Research Article

Dependence Properties of Sol-Gel Derived CuO@SiO$_2$ Nanostructure to Diverse Concentrations of Copper Oxide

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Various concentrations of copper oxide were embedded into silica matrix of xerogel forms using copper source Cu(NO$_3$)$_2$·3H$_2$O. The xerogel samples were prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) with determination of new molar ratios of the components by the sol-gel method. In this paper, three samples of copper oxide were doped into silica matrices using different concentrations. We obtained 10, 20, and 30 wt.% of copper oxide in silica matrices labeled as A, B, and C, respectively. The absorption and transmittance spectra of the gel matrices were treated at different concentrations by Uv-vis spectrophotometer. Quantities of water and transparency in the silica network change the spectral characteristics of Cu^{2+} ions in the host silica. Absorption spectra of the samples heated to higher concentration complete the conversion of Cu^{2+} ions to Cu$^+$ ions. The effects of concentration of copper oxide were characterized by X-ray diffraction (XRD) patterns, and the transmission electron microscope (TEM) micrographs. Also, textural properties of samples were studied by surface area analysis (BET method) at different concentrations.

1. Introduction

Sol-gel processing is a relatively new technique in the preparation of glasses and primarily to get potentially high purity and homogeneity as well as low processing temperatures compared with the traditional glass melting techniques [1]. Hydrolysis and polycondensation of alkoxide precursors followed by aging and drying are of the best methods used for making sol-gel of silica monolith [2]. The monoliths processed by sol-gel method allowed metal ions and rare earth ions to incorporate transition metal in their matrices. Introducing transition metals into hydrolysable precursors through sol-gel method permits the formation of numerous novel materials that exhibit important optical and/or catalytic properties [3, 4]. Copper or copper oxides in oxide matrixes have attracted sustained interest due to their unusual properties [5]. Mohanan and Brock [6] have studied copper oxide silica aerogel composites by varying pH values, copper

precursor salts, and treatment temperatures. They found that based-catalyzed gels underwent a gradual change from bonded Cu^{+2} ions to segregated copper oxide at different heating conditions. Parler et al. [7] observed silicon-oxygen-metal bond formation during both the synthesis and drying stages at low temperatures. Host matrices embedded with copper have been produced to study their properties as tunable visible light solid-state lasers and colored coatings [8, 9]. The mechanical properties of Cu-doped silica gels in the form of xerogels, coatings, and powders have been studied extensively [10]. The structural evolutions of copper-doped porous silica gels treated at different temperatures have also been studied [11, 12]. So far no reports have been seen on different concentrations effect of copper oxide on the optical, structural, and textural properties of CuO@SiO$_2$ nanostructures. The aim of present work is understanding the effect of concentration on the spectroscopic properties of different copper concentrations (10, 20, and 30 wt.%).

2. Experimental Procedure

2.1. Sample Preparation. In this work, the raw materials consisting of tetraethyl orthosilicate (TEOS) (Fluka, 98%), ethanol absolute (EtOH) (Merck), and copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (Merck), as initial solution, and nitric acid (HNO_3) (Merck, 65%) and acetic acid (CH_3COOH) (Merck, 99-100%), as catalysts, were used. Three samples of CuO@SiO$_2$ nanocomposite in xerogel form were prepared by the sol-gel method, and the fourth sample was prepared as a blank using TEOS hydrolyzed with HNO_3, CH_3COOH, EtOH and deionized (DI) water in the new total molar ratio of $TEOS : ETOH : H_2O = 1 : 1.3 : 6.2$ [12].

The appropriate amounts of trihydrated copper nitrate were added to the solution, so that the concentrations of copper oxide in the final products reached 10, 20, and 30 wt.% (labeled as A, B, and C, resp.). Then the solutions were mixed by magnetic stirrer for 1.5 hours to make them more homogeneous. The solution acidity (pH) was measured by pH meter as 2.4. The samples were kept in a close container at 25–30°C. The soft gel was prepared till a dark-blue color appeared within 84 hours via gelatin treatment. Then the gel samples were dried in an oven at 80–110°C in air for 1 hour to complete the gelatin process [13]. The gel samples were then annealed at the temperature range of 100–1000°C with rate of 50°C/h for 2 hours, using electric furnace to form the condense nanocomposites [14–16]. The blank solution was prepared using the above-mentioned procedure but with no $Cu(NO_3)_2 \, 3H_2O$ application.

