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Synthesis and electrochromic study of sol–gel cuprous oxide nanoparticles accumulated on silica thin film

O. Akhavan *, H. Tohidi, A.Z. Moshfegh

Department of Physics, Sharif University of Technology, P.O. Box 11155-9161, Tehran, Iran

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ABSTRACT

In this study, electrochromic properties of cuprous oxide nanoparticles, self-accumulated on the surface of a sol–gel silica thin film, have been investigated by using UV–visible spectrophotometry in a lithium-based electrolyte cell. The cuprous oxide nanoparticles showed a reversible electrochromic process with a thin film transmission reduction of about 50% in a narrow wavelength range of 400–500 nm, as compared to the bleached state of the film. Using optical transmission measurement, we have found that the band gap energy of the films reduced from 2.7 eV for Cu_2O to 1.3 eV for CuO by increasing the annealing temperature from 220 to 300 °C in an N_2 environment for 1 h. Study of the band gaps of the as-deposited, colored and bleached states of the nanoparticles showed that the electrochromic process corresponded to a reversible red–ox conversion of Cu_2O to CuO on the film surface, in addition to the reversible red–ox reaction of the Cu_2O film. X-ray photoelectron spectroscopy indicated that the copper oxide nanoparticles accumulated on the film surface, after annealing the samples at 200 °C. Surface morphology of the films and particle size of the surface copper oxides have also been studied by atomic force microscopy analysis. The copper oxide nanoparticles with average size of about 100 nm increased the surface area ratio and surface roughness of the silica films from 2.2% and 0.8 nm to 51% and 21 nm, respectively.

1. Introduction

Metal oxide nanostructures, as promising materials, have attracted much attention because of their extraordinary properties in different fields of optics, optoelectronics, catalysts, biosensors and so on. In this regard, copper oxide-based materials with nanostructures have been widely investigated [1–6] due to their potential applications in chemical, photochemical and electrochemical fields, particularly in water splitting under visible light irradiation [7], windows for solar energy conversion [8] and catalytic [9] as well as electrochromic [10] applications.

Copper oxide thin films has been prepared by several different methods, such as electro-deposition, sono-chemical method, thermal relaxation liquid phase reduction, thermal evaporation, sputtering and also sol–gel. Among them, sol–gel technique has been utilized as a potentially useful technique for preparation of even nanoparticles of copper and copper oxide materials [11–15].

Copper oxide is known to exist in two semiconducting phases, namely cupric oxide (CuO) and cuprous oxide (Cu_2O) having monoclinic p-type and cubic p-type crystal structures, respectively. Cuprous oxide is a semiconductor with various characteristics due to the stoichiometric deviations arising from its preparation methods and parameters [16–19].

In addition to the numerous studies on the solar cell application of cuprous oxide thin films [20,21], it has recently been found that Cu_2O thin films exhibit cathode electrochromism [10,22–25], *i.e.* they are transparent for visible light in their oxidized state, and almost black when switched to their reduced state. Electrochromic materials are able to reversibly change their optical properties upon charge insertion–extraction induced by an external voltage. These materials can be interesting because of possibilities to modulate optical transmission, reflection, absorption, and emission. So far, there is very limited number of scientific publication on the electrochromic properties of cuprous oxide thin films [25]. For example, in an investigation [22], copper oxide films were deposited by thermal evaporation technique and it has been shown that the films had a reversible optical switching from the colored to bleached state. Optical transmittance of the copper oxide films with 500–600 nm thickness on indium tin oxide (ITO)/glass substrate varied from 85 to 40% during the coloring process. In another research [10], copper and copper oxide thin films with 25 nm in thickness were deposited on fluorine doped tin oxide (FTO)/glass substrates by DC magnetron sputtering, and then electrochromical cycling has been carried out in 0.1 M NaOH electrolyte. The visible transmission varied by 50% between the bleached and colored states, with a similar modulation of reflectance in the near-infrared. Recently, the electrochromic properties of cuprous oxide thin films with 150–200 nm thickness deposited on FTO/glass substrates were studied and it was shown that change in the

* Corresponding author. Tel.: +98 21 6616 4566; fax: +98 21 6602 2711.
E-mail address: oakhavan@sharif.edu (O. Akhavan).

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transmittance between the colored and the bleached state was about 50% [25]. Also, in this context, studies of electrochromic properties of metal and metal oxide nanostructures, such as Ag and WO_3 nanoparticles, have attracted much attention, due to better electrochromical performance than the common thin films [26–28]. Beside the limited investigations on electrochromic properties of cuprous oxide thin films, the electrochromic properties of cuprous oxide nanoparticles have not also been studied, yet.

In this work, silica thin films containing copper oxide nanoparticles accumulated on the film's surface have been synthesized using the sol–gel technique. The silica thin film was used as a matrix for producing cuprous oxide (Cu_2O) nanoparticles at a suitable annealing temperature. It was previously found that low-temperature heat-treatment of aqueous sol–gel silica thin films results in a self-accumulation of the metallic/metal oxide nanoparticles, initially dispersed within the film, on the film surface [14,29]. The copper oxide nanoparticles accumulated on the surface can produce a rough surface with a high surface area ratio, suitable for electrochromic process. The optical properties of the films, including the optical band gap energy, have been investigated for the different annealing temperatures and also for the thin films in colored and bleached states of the electrochromic process. The electrochromic properties of the cuprous oxide nanoparticles have been characterized in a lithium-based electrolyte cell.

