

# Comparision of Synthesis and Characterization of Copper Species Nanostructures on the Silica Matrix

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## **Abstract:**

*Incorporation of copper species into silica matrix was performed by the sol-gel method. Copper ions and copper particles were doped using two different copper sources;  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and copper particles chemically synthesized. The particles of copper metallic, cuprous and cupric oxide were prepared and the synthesis and characterizations of copper species were compared together. On the other hand, their structures were analyzed by furrier transformation infra red spectroscopy and X-ray diffraction at 200, 400 and 600°C. Three main region contain Rocking (R), Bending (B) and Stretching (S) were recognized on their vibration structure using furrier transformation infra red spectra. Also, the scanning electron micrographs and chemical analysis of Cu and  $\text{CuO}/\text{SiO}_2$  were performed by energy dispersive X-ray spectroscopy. Average sizes of particles were determinated about 50 nm for  $\text{CuO}/\text{SiO}_2$  and were analyzed about 200 nm by transmission electron microscopy for the particles of  $\text{Cu}/\text{SiO}_2$ .*

**Keywords:** Synthesis and Charactrization, Sol-Gel, Copper Species

## **1. INTRODUCTION**

The sol-gel method is a versatile technique for preparation of glass coating and powdered samples that allows the incorporation of metals sand other materials in their matrixes [1,2]. The incorporations of different elements, post deposition treatments and the interactions of the elements with the host matrix lead to the modifications of the glass structure [1].

The introduction of transition metals in a  $\text{SiO}_2$  glass matrix has a strong influence on the optical visible absorption spectrum [3]. Nano and microsized particles of various materials embedded in the glass matrix produce quantum and non linear optical effects when the particles have some critical size [4]. In the sol-gel method, metal ions can be doped into ionic oxide network,

which then converted to more stable compounds compared to the other methods [5,6]. The sol-gel polymerization of metal alkoxides in presence of inorganic salts lead to the formation of ceramic oxides materials with important microstructural properties [7]. Several authors have reported the works concerning sol-gel prepared silica samples containing copper [8,9].

They have also checked various steps of preparation  $\text{CuO}/\text{SiO}_2$  by the sol-gel method [10]. To our knowledge, none have compared the preparation and characterization of different copper species by analytical instruments. The main suggestion of this investigation is to dope the copper species in the silica network by thermal treatment and explore the nanostructure of the support material and the evolution of metallic species in the silica network.

## 2. EXPERIMENTAL

### 2.1. Materials

In this investigation, the raw materials contain tetraethyl orthosilicate (Fluka, 98%) (TEOS), ethanol absolute (Merck) (EtOH), copper nitrate tri-hydrated (Merck),  $\text{HNO}_3$  (Merck, 65%),  $\text{CH}_3\text{COOH}$  (Merck, 99-100%) were used.

### 2.2. Synthesis of copper species

Initially, samples were prepared by sol-gel method as  $\text{CuO/SiO}_2$  nanocomposite xerogel [10]. The Initial solution for  $\text{CuO/SiO}_2$  xerogel was prepared with mixture of TEOS,  $\text{H}_2\text{O}$ , EtOH,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 3M  $\text{HNO}_3$ , 4M  $\text{CH}_3\text{COOH}$ , with total molar ratios of 1:1.3:6.2 for TEOS: EtOH: $\text{H}_2\text{O}$ . Subsequently, 0.2 moles of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $5 \times 10^{-3}$  moles of 3 M  $\text{HNO}_3$ ,  $4 \times 10^{-3}$  moles of 4 M  $\text{CH}_3\text{COOH}$  were added to 1mole of TEOS for catalyzing the hydrolyzation and condensation reactions. A homogenous solution of all components was obtained after mixing them for 2.5 hours by a magnetic stirrer. The final pH of all the samples was about 2.4. The solution was kept in a close container at 25-30°C. The soft gel was prepared to dark- blue color in 84 hours (3.5 days) by gelation treatment. Then gel samples were dried in an air oven at about 100°C for 2 hours and the gelation procedure was thus completed. Copper particles were obtained using a water oil microemulsion and using  $\text{NaBH}_4$  as the reducing agent.

