



Preparation of TiO₂/Ag colloids with ultraviolet resistance and antibacterial property using short chain polyethylene glycol

W. Su, S.S. Wei, S.Q. Hu, J.X. Tang*

Key Laboratory of Green Packaging and Application Biological Nanotechnology of Hunan Province, Hunan University of Technology, Zhuzhou 412008, People's Republic of China

ARTICLE INFO

Article history:

Received 28 November 2008

Received in revised form 12 July 2009

Accepted 14 July 2009

Available online 22 July 2009

Keywords:

TiO₂/Ag

PEG-600

Complex antibacterial agents

Ultraviolet resistance

Growth inhibition rates

ABSTRACT

TiO₂/Ag nano-antibacterial material was prepared at low temperature using polyethylene glycol (PEG-600) as reducing and stabilizing agent. The size and shape as well as the optical properties of the nano-materials were characterized with transmission electron microscopy (TEM) and UV–vis spectroscopy (UV–vis). The results showed that the average particle size of TiO₂ among these nano-materials was around 50–150 nm, and the average particle size of nano-silver was around 20 nm. Formation of Ag nano-particles on the surface of TiO₂ was confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and the antibacterial activity was also investigated. By the antibacterial activity study and ultraviolet resistance test, it is noted that growth inhibition rates against *E. coli* was 99.99% as the concentration of nano-particles dispersion solution was 10 ppm, the minimum UV protective effect could be achieved as the concentration was 290 ppm.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Ultraviolet has many functions such as disinfection, sterilization and promoting the synthesis of vitamin D. Exposure to ultraviolet radiation at adequate intensity can enhance the body's resistance, but to ultraviolet radiation at excessive intensity would lead to increased melanin, the aging of skin, declining immunity. Therefore, clothing of field staff, clothing of the staff at high altitude, beach clothing, sportswear, etc. have an urgent requirement against ultraviolet rays. For these reasons, UV shielding agent has become the focus of the current study to achieve such goal. In general, the UV shielding agents applied include TiO₂, ZnO, and MgO.

In addition to the UV shielding effect, nano-TiO₂ has photocatalytic ability realized by using sunlight, fluorescent light as the UV excitation source, thus the nano-TiO₂ are widely used for removal of toxic, harmful or hazardous pollutants, sewage treatment because of its physical and chemical stability, low cost, ease of availability, non-toxicity and electronic and optical properties [1]. However, the photo quantum efficiency of TiO₂ is greatly limited because of the quick recombination of photogenerated electrons and holes. Thus, it is of current interest to develop techniques to depress the electron-hole recombination in TiO₂. TiO₂ surface modification with Ag has been proved as an effective technique to depress the recombination of photogenerated electrons and holes in TiO₂ and improve its bactericidal activities [2]. Owing to the antibacterial effect of

Ag and Ag⁺, TiO₂ surface modification with Ag could be endowed with ultraviolet resistance and antibacterial effect, which is of great significance for functional textile products.

Regarding the synthesis of hydrophilic TiO₂/Ag composite antibacterial materials, there are two common methods reported. The first is *in situ* synthesis of TiO₂/Ag reported by Mohseni and co-workers [3], in which Ag is anchored to TiO₂ nano-particles surface in the preparation of TiO₂ using titanium alkoxides as raw materials [4,5]. In another route, nano-TiO₂ is applied as raw materials, Ag⁺ is deposited on the nano-TiO₂ surface or nano-TiO₂ lattice by using DMF [6], sodium citrate [7], H₂O₂ [8], hydrazine [9], sodium borohydride [10] as reducing agent or by photochemical method [11–13].

As polyethylene glycol has excellent water solubility, biocompatible lubricity, thermal stability plus its features of non-toxic, non-irritating and moisturizing, so many researches have reported preparation of TiO₂/Ag using polyethylene glycol. Nasr-Esfahani and Mohammad [14], Kodaira et al. [15] have dealt with the preparation of TiO₂/Ag film, Mallick et al. [16] has used a methoxy polyethylene glycol (MPEG) template to synthesize Ag film, Popa et al. [17] has reported a 'one pot' facile method for environmentally benign production of stable Ag colloids, using short chain polyethylene glycol as solvent, reducing agent and stabilizer.

Though these published works have reported synthesis of TiO₂/Ag composite, they were almost concerned on photocatalytic activity, its ultraviolet resistance and antimicrobial effects were not properly studied simultaneously.

