SYNTHESIS AND CHARACTERIZATION OF Ag/TiO_2 NANOCOMPOSITE THIN FILMS

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Introduction

TiO_2 has been widely studied as an effective photocatalyst for environment purification [1,2], such as bactericidal material [3] and due to its hydrophobic and superhydrofilic property [4]. However, the semiconductor TiO_2 has a wide band gap, which only can be activated by near-UV radiation. Also, the photogenerated electron–hole pairs tend to recombine easily, leading to very low quantum yields. These problems have motivated scientists to find ways of increasing the TiO_2 photoresponse by shifting its absorption to the visible light region and preventing the recombination of electron and holes [5]. To solve the electron–hole recombination problem, the TiO_2 surface has been modified by noble metal such as Ag [6]. This serves the purpose of to mediate the electrons away from the TiO_2 surface, preventing their recombination with the holes [7]. Chemical routes, such as sol-gel processing, possess the advantage of low investment cost with respect to physical synthesis methods [8]. Nanocomposites made of oxide films containing nano-sized semiconductor or metal particles allow systems with peculiar optical and electrical properties. In this study, we used a colloidal solution prepared with silver nitrate and titanium alkoxide dissolved in its equivalent alcohol to prepare transparent and adherent oxide films. The films, deposited in glass plates, were thermally treated and morphologically, optically, structurally, and texturally characterized.

Experimental

Ag/TiO_2 coatings were prepared by sol-gel process from alcoholic starting solution containing silver nitrate and tetraisopropyl orthotitanate dissolved in a mixture of isopropyl alcohol and hydrocloric acid. The atomic ratio Ag:Ti chosen was equal to 1:6. The starting solution was sonificated at room temperature during 1 hour and was submitted to UV irradiation treatment in air for 8 hours to produce Ag by reduction of Ag^+. To obtain films free of defects, the solution pH was kept between 2 and 4 and the viscosity between 2 and 5 cP. Surface tension and density measurements also were carried out. The films were dip-coated onto clean glass substrates with withdrawal speed of 1.5 cm/sec, dried in air for 30 min and thermally treated for 1 hour at 100 and 400 °C. The change of the crystalline structure was observed by low angle X-ray diffractometry (incidence angle of 5θ) using radiation of 1.5424Å. The particle size and roughness of the films were evaluated by atomic force microscopy (Nanoscope II and a Dimension 3000, Digital Instruments) equipped with an extended modulus for phase imaging. The images were generated through the intermittent contact mode, using a silicon probe tip with 5 nm of curvature radius. The transmittance was measured using an UV-visible spectrometer (U3010-Hitachi). Thicknesses and refractive indices were evaluated by Fresnel´s equation using the transmittance spectrum data of layers deposited onto one side of the glass substrate. Surface morphologies of the films were observed by scanning electron microscopy (SEM, Quanta 200 FEG - FEI) with an accelerating tension of 30 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI TECNAI G2-20 at acceleration tension of 200 kV. Those techniques were used to determine the morphology and size, and to identity the nanocrystal particles in the composite films.

Results and discussion

The surface tension and density values of the Ag/TiO_2 precursor solution were (38.0 ± 0.2) $m.Nm^{-1}$ and (0.82 ± 0.01) $g.cm^{-3}$, respectively. X-ray diffraction (XRD) patterns of $Ag-TiO_2$ samples calcined at 100 and 400 ºC are shown in Figure 1. Only anatase phase was identified for both 100 and 400 °C drying temperature. Peaks attributable to cubic metallic Ag were observed for the films calcined at 400 °C.

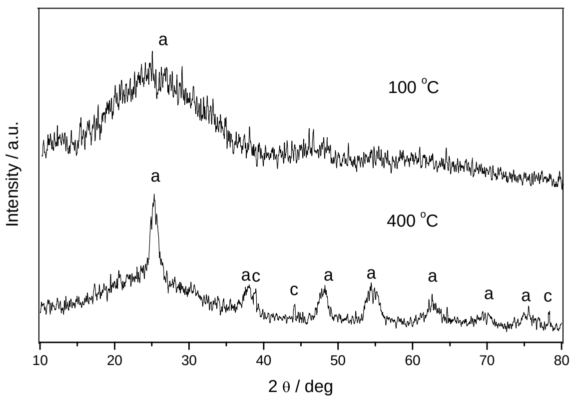

Fig. 1 X-ray diffraction patterns of Ag/TiO_2 calcined in indicated temperatures (a=anatase and c = metallic Ag).

AFM analysis (Fig. 2) revealed that the films calcined at 100 and 400 °C exhibit a grain-type surface morphology. For Ag/TiO_2 films calcined at 100 °C, the surface roughness was determined as equal to about 0.9 nm and the average particle size was estimated to be 6 nm. In the line profile shown in Fig. 2 (d) a similar surface roughness of 1.0 nm was observed for Ag/TiO_2 films calcined at 400 °C. Otherwise, the average particle size increases to 12 nm. The values (Table 1) determined from optical transmission spectrum show that the thickness decreases and the refraction index increases with the increase in temperature. Fig. 3 (a) and (b) show the SEM micrographies of Ag/TiO_2 films calcined at 100 °C. It is possible to observe the presence of microporous and the film thickness of 90 nm, confirming the UV-visible spectroscopy results. TEM images (Fig. 3 (c) and (d)) show that the films calcined at 100 °C are formed by particles of Ag of about 10 nm dispersed in a TiO_2 amorphous matrix. HRTEM images (Fig. 3 (e) and (f)) show that the films calcined at 400 °C are formed by nanocrystalline particles of Ag dispersed into TiO_2 anatase matrix. The lattice planes of anatase (1 0 1) and Ag (1 1 1) with interlayer spacing of 3.51 and 2.35 Å, respectively, were clearly displayed. These results agreed with X-ray analyses. This close interconnection is important to the photogenerated electron transfer between the silver and titanium dioxide.