Microemulsions were prepared by dissolving aqueous  $\text{CuCl}_2$  or  $\text{NaBH}_4$  solution into a surfactant/hexanol/hexane solution.  $\text{CuCl}_2$  is dissolved in one solution and  $\text{NaBH}_4$  in the other one, where, the salt concentration in the aqueous phases were 0.1 M in  $\text{CuCl}_2$  and 0.3 M in  $\text{NaBH}_4$ . Preparation of copper particles was carried out by rapidly mixing equal volumes of each water/microemulsion ratio; and pH of  $\text{CuCl}_2$  solution, the amount of  $\text{Cu}_2\text{O}$  present in the copper particles can vary drastically. The copper particles are made at room temperature without removing the oxygen [8]. For the particle-doped xerogels, they were mixed with ethanol directly to the homogenous  $\text{H}_2\text{O/TEOS}$  solution and hence the final solution was obtained. The solution was then

stirred for about 15 minutes by a magnetic stirrer. The two solutions were placed in a container at constant temperature bath at 35°C. The samples were labeled set A for the copper nitrate and set B for the particles one. In both sets of samples, soft species were obtained after about 48 hours. The B solutions were heated in an oven in air atmosphere at about 100°C to produce rapidly dried the solution and thus accelerating the gelation process. For subsequent annealing, the samples were introduced in the oven at the desired temperature for 25 minutes in air. These species were ground to form a fine powder.

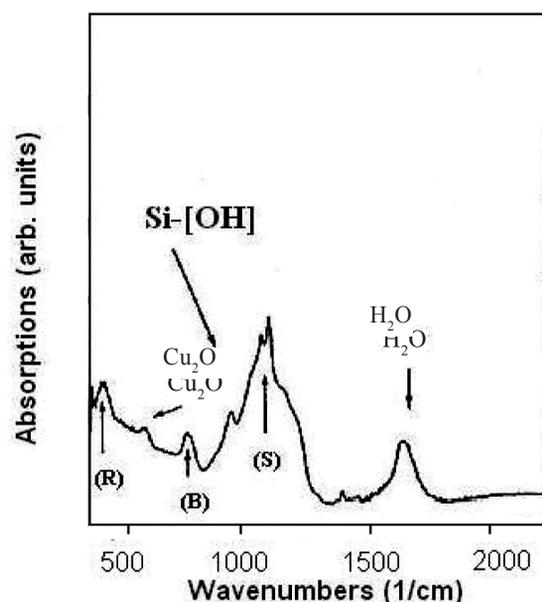
- The infrared spectra was prepared in a FTIR spectrometer of Genesis system- model ATI, using 0.05 gr of powder sample with 0.3 gr of KBr.
- TEM micrographs were prepared using a Phillips system- model Em208S at 100 kV. The dry samples were ground and suspended in dry Cyclohexane, and sonicated for 1-2 minutes. Then, the solution was allowed to settle and a droplet of the resulting supernatant was placed on a carbon film and dried.
- The x-ray diffraction (XRD) patterns were Prepared by a Philips instrument using PW1800 Diffractometer and radiation of Copper Anodic Tube  $\lambda=1.54\text{\AA}$ .
- Scanning electronic microscopy (SEM) was performed by SEM XLC Philips instrument.
- The acidity of solution (PH) was measured by Omega PH meter-model 744.
- The condensation of samples was done in a heat furnace (Oxaiton model) with high thermal capacity (1500°C).

## 3. RESULTS AND DISCUSSION

### 3.1. FTIR Spectroscopy

The bonding and molecular structure of  $\text{Cu,CuO/SiO}_2$  nanocomposites were studied using in bonding vibrational mode in the range of 400 to 2200  $\text{cm}^{-1}$  by FTIR spectrum. Figures 1 and 2 present the FTIR absorption spectrum for  $\text{SiO}_2 : \text{CuO}$  and  $\text{SiO}_2 : \text{Cu}$  in powdered sample form. We can see three main regions from 400 to 1300 $\text{cm}^{-1}$  and

