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Impact of the chemical precursor on the crystalline constitution of nano-CuO/TiO_2 films

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ABSTRACT

More and more interest is dedicated to nano-CuO/TiO_2 mesoporous films which could be used in solar energy converting structures, sensors and photocatalysis applications. In this work we have studied the synthesis of CuO/TiO_2 nanocomposite films using a low temperature modified wet-impregnation technique. Copper(II) formate and copper(II) acetate aqueous solutions with varying concentrations are used as precursors for deposition of cupric oxide inside mesoporous TiO_2 layers. The obtained nanocomposite is characterized using XRD, SEM, AFM and UV–vis spectroscopy. Results show that the optical absorption spectrum of TiO_2 is extended significantly in the visible region and a CuO energy gap $E_g = 1.4$ eV is deduced from the absorption edge. XRD experiments show evidence of CuO nanocrystals when using cupric formate aqueous solution as a precursor while for cupric acetate-prepared compound, no XRD peaks are observed suggesting a disordered CuO phase in that case.

1. Introduction

Nano-CuO/TiO_2 is studied at present since it can be used in solar energy conversion [1–3], sensors [4] and photocatalysis [5,6] applications. For the majority of these applications, it is convenient to use a film or layer of nano-CuO/TiO_2. CuO has also been reported anchored to other materials like graphene [7] and ZnO [8].

When a layer of TiO_2 nanocrystals is heat-treated adequately, necking among them occurs and a nanocrystalline film with mesopores is formed. The resultant internal surface (much larger than the external surface) can be viewed as wrapped or packed in the film or layer volume. If CuO is somehow deposited on the real (internal) surface, a nanostructured composite with a large CuO/TiO_2 interface area may result. Different technologies have been used to fabricate CuO/TiO_2 interfaces as, wet-impregnation [1–3,5,6], sol–gel [9], and photoelectrochemistry [10,11].

Adequate position for water splitting of CuO band edges relative to that of TiO_2 has been reported for nanocrystals showing quantum confinement [2] as well as electron injection from CuO to TiO_2 [8]. This is fundamental in order to use CuO/TiO_2 interface for conversion of solar energy to electricity. The literature shows that the CuO/TiO_2 interface has not been studied sufficiently, particularly, regarding relative band positions and bandgap. For example, disagreements exist with respect to both; CuO bandgap type and bandgap value [12–16]. Furthermore, different values for the conduction band position relative to vacuum are reported [13,14] [13,14 and references there in]. Existing uncertainties imply that nanostructured CuO/TiO_2 interface might behave better than Cu_2O/TiO_2 taking advantage of its lower bandgap for solar spectrum absorption.

In this work, we report a facile technique to deposit CuO within a TiO_2 mesoporous matrix using cupric formate and cupric acetate as chemical precursors. This has not been done before to the best of our knowledge. Besides ease of fabrication, an additional advantage with respect to other reported low-bandgap/high-bandgap three dimensional heterostructures is that the employed oxides are innocuous. On the other hand, penetration of nano-sized interstices is a difficult task encountered with the majority of deposition techniques used to form three dimensional interfaces. They tend to clog pores and penetration is hindered. The proposed technique is designed so that CuO completely penetrates the mesoporous TiO_2 and CuO nanoparticles form inside the pores.

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Samples are analyzed using scanning electron microscopy (SEM), optical microscopy and atomic force microscopy (AFM) for morphological characterization. UV–vis spectroscopy together with profilometry allowed finding an effective absorption coefficient. Finally, XRD was employed to characterize the phase constitution of the material.

2. Experimental procedures

2.1. Fabrication of CuO/TiO$_2$ films

Single layers of mesoporous TiO$_2$ were prepared using TiO$_2$ nano-powder Degussa P25 (particle diameter ca. 25 nm) and the well-known "doctor blade" technique developed for DSSC [17]. Air drying of the TiO$_2$ layer was followed by heat treatment in air for an hour at 450 °C. The porous TiO$_2$ films were then immersed in the precursor solution during 18 h so that the solution filled completely the TiO$_2$ mesopores. Precursor solutions based on Cu (II) formate and Cu(II) acetate with different concentrations were used, as shown in Table 1.

Fig. 1 shows separation distance between molecules in precursor solution relative to nanocrystal and pore sizes for the case of 40 mM Cu(II) formate. For this condition, the distance between cupric formate molecules is ca. 3 nm. Considering this value, in this case, there should be around 80 molecules of cupric formate inside a pore with diameter $\varphi\sim18$ nm (pores are formed by the nanocrystals interstices). Precursor molecules should move easily through the mesoporous structure and penetrate pores. After immersion, the samples were heat treated in air for three hour at 500 °C. In this process, water evaporates, Cu(II) salts decompose and CuO is formed.

