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One step room temperature photodeposition of Cu/TiO_2 composite films and its conversion to CuO/TiO_2

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ABSTRACT

Cu/TiO_2 composite films were prepared at low temperature on glass substrates by a photodeposition method. Films were deposited by irradiating the substrate while in contact with an aqueous TiO_2 suspension containing copper(II) nitrate and ethanol. Cu/TiO_2 composite films of 500 nm in thickness were deposited at room temperature after a short irradiation time (15 min) with a 125 W mercury vapour lamp. According to scanning electron microscopy observations, the obtained films were homogeneous and porous. Energy dispersive X-ray spectroscopy analysis revealed a 3:1 Cu:Ti atomic ratio. Grazing angle X-ray diffraction analysis showed that the films contained Cu and TiO_2 as major components and Cu_2O as a minor component. Heat treatment at 400 °C in air for a period of 3 h transformed the initial material into a CuO/TiO_2 composite, improved the adhesion to the substrate and favoured a more regular distribution of copper oxide according to backscattering micrographs.

1. Introduction

Chemical bath deposition (CBD) technique has numerous advantages to deposit metal chalcogenides and metal oxide films due to its simplicity. Special equipments are not required for this deposition. Usually, temperature measurement is enough and there is no need for controlled atmosphere, high pressure and/or high temperature. As a consequence, the energy consumption is low. This technique can help to reduce the negative environmental impacts caused by using other deposition methods, especially if the chemicals present in the bath are not pollutant. In addition, it is an easily scalable method applicable to substrates with complex morphology [1–3].

Photodeposition methods have been explored as a strategy to enhance standard CBD technique [1]. It has been mostly used to deposit films of transition metal chalcogenides. Light irradiation may have different effects. In some of these processes, light is absorbed by soluble species such as thiosulphate or sulfite, that after being activated produce the species that initiate the chemical reaction responsible for film growth [4–7]. In other cases, the semiconductor nature of the chemically deposited material allows the absorption of light of adequate wavelength, thus generating redox active species. These have a synergic effect and accelerate the deposition rate. In these cases, radiation also increases the size of the nanocrystals that constitute the film. This leads to changes in physico–chemical properties associated with crystal size [8–10].

Titanium dioxide is an extensively studied material with well known photoactivity [11,12]. Absorption of ultraviolet photons (wavelength$<$400 nm) by this semiconductor promotes electrons from the valence band into the conduction band, leaving positively charged holes in the valence band. Both charge carriers promote redox reactions if they reach the TiO_2 surface [11,12]. Although TiO_2 is insoluble, by using nanocrystalline powder highly homogenous aqueous suspensions can be obtained. This allows their use to activate soluble species. In the photodeposition technique reported here, we take advantage of the fact that suspended TiO_2 particles could stick to the growing film (or the substrate) and be trapped in the deposit, thus leading to composite deposition. This is advantageous considering the large variety of applications of composite materials in which the TiO_2 is a key component [13–16].

The reduction of aqueous copper(II) over illuminated TiO_2 is well documented. For instance, TiO_2 photocatalysis has been studied for the recovery of Cu(II) from wastewater [17–19]. Recently, a soft method to modify TiO_2 photocatalyst by photodeposited copper has been proposed as a way to improve the performance of this photocatalyst [20–22].

Cu/TiO_2 composite materials have also been explored as photoelectrodes [23]. Cu/TiO_2 films heated in air allow obtaining copper oxide/TiO_2 composite films, a material with prospective applications in all inorganic solar cells [24,25]. Moreover, the electrochemical properties of CuO/TiO_2 nanostructured films have been reported as

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advantageous for photocatalysts of hydrogen production from H_2O [26–28]. Recently, it has been reported that irradiation of Cu_2O/TiO_2 composite films with visible light can be used to produce hydrogen peroxide in aerated aqueous suspensions [29].

In this work, we have explored the use of TiO_2 semiconductor to promote the photodeposition of Cu/TiO_2 composites. Copper(II) from the precursor solution is reduced with the electrons photogenerated on the TiO_2 surface. Additionally, an easily oxidable compound must be present in the system to assure that holes are consumed, directly or indirectly, via hydroxyl radical formation; thus avoiding their accumulation on the photocatalyst surface. This could stop photocatalyst activity or cause copper reoxidation. Reduction of aqueous copper(II) on TiO_2 has been studied using either suspended TiO_2 powder [17,19,30] or TiO_2 films [20,31–33]. To our knowledge, the direct deposition of Cu/TiO_2 composite films on bare glass has not been reported. Films were characterized using grazing angle X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet-visible extinction spectroscopy.