2. Experimental details

Silica thin films containing copper oxide particles were prepared by sol–gel method on ITO/glass substrates. The silica sol was prepared by mixing tetraethylorthosilicate (TEOS, Merck,>98%), ethanol (C_2H_5OH, Merck,>99.9%) and deionized water in molar ratio of 1:4:11, respectively. To prepare the copper oxide doped SiO_2 sol, copper nitrate (50 wt.% of the final product with total metal oxidation assumption) was added to the solution. Also HNO_3 (Merck, 65%) with the molar ratio of 0.03 relative to TEOS was used as a catalyst to promote the hydrolysis process. In the first stage of sol preparation, TEOS and ethanol were mixed by using a magnetic stirrer. After 30 min of stirring, a solution containing the water, the copper nitrate and the nitric acid was added to the sol drop-by-drop, while it was vigorously stirred at room temperature. A blue-color as well as homogenous solution of all the components was obtained after mixing them. The sols were left 24 h for ageing until the viscosity reached approximately about 5 cP. A similar sol–gel process for synthesis of Ag nanoparticles in silica matrix was also reported, previously [30]. The coating of films was performed by dipping the ITO/glass substrates (with electrical sheet resistance of 100 Ω/□ and thickness of 1 μm) in the sol for 60 s and then by pulling them with a rate of 1 mm/s. The films were dried at 100 °C in air for 1 h and then heat-treated at temperature range of 200–300 °C in an N_2 environment for another 1 h. The prepared samples heat-treated at 220 °C were transparent and slight green in color. Thickness of the silica films was measured about 250–300 nm by an interference optical method.

An UV–visible spectrophotometer (Jasco-V530) was used to investigate the optical properties of the films in the wavelength range of 300–1100 nm with 1 nm resolution. X-ray photoelectron spectroscopy (XPS) was employed to study the atomic composition and chemical state of the film's surfaces. A hemispherical energy analyzer (Specs EA 10 Plus) with an Al Kα X-ray source at energy of 1486.6 eV operating in a vacuum better than 10^{-7} Pa was used for the binding energy analysis. All binding energy values were calibrated by fixing the C(1s) line to 285.0 eV. The surface morphology and the particle size distribution were also examined by using Park scientific-Auto probe CP atomic force microscopy (AFM) with a silicon tip of 10 nm in radius operating at the contact mode.

The coloration-bleaching kinetics and the optical modulation of the copper oxide nanoparticles in the silica thin films were studied in a 1 M $LiClO_4$ + propylene carbonate (PC) electrolyte cell. A simple two-electrode electrochromic cell, which was previously applied for the study of other electrochromic thin films [31], was also considered here for the same purpose. It consisted of two ITO/glass plate electrodes with a perpendicular position relative to each other. One plate was coated with WO_3 film (as a counter electrode) and another with the copper oxide–silica composite film (as the work electrode). The perpendicular position provided the conditions by which the light beam could make an incidence only on the copper oxide film surface so that we could eliminate the effects of WO_3 layer on our results. Although one of the simplest counter electrodes is ITO itself, we have observed that the bare ITO electrodes were not completely reversible in our experimental conditions (particularly due to the applied coloring voltage of −5 V). However, the WO_3/ITO/glass electrode reversibly worked as a counter electrode at such a voltage [31], due to preventing the Li ion diffusion into the ITO by using the WO_3 thin film. Some details about the characteristics of the WO_3 layer can be found elsewhere [32,33]. By applying a constant coloring voltage (−5 V), the optical transmittance of copper oxides–silica thin films was measured *in-situ* as a function of time at a constant wavelength (500 nm) and also as a function of wavelength at a constant time (90 s after applying the voltage). The bleaching process was done by changing the polarity of the applied voltage (*i.e.* applying +5 V), 100 s after applying the coloring voltage.

3. Results and discussion

Fig. 1 shows the transmission spectra of the silica films containing copper oxide nanoparticles annealed in a temperature range of 200–300 °C, after eliminating the optical effect of the substrate. Meantime, for comparison, the transmission spectra of the annealed silica thin films (without any copper oxide doping) at 200 and 300 °C have also been presented in Fig. 1. The doped copper oxide films heat-treated at 200 °C had a light blue color, showing a trace of the initial copper nitrate in the films. The transmission of the samples improved by increasing the annealing temperature to 220 °C. At 220 °C the films were transparent with a light green color, due to complete formation of cuprous oxide in the film. However, by increasing the annealing temperature from 220 to 300 °C the transmission of the films gradually decreased from about 85 to 7% at wavelength of 500 nm, and their color changed to light and dark brown which the latter is an indicative for substantial formation of cupric oxide in the film.

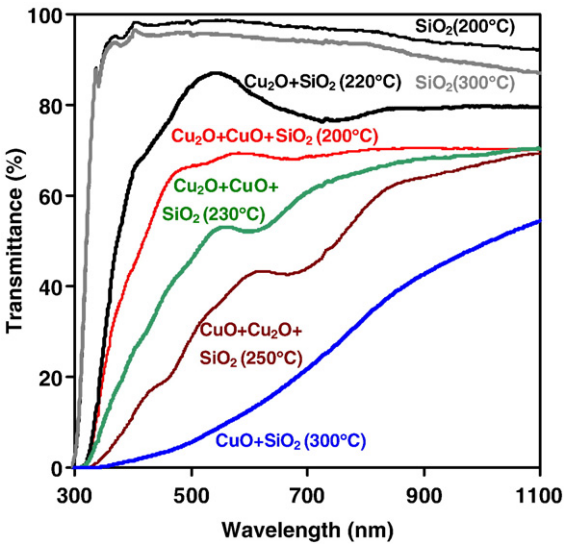

Fig. 1. Optical transmission spectra of the annealed silica thin films containing copper oxide nanoparticles in a temperature range of 200–300 °C in N_2 environment, as compared with the spectra of the pure silica films heat-treated at 200 and 300 °C.