

## Synthesis and characterization Au doped TiO<sub>2</sub> film for photocatalytic function

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**Abstract** Au doped TiO<sub>2</sub> nanoparticles have been synthesized using a reverse micelle technique combined with metal alkoxide hydrolysis and condensation. Au doped TiO<sub>2</sub> was coated with glass substrate. The size of the particles and thickness of the coating can be controlled by manipulating the relative rates of the hydrolysis and condensation reaction of TTIP within the micro-emulsion. The average size of synthesized Au doped TiO<sub>2</sub> nanoparticle was about in the size range of 15 to 25 nm and the Au particles formed mainly the range of 2 to 10 nm in diameter. The effect of synthesis parameters, such as the molar ratio of water to TTIP and the molar ratio of water to surfactant, are discussed. The synthesized nanoparticles were coated on glass substrate by a spin coating process. The thickness of thin film was about 80 nm. The degradation of MB on a TiO<sub>2</sub> thin film was enhanced over 20 % efficiency by the incorporation of Au.

**Key words** Au doped TiO<sub>2</sub>, Photocatalyst, Thin film, Reverse Micelle and Sol-Gel Process

### 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) has attracted interest due to its potential applications in water and air purification systems, self-cleaning coatings and photocatalytic and photovoltaic applications [1-6]. TiO<sub>2</sub> films can be coated by several methods including sol-gel, chemical vapor deposition, magnetron sputtering, layer-by-layer deposition, spin coating and spray pyrolysis [2]. One of these processes, the spin coating is the common process due to its simplicity and ease of control over the chemical composition of the films. The large band gap (3.2 eV) of TiO<sub>2</sub> is one of the crucial issues that it limits the applications of the TiO<sub>2</sub> nanostructures under visible light. Thus, the development of a TiO<sub>2</sub> photocatalyst with visible light activity has attracted much attention over the past several years. Typical pioneering efforts to modify TiO<sub>2</sub> include anion doping [7-10], transition metal ion implantation [11, 12], dye sensitization [13-16], nitrogen doping [17], Pt modification [18] and hybridization with noble metals. Among these, composites of noble metal and TiO<sub>2</sub> have been shown to have a high quantum yield of TiO<sub>2</sub> photocatalytic activity by prohibiting the fast recombination of photogenerated charge carriers [19]. The metal doping with well defined and dispersed is a key point of composite nanomaterials.

Several kind of approaches have been explored for the preparation of spherical ultrafine particles, including the use of colloids, polymers, glasses, and micelles to successfully control aggregation [20]. New and unusual physical and chemical properties also arise as particles attain nanosize dimensions [21]. Compared to conventional solid-state reaction methods, solution-based synthesis results in higher levels of chemical homogeneity. Also, in solution systems, mixing of the starting materials is achieved at the molecular level, and this is especially important when multi-component oxides are being prepared. In this study, we studied that Synthesis and Efficient PhotoCatalytic of Au doped TiO<sub>2</sub> thin film by a reverse micelle [22, 23] and sol-gel process [23]. Also, we demonstrate that the well defined and dispersed Au nanoparticles improved a photocatalytic activity.

### 2. Experiment

#### 2.1. The preparation of Au doped TiO<sub>2</sub> sol and thin film

Au doped TiO<sub>2</sub> sol was prepared by reverse micelle and sol-gel process. Reverse micelles were prepared from nonionic surfactant which was poly (oxyethylene) nonylphenyl ether (Igepal CO-520, Aldrich Chemical Co.). The surfactant was used without further purification. Other chemicals, such as Titanium(IV) isopropoxide (TTIP, Aldrich Chemical Co.), Hydrogen tetrachloroau-

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rate(III) trihydrate (ACS, 99.99 %, Alfa Aesar) cyclohexane, and NH<sub>4</sub>OH (28 %) (Fisher Scientific) were used as received. Typically, micro-emulsions of total volume 20 mL were prepared at ambient temperature with rapid stirring, and they consisted of Igepal CO-520, Cyclohexane, HAuCl<sub>4</sub> · 3H<sub>2</sub>O metal solution, and deionized water. The core size was controlled by varying the metal solution ratio C [24]. After nanosize water droplets were formed while stirring, TEOS was added into the stirred micro-emulsion. NH<sub>4</sub>OH was injected into the micro-emulsion to accelerate the condensation reaction of metal alkoxide precursors. This sol was used for deposition of thin film on soda-lime glass. The sol was coated on soda-lime glass by a spin-coating process. The sol was spin coated onto the substrate at 2000 rpm for 30 s. As-deposited film was dried at 80°C for 3 hours and heat treatment at 500°C for 1 h.