Here, we report for the first time a simple and economical recovery method for silver-deposited TiO₂, this method needs no other

* Corresponding author. Tel.: +86 25 2182107; fax: +86 25 2182107.

E-mail addresses: jxtang0733@163.com, ssswww13@163.com (J.X. Tang).

reductant or surfactant except polyethylene glycol, which can save raw material and reduce cost, thus it is very suitable for industrial production of TiO₂/Ag. In our research, PEG-600 was used as a stabilizing agent and reducing agent to synthesize nano-sized TiO₂/Ag composite colloids, which showed excellent dispersion stability. This novel deposition precipitation (DP) method needs no calcinations, which is different from traditional deposition precipitation method. Since neither calcinations nor long-term UV irradiation was needed in this DP method, the agglomeration of Ag particles on the TiO₂ could be nearly avoided. At the same time, its ultraviolet resistance and antimicrobial activity were investigated in our study. As TiO₂/Ag composite colloids had excellent ultraviolet resistance and antimicrobial activity, it can be applied in many fields such as coating, textiles, plastics, and packaging.

2. Experimental

2.1. Materials

TiO₂ in industrial grade was purchased from Hunan Zhuzhou Chemical Industry Group Co. Ltd. and silver nitrate (AgNO₃) with analytical grade obtained from Shanghai Institute of Fine Chemical Materials was used as silver sources for preparation of TiO₂/Ag. Polyethylene glycol (PEG-600) in reagent grade taken from Guangdong Guanghua Chemical was used as solvent for the TiO₂/Ag and reducing agent of AgNO₃. *E. coli* and *Streptomyces* were taken to investigate antimicrobial activity of TiO₂/Ag. Phosphate Buffered Saline (PBS) buffer solution was used as diluent, nutrient broth and agar medium were used for the liquid culture medium and solid culture medium of bacteria, respectively.

2.2. Analytical techniques

Transmission electron microscopy (TEM, TSM6360) was employed to investigate the size and distribution of Ag-deposited TiO₂. X-ray photoelectron spectra (XPS) analysis was performed under a pressure of 1.33×10^{-7} Pa on the ESCA LAB MK2 instrument with Mg K-Alpha as source and a step of 0.05. The C (1s) level (285.0 eV) was taken as the reference binding energy. TU-1901 two-beam UV–vis spectrophotometer (Beijing Cape Analysis of General Instruments Limited Liability Company) was used to measure the optical properties and ultraviolet resistance properties of TiO₂/Ag colloids; X-ray diffraction (XRD) patterns was recorded using a Bruker D8 Advance XRD diffractometer equipped with a Gobel mirror, using Cu K α radiation.

2.3. Preparation of TiO₂/Ag colloids

For the preparation of TiO₂/Ag composite colloids, firstly, 30 g industrial TiO₂ dispersed in 200 mL deionized water was grinded into nano-TiO₂ at 3000 rps for 30 min using nanometer grinder. Then, 5 mL of TiO₂ slurry and 1 g of AgNO₃ were dispersed in 100 mL of PEG-600 at continuous stirring using magnetic stirrer. Reactions were carried out for 4 h at 60 °C. To get TiO₂/Ag powder, the TiO₂/Ag colloids were centrifuged at rate of 3000 rps for 60 min and washed with ethyl alcohol, at last dried in vacuum at 80 °C for 24 h.

2.4. Antibacterial properties study

First of all, liquid culture medium and solid culture medium were collocated for bacteria. Briefly, bacteria and 1 ppm, 4 ppm, 7 ppm, 10 ppm of TiO₂/Ag colloidal dispersions were added to 100 mL liquid culture medium, respectively in the Erlenmeyer flask shaking in thermostat shaker at rate of 170 rps. 0.1 mL so-made bacteria–TiO₂/Ag mixture was diluted with 0.9 mL. Phosphate Buffered Saline buffer solution, and completely mixed by vortex.

No TiO₂/Ag colloids were added to one Erlenmeyer flask containing 100 mL liquid culture medium, which was served as a control sample.