2.2. Characterization. Characterizations of ultraviolet-visible (Uv-vis) spectra of samples were prepared under experimental conditions by Uv spectrophotometer, model BEKMAN (DU-600).

The X-ray diffraction (XRD) patterns were prepared by a Philips instrument using PW1800 diffract meter and radiation of copper anodic tube $\lambda = 1.54$ Å.

A transmission electron microscope (TEM), Em208S series (Philips Company), operating at 100 kV was used in this work. The dry samples were ground, suspended in dry cyclohexane, and sonicated for 30 minutes. Then the solutions were allowed to settle, and a droplet of the resulting supernatants was placed on a holey carbon film and dried.

The porosities of the samples were analyzed by nitrogen adsorption/desorption measurements fitted to a BET isotherm using an Autosorb instrument (Quanta-chrome, Nova 1200). The samples were pretreated for 3 hrs under vacuum at 100°C (for the sample dried at 100°C) and at 200°C (for samples treated at 400, 800, and 1000°C). Gaseous nitrogen was used with a 5-hour adsorption/desorption cycle.

The condensation and annealing of the samples were performed in a heat furnace with high thermal capacity (1500°C).

3. Results and Discussion

3.1. Spectroscopy Characteristics. Figure 1 exhibits the absorption spectra of the samples A, B, and C heated at 200°C. As shown, all of the doped gel samples present an absorption
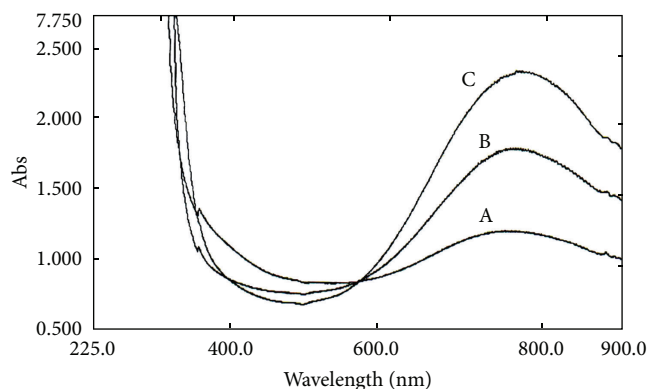

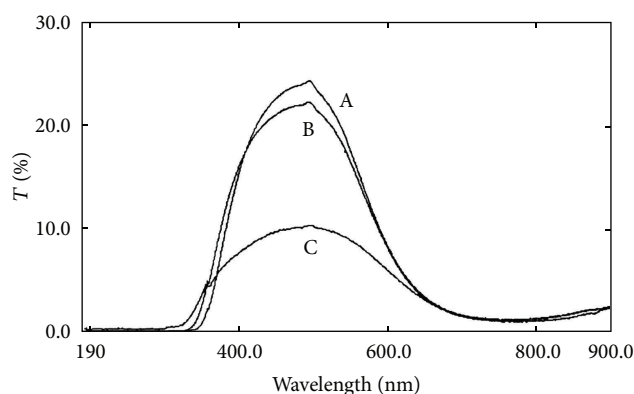Figure 1: Absorption spectra of the samples A, B, and C heated at 200°C.

Figure 2: The transmittance spectra of the samples A, B, and C.

band around the 780 nm wavelength, which explains the presence of Cu^{+2} ions in the gel matrix. This absorption intensity increases for higher concentrations of copper ions in volume unit. This figure presents with increasing of concentration copper oxide, the intensity of peaks increases and amounts Cu^{2+} raises in volume unit. Also, the incorporation of copper ions in the matrix up to 700°C was confirmed by the absorption spectra [16].

It is known that impurity of water in oxides appearing in the form of hydroxyl groups produces absorption band in the NIR region. Sometimes it has been observed that an absorption band in the violet region (400 nm) exhibits copper oxide colloidal particles in the matrix. But it is surprising that no absorption band has been seen in this range due to low concentration of the copper ions and low acidity of the samples. Figure 2 presents the transmittance spectra of the samples A, B, and C at different concentrations. The dark-blue color of gel samples is related to the transmittance spectrum indicating maximum transmittance in the 400–600 nm range.