## 2.2. Characterization

The morphological feature of the synthesized Au doped TiO<sub>2</sub> sol was characterized was studied by transmission electron microscope (TEM) (JEM 2100F). The crystalline structures were observed by selected area electron diffraction (SAED). The structure of Au doped TiO<sub>2</sub> coated glass substrate was characterized by X-ray diffraction (XRD) (Model MiniFluxII; Rigaku Co., Tokyo, Japan) with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The coating morphology and thickness was studied by field emission scanning electron microscope (FE-SEM) (MIRA II LMH, H.S. Code : 9012. 10. 1000). Photocatalytic degradation of methylene blue (MB) was measured by UV-Visible Spectra Photometer analysis (UV-visble).

## 3. Results and Discussion

Au doped TiO<sub>2</sub> sol was obtained in reverse micelles

followed by in situ hydrolysis and condensation in the micro-emulsion. Fig. 1 shows that Au doped TiO<sub>2</sub> was obtained and Au core (2~10 nm) was well-dispersed in TiO<sub>2</sub>. The Au particles as core were formed by a homogeneous nucleation and growth process. The TiO<sub>2</sub> sol was most likely formed through heterogeneous nucleation and growth. There are two different mechanism and controlling to synthesis Au doped TiO<sub>2</sub> sol. The first step was rapid, complete reduction of the metal to the zero valence state. The second step was growth via reagent exchanges between micelles [25].

Fig. 2 was the spectrum of Au doped TiO<sub>2</sub> by TEM - EDS analysis. Fig. 2 a) core particles appear Au pattern peaks and Fig. 2 b) shells appear TiO<sub>2</sub> pattern peaks. Typically, Fig. 3 was characterized with SEAD to investigate crystal faces of the Au (111), (200), (220) and (311) [26]. An attempt to characterize the Au doped TiO<sub>2</sub> sample by EDS was not successful, because no characteristic pattern peaks of Au crystalline were observed. The crystalline phase present in the Au doped TiO<sub>2</sub> sample could be confirmed by selected area electron diffraction (SAED). The characteristic diffraction rings and spots of Au crystalline were observed clearly, indicating the Au cores exhibited polycrystalline structure. The SAED patterns of the sample consisted of a few relatively broad diffuse rings, which resulted from its very small dimensions. The broad rings indicated a very small grain size.

Fig. 4 was XRD patterns of the Au doped TiO<sub>2</sub> thin films calcined at 500°C for 1 h. As is widely known, the anatase-to-rutile phase transformation took place at temperatures of 600~800°C [27, 28] anatase phase TiO<sub>2</sub> was the most efficient for photocatalysis. So 500°C was chosen and we obtained anatase phase TiO<sub>2</sub> thin film.

Fig. 5 shows the typical SEM images of Au doped TiO<sub>2</sub> on glass substrate that were fabricated by repeating spin-coating 5 times. Fig. 4 a) was the surface of the film. It became smooth without delaminating or crack-

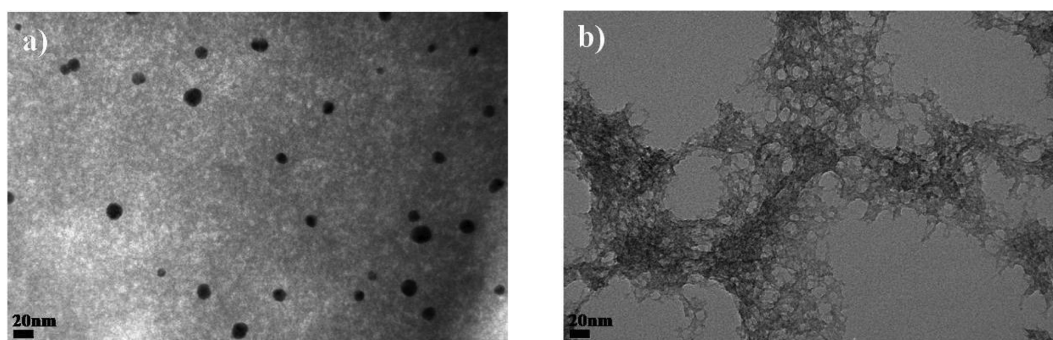


Fig. 1. TEM images of TiO<sub>2</sub> sol; a) Au doped TiO<sub>2</sub> nanoparticles and b) TiO<sub>2</sub> nanoparticles.