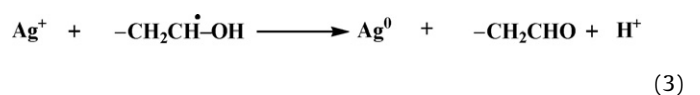
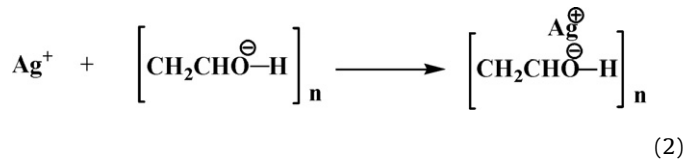
Subsequently, the bacteria suspension was diluted 10⁵ times. After the serial dilution had been carried out, 0.2 mL of each bacteria–TiO₂/Ag mixture was added to a Petri dish containing 10 mL warm agar medium. One additional plate was poured containing 10 mL of nutrient agar for control purposes. The plates were incubated for 24 h at 37 °C and then analyzed for the number of bacterial colonies to determine the growth inhibition rates of TiO₂/Ag in accordance with the Eq. (1)

$$R(\%) = \frac{A - B}{A} \times 100 \quad (1)$$

where R = the growth inhibition rates, A = the number of bacterial colonies from control sample, and B = the number of bacterial colonies from TiO₂/Ag sample.

3. Results and discussion

Polyethylene glycol (HOCH₂(CH₂OCH₂)_{*n*}CH₂OH) is non-electrolyte, having many polar groups such as C–O, C–H, H–O so that it can be absorbed onto TiO₂ by hydrogen bonding [18] and supposed to enhance the steric hindrance effect on surface of nano-TiO₂ to prevent agglomeration of TiO₂. In the presence of AgNO₃, Ag⁺ was bonded to the polar side groups such as C–O, C–H, H–O in PEG-600 according to Eq. (2), so that the reduction of silver ions on the surface of TiO₂ in the PEG solution can occur while hydroxyl groups of PEG was oxidized to aldehyde groups (CH₂CH₂OH → CH₂CHO) based on Eq. (3). The merit of method for preparation of TiO₂/Ag composite nano-material, which extends PEG-based routes toward a more environment-friendly production of Ag nano-particles on the surface of TiO₂, is the use of longer chain polymer as both solvent and reducing agent, which leads to an increase stability of the obtained TiO₂/Ag colloids and eliminates the need of co-stabilizers.



3.1. Morphological analysis

Fig. 1 is TEM image of TiO₂/Ag composite colloids, which enable identification of the location, distribution and size of Ag-deposited TiO₂. As result of hydroxyl and polyethylene glycol absorbed on the surface of TiO₂, it can be enhanced as adsorbent or carriers for metal, which is beneficial for the deposition of conductive silver. Since density of silver particles is higher than that of TiO₂, the TEM image of silver particle is significantly darker than that of TiO₂. This makes it easy to identify Ag spherical nano-particles from TiO₂ particles. In Fig. 1, it is clear that Ag particles with size of 20 nm were successfully deposited on the surface of TiO₂ (50–150 nm), which would be beneficial for the UV shielding capability of TiO₂. It is confirmed by the fact that the absorbance of the Ag-deposited TiO₂ sample is higher than that of the pure TiO₂ powders below 462.5 nm. Fig. 1 also shows that TiO₂/Ag nano-particles dispersed evenly, which is attributed to the stabilizing of PEG-600 [19,20]. In

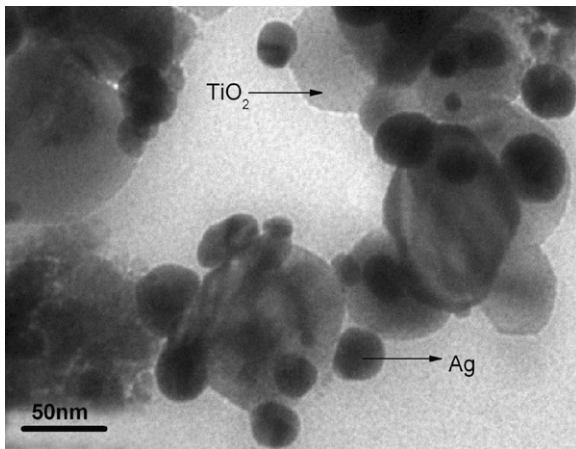


Fig. 1. TEM images of TiO_2/Ag .

Fig. 1, no free Ag particles are found in the mixture, indicating that silver particles are strongly anchored to the TiO_2 supports.

