,* 3(2010), 66-72.
3. M. Alzamani, A. Shokuhfar, S. Mastali, E. Eghdam, M. A. Hossaini, On the investigation of sol-gel TiO_2 nanostructured films applied on windshields pre-coated with SiO_2 layer by dip-coating method, *Prog. Color Colorants Coat.,* 6(2013), 51-59.
4. N. Barati, M. A. Faghihi Sani, Coating of titania nanoparticles on stainless steel using an alkoxide precursor, *Prog. Color Colorants Coat.,* 2(2009), 71-78.
5. H. Choi, E. Stathatos, D. D. Dionysiou, Photocatalytic TiO_2 films and membranes for the development of efficient wastewater treatment and reuse systems, *Desalination*, 202(2007), 199-206.
6. H. Choi, E. Stathatos, D. D. Dionysiou, Sol-gel preparation of mesoporous photocatalytic TiO_2 films and TiO_2/Al_2O_3 composite membranes for environmental applications, *Appl. Catal., B*, 63(2006), 60-67.
7. C. J. Tavares, J. Vieira, L. Rebouta, G. Hungerford, P. Coutinho, V. Teixeira, J. O. Carneiro, A. J. Fernandes, Reactive sputtering deposition of photocatalytic TiO_2 thin films on glass substrates, *Mater. Sci. Eng., B*, 138(2007), 139-143.
8. A. Alem, H. Sarpoolaky, M. Keshmiri, Titania ultrafiltration membrane: preparation, characterization and photocatalytic activity, *J. Eur. Ceram. Soc.,* 29(2009), 629-635.
9. A. Alem, H. Sarpoolaky, M. Keshmiri, Sol-gel preparation of titania multilayer membrane for photocatalytic applications, *Ceram. Int.,* 35(2009), 1837-1843.
10. A. A. Habibpanah, S. Pourhashem, H. Sarpoolaky, Preparation and characterization of photocatalytic titania–alumina composite membranes by sol–gel methods, *J. Eur. Ceram. Soc.,* 31(2011), 2867-2875.
11. H. Hao, J. Zhang, Low temperature synthesis of crystalline mesoporous titania with high photocatalytic activity by post-treatment in nitric acid ethanol solution, *Mater. Lett.,* 63(2009), 106-108.
12. T. H. Meen, W. Water, W. R. Chen, S. M. Chao, L. W. Ji, C. J. Huang, Application of TiO_2 nano-particles on the electrode of dye-sensitized solar cells, *J. Phys. Chem. Solids,* 70(2009), 472-476.
13. J. W. Lee, M. R. Othman, Y. Eom, T. G. Lee, W. S. Kim, J. Kim, The effects of sonification and TiO_2 deposition on the micro-characteristics of the thermally treated SiO_2/TiO_2 spherical core-shell particles for photo-catalysis of methyl orange, *Microporous Mesoporous Mater.,* 116(2008), 561-568.
14. Y. Badr, M. A. Mahmoud, Photocatalytic degradation of methyl orange by gold silver nano-core/shell nano-shell, *J. Phys. Chem. Solids,* 68(2007), 413–419.
15. D. H. Ryu, S. C. Kim, S. M. Koo, Deposition of titania nanoparticles on spherical silica, *J. Sol-Gel Sci. Technol.,* 26(2003), 489-493.
16. J. W. Lee, S. Kong, W. S. Kim, J. Kim, Preparation and characterization of SiO_2/TiO_2 core-shell particles with controlled shell thickness, *Mater. Chem. Phys.,* 106(2007), 39-44.
17. S. Kamaruddin, D. Stephan, The preparation of silica-titania core-shell particles and their impact as an alternative material to pure nano-titania photocatalysts, *Catal. Today,* 161(2011), 53-58.
18. S. Kalele, R. Dey, N. Hebalkar, J. Urban, S. W. Gosavi, S. K. Kulkarni, Synthesis and characterization of silica-titania core-shell particles, *Pramana J Phys,* 65(2005), 787-791.
19. K. Gude, V. M. Gun'ko, J. P. Blitz, Adsorption and photocatalytic decomposition of methylene blue on surface modified silica and silica-titania, *Colloids Surf., A,* 325(2008), 17-20.
20. O. Kesmez, H. E. Çamurlu, E. Burunkaya, E. Arpac, Sol-gel preparation and characterization of anti-reflective and self-cleaning SiO_2-TiO_2 double-layer nanometric films, *Sol. Energy Mater. Sol. Cells,* 93(2009), 1833-1839.
21. W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interface Sci.,* 26(1968), 62-69.
22. A. Imhof, Preparation and characterization of titania-coated polystyrene spheres and hollow titania shells, *Langmuir,* 17(2001), 3579-3585.
23. L. Zhou, S. Yan, B. Tian, J. Zhang, M. Anpo, Preparation of TiO_2–SiO_2 film with high photocatalytic activity on PET substrate, *Mater. Lett.,* 60(2006), 396-399.
24. Z. Li, B. Hou, Y. Xu, D. Wu, Y. Sun, W. Hu, F.

Deng, Comparative study of sol–gel-hydrothermal and sol–gel synthesis of titania–silica composite nanoparticles, *J. Solid State Chem.,* 178(2005), 1395-1405.

25. K. M. S. Khalil, A. A. Elsamahy, M. S. Elanany, Formation and characterization of high surface area thermally stabilized titania/silica composite materials via hydrolysis of titanium(IV) *tetra*-isopropoxide in sols of spherical silica particles, *J. Colloid Interface Sci.,* 249(2002), 359-365.
26. Y. Djaoued, S. Badilescu, P. V. Ashrit, D. Bersani, P. P. Lottici, J. Robichaud, Study of anatase to rutile phase transition in nanocrystalline titania films, *J. Sol-Gel Sci. Technol.,* 24(2002), 255-264.
27. S. Mozia, A. W. Morawski, M. Toyoda, M. Inagaki, Application of anatase-phase TiO_2 for decomposition of azo dye in a photocatalytic membrane reactor, *Desalination,* 241(2009), 97-105.
28. D. Beydoun, R. Amal, Implications of heat treatment on the properties of a magnetic iron oxide-titanium dioxide photocatalyst, *Mater. Sci. Eng., B*, 94(2002), 71-81.