Journal of Alloys and Compounds 515 (2012) 1–3

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Low-temperature sol–gel synthesis photochromic Cu/TiO_2 films

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ARTICLE INFO

Article history:
Received 29 September 2011
Received in revised form 1 November 2011
Accepted 1 November 2011
Available online 9 November 2011

Keywords:
Coating materials
Nanostructured materials
Thin films
Sol–gel processes
Photoconductivity and photovoltaics

ABSTRACT

Synthesis of photochromic, highly photoactive $Cu@TiO_2$ films by low-temperature sol–gel route has been reported. The photoelectric properties of nanostructured non-calcined composite film are higher than that in individual compounds. Synthesized films are characterized by AFM, UV–vis absorption spectra and X-ray diffraction. The functional properties are estimated by photopolarization measurement. Titania films were soaked with a copper salt solution and chemical reduction treatments are performed using $NaBH_4$. We used P123 for protection metal surface and decreasing agglomeration activity. Also, the utilization of a mesoporous titania substrate allows to control the nanoparticle size and the interparticle distance. UV–vis absorption spectra experiments provide the evidence that UV illumination induces a strong accumulation of copper nanoparticles in the subsurface of the layer.

1. Introduction

Metal oxide nanocomposites are a versatile material with many scientific and industrial applications [1]. Synthesis of high-quality ordered functional coatings with respect to chemical purity, phase selectivity, crystallinity, and homogeneity in particle size with controlled state of agglomeration in a cost-effective procedure is still a challenge to material chemists [2]. Titania–copper nanocomposites with highly ordered surface structure are promising material for multicolor device technology, low-cost photovoltaic cells and photochromic coatings [3]. The pore size and the specific surface area greatly impact the physical properties of these materials and can play a relevant role in their activity. For instance, photochromic applications require an adjustable porosity to optimize the diffusion rate of metal nanoparticles towards the adsorption sites and a high surface area to maximize the interface between the metal and the TiO_2 surface [4]. The photochromism of copper species adsorbed on colloidal titania is unstudied at this time. The photochromism on colloidal titania has been known for a long time. A darkening of these systems upon illumination can be found reversible and the oxidation of copper species was proven to explain the bleaching in these systems. By UV irradiation, electrons at the valence band of titania are excited to the conduction band and then migrate to Cu^{2+} species reducing them to Cu^0. Copper nanoparticles interact with visible light through their surface plasmon resonance, and their electrons migrate to the conduction band of titania, which induces the Cu^0 oxidation into Cu^{2+} species [5], like silver UV-reducing [6]. At the same time, an investigation on such a mechanism of oxidation–reduction reactions with participation of copper nanoparticles on nanostructured titania surface obtained using sol–gel method has not been carried out, as for realization of reductive transition Cu^{2+}–Cu^0 the use of highly active anatase possessing a highly developed surface is needed. Considering the need for drawing ultradispersed metal nanoparticles and their propensity to agglomerate, one requires to minimize their accumulation and formation of large particles. For protection from agglomeration using special polymers (for example, polyvinyl alcohol) [7] or molecules (usually containing nucleophilic atoms, such as thiols, amines or phosphines) [8].

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 described in [8] allows to obtain the TiO_2 particles with size of about 10 nm generated from the anatase-brookite form nanocrystals, and, in contrast to existing [9] approaches, does not require the subsequent calcination. 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 [3,10].

In the given work we consider an approach to obtaining highly photoactive nanostructured films using drawing copper nanoparticles onto the surface of nanostructured non-calcined film of TiO_2.

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doi:10.1016/j.jallcom.2011.11.004

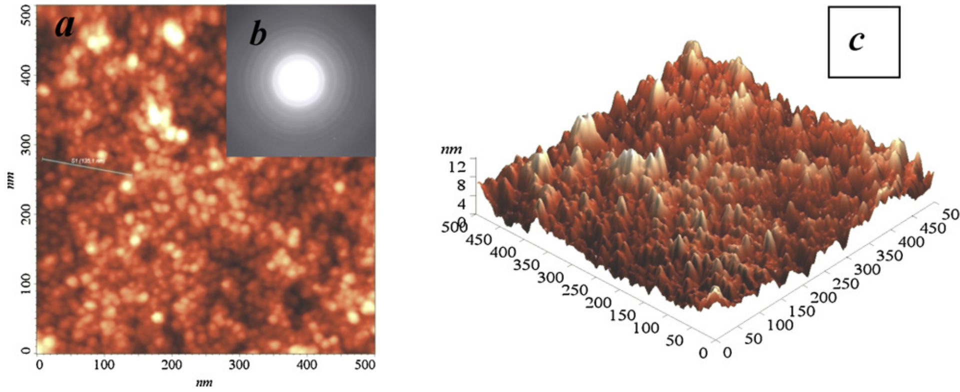

Fig. 1. The AFM images with size 0.5 × 0.5 μm of titania film without copper nanoparticles: (a) 2-D top-view image; (b) electron transmission diffraction pattern; (c) 3-D image.

Table 1
Photo-emf response of the films under UV irradiation.

Sample	Photo-emf (non-calcined) (mV)	Conductivity type
Cu(CuO)	6	p-
TiO_2 non-modified	15	n-
TiO_2 + Cu	32	p-

2. Experimental

Synthesis of nanostructured titania was carried out in a single stage using for this purpose a prepared solution by mixing 12 ml of isopropanol (Aldrich) and 16 ml of isopropoxide titania $Ti(OC_3H_7)_4$ (98%), into which after stirring for 2 h there was added drop by drop a peptizing solution heated to 70 °C and consisting of 100 ml of bidistilled H_2O and 0.7 ml of concentrated HNO_3. As a result, the aggregated amorphous precipitate in the process of peptization and long exposure to temperature (70 °C for 8 h) was transferred into a colloidal solution of the TiO_2 sol which was used for drawing films onto the surface of preliminarily washed and dried integumentary glass. Then films were exposed to vacuum drying at 70 °C for 1 h. This route uses a cheap and non toxic solvent (water) and gives crystalline films with potential applications for coating low thermal stability substrates (polymers).

Synthesis of copper nanoparticles was carried out by reduction of Cu^{2+} from a solution containing 0.35 g of $CuSO_4{\cdot}5H_2O$ (99% Aldrich), 7 ml of H_2O and 0.5 g of Pluronic P123 (Aldrich Mr = 5800) with a solution of 0.022 g $NaBH_4$ in 2 ml of H_2O instilled drop by drop upon intensive stirring. Simultaneously there took place the formation of brown colloidal solution of colloid copper. Addition of polymer P123 allowed avoiding the aggregation of nanoparticles during reduction.

Drawing the metal nanoparticles onto the surface of a TiO_2 film was also carried out by centrifugation, with the subsequent vacuum drying at 70 °C for 1 h, then films were exposed to the structural analysis, UV–vis spectroscopy and photopolarization measurements.

The AFM image (SPM Solver P47H-PRO microscope) of an empty titania film before the copper nanoparticles plate is shown in Fig. 1. The 2D, 3D top-view image (Fig. 1a and c) is present spherical nanoparticles with narrow size distribution, approximately 10 nm. According to the general diffraction data (Fig. 1b), the material is constructed from the anatase-brookite form crystallites, with size of about 5 nm (according to ring broadening).

The TiO_2 crystal phase formed during temperature dehydration possesses high photoactivity (see Table 1) as the generated nanoparticles size of about 10 nm is an “optimum” for the most effective absorption of the light quantum and generation of electron–hole pairs on the surface [11].

Drawing the second layer of metal nanoparticles was also carried out by 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 obtained were performed using AFM and X-ray diffraction (Bruker Nanostar). The obtained results are shown in Fig. 2.

Following the main goal of the work, it was planned to perform a modification of the surface of the TiO_2 film by various metals in colloidal condition, such as Cu, which would allow, on the one hand, to achieve photochromic effect without the traditional usage of Ag, Pt, Pd and, on the other, to increase the photoactivity of the generated composites for improve photocatalytical and photoelectrochemical properties. 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. As a result of processing the AFM images, it was revealed that the copper nanoparticles generated in the conditions of the Cu^{2+} reduction using sodium tetrahydroborate (Fig. 2b) possess broad NPs size distribution (5–100 nm) and different morphology.

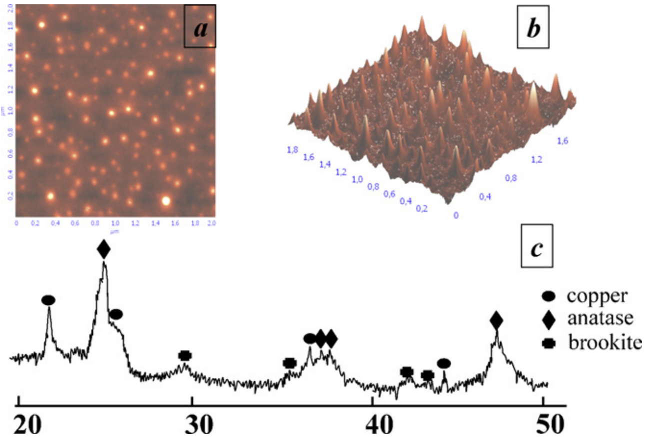

Fig. 2. Structure and phase analysis of TiO_2@Cu nanoparticles: (a) the 2-D surface of the Cu@TiO_2 film with size 2 × 2 μm; (b) the 3-D surface of the Cu@TiO_2 film; (c) XRD analysis scraped film after UV illumination (15 min).