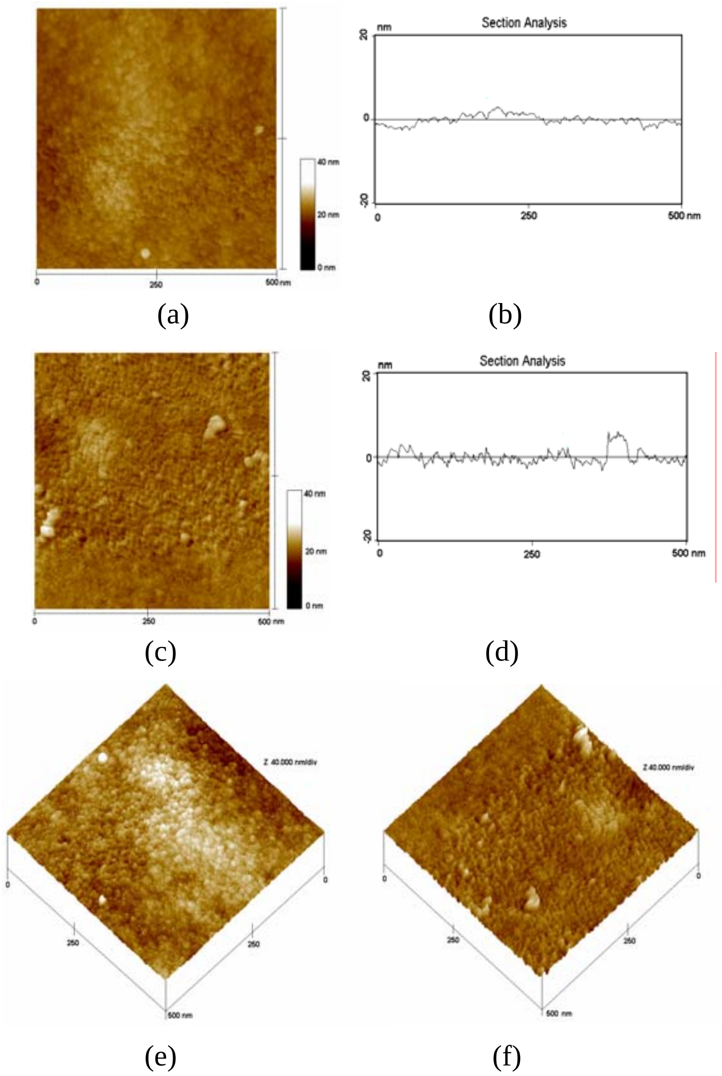

Fig. 2 Top-view AFM images of Ag/TiO_2 calcined at (a) 100 °C, (b) line profile (c) 400 °C, (d) line profile, (e) 3D (100 °C) and (f) 3D (400 °C).

Table 1 Thickness and refraction index of Ag/TiO_2

Temperature	Thickness	Refraction index
100 °C	80 nm	1,95
400 °C	75 nm	2,20

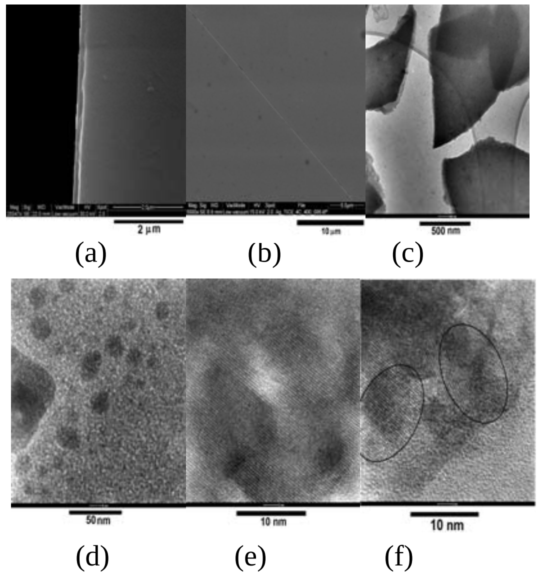

Fig. 3 (a) and (b) SEM of the films calcined at 100 °C, (c) and (d) TEM of the films cacined at 100 °C, (e) and (f) HRTEM of films calcined at 400°C.

Conclusion

Nanocomposite thin films of Ag/TiO_2 were successfully prepared by sol-gel dip-coating technique. The films obtained were transparent, adherent, homogeneous and free of microcracks. Subsequent heat treatment of the as-deposited amorphous thin films led to the formation of Ag nanocrystalline particles with average grain size of 10 nm dispersed in an anatase titania matrix.

References

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