3.2. XRD analysis

The XRD patterns of TiO_2/Ag and TiO_2 sample are shown in Fig. 2. To our best knowledge, it is widely known that the formation of metallic silver particles crystallized in the face centered cubic (fcc) structure is in accordance with the JCPDS file No. 4-0862, the peaks at 38.1° , 44.6° , 64.7° , 77.5° assigned to diffractions from the (1 1 1), (2 0 0), (2 2 0) and (3 3 0) planes are of fcc silver. A and R represent the anatase and rutile diffraction peak absorption of TiO_2 , respectively. The TiO_2 sample exhibit well-crystallized anatase phase in Fig. 2(a), XRD peaks at 25° (major), 37° , 48° , 55° , 56° , 62° , 71° , and 75° appear significantly. In Fig. 2(b), weak peaks corresponding to metal Ag can be found at $2\theta = 44.3^\circ$ (2 0 0), 64.4° (2 2 0), 77.4° (3 3 0). It indicated that Ag had successfully anchored to the TiO_2 supports. Unfortunately, due to the strong diffraction peaks of the TiO_2 supports and the low amounts of the metals present [5,8], the intense peak corresponding to metal Ag at $2\theta = 38.1^\circ$ (1 1 1) is covered up by peaks corresponding to TiO_2 at $2\theta = 37.8^\circ$ (0 0 4), 38.6° (1 1 2). Owing to deposits of Ag, TiO_2/Ag showed some rutile structures on the pattern at $2\theta = 27.5^\circ$, 36.4° [21]. However, the peak for the anatase structure of pure TiO_2 was weaker and broader compared to that for TiO_2/Ag . Generally, the

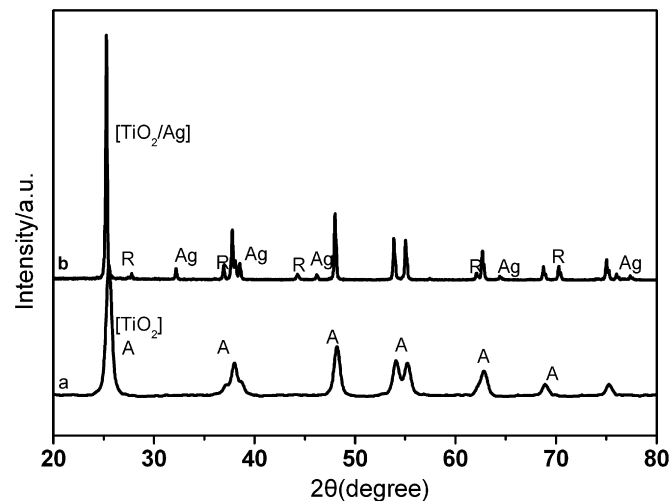


Fig. 2. XRD patterns of TiO_2 and TiO_2/Ag (a) synthesized mesoporous TiO_2 ; (b) 25% Ag on TiO_2/Ag .

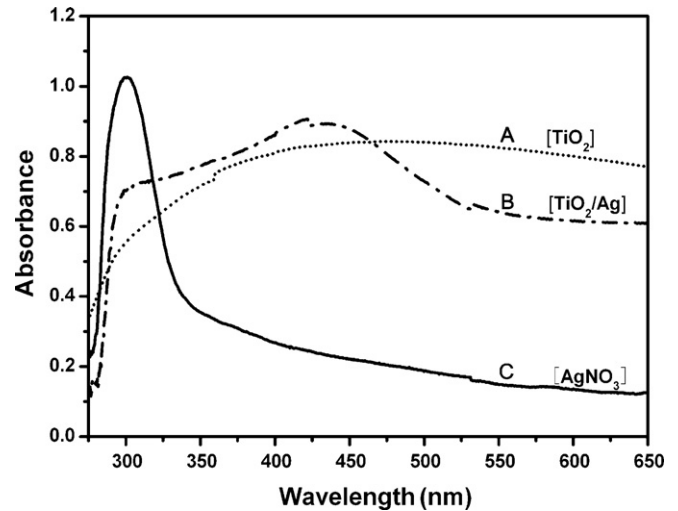


Fig. 3. UV-vis absorption spectra of AgNO_3 , pure TiO_2 , TiO_2/Ag colloid dispersed in PEG-600 (A) pure TiO_2 ; (B) TiO_2/Ag colloid containing 5000 ppm Ag; (C) AgNO_3 containing 5000 ppm Ag.

broader the peaks, the smaller the crystallites are; our samples were characterized by relatively large crystallite sizes of 50–150 nm and 70–170 nm for the anatase structures of TiO_2 and TiO_2/Ag , respectively.