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

3. Results and discussion

For investigating the photochromism effect the obtained TiO_2–Cu films were exposed to an ultra-violet irradiation for 15 min (two 6 W lamps with wavelengths of 254 and 366 nm, respectively, were the UV-source). Then the comparative analysis of materials before (Fig. 3a and c) and after (Fig. 3b and d) UV irradiation was carried out. The efficiency of color change may be determined by

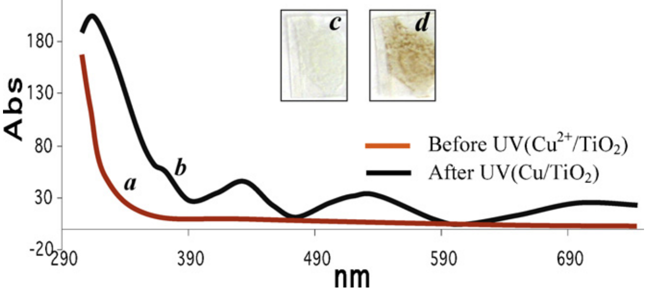

Fig. 3. UV–vis absorption spectra (a and b) and photographs(c and d) of films containing copper nanoparticles on the TiO_2 surface before (a and c) and after (b and d) UV illumination (15 min).

the quantity of the formed photogenerated charge carriers [12]. In the process of photogeneration of electrons and their transport the certain ion sites are reduced to Cu^0. The data implying high photoactivity of the Cu@TiO_2 composite are confirmed by the greatest photoresponse value of 32 mV (Table 1). After UV irradiation the excited electrons move to the TiO_2 conductivity zone, and holes move to the valency zone through interface. Thus, the separation of the photogenerated electron–hole pairs in a heterostructured film is more efficient than in individual, non-modified one. Hence, the recombination of the photogenerated charge carriers also proceeds more efficiently, and that is proved by an increase in the photoresponse value for the TiO_2–Cu used. The use of copper nanoparticles also promotes the increase in photocatalytic activity of a film (Table 1) owing to larger water adsorption on the surface of a TiO_2–Cu film due to the nanoparticle surface effect [8], which is promoted by a high concentration of the photogenerated holes, because the main factor determining the type of conductivity mostly depends on upper layer, consisting of copper nanoparticles, whose presence is confirmed by TiO_2–Cu conductivity type (Table 1).

4. Conclusions

Obtaining the crystalline TiO_2 using sol–gel method without calcination allowed to form highly photoactive heterostructured nanomaterials. The presence of two main photoactive titania phases provides not only high photoactivity but also high photochromic properties compared with silver based titania, obtained after calcination. These are based on nanostructured TiO_2, which is coated by metal nanoparticle layer. Drawing the Cu nanoparticles onto the surface, which are transformed into ionic forms upon interaction with air oxygen and moisture, has lead to the achievement of photochromic effect. According to the AFM and UV–visible spectroscopy data the morphology of formed nanoparticles is estimated. The Cu@TiO_2 nanocomposites described in this work are expected to find important applications for the fabrication of photochromic materials, photoelectrochemical cells, or sensors.

Acknowledgement

This work was supported by the Russian Foundation for Basic Research, Project Nos. 09-03-97553, 11-03-12063, 11-03-00639 and 10-03-92658.

References

[1] J.P. Jolivet, Metal Oxide Chemistry and Synthesis, Wiley, Chichester, 2000.
[2] J.P. Jolivet, S. Cassaignon, C. Chaneac, Chiche, D. Tronc, J. Sol-Gel Sci. Technol. 46 (2008) 299–305.
[3] J. Liu, X. Huang, Y. Li, K.M. Sulieman, X. He, F. Sun, J. Mater. Chem. 16 (2006) 4427–4434.
[4] M.N. Patel, R.D. Williams, R.A. May, H. Uchida, K.J. Stevenson, K.P. Johnston, Chem. Mater. 20 (2008) 6029–6040.
[5] A. Henglein, J. Phys. Chem. B 104 (2000) 1206–1211.
[6] L. Bois, F. Chassagneux, Y. Battie, F. Bessueille, L. Mollet, S. Parola, N. Destouches, N. Toulhoat, N. Moncoffre, Langmuir 26 (2010) 1199–1206.
[7] D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed. 44 (2005) 7852–7872.
[8] P. Alphonse, A. Varghese, C. Tendero, J. Sol-Gel Sci. Technol. 56 (2010) 250–263.
[9] A.L. Castro, M.R. Nunes, A.P. Carvalho, F.M. Costa, M.H. Florencio, Solid State Sci. 182 (2009) 1838–1845.
[10] A.V. Agafonov, A.V. Vinogradov, J. Sol-Gel Sci. Technol. 49 (2009) 180–185.
[11] C. Agrafiotis, A. Tsetsekou, J. Eur. Ceram. Soc. 20 (2000) 825–834.
[12] Y.J. Cheng, L. Zhi, W. Steffen, J.S. Gutmann, J. Chem. Mater. 20 (2008) 6580–6582.