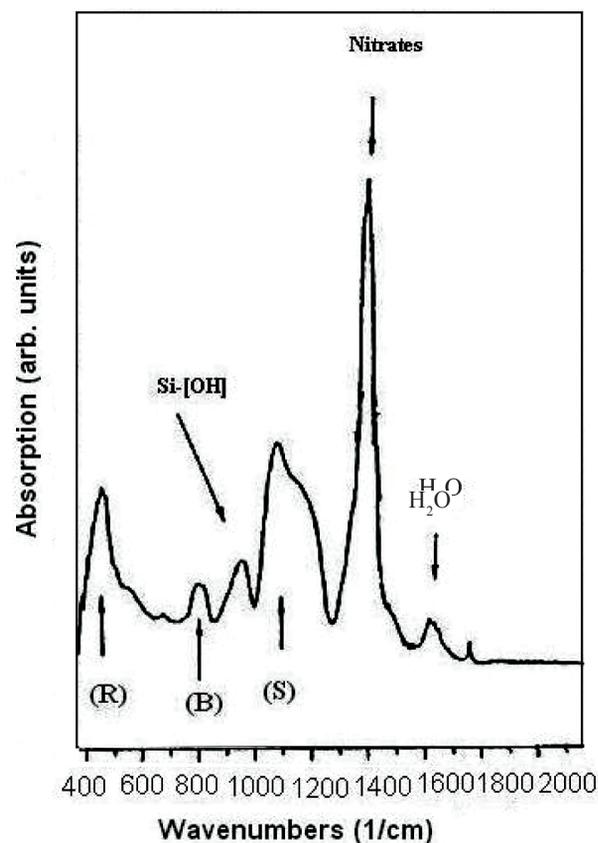
labeled (R), (B) and (S) respectively. Each of the three major features related to transversal optical (TO) absorption bands is shown in figures 1 and 2 which can be characterized in terms of a particular vibration mode of the oxygen atom with respect to the silicon atom that can be linked. Rocking (R) behavior of the oxygen atom about an axis through the two Si atoms characterize the vibrational behavior at 450-490 $\text{cm}^{-1}$ . Also, bending (B) behavior of the oxygen atom along a line bisecting formed by the two silicon atoms characterizes the vibrational mode of band at 780-810 $\text{cm}^{-1}$  [11]. The remaining TO band and its high frequency shoulder are due to an asymmetrical stretch (S) motion in which the oxygen atom moves back and forth along a line parallel to the axis through the two silicon atoms [12].



**Figure 1:** FTIR spectrum of  $\text{CuO}/\text{SiO}_2$  nanocomposite

The main band of the  $\text{SiO}_2$  FTIR spectrum corresponds to the asymmetrical stretching (S) mode at 1100 $\text{cm}^{-1}$ . It has been reported that the FTIR spectrum in which a shoulder, in the frequency range of 1150 to 1250  $\text{cm}^{-1}$ , has an amplitude comparable or bigger than the main stretching band at 1100 $\text{cm}^{-1}$  [13,14]. This has been achieved in vitreous  $\text{SiO}_2$  samples prepared by the sol-gel method using specific preparation

conditions. Also, from Figures 1 and 2 we can observe a band at 850-990  $\text{cm}^{-1}$  assigned to the vibration of the [Si—OH] group. In Figure 1, we have this band and bending band Si—O (B) that observed to separate peak type of stretching frequency Si—O (S) in set A, but in Figure 2, we can see the overlap of Si—OH band and stretching frequency Si—O (S) in ambient temperature in set B [15]. By comparing this bond for the as prepared samples in both figures, it can be seen in Figure 1 that the [Si—OH] band and Si—O (S) stretching band do not have any overlap, while in Figure 2, the overlapping is quite evident. It has been reported that the Cu—O vibration in cupric oxide has IR active modes at 420, 425 and 528 $\text{cm}^{-1}$  [13].



**Figure 2:** FTIR absorption of  $\text{Cu}/\text{SiO}_2$  powdered sample

Figure 1 shows two separate peaks related to (R) and Cu—O, but, Figure 2 confirms overlapping of these two peaks in this range. Therefore, the relative

increase in the intensity of the (R) band could be the consequence of overlapping of the (R) band and Cu–O bands. In spectrum of B samples, there is an additional band at about  $620\text{cm}^{-1}$  that could be due to vibrational modes of Cu–O in  $\text{Cu}_2\text{O}$  phase [14]. There are two additional bands at about  $1450$  and  $1650\text{ cm}^{-1}$  related to the nitrate groups and free molecular water vibrations respectively [16]. In set B, the peak of nitrate groups is very sharp, but, in set A this peak is very small, because small amounts of nitric acid has been added to catalyze the hydrolysis/condensation reactions.

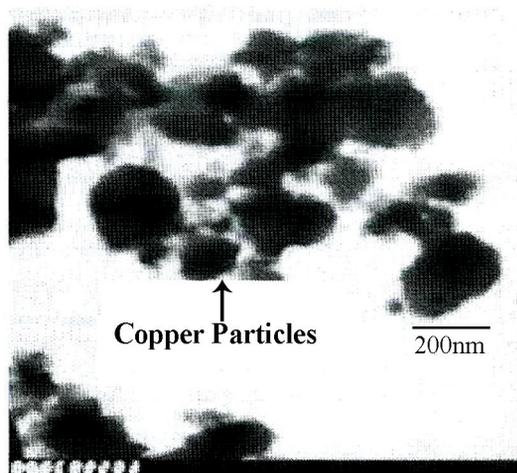


Figure 3: TEM micrograph of  $\text{Cu}/\text{SiO}_2$  nanocomposite at  $400^\circ\text{C}$ .