3.3. Optical properties

Fig. 3 illustrates the absorption spectra of AgNO_3 , pure TiO_2 , TiO_2/Ag composite colloids in the wavelength range 275–650 nm. In Fig. 3, short dot line, dash dot line and solid line represent absorption spectra of pure TiO_2 , TiO_2/Ag composite colloids and AgNO_3 , respectively. It reveals that absorption peak of TiO_2/Ag appeared at 420 nm attributed to the classical surface plasmon excitation of the Ag nano-crystals. However, the peak is widen due to the deposition of Ag on anatase TiO_2 . As shown in Fig. 3, the absorbance of the Ag-deposited TiO_2 sample is higher than that of the pure TiO_2 below 462.5 nm, and is lower than that of the pure TiO_2 at long wavelengths (>462.5 nm). That is beneficial for the UV shielding capability of TiO_2 . These results appeared due to the presence of Ag particles and their interaction with TiO_2 particles [9,13]. The difference in UV-vis absorption spectroscopy between AgNO_3 and that of TiO_2/Ag could be employed to determine the extent to which Ag^+ is reduced to Ag. Actually, the color of colloidal solution changed from white to yellow and finally colored in grayish brown due to deposition of finely dispersed silver on TiO_2 in the process of TiO_2/Ag preparation.

3.4. Ultraviolet resistance

Ultraviolet light spectrum could be divided into UVA (400–320 nm), UVB (320–280 nm), UVC (280–200 nm) as well as vacuum ultraviolet (200–100 nm). The UVC has little effect on human body as it is absorbed by the ozone layer before arriving on the earth comparing with UVA and UVB. Therefore, we could evaluate the anti-ultraviolet effects by study of UV absorption capability of TiO_2/Ag colloids with UV spectrum in the range of 280–400 nm. TiO_2/Ag colloid was diluted with PEG600 to 2.37 mg/mL, 1.18 mg/mL, 0.59 mg/mL and 0.29 mg/mL, whose UV absorbance performances were investigated by spectrophotometer scanning from 200 nm to 400 nm.

Fig. 4 demonstrates UV absorbance of TiO_2/Ag composite colloidal solution at different concentrations. Due to higher concentrations of TiO_2/Ag , the absorbance values vary from 0 to 5.

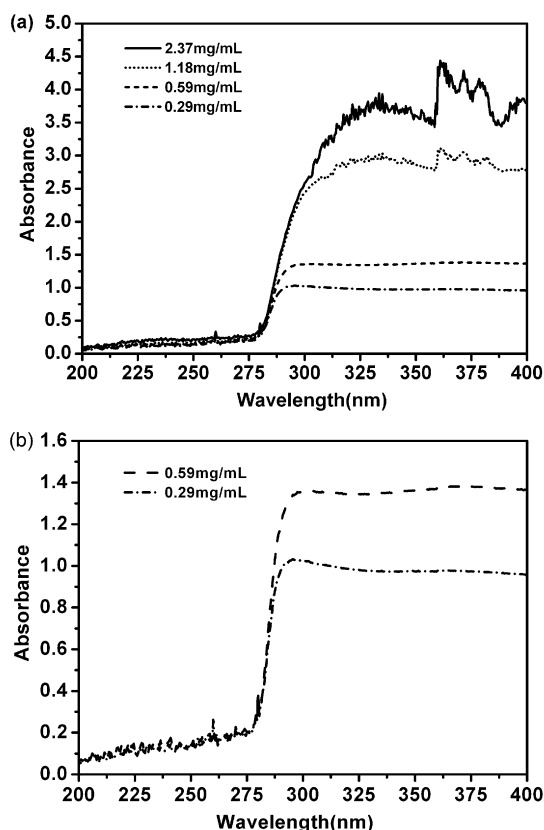


Fig. 4. UV absorbance of TiO_2/Ag colloids at different concentrations. (a) UV absorbance of all the TiO_2/Ag colloid; (b) high-resolution UV absorbance of TiO_2/Ag at 0.59 mg/mL and 0.29 mg/mL.

Fig. 4(a) is UV absorbance of all the TiO_2/Ag colloids, Fig. 4(b) is high-resolution UV absorbance of TiO_2/Ag at 0.59 mg/mL and 0.29 mg/mL. From the figure it is noted that the ultraviolet absorption value of all the TiO_2/Ag colloids is below 0.25 with $\lambda < 275$ nm, and rise sharply at wavelengths from 275 nm to 310 nm. This phenomenon can be explained as follow. TiO_2 was coated by a large number of Ag nano-particles, which was confirmed by the fact that the UV absorbance of TiO_2/Ag colloids is lower than that of pure TiO_2 in Fig. 3. However, the absorption of ultraviolet does not vary obviously above 310 nm. According to evaluation form on the effect of sunscreen comprehensive in "UV absorbance Law" [22] in which the material with absorbance values between 0.5 and 1.0 is defined to have the smallest UV protective effect, the middle UV protective effect from 1.1 to 1.5, effective protection ultraviolet radiation in the range of 1.6–2.0, full protective ultraviolet radiation above 2.1. Thus, complex colloidal solution with concentration at 0.29 mg/mL has smallest UV protective effect, moderate UV protective effect as the concentration is 0.59 mg/mL, and fully protective ultraviolet radiation effect as the concentration is 1.19 mg/mL.