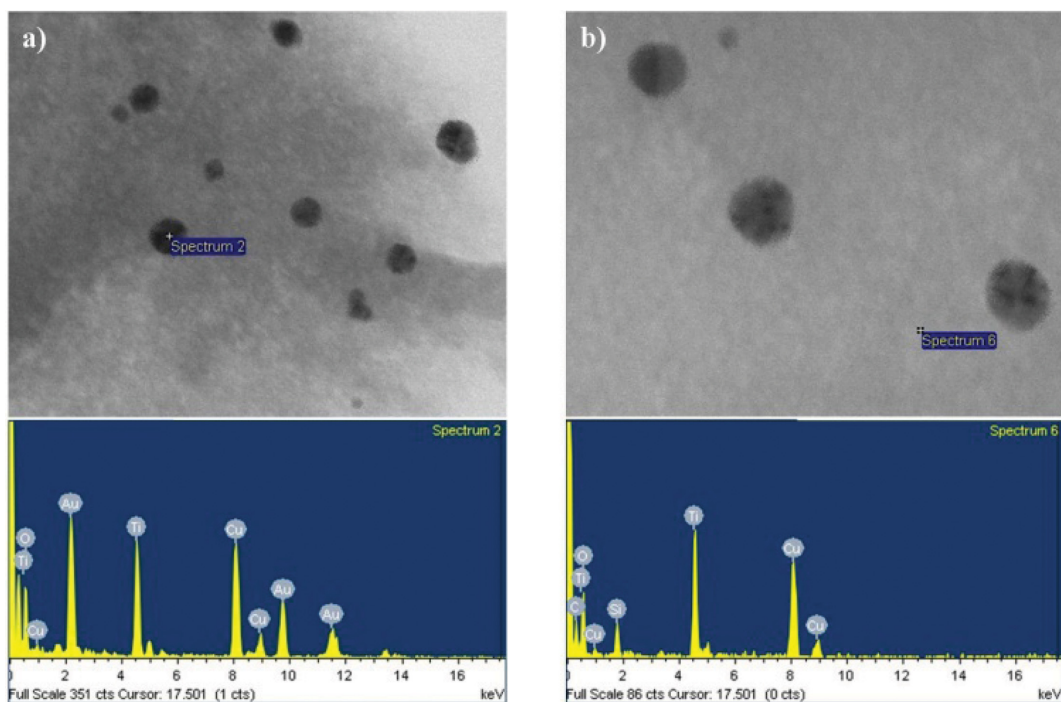


Fig. 2. TEM-energy dispersive spectroscopy (EDS) mapping of Au doped  $\text{TiO}_2$ ; a) Core spectrum and b) Shell spectrum.

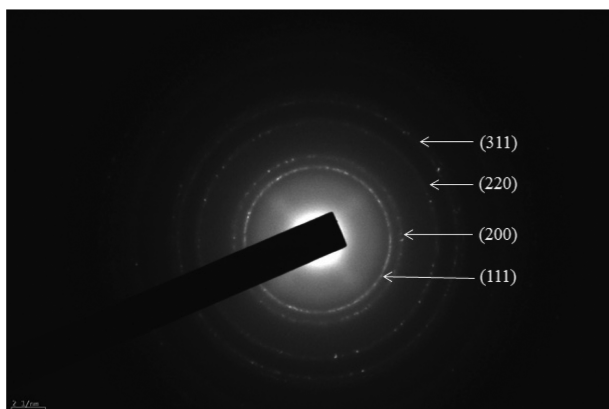


Fig. 3. Selected area electron diffraction (SAED) micrographs mapping of Au core particles diffraction pattern.

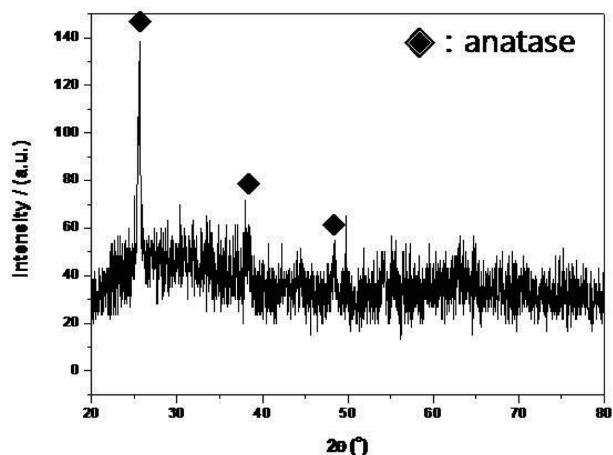


Fig. 4. XRD patterns of Au doped  $\text{TiO}_2$  thin film on glass substrate calcined at  $500^\circ\text{C}$  for 1 h.

ing. Fig. 4 b) was the cross-section of the film. The  $\text{TiO}_2$  layer was clearly observed. Also, it covered the substrate without delaminating or cracking. The thickness of the film was 70 to 80 nm, respectively.