2. Experimental details

2.1. Reagents and substrate

$Cu(NO_3)_2 \cdot 3H_2O$ (Fluka) and ethanol were of analytical grade (Panreac) and were used as received without further purification. TiO_2 powder P25 supplied by Degussa AG (80% anatase and 20% rutile, non porous, Brunauer–Emmett–Teller specific surface area: 50 m^2 g^{-1}, and average primary particle size of about 30 nm) was used as starting material. Ultrapure double distilled and deionised water (Milli-Q system, conductivity lower than 0.05 μS/cm) was employed for solution preparation, as well as, for cleaning procedures. Analytical grade phosphoric acid (Panreac) was used for substrate cleaning.

2.2. Preparation of glass substrates

The substrates used were bare glass (microscope slides, IDL). Slides, 75 × 25 mm, were cleaned with detergent solution and repeatedly rinsed with water. They were placed in a 15% H_3PO_4 solution during 3 h, washed thoroughly with deionised water and dried in a nitrogen gas flow.

2.3. Bath composition

TiO_2 powder (0.50 g) was dispersed in 100 mL of water using ultrasound for 5 min. After adding $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 g), the mixture was further sonicated during 5 min. Ethanol (1.0 mL) was then added and the sonicating procedure was carried out for 5 min. more. Obtained suspensions had a milky aspect.

2.4. Photodeposition

A 30 ml plastic container was filled completely with the suspension. A just-cleaned glass substrate was then placed horizontally on top of the container. Thus, only one side of the substrate was in direct contact with the bath suspension. Care was taken to avoid that any gas bubble adhered to the substrate since this cause non-homogenous deposits. Substrates were irradiated by the other side with UV light using a 125 W mercury lamp manufactured by Cathodeon (HPK). The lamp was placed at 15 cm distance from the sample and the standard irradiation time was 15 min. After deposition, the glass substrate was removed and gently rinsed with deionised water. Finally, it was dried in an oven (Memmert) at 85 °C during 5 min.

Initially, bath and substrate were both at room temperature. During irradiation they were gradually heated; although, for the short irradiation times used, only moderate temperatures increases occurred (<5 °C) in the bath. Therefore, no substantial solvent evaporation was observed. Precaution and protection measures were taken during mercury vapour lamp manipulation.

2.5. Heat treatment

Samples were placed in a cold furnace (Heron) which was then set to 400 °C. Once the furnace reached 400 °C, samples were left at this temperature for 3 h. After the furnace was switched off samples were allowed to cool before taking them out.

2.6. Characterisation techniques

Film surface morphology was investigated using SEM on gold covered samples with a JEOL JSM-3600 scanning electron microscope (operating voltage 10–30 keV). Backscattering images were taken in the same apparatus equipped with an energy dispersive X-ray spectrometer (EDX, Link ISIS-200) used for microanalysis. The XRD patterns were registered on a Siemens D-500 apparatus at an incidence angle of 1° using Cu K_α radiation. UV–visible extinction measurements in the films were performed in the standard transmission geometry mode with a Heλios γ spectrophotometer (Thermo Electron Corporation). A cleaned bare glass substrate was used as the reference. The film thickness was measured with a KLA Tencor P15 stylus profilometer.

3. Results and discussion

In the deposition method used in the present work, ultraviolet light was absorbed by a solid homogenously suspended in the bath, i.e., TiO_2 which acted as photocatalyst. The use of TiO_2 Degussa P-25, a powdered material composed of loosely aggregated nanocrystals, and the sonication treatment assured that most of the TiO_2 remained in suspension for a time long enough to perform the experiments. The presence of this opaque solid introduces differences in our process with respect to standard CBD. First, the suspension used limited light penetration. Therefore, only the suspension closer to the substrate was effectively illuminated. Second, the suspended solid was codeposited, and a composite material was obtained.

Concentration of copper(II) nitrate and ethanol, i.e., bath composition, as well as the amount of suspended TiO_2, influence characteristics of the deposited material. Copper nitrate was selected as the metal source because the nitrate anion is not generally adsorbed on oxide surfaces. Thus, obtaining a clean final material was expected. In addition, an organic species was necessary as hole scavenger and to favor copper ions reduction. Its nature will influence the deposition rate and the chemical nature of the species produced [17]. In this respect, good quality films were deposited by adding ethanol. Reactive species concentration determined the film properties if illumination time is kept constant. Results presented here were obtained using an optimised bath composition based on the criteria of homogenous films production at shortest possible time (15 min). Experiments performed showed that deposition rate was enhanced by increasing the irradiation power. At low irradiation power (6 W blacklight fluorescent lamp) no deposition or bad quality films were produced even after long illumination periods.

Deposited films using optimised procedure had a red brown uniform appearance. Film thickness, measured by profilometry, was around 500 nm. Even though as-deposited films were not well adhered to the substrate, after heat treatment films were noticeably well-adhered and, resisted the Scotch-tape adhesion test, although films did not resist more aggressive treatments as immersion in an ultrasound bath. Thermal treatment also led to darkening of the samples, suggesting oxidation of the copper to copper(II) oxide. In order to improve the adhesion, different methods of glass pretreatment were tested and it was found that a 3 h treatment with phosphoric acid improved the adhesion significantly.