3.5. XPS analysis

X-ray photoelectron spectroscopy (XPS) experiments were performed to elucidate both the TiO_2 structure and the chemical state of Ag particles. Fig. 5 shows the XPS survey spectrum of TiO_2/Ag powders prepared by the deposition precipitation method. XPS peaks show that the TiO_2/Ag powders contain only Ti, O, and Ag elements and a trace amount of carbon. The C element is ascribed to the adventitious hydrocarbon from XPS instrument itself. The evaluation of binding energy values for the Ti2p and O1s peaks show that they are in the ranges 458.2–458.8 eV and 530.0–530.2 eV, respec-

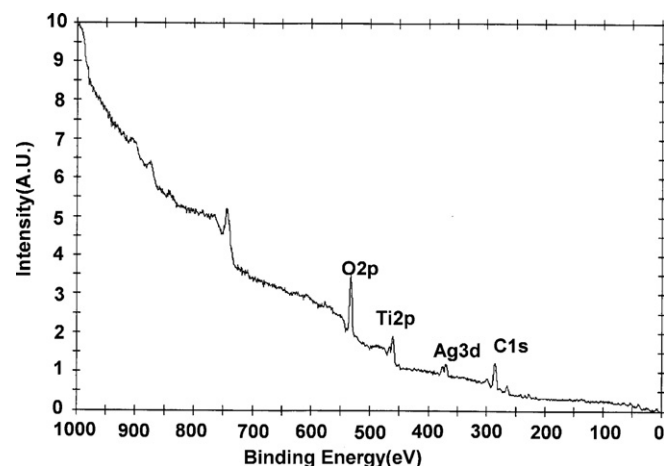


Fig. 5. XPS survey spectrum of TiO_2/Ag .

Table 1
XPS Data of TiO_2/Ag .

Element	Area (cts-eV/s)	Sensitivity factor	Concentration (%)
Ag3d	8855	5.200	1.56
O1s	28,603	0.660	39.78
C1s	13,423	0.250	49.28
Ti2p	18,378	1.800	9.37

tively. These values can be attributed to Ti^{4+} and O_2 in TiO_2 . No Ti2p peak that attributed to Ti^{3+} was observed. Spectral data are summarized in Table 1.

Previous studies show that the Ag3d5/2 binding energies for the Ag, Ag_2O and AgO are 368.2 eV, 367.8 eV and 367.4 eV, respectively. Fig. 6 shows the high-resolution XPS of the Ag3d and Ti2p region of the TiO_2/Ag sample. In Fig. 6(a), the XPS curve of the TiO_2/Ag can be well fitted with a distribution of which there are two peaks centered at 369.2 eV and 375.7 eV corresponding to Ag3d5/2 and Ag3d3/2, respectively. No peak corresponding to Ag_2O (367.8 eV) or AgO (367.4 eV) was observed in the XPS spectra of TiO_2/Ag , this indicates that the Ag species deposited on TiO_2 powders are all in form of metal Ag, but not Ag_2O or AgO. Fig. 6(b) provides the titanium Ti2p and oxygen O1s XPS spectra of the TiO_2 . The Ti2p spectrum showed peaks at 460.2 eV and 466 eV that correspond to the 2p3/2 and 2p1/2 lines for Ti in the 4⁺ oxidation state, no reduction in the valence state of titanium were observed in the TiO_2/Ag sample.

3.6. Antimicrobial activity study

The antibacterial activity study of TiO_2/Ag was carried out against *E. coli* and *Streptomyces*. Table 2 summarizes the results obtained for growth inhibition rates of the TiO_2/Ag particles against *E. coli* and *Streptomyces*. Evidently, TiO_2/Ag has strong antibactericidal effect. Based on growth inhibition rates shown in Table 2, it is clear that the growth inhibition rates against *E. coli* was 99.9% as the concentration of TiO_2/Ag was 10 ppm, but it weakened significantly with decrease of TiO_2/Ag concentrations; the growth inhibition rates against *Streptomyces* was 97.9% as the concentration of TiO_2/Ag

Table 2
Growth inhibition rates of TiO_2/Ag against *Streptomyces* and *E. coli*.