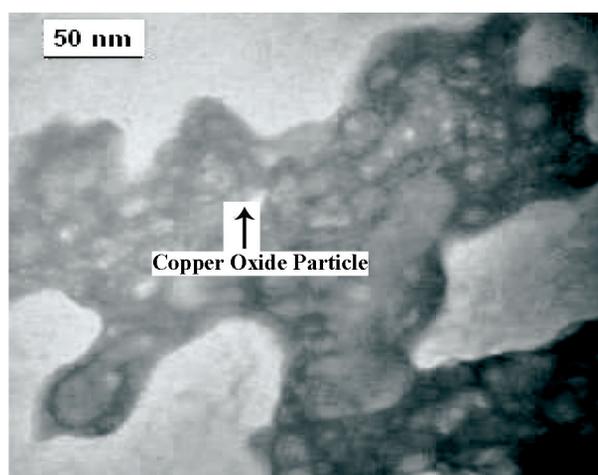


Figure 4: TEM micrograph of  $\text{CuO}/\text{SiO}_2$  nanocomposite at  $400^\circ\text{C}$ .

### 3.2. TEM micrograph

The microstructure of the xerogel was examined by transmission electron microscopy (TEM). Powders with copper particles and copper ions after ambient drying and thermal treatment at  $400^\circ\text{C}$  in air for 1 hour were imaged on TEM. The TEM micrograph of dried sample  $\text{Cu}/\text{SiO}_2$  is shown in Figure 3. This figure confirms the formation of particles with average size of  $150\text{-}200\text{ nm}$ .

The TEM micrograph of dried sample  $\text{CuO}/\text{SiO}_2$  is shown in Figure 4. This figure confirms the formation of particles with average size ranging  $50\text{-}80\text{ nm}$ .

### 3.3. XRD Diffraction

Figure 5 presents the x-ray pattern of the A set of  $\text{CuO}/\text{SiO}_2$  samples annealed at  $200$ ,  $400$  and  $600^\circ\text{C}$ . For the  $200^\circ\text{C}$  sample, the pattern corresponding to the copper nitrate is still presented as the partially hydrolyzed phase of  $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ . Although the amount of the copper nitrate added, is below the solubility limit, and all precautions were taken to dissolve it, but two states could occur during the thermal treatment of the gel which explains the later fact:

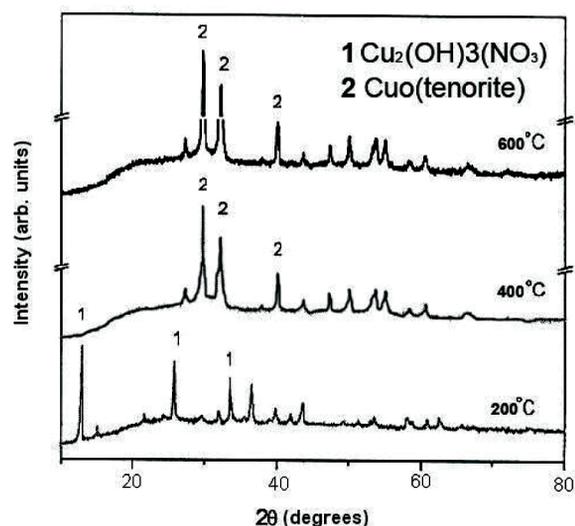
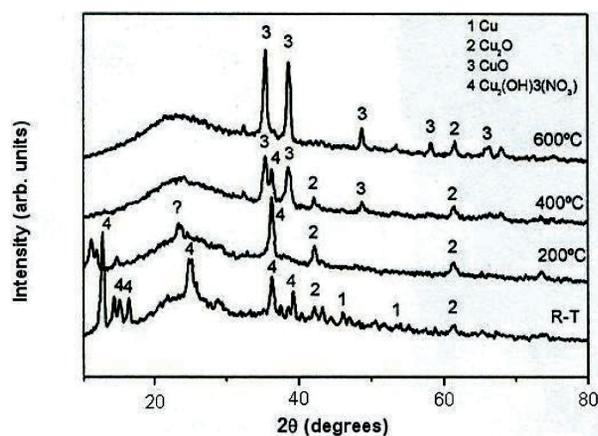


Figure 5: X-ray pattern  $\text{CuO}/\text{SiO}_2$  sample annealed at  $200$ ,  $400$  and  $600^\circ\text{C}$ .

the precipitation of the compounds or separated ions lead to formation of compounds during annealing. For the samples annealed at  $400$  and  $600^\circ\text{C}$ , it can be seen that the X-ray pattern is corresponding to

the CuO phase [17]. From this results, it can be concluded that there is no evidence of the presence Cu<sub>2</sub>O species in these samples.