In order to study any synergistic property of Au core particles, the photocatalysis efficiency was very important. Fig. 6 shows the results of the degradation of methylene blue (MB) under UV-vis. The Au doped  $\text{TiO}_2$  thin film was immersed in a UV cuvette filled with 10ppm aqueous MB solution and irradiated with UV light of 365 nm wavelength for a specified length of time. The MB absorbance peak was 664nm and before and after irradiation ( $I/I_0$ ) was correlated and displayed in Fig. 6.

It was found that the degradation of MB on a  $\text{TiO}_2$  thin film was significantly enhanced by the incorporation of Au cores, about a over 20 % enhancement of the photocatalytic activity. The enhanced photocatalytic activity can be explained through the energy band diagram and SPR effect [31]. The mechanism for photocatalytic is illustrated in Fig. 7 [31]. The inhibition of the recombination between photoinduced electron-hole pairs is believed to be responsible for the enhanced photocatalytic activity of Au doped  $\text{TiO}_2$  [29, 30]. The  $\text{TiO}_2$  film that was incorporated Au cores was shown to have higher photocatalytic degradation capability than neat

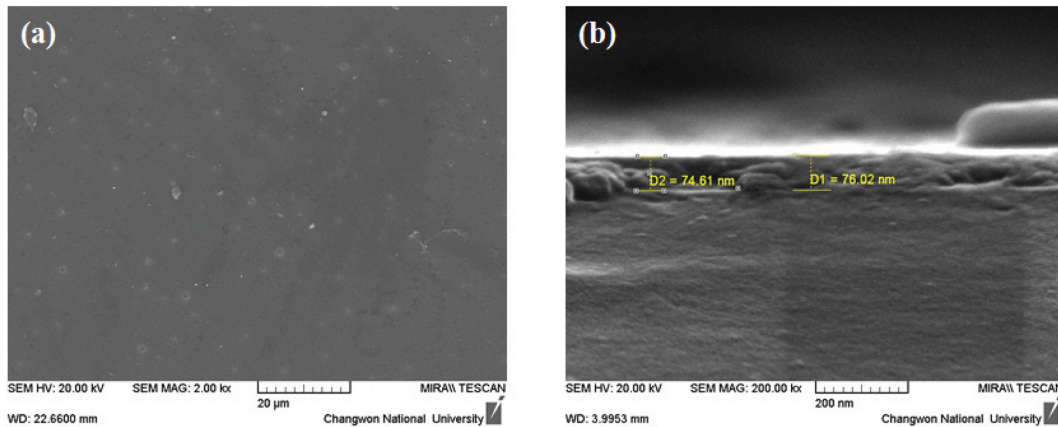


Fig. 5. FE-SEM images of Au doped TiO<sub>2</sub> thin film by spin coating process; a) Surface and b) Cross-Section.

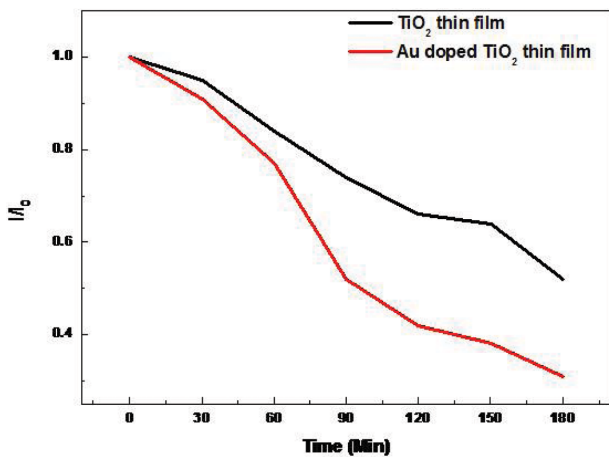


Fig. 6. Photocatalytic degradation of methylene blue (MB); ratio of the intensity of the peak at 664 nm ( $I/I_0$ ).