2.2. Characterization

The phase identification of the films was performed by X-ray diffraction (XRD) with an Empyrean Panalytical apparatus in the range $10^\circ < 2\theta < 60^\circ$. Cu K$\alpha$ radiation (λ = 1.5406 Å) was used for all X-ray diffraction experiments. The Panalytical sofware for XRD HighScore version 3.0 (2012) was used for XRD pattern analysis. Sample surface was observed by optical microscopy. Also scanning electron microscopy (SEM) was conducted with a Hitachi SU8020 scanning electron microscope. Film thickness was monitored using surface profiler Dektak 150. Atomic force microscopy (AFM) was carried out in air at ambient conditions using a Nanoscope Multimode equipment. The presence of CuO and optical properties of the films were determined from transmission experiments with a UV–vis–NIR double beam spectrophotometer Cary 5G. Spectra were measured from 200 to 1300 nm.

3. Results and discussion

Optical microscopy observations showed that CuO is deposited on the surface due to the thin wetting film that remained on it after withdrawal from the precursor solution. According to Fig. 2, crystals form more readily when using Cu(II) formate than when using Cu(II) acetate. Smaller and more widely dispersed CuO particles are observed for Cu(II) acetate that could be attributed to a different surface wettability of the solution. Also different crystal morphologies are observed for low and for high concentrations of cupric formate: rod-, chrysanthemum- and leaf-like CuO nanostructures. Other authors have also observed these different morphologies for CuO nanocrystals depending on growth conditions [18–21].

Table 1
Analyzed samples.

Sample name	Solute in aqueous precursor	Concentration (mM)
160 F	Cu(II) formate ($Cu(HCOO)_2$)	160
160 A	Cu(II) acetate ($Cu(CH_3COO)_2$)	160
40 F	Cu(II) formate ($Cu(HCOO)_2$)	40
40 A	Cu(II) acetate ($Cu(CH_3COO)_2$)	40

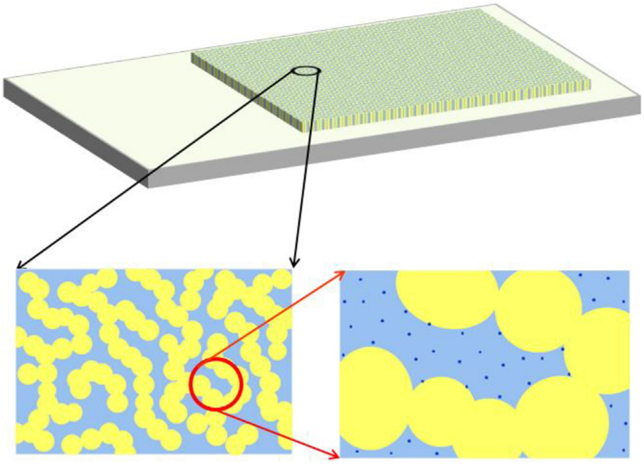

Fig. 1. The two bottom figures show relative dimensions of TiO$_2$ nanocrystals, pores, solute molecules and separation distance between precursor molecules when 40 mM Cu(II) formate is used as precursor solution. TiO$_2$ structure is shown in yellow (white) and the precursor solution in blue (gray). In the last diagram, which corresponds to the largest magnification, molecules are shown in dark blue (black). Molecules can flow easily through pores according to relative dimensions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As a consequence, sample surfaces were then always thoroughly dried after withdrawal from precursor solution to avoid this phenomenon.

SEM cross-sections are presented in Fig. 3 in which it can be seen that the resulting composite is nanostructured whatever the precursor used (cupric formate or acetate). Fig. 3d and e show the images corresponding to samples A40 and F40, respectively. Their comparison show that particles are bigger for sample A40. This could be attributed to CuO surrounding the surface of the TiO$_2$ nanocrystals. SEM images in Fig. 3 show that the CuO/TiO$_2$ mesoporous structures are not appreciably denser than the TiO$_2$ structure. The existing pores allow penetration by an electrolyte or other media required by some devices based on the CuO/TiO$_2$ interface.

AFM images for the four types of samples are shown in Fig. 4. Analysis using AFM showed similar surface roughness for all the studied samples. Surface roughness, R_a, is the mean roughness value given by the arithmetic average of the absolute values of surface height deviations measured from the mean plane given by 0 in Fig. 4. R_a is less than 30 nm for all samples. This seems to be determined by the TiO$_2$ nanocrystals used to deposit the mesoporous TiO$_2$ layer.

TiO$_2$ mesoporous films that were immersed in the precursor solutions showed a light blue color after withdrawal (even when their surfaces were carefully dried). This color changed to brownish in all cases after heat treatment showing that precursor cupric salts had decomposed. Samples were darker for higher precursor solution concentration. In order to analyze the cupric oxide formed within the mesoporous TiO$_2$, optical transmission experiments were performed. Since thicker samples retain more precursor solution within its pores, samples thickness was measured and used to find an effective absorption coefficient $\alpha(h\nu)$ according to the expression: