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Sol-gel synthesis of photochromic films *via* silver–titania nanocomposites prepared without heat treatment

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Highly photoactive nanocomposites were obtained by drawing silver nanoparticles onto the surface of a nanostructured non-calcined film of TiO_2 prepared by a sol-gel technique.

Titania coatings with high specific surface areas and narrow pore size distributions have potential applications in solar energy conversion,[1] photocatalysis[2,3] and photoelectrochromic coatings.[4] The photochromism of silver species adsorbed on colloidal titania is well known.[4] A darkening of these systems upon illumination is reversible, and the oxidation of silver species explains the bleaching of these systems. By UV irradiation, electrons at the valence band of titania are excited to the conduction band and then migrate to Ag^I species reducing them to Ag^0. Silver nanoparticles interact with visible light through their surface plasmon resonance, and their electrons migrate to the conduction band of titania, which induces the Ag^0 oxidation into Ag^I species.[5] The main problem in the synthesis of such photochromic films consists in the production of crystalline titania nanoparticles with high interface reaction with metal layer. Considering the need for drawing metal nanoparticles and their propensity to agglomerate, one requires to minimize their accumulation and formation of large particles. For protection from agglomeration, the protective levels on the metal surface are formed using special polymers (*e.g.*, polyvinyl alcohol)[6] or molecules containing nucleophilic atoms (such as thiols, amines or phosphines).[7]

In this work, the synthesis of titania was carried out using alkoxide hydrolysis in water solution with the subsequent peptization of the HNO_3 particles.† This method[8] allows one to obtain ~10 nm TiO_2 particles generated from the anatase-brookite nanocrystals; it does not require the subsequent calcination (*cf*. ref. 9). The crystalline structure was formed without calcination by regulating the conditions of synthesis. Spin-coating films obtained from these colloidal solutions have a very high specific surface area and are often considered as a way to adjust electronic, optical or catalytic properties.[2,3]

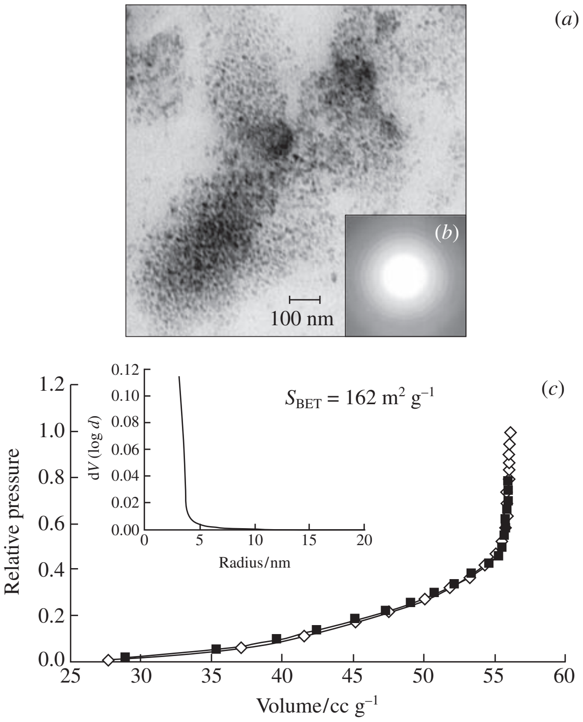

Figure 1 TEM images of a titania film without silver nanoparticles: (*a*) top-view; (*b*) electron transmission diffraction pattern and (*c*) adsorption–desorption isotherms of nitrogen and pore size distribution.