Growth inhibition rates (%)					
	Concentrations	1 ppm	4 ppm	7 ppm	10 ppm
<i>E. coli</i>		35%	60%	66.7%	99.9%
<i>Streptomyces</i>		85.3%	90.5%	96%	97.9%

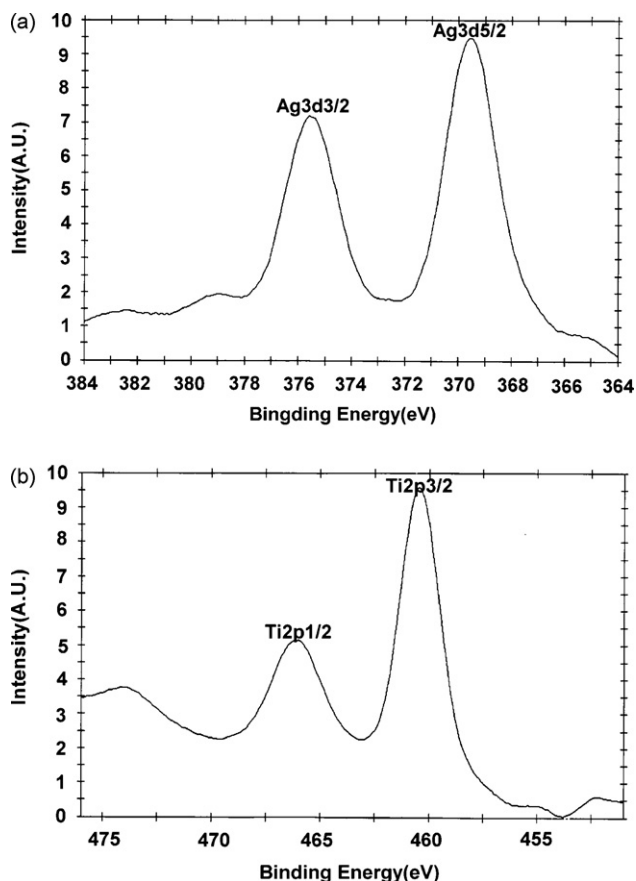


Fig. 6. Ag 3d and Ti 2p high-resolution XPS spectrum of TiO_2/Ag (a) Ag 3d; (b) Ti 2p.

was 10 ppm, but changes of inhibition rates are not very obvious with the decrease of concentration of TiO_2/Ag .

4. Conclusions

It is clear that PEG monomer chains have stabilizing effect on TiO_2/Ag nano-particles, as both TEM and UV-vis experimental data confirmed. Experiments on the synthesis and stability of TiO_2/Ag colloids with longer chain PEG and P-25 (Degussa) are now underway. As result of hydroxyl on the surface of TiO_2 , it can be enhanced as adsorbent or carriers for metals, which is beneficial for the deposition of conductive silver, XPS and XRD revealed that formation of Ag nano-particles on the surface of TiO_2 .

The antimicrobial activity study suggested that TiO_2/Ag composites exhibits satisfactory antibacterial property, the growth inhibition rates against *E. coli* was 99.99% as the concentration of TiO_2/Ag was 10 ppm. The minimum UV protective effect could be achieved as the concentration of TiO_2/Ag was 290 ppm according to Ultraviolet Resistance test. The post-reaction TiO_2/Ag particles were proven to have antibacterial capabilities that render them potentially useful as antibacterial agents for a variety of applications. Materials coupled with this kind of TiO_2/Ag composites could be grafted with ultraviolet resistance and antibacterial properties.

Acknowledgements

This research was supported by the Chinese 863 High-Tech project (2006AA03Z357), the Natural Science Foundation of China (60571001), Postdoctoral Science Foundation (20060390887), the project of Educational Department of Hunan Province (06C262). Hunan Provincial Innovation Foundation For Postgraduate (CX0801). Technology project of Hunan Province (2008FJ4185)