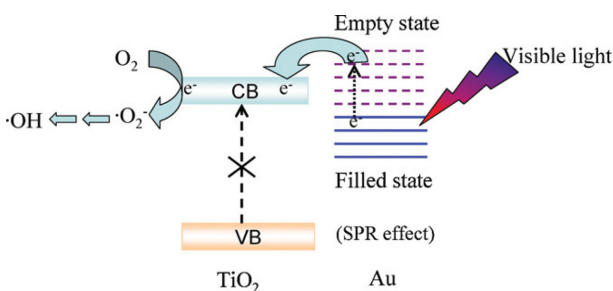


Fig. 7. The mechanism for photocatalytic of Au/TiO<sub>2</sub> catalysts [31].

TiO<sub>2</sub> one.

#### 4. Conclusions

We fabricate TiO<sub>2</sub> sol incorporated Au cores by reverse micelle and sol-gel process. The crystallized Au doped TiO<sub>2</sub> was confirmed by selected area electron dif-

fraction (SAED). The nanosized core particles were well dispersed and around 2~10 nm. The enhanced photocatalytic degradation of MB has been observed in Au doped TiO<sub>2</sub> thin films due to the inhibition of photoinduced electron-hole recombination as a result of an effective charge transfer.

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#### References

- [ 1 ] A. Fujishima and X. Zhang, "Titanium dioxide photocatalysis: Present situation and future approaches", *C. R. Chim.* 9 (2006) 750.
- [ 2 ] X. Chen and S.S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications", *Chem. Rev.* 107 (2007) 2891.
- [ 3 ] J.L. Gole, J.D. Stout, C. Burda, Y. Lou and X. Chen, "Highly efficient formation of visible light tunable TiO<sub>2-x</sub>N<sub>x</sub> Photocatalysts and Their Transformation at the Nanoscale", *J. Phys. Chem. B* 108 (2004) 1230.
- [ 4 ] A. Mills, G. Hill, S. Bhopal, I.P. Parkin and S.A. O'Neil, "Thick titanium dioxide films for semiconductor photocatalysis", *J. Photochem. Photobiol., A* 160 (2003) 185.
- [ 5 ] G.E. Brown, V.E. Henrich, W.H. Casey, D.L. Clark, C. Eggleston, A. Femly, D.W. Goodman, M. Gratzel, G. Macial, M.I. McGarthy, K.H. Neelson, D.A. Sverjensky, M.F. Toney and J.M. Zachara, "Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms", *Chem. Rev.* 99 (1999) 77.
- [ 6 ] S.A. Bilmes, P. Mandelbaum, F. Alvarez and N.M. Vic-

- toria, "Surface and electronic structure of titanium dioxide photocatalysts", *J. Phys. Chem.* 104 (2000) 9851.
- [ 7 ] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides", *Science* 293 (2001) 269.
- [ 8 ] Y. Sakatani, K. Okusako, H. Koike and H. Ando, "Development of TiO<sub>2</sub> photocatalysis with visible light response", *Photocatalysis* 4 (2002) 51.
- [ 9 ] H. Irie, Y. Watanabe and K. Hashimoto, "Nitrogen-concentration dependence on photocatalytic activity of TiO<sub>2-x</sub>N<sub>x</sub> Powders", *J. Phys. Chem. B* 107 (2003) 5483.
- [10] K. Kobayakawa, Y. Murakami and Y. Sato, "Visible-light active N-doped TiO<sub>2</sub> prepared by heating of titanium hydroxide and urea", *J. Photochem. Photobiol., A* 170 (2005) 177.
- [11] D. Wang, H. Lin and C. Yen, "Influence of metal plasma ion implantation on photo-sensitivity of anatase TiO<sub>2</sub> thin films", *Thin Solid Films* 515 (2006) 1047.
- [12] M. Anpo, "Photocatalysis on titanium oxide catalysts: Approaches in achieving highly efficient reactions and realizing the use of visible light", *Catal. Surv. Jpn.* 1 (1997) 169.
- [13] J. Hodak, C. Quinteros, M.I. Litter and E. San Roman, "Sensitization of TiO<sub>2</sub> with phthalocyanines. Part I. Photo-oxidations using hydroxoaluminium tricarboxy-monoamid-epthalocyanine adsorbed on TiO<sub>2</sub>", *J. Chem. Soc., Faraday Trans.* 92 (1996) 5081.
- [14] Y. Cho, C.H. Lee, T. Hyeon and H.I. Lee, "Visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO<sub>2</sub>", *Environ. Sci. Technol.* 35 (2001) 966.
- [15] D. Chatterjee and A. Mahata, "Demineralization of organic pollutants on the dye modified TiO<sub>2</sub> semiconductor particulate system using visible light", *Appl. Catal., B* 33 (2001) 119.
- [16] E. Bae, W. Choi, J. Park, H.S. Shin, S.B. Kim and J.S. Lee, "Effects of surface anchoring groups (carboxylate vs phosphonate) in ruthenium-complex-sensitized TiO<sub>2</sub> on visible light reactivity in aqueous suspensions", *J. Phys. Chem. B* 108 (2004) 14093.
- [17] H. Fu, L. Zhang, S. Zhang, Y. Zhu and J. Zhao, "Electron spin resonance spin-trapping detection of radical intermediates in N-doped TiO<sub>2</sub>-assisted photodegradation of 4-chlorophenol", *J. Phys. Chem. B.* 110 (2006) 3061.
- [18] K.W. Park, "Influence of Pt nanocrystallinity on electrochromism of TiO<sub>2</sub>", *Inorg. Chem.* 44 (2005) 3190.
- [19] J. Sa, M. Fernandez-Garcia and J.A. Anderson, "Photoformed electron transfer from TiO<sub>2</sub> to metal clusters", *Catal. Commun.* 9 (2008) 1991.
- [20] Y.M. Tricot and J.H. Fendler, "In situ generated colloidal semiconductor CdS particles in dihexadecyl phosphate vesicles: Quantum size and asymmetry effects", *J. Phys. Chem.* 90 (1986) 3369.
- [21] N. Ichinose, Y. Ozaki and S. Kashi, "Superfine particle technology", Springer-Verlag, New York (1988) 27.
- [22] D.S. Bae, K.S. Han and J.H. Adair, "Synthesis of nanosize SiO<sub>2</sub> particles by a reverse micelle and sol-gel processing", *J. Korean Cryst. Growth Cryst. Technol.* 11 (2001) 67.
- [23] J.W. Eun, D.K. Oh, K.J. Kim, T.U. Hong, S.M. Jeong, B.G. Choi and K.B. Shim, "Thermal stabilizing effect of Yb<sup>3+</sup> Er<sup>3+</sup> codoping into TiO<sub>2</sub> powder prepared by sol-gel method and its up conversion characteristic", *J. Korean Cryst. Growth Cryst. Technol.* 20 (2010) 173.
- [24] J.H. Son, H.Y. Park, D.P. Kang and D.S. Bae, "Synthesis and characterization of Ag/Pd doped SiO<sub>2</sub> nanoparticles by a reverse micelle and sol-gel processing" *Colloids and Surfaces A: Physicochem. Eng.* 313 (2008) 105.
- [25] T. Li, J.J. Mecholsky, D.R. Talham and J.H. Adair, "Preparation of Ag/SiO<sub>2</sub> nanosize composites by a reverse micelle and sol-gel technique", *Langmuir* 15 (1999) 4328.
- [26] S.W. Zhang, B.P. Zhang, S. Li, X.Y. Li and Z.C. Huang, "SPR enhanced photocatalytic properties of Au-dispersed amorphous BaTiO<sub>3</sub> nanocomposite thin films", *J. Alloy Comp.* 654 (2016) 112.
- [27] N. Negishi and K. Takeuchi, "Structural changes of transparent TiO<sub>2</sub> thin films with heat treatment", *Mater. Lett.* 38 (1999) 150.
- [28] J.H. Ryu, C.S. Lim, W.C. Oh and K.H. Auh, "Preparation of TiO<sub>2</sub> nanopowder using titanium terta-isopropoxide and effect of pH", *J. Korean Cryst. Growth Cryst. Technol.* 12 (2002) 91.
- [29] Y. Zheng, L. Zheng, Y. Zhan, X. Lin, Q. Zheng and K. Wei, "Ag/ZnO heterostructure nanocrystals: synthesis, characterization, and photocatalysis", *Inorg. Chem.* 46 (2007) 6980.
- [30] T. Hirakawa and P.V. Kamat, "Charge separation and catalytic activity of Ag@TiO<sub>2</sub> core-shell composite clusters under UV-irradiation", *J. Am. Chem. Soc.* 127 (2005) 3928.
- [31] S. Zhu, S. Liang, Q. Gu, L. Xie, J. Wang, Z. Ding and P. Liu, "Effect of Au supported TiO<sub>2</sub> with dominant exposed {0 0 1} facets on the visible-light photocatalytic activity", *Appl. Catal. B Environ.* 119 (2012) 146.