The TEM image (LEO-906E transmission electron microscope operating at 100 kV) of an empty titania film before the silver nanoparticle plate is shown in Figure 1. The top-view image

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† The one-step synthesis of nanostructured titania was carried out using a solution of titanium(IV) isopropoxide in anhydrous isopropanol (Pr^iOH:Ti = = 3.5), which was added with stirring to hot (70 °C) water (H_2O:Ti ≈ 90) acidified with nitric acid (H^+:Ti = 0.2). A white precipitate was obtained and the mixture was stirred at 80 °C for 16 h. The white suspension changed gradually to a translucent sol by peptization. During the first 6 h, the reaction flask was kept uncovered in order to allow isopropanol to evaporate (the boiling point of the isopropanol–water azeotrope 87.4:12.6 is 80.3 °C). At the end of peptization the pH of the sol was about 1.4 and the molar concentration of Ti was 0.6–0.65 mol dm^{-3}.

Silver nanoparticles were synthesised by the reduction of Ag^+ ions. For this purpose, a solution was prepared by mixing 0.07 g of $AgNO_3$ and 5 ml of ethanol upon heating to 80 °C. The second solution acting as a stabilizer was prepared by dissolving 1.45 g of poly(2-hydroxypropylmethacrylate) (PHPM) in 25 ml of ethanol at 50 °C. Then, both solutions were mixed upon sharp cooling to 20 °C and stirred for 3 h. Reduction occurred upon addition of 0.03 ml Super-Hydride $LiBEt_3H$ (Aldrich) to form dark-brown colloidal solution. Then, the suspension was centrifuged at 2000 rpm for 30 min to isolate the nanoparticles, which remain in the supernatant. The supernatant containing the Ag nanoparticles was centrifuged twice at 6000 rpm for 30 min to separate the particles. We discard the supernatant containing PHPM, and other impurities. After the final centrifugation, the precipitate of silver nanoparticles was dispersed in 5 ml of isopropanol.

Drawing the metal nanoparticles onto the surface of a TiO_2 film was carried out by a spin-coat method with the subsequent vacuum drying at 70 °C for 1 h; then, the films were exposed to the structural analysis, UV-VIS spectroscopy and photopolarization measurements.

Table 1 Photoactivity and conductivity type of modified and non-modified titania films.

Sample	Photo-emf (non-calcined)/mV	Conductivity
TiO_2 + Ag	46	p-
Ag	4.7	p-
TiO_2 non-modified	15	n-

[Figure 1(*a*)] is coherent with disordered crystalline nanoparticles with narrow particle size distribution, approximately 10 nm. According to the general diffraction data [Figure 1(*b*)], the material is constructed from the anatase-brookite form crystallites, with size of about 5 nm (according to ring broadening). According to the low-temperature nitrogen adsorption–desorption data (Nova 1200e), the specific surface area of such a material was 162 $m^2 g^{-1}$ [Figure 1(*c*)].

The TiO_2 crystal phase formed during temperature dehydration[8] possesses high photoactivity (Table 1) as the generated nanoparticles size of about 10 nm is an optimum for the most effective absorption of a light quantum and the generation of electron–hole pairs on the surface.

Drawing the second layer of metal nanoparticles was also carried out by a spin-coating method from colloidal solution for keeping the metal–TiO_2 interaction strong. The analysis of the surfaces and phase analysis of the heterostructures was performed using an SPM Solver P47H – PRO atomic force microscope with different resolutions [Figures 2(*a*),(*b*)] and X-ray diffraction (Bruker Nanostar) [Figure 2(*c*)].

According to the AFM results, the TiO_2 film generated using $Ti(OPr^i)_4$ in the HNO_3 medium was formed by spherical roundish shaped nanoparticles with an average diameter of about 10 nm.

The modification of the TiO_2 surface film by colloidal silver was expected to provide, on the one hand, a photochromic effect without the traditional usage of platinum and palladium, and, on the other, an increase in the photoactivity of the generated composites. Thus, the necessary factor was obtaining the nanoparticles with sizes in the range of 10 nm, leading to the generation of heterostructures of the metal nanoparticles plasmon resonance in the system. According to Figure 2, the generated crystalline silver nanoparticles represent triangular nanoprisms with the average size of ~5 nm distributed in regular intervals on the TiO_2 surface.