References

- [1] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1–21.
- [2] S.W. Lam, K. Chiang, T.M. Lim, The effect of platinum and silver deposits in the photocatalytic oxidation of resorcinol, *Appl. Catal. B: Environ.* 72 (2007) 363–372.
- [3] M.S. Lee, S.S. Hong, M. Mohseni, Synthesis of photocatalytic nanosized TiO_2 -Ag particles with sol-gel method using reduction agent, *J. Mol. Catal. A: Chem.* 242 (2005) 135–140.
- [4] A. ValentineRup, D. Manikandan, D. Divakar, Effect of deposition of Ag on TiO_2 nanoparticles on the photodegradation of reactive yellow-17, *J. Hazard. Mater.* 147 (25) (2007) 906–913.
- [5] S. Rengaraj, X.Z. Li, Enhanced photocatalytic activity of TiO_2 by doping with Ag for degradation of 2,4,6-trichlorophenol in aqueous suspension, *J. Mol. Catal. A: Chem.* 243 (2006) 60–67.
- [6] L.M. Zhang, D.X. Xia, Q. Shen, Synthesis and characterization of Ag@ TiO_2 core-shell nanoparticles and TiO_2 nanobubbles, *J. Nanopart. Res.* 8 (2006) 23–28.
- [7] H.W. Wang, H.C. Lin, C.H. Kuo, Synthesis and photocatalysis of mesoporous anatase TiO_2 powders incorporated Ag nanoparticles, *J. Phys. Chem. Solids* 69 (2008) 633–636.
- [8] X.F. You, F. Chen, J.L. Zhang, A novel deposition precipitation method for preparation of Ag-loaded titanium dioxide, *Catal. Lett.* 10 (2005) 3–4.
- [9] K.D. Kim, D.N. Han, J.B. Lee, Formation and characterization of Ag-deposited TiO_2 nanoparticles by chemical reduction method, *Scripta Mater.* 54 (2006) 143–146.
- [10] F.L. Toma, G. Bertrand, S. Begin, Microstructure and environmental functionalities of TiO_2 -supported photocatalysts obtained by suspension plasma spraying, *Appl. Catal. B: Environ.* 68 (2006) 74–84.
- [11] L.Z. Zhang, J.C. Yu, A simple approach to reactivate silver-coated titanium dioxide photocatalyst, *Catal. Commun.* 6 (2005) 684–687.
- [12] U. Backman, U. Tapper, J.K. Jokiniemi, An aerosol method to synthesize supported metal catalyst nanoparticles, *Synth. Met.* 142 (2004) 169–176.
- [13] N. Sobana, M. Muruganadham, M. Swaminathan, Nano-Ag particles doped TiO_2 for efficient photodegradation of direct azo dyes, *J. Mol. Catal. A: Chem.* 258 (2006) 124–132.
- [14] M. Nasr-Esfahani, H.H. Mohammad, Silver doped TiO_2 nanostructure composite photocatalyst film synthesized by sol-gel spin and dip coating technique on glass, *Int. J. Photoenergy* (2008), doi:10.1155/2008/628713.
- [15] S. Kodaira, S.W. Lee, T. Kunitake, Photoinduced micropatterning of silver nanoparticles in titaniumdioxide/poly(acrylic acid) alternate thin film, *Chem. Lett.* 37 (2008) 168–169.
- [16] Kaushik Mallick, Mike J. Witcomb, Mike S. Scurrill, Self-assembly of silver nanoparticles: formation of a thin silver film in a polymer matrix, *Mater. Sci. Eng. C* 26 (2006) 87–91.
- [17] M. Popa, T. Pradell, D. Crespo, Stable silver colloidal dispersions using short chain polyethylene glycol, *Colloids Surf. A: Physicochem. Eng. Aspects* 303 (2007) 184–190.
- [18] S.C. Liu-Fu, H.L. Xiao, Y.P. Li, Polyethylene glycol adsorption behavior on nanoparticulate TiO_2 and its stability in aqueous dispersions, *J. Inorg. Mater.* 20 (2005) 310–316.
- [19] M.D. Chadwick, J.W. Goodwin, B. Vincent, Rheological behaviour of titanium dioxide (uncoated anatase) in ethylene glycol, *Colloids Surf. A: Physicochem. Eng.* 196 (2002) 235–245.
- [20] S.J. Bu, Z.G. Jin, X.X. Liu, Synthesis of TiO_2 porous thin films by polyethylene glycol templating and chemistry of the process, *J. Eur. Ceram. Soc.* 25 (2005) 673–679.
- [21] C. He, Y. Yu, C.H. Zhou, Influence of Ag additive on the microstructure of TiO_2 , *J. Inorg. Mater.* 18 (2003) 457–464.
- [22] QB/T2410-1998 UVB sunscreen cosmetics area method evaluation of the effect of sunscreen (China).