Because of high purity and low volume of water, these samples show high transmittance. These observations indicate that the samples have filtering effect in the 400–600 nm range.
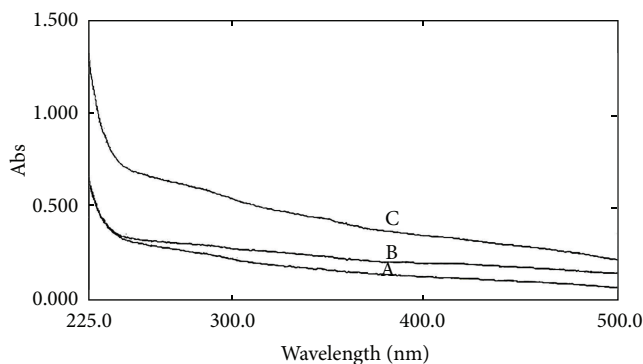
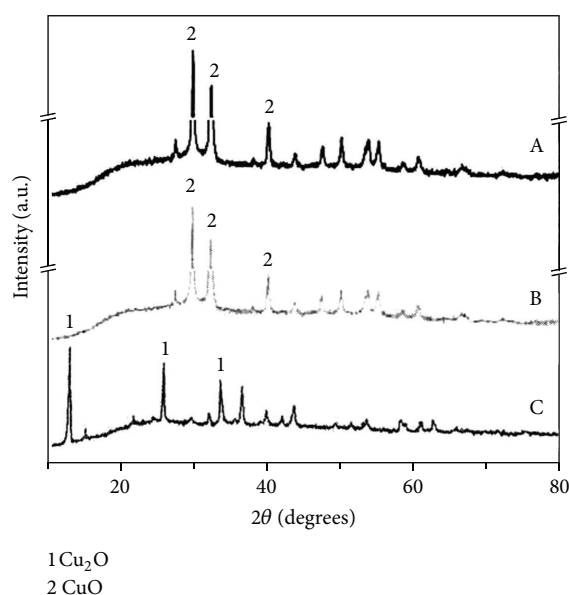FIGURE 3: The absorption spectra of the samples A, B, and C heated at 1000°C.

1 Cu$_2$O
2 CuO

FIGURE 4: X-ray patterns of CuO/SiO$_2$ sample concentrated at A, B, and C samples.

Figure 3 shows the absorption spectra of the samples A, B, and C heat-treated at 1000°C. The powdered samples showed similar absorption spectra to those of Cu$^+$ ions. The broad absorption around 780 nm was completely disappeared from all the samples. Therefore, it seems that, at 1000°C, the Cu^{2+} ions might be converted into Cu$^+$ ions or Cu$_2$O. Thus, the reaction of copper metal and oxygen initially yields copper oxide, which is then converted into Cu$_2$O during the longer reaction times or at higher concentrations and temperatures [17, 18].

Figure 4 presents the X-ray pattern of the CuO@SiO$_2$ sample sets annealed at A, B, and C. For the sample annealed at C label, the pattern corresponding to the copper nitrate is presented to be Cu$_2$O of Cu^{1+} form. Although the amount of the added copper nitrate is below the limit of solubility and all precautions were taken to dissolve it, two states could occur during the thermal treatment of the gel, which explain the later fact that the precipitation of the compounds or

separated ions leads to formation of the compounds during the annealing. For the samples concentrated at A and B, it demonstrated the X-ray pattern corresponding to the copper oxide phase in tenorite structure. According to the results, it was shown that there is no evidence of the presence of Cu$_2$O species in these samples, but for the sample of C X-ray diffraction patterns are not clear at this concentration. In the authors, view, in high concentration CuO decomposition occurred is and converted to Cu$_2$O.

The nanostructural characterization of the xerogel was studied by TEM. Powder samples with 10, 20, and 30 wt% copper oxide, after ambient drying and thermal treatment at 400°C in air for 1 h, were objected to TEM using bright field, and the resulted images are shown in Figure 5. No crystalline species were detected without thermal treatment, and the bright field image shows a typical amorphous xerogel. Figure 5(a) exhibits A sample with 10 wt% in silica matrix that is a network of pores with different average sizes about 50 nm. Also, Figure 5(b) presents the copper ions with 20 wt% doped into the pores of silica matrix after annealing at 400°C.

In this figure, the different particles with average size of about 75 nm that doped and completed the pores of silica matrix can be seen. Figure 5(c) presents TEM micrograph of sample C with 30 wt% that has average size about 150 nm. It was shown that with increasing concentration particle size increased, but a deformation in micrographs was appeared. With increasing of concentration, numbers of copper ions raises in volume unit and structure move to formation of nanoclusters from Cu–O–Cu that is connected to silica matrix directly. The XRD confirms formation of Cu^{1+} in sample C that is unuseful for optical properties. Sample A is the most important sample with the highest transmittance that shows low amount of water and high purity.