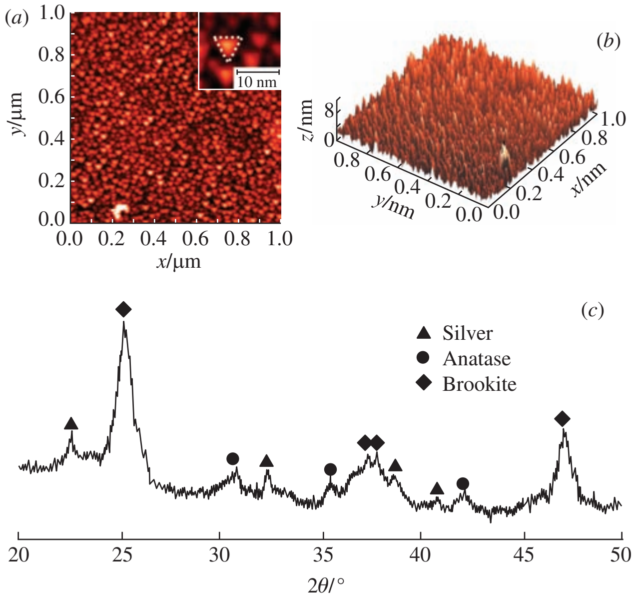

Figure 2 Structure and phase analysis of TiO_2–Ag nanoparticles: (*a*) the 2-D surface of the Ag–TiO_2 film; (*b*) the 3-D surface of the Ag–TiO_2 film and (*c*) XRD analysis of scraped film after UV illumination (15 min).

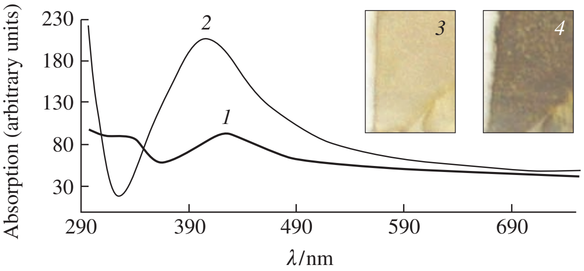

Figure 3 (*1*),(*2*) UV-VIS absorption spectra and (*3*),(*4*) photographs of films containing silver nanoparticles on the TiO_2 surface (*1*),(*3*) before and (*2*),(*4*) after illumination (15 min).

The experimental data are confirmed by the characteristic profile of a plasmon peak[10] (Figure 3).

In this case the highly conducting silver nanoparticles having a high concentration of free charge carriers show the surface plasmon effect, and the quanta of fluctuations in metal free electrons density are distributed only along the boundary of particle surface.

For investigating the photochromism, the composite films were UV-irradiated for 15 min (two 6 W lamps with wavelengths of 254 and 366 nm). The results show similar photochromic activity in materials prepared with the preliminary calcination of TiO_2.[4] The color change efficiency may be determined by the quantity of photogenerated charge carriers. In the photogeneration of electrons and their transport, certain ion sites are reduced to Ag^0. The data implying high photoactivity of the Ag–TiO_2 composite are confirmed by the greatest photoresponse of 46 mV (Table 1). After UV irradiation, the excited electrons move to the TiO_2 conductivity zone and holes move to the valency zone through the interface. Thus, the separation of the photogenerated electron–hole pairs in a composite film is more efficient than in pure non-modified one. Hence, the recombination of the photogenerated charge carriers also proceeds more efficiently. The use of silver nanoparticles also promotes an increase in the photoactivity of a film (Table 1) owing to larger water adsorption on the surface of a composite due to the nanoparticle surface effect,[8] which is promoted by a high concentration of the photogenerated holes whose presence is confirmed by composite conductivity type.

Thus, the Ag–TiO_2 nanocomposites described in this work are expected to find important applications to the fabrication of photochromic materials, optical filters or sensors.

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