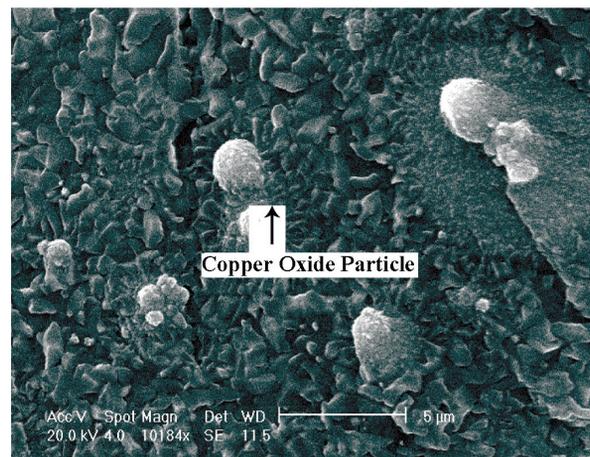


**Figure 6:** X-ray pattern of Cu/SiO<sub>2</sub> sample annealed at 200, 400 and 600°C.

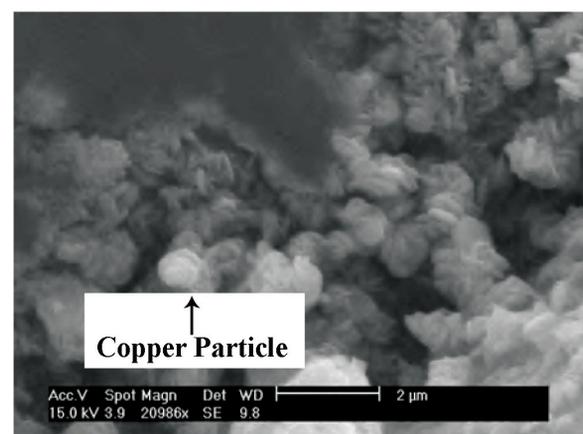
Figure 6 shows the x-ray results of the set of samples B. For the prepared sample it is possible to see a x-ray pattern with a lot of small peaks due to copper species such as; metallic copper, copper nitrate partially hydrolyzed and cuprite oxide (Cu<sub>2</sub>O). Sample B annealed at 200°C has the peaks corresponding to metallic copper, and partially hydrolyzed copper nitrate diminishes noticeably and Cu<sub>2</sub>O peaks are predominant. For samples at 400°C, CuO and Cu<sub>2</sub>O-related peaks can almost be seen. Finally, for samples at 600°C the peaks related to CuO are predominant and Cu<sub>2</sub>O species have a very small contribution. From FTIR and X-ray results, it can be concluded that in CuO/SiO<sub>2</sub> samples, there is formation of the Copper oxide particles mainly in form of a *Tenorite*.

The evolution of copper species goes from copper nitrate to copper oxide species. For the copper-particle-doped samples (set B), the evolution is from Cu to Cu<sub>2</sub>O, through an intermediate phase Cu<sub>2</sub>(OH).3(NO<sub>3</sub>), and then, when nitric acid is used, it is converted to CuO. We have already mentioned, for both set A and B samples, there are differences for FTIR and XRD results. Both 980, 1078 cm<sup>-1</sup> bands are separated from each other, whereas in B samples overlapping of these bands is evident. It can be concluded that at these temperature in set

A samples copper is mainly incorporated into SiO<sub>2</sub> matrix as copper nitrate. There are no copper oxide particles, or the concentration is low. After copper nitrate is decomposed by thermal treatment, copper oxide particles are formed and then interact with SiO<sub>2</sub> matrix via OH groups [18]. For set B samples, copper is incorporated to form particles or aggregates; copper particles are oxidized to form Cu<sub>2</sub>O and CuO species depending on the thermal treatment.



