

## The effect of time and temperature on the growth and morphology of copper oxide nanostructures

Mohamad Mohsen Momeni<sup>\*a</sup>, Mohadesah Hakimiyan<sup>b,c</sup>, Ali Kazempour<sup>b,c</sup>, Mahboubeh Mirhosseini<sup>d,e</sup>, Zohre Nazari<sup>c</sup>, Seyed Mostafa Mirhoseini<sup>c</sup>, Hadi Kargar<sup>f</sup>

<sup>a</sup>Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

<sup>b</sup>Department of Physics, Payame Noor University, P.O. BOX 119395-3697, Tehran, Iran

<sup>c</sup>Department of Physics, Payame Noor University, Iran Nano Structured Coatings Institute, Yazd Payame Noor University, P.O. BOX 89431-74559 Yazd, Iran

<sup>d</sup>Department of Biology, Payame Noor University, P.O. BOX 119395-3697, Tehran, Iran

<sup>e</sup>Department of Biology, Payame Noor University, Iran Nano Structured Coatings Institute, Yazd Payame Noor University, P.O. BOX 89431-74559 Yazd, Iran

<sup>f</sup>Department of Chemistry, Payame Noor University, P.O. BOX 119395-3697, Tehran, Iran

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### Abstract

Copper Oxide structures with a variety of novel morphologies are synthesized using copper foil as substrate via a solution route. The structure, morphology and phase of the as-synthesized nanostructures are analyzed by various techniques. SEM images show gradual development of hierarchical structures of copper oxide with different morphology. In order to study the effect of reaction time and temperature on the morphology of the CuO samples, experiments were carried out at temperatures 0 °C and 25 °C for 10 min up to 12 h. Results showed that the prepared samples exhibited some novel morphology such as nanorods, nanosheets, microflowers, cubic shaped structures and Tulip flower-shaped structures.

**Keywords:** Nanostructures; copper oxide; morphology.

### Introduction

CuO is a p-type semiconductor with the band gap of 1.7 eV. It possesses a great variety of unique physical and chemical properties, which enable its wide use in different application [1,2]. It has been reported that the practical performances of CuO which are relative to its morphology and size would ultimately depend on the preparation methods and conditions [2-5]. Therefore, so far, much effort has been devoted to the

synthesis of CuO nanomaterials with different characteristics using different methods such as hydrothermal [6,7], solvothermal [8,9], thermal oxidation [10,11], sonochemical [12,13] and microwave irradiation [14,15]. However, with most of the developed methods it is hard to produce large scale CuO nanomaterials at low cost in an environmentally-friendly way. Over the past decade, green synthesis chemistry, which aims at total

\*Corresponding author: Mohamad Mohsen Momeni  
Tel: +98 (311) 3912237; Fax: +98 (311) 3912350  
E-mail: mm.momeni@cc.iut.ac.ir

elimination or at least minimization of the use and generation of hazardous substances, has received much more attention. A green synthesis strategy usually adopts nontoxic and environmentally benign reactants and solvents, and releases no unwanted byproducts and pollution [16-20]. This article reports on the investigation of the effects of both temperature and reaction time on the morphology of nanostructured CuO thin films. In this paper; a simple and easy method was developed for the synthesis of nanostructured CuO thin films on Cu foils by a wet chemical method without using any templates or seeds on top. The proposed method is green, simple and cost effective, and thus could be suitable for large scale production of CuO nanomaterials. The resulting CuO thin films were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and fourier transform infrared (FT-IR).

## Experimental

### *Synthesis of copper oxide thin films*

All reagents in this experiment were analytical grade and were used without further purification. Copper oxide nanostructures were grown on Cu foils (purity: 99.9% Cu) by the following sequence. A large piece of Cu foil with 0.15 mm thick was cut into several 10 mm × 10 mm test coupons. Then copper foils were burnished by abrasive paper orderly, and afterwards they cleaned with absolute ethanol and distilled water to remove adsorbed dust and surface contamination. During the next step, the Cu foils were etched by 4 M HCl aqueous solution to get rid of the residual oxide layer. In a typical procedure, Cu foil were immersed in to 20 mL of 1 M NaOH aqueous solution containing 35 mM (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at temperatures 0 and 25 °C for different

duration time to obtain CuO films. After a given reaction time (about 10 min-24 h), the copper foil was taken out of the solution, washed several times with distilled water, and then dried in air.

## Characterizations

Crystal structure of the CuO nanostructures were characterized by means of X-Ray diffraction (XRD) with Equinox 3000 diffractometer (Inel, France). The diffraction angles (2θ) were fixed between 20° and 80°. The morphology and elemental composition of the prepared particles was characterized by energy dispersive spectroscopy (EDS) attached using SEM instrument (Phenom pro X, Netherlands). FT-IR absorption measurements were done using a Shimadzu IR prestige-21 spectrometer through KBr pellet technique in the range of 4000 to 400 cm<sup>-1</sup>.

## Results and discussion

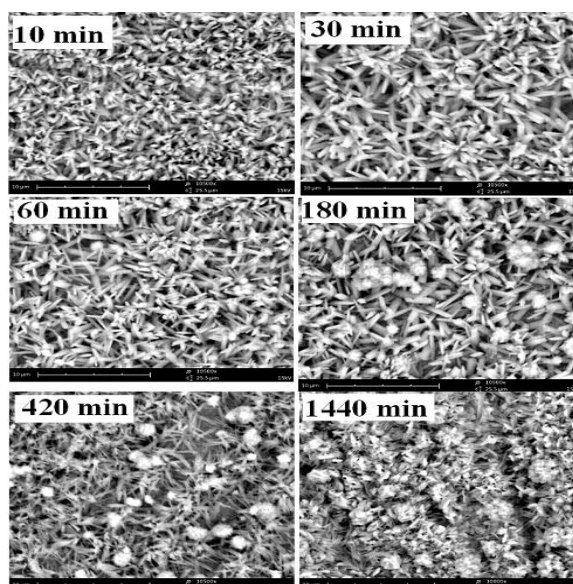
### *The morphology of the CuO nanostructures*

Morphologies of the copper oxide films grown on copper foils along with reaction time at two temperatures 0 °C and 25 °C were characterized by scanning electron microscopy. Figure 1 shows morphologies of the copper oxide films grown on copper foils along with reaction time at 0 °C. It shows that CuO nanorod-like structures were formed on copper and their morphology had not changed with time