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Combination of photocatalytic and antibacterial effects of silver oxide loaded on titania nanotubes

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ABSTRACT

Silver nanoparticles were photodeposited on titania nanotubes and their antibacterial activity was tested. Investigation of the structure and morphology of the nanostructures showed nanometer size silver oxide particles homogeneously distributed on titania nanotubes. Furthermore the modified titania nanotubes were spin-coated as thin films and their antibacterial activity was examined under visible light irradiation and in complete darkness. Although silver oxide loaded titania nanotubes (TiNT-AgO) has a potential for antibacterial activity in both conditions with and without light irradiation, enhanced activity was observed in visible light irradiation condition.

1. Introduction

Recently, significant efforts have been made to develop nanomaterials that can interact with biological organisms to inactivate their toxicity, and titanium dioxide mediated systems proved to be excellent candidates. Ag-loaded TiO_2 nanoparticles have been profoundly investigated over the past few decades [1], but only little work has been conducted on silver-loaded titanate nanotubes and especially for biological agents' detoxification. Furthermore, one-dimensional nanomaterials are particularly of importance for light harvesting systems because of their unique way to conduct electrons through one axis. Wang et al. showed the exchangeability of H^+ in nanotubes by Ag^+, where a great number of clusters are formed [2]. Some authors suggested hybridization of Ag4*d* and O2*p* to form a different valence band with a visible light response appearing [3,4]. Li et al. tested the photocatalytic degradation of methyl orange in water and showed that a suitable amount of silver demonstrates a great improvement in the activity compared to pure TiNT [5]. More recently, Paramasivam et al. studied the photocatalytic activity of titania nanotube arrays loaded with Ag nanoparticles, and concluded that TiNT arrays are more efficient than compact surfaces, and their performance can be enhanced when loaded with a certain amount of Ag nanoparticles [6]; Guin et al. studied tests for antibacterial outcomes using silver on TiO_2 nanotubes and showed efficiency toward destroying the Gram negative bacteria *Escherichia coli* [7].

Resistance of bacteria to antimicrobials and especially silver is also a serious problem. Silver-resistant organisms have been reported in clinical [8] and environmental [9] samples. By using both photocatalysis and the antibacterial effect of silver, we could reach a high level of bacterial inactivation. We therefore present here investigations of silver deposited on titanate nanotubes as a possible anti-biological material under irradiation or in complete darkness.

2. Experimental

2.1. Synthesis of nanotubes

Titanate nanotubes were synthesized by the method developed by Kasuga et al. [10]. In a typical synthesis procedure, commercial TiO_2 powder (1.5 g, P25 Degussa-Evonik) was first mixed with 10 M NaOH (100 ml) for 1 h. The mixture was then treated at 130 °C for 24 h. After cooling to room temperature, excess NaOH was removed and the resultant powder was dispersed in a large volume of distilled water (500 ml), filtered and re-dispersed in the same volume of HCl 1 M for 2 h before vacuum drying; the dispersion was then washed with distilled water until neutral pH. The resultant white powder was finally filtered and dried 1 h at 100 °C.

Silver nanoparticles were loaded onto the nanotubes by soaking them in a $AgNO_3$ solution made of 80% ethanol at a concentration of 0.5 wt.% for 12 h and then irradiated for 2 h with a 368 nm 8 W ultraviolet lamp at ambient temperature and pressure. The resultant powder was washed several times with distilled water to ensure complete removal of nitrate ions. The dark brownish precipitate was then dried at 100 °C and used for further studies. The suitable amount

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of silver for homogeneous and fine diameter nanoparticle distributions has been experimentally determined to be around 0.5 wt.% and was thereby used in this contribution.

2.2. Antibacterial assay

First, a TiNT-AgO suspension at 1 g/L (in EtOH/H_2O 50:50) was prepared and spin-coated on glass slides (2 2 cm) at 2000 rpm and dried at 70 °C overnight. This technique enabled us to obtain a film thickness of around 500 nm with acceptable reproducibility.

E. coli DH5a cells precultured in LB broth were collected by centrifugation at 3000 rpm for 3 min, and resuspended into 1% NaCl solution at a concentration of ca. 1.5×10^8 cells/ml. Then 10 μl of *E. coli* suspension was put onto the glass slides coated with TiNT and TiNT-AgO, and covered with a cover glass. The glass slides were kept at room temperature in a humidified chamber in the dark and under illumination, respectively. Illumination was carried out at a distance of 15 cm from the lamp (incandescent lamp, 60 W, Philips) to prevent overheating of the photocatalyst substrates and preventing drying. After 30 min, cells were recovered by washing out from the glass slide surface using 3 ml of 1% NaCl solution, and then diluted 10- and 100-fold in the same solution. Ten microliters of the diluted cell suspension was plated out onto LB agar, and the number of colonies was counted after overnight incubation at 37 °C.

3. Results

3.1. Characterization of Ag/titanate nanotubes

The XRD patterns of the obtained nanotubes before and after 0.5 wt.% silver photoreduction are presented in Fig. 1a. The patterns of as-prepared nanotubes are quite similar to those reported for monoclinic symmetry whose crystallographic phase is tri-titanate [11], even if the exact composition is still under discussion. After photodeposition, we could not detect any peaks related to any silver related phase in the spectra which may be due to the small amount loaded on the titania nanotubes. Fig. 1b illustrates the diffuse reflectance spectra (DRS) of the pristine TiNT and Ag-loaded TiNT sample. DRS clearly indicate the visible absorption of the silver-loaded sample with a characteristic band absorption around 500 nm corresponding to surface plasmon absorption, where TiNT has no response for visible light.

Fig. 2 shows TEM images of the as-prepared sample before and after 0.5 wt.% silver photodeposition. A micrograph of TiNT on Fig. 2a shows multiwalled nanotubes with both ends opened, with a length of hundreds of nanometers and an average diameter of 15 nm. SAED analysis indicates the presence of a polycrystalline material with poor crystallization. When the amount of silver is 0.5 wt.%, Ag-based nanoparticles are clearly seen in contrast to titania nanotubes (Fig. 2b), with an average diameter of 20 nm and a homogenous

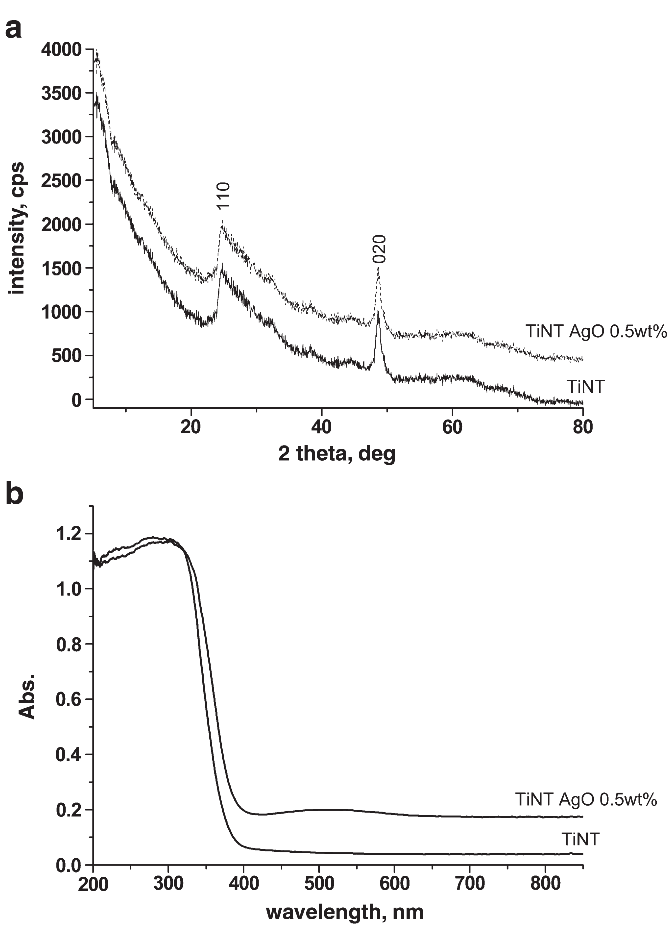

Fig. 1. a) X-ray diffraction pattern, and b) UV—Vis spectra of pristine titania nanotubes and loaded with 0.5 wt.% of silver TiNT-AgO.

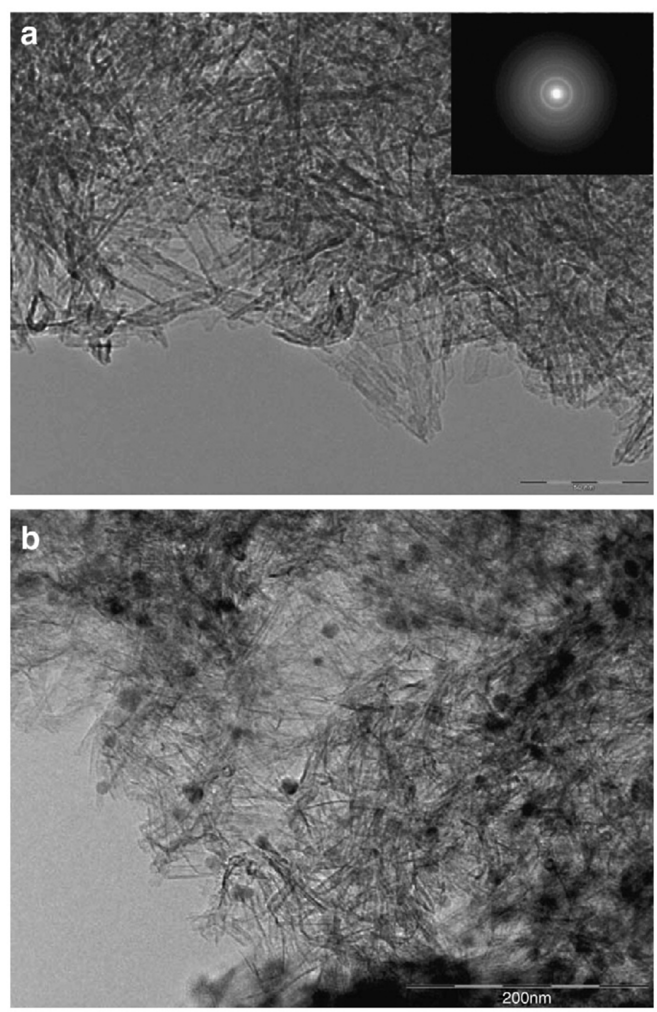

Fig. 2. TEM images of a) neat titania nanotubes, and b) TiNT-AgO composite.