**Figure 7:** SEM micrograph of Cu-O particles on the silica matrix



**Figure 8:** SEM micrograph of copper particles on the silica

### 3.4. SEM Images

Scanning electron microscope (SEM) images of Figure 7 are used to study of sample morphology. At 200°C, it can be seen that the copper nitrate particles are embedded onto the silica matrix. Increasing temperature to 400-800°C causes copper

nitrate particles to decompose and convert to copper oxide particles that dope into silica matrix. SEM images show an inorganic polymerization that can form oxide network containing metal oxide clusters Cu-O. The exact composition of clusters depends on the annealing temperature and molar ratio of components. Figure 8 presents SEM micrograph of copper particles on the silica matrix with high porosity. The copper particles can be aggregated together and form nano-scale porosity with average pore size of about 150 nm.

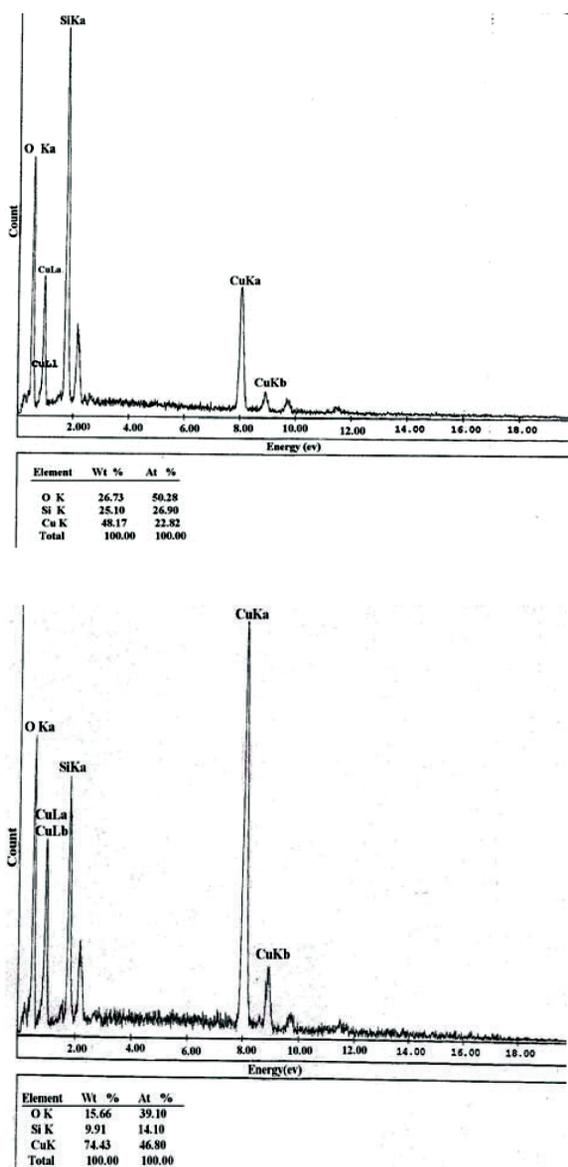


Figure 9: EDX of CuO and Cu particles on the silica matrix

### 3.5. Chemical Analysis

Figure 9 represents chemical analysis as measured by electronic microprobe (EDX). This method of chemical analysis is a known method for fast elemental analysis of samples. Elemental analysis presents weight and atomic percent of oxygen, silicon and copper. Figure 9 shows the ratios of Cu/O (wt.%)=1.8, and Cu/Si (wt.%)= 1.91. This data confirms that the structure of clusters can be of the Cu-O-Si form. In figure 9, we can see ratio of Cu/O (wt.%)=4.75, Cu/Si (wt.%)=7.51, which shows that many copper particles have doped on the silica support with high porosity [17].

### 4. CONCLUSION

We have studied and compared nanostructures of copper oxide and copper based particles on the silica matrix. The exact composition of structures depends on copper source, molar ratio of components and annealing temperature. We can produce particles of metallic copper, cuprous and cupric oxide and compare these particles for synthesis method and characterization. Thus, their structures analyzed by FTIR spectroscopy and XRD system at 200, 400 and 600°C temperatures. We have recognized three main regions contain Rocking (R), Bending (B) and Stretching (S) on their structure using FTIR spectrum. The SEM micrographs and chemical analysis are compared by EDX of Cu and CuO/SiO<sub>2</sub> together. Average size of particles was determined to be 150-200 nm for copper particles and about 50 nm for copper ions using TEM micrograph. These nanocomposites have excellent stability and useful applications [18].

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