The effects of the concentration on the textural properties of the sol-gel samples were presented in Table 1. The obtained data have shown that the treatment at 400°C of A sample produced the largest surface area, pore size radius with the lowest density. These results indicate the loss of volatile compounds from the porous structure. Once the volatile compounds were eliminated from the network, an increase occurs in the porosity, and the gas pores interact [19–21]. Despite this weight loss, a little shrinkage was observed for the material treated at 400°C, resulting in density decrease. It is interesting for the sample treated at 400°C of B sample, which the surface area reduces by 41.9% (from 420 to 244 m$^2 \cdot$g^{-1}), whereas the pore volume shows a much more pronounced decrease of 68.4% (from 680 to 214.5 cm$^3 \cdot$g^{-1}).

For the sample of C treated at 400°C, the surface area decreases by about 53.7%, whereas the pore volume shows 54.3% reduction. In the authors' view, it was related to the size and shape of micro-, meso-, and macropores, which modify the samples treated at 400°C. For another sample, the surface area and porosity strongly decrease due to densification process. The results have presented a significant contribution to micropores in the material treated at 400°C. Comparison of surface area, porosity, density, and pore volumes for these samples and obtained results show that A sample is the best material for catalytic activity [22].

(a)   (b)   (c)
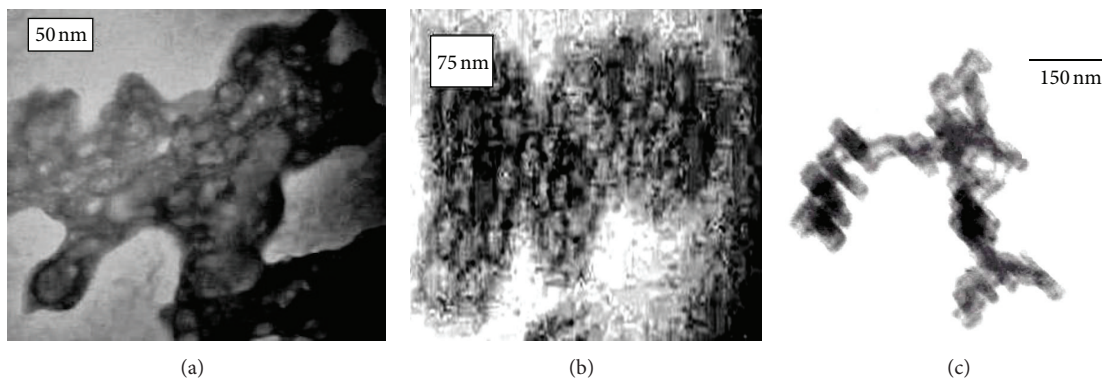
FIGURE 5: TEM micrograph of (a) sample A (10 wt%), (b) sample B (20 wt%), and (c) sample C (30 wt%).

TABLE 1: Textural properties of A, B, and C samples.

Sample	Surface area $(m^2\,g^{-1})$	Pore radius (Å)	ρ_{pic} g/cm^3	V_p cm^3/g
A	420.0	21.0	0.72	680.0
B	244.0	16.0	0.78	214.5
C	112.8	8.0	0.86	98.0

4. Conclusion

The broad absorption band of Cu^{2+} ions in around 780 nm was related to the legend field splitting of d levels. The transmittance spectra of high temperature treated copper ions doped into silica matrices indicate that the broad bond with filtering effect. Uv-vis spectroscopy presents the sample of A is the most important sample with the highest transmittance that shows low amounts of water and high purity. XRD patterns presents in A and B samples, there are copper ions to Cu^{2+} to tenorite structure, but in C sample, there are copper ions to Cu^{1+} form, mainly. Also, the TEM micrographs confirmed the formation of colloidal particles of about 50, 75, and 150 nm for A, B, and C samples, respectively. Also, surface area, porosity, density, and pore volumes compared for these samples and obtained results show that A sample is the best material for catalytic activity. A sample shows the highest surface area and results in the best catalytic activity. The lower concentrations are not suitable for catalytic activity, because the copper oxide quantities are very low. But in case of B and C samples, these are not good for catalytic activity, because copper oxide particles are coagulated together, stay in pores, and do not come to surface for reaction with other molecules to present catalytic activity. According to the results, the exact compositions of nanocomposites depend on the annealing temperatures, the choice of appropriate copper source, and suitable concentration of copper ions in the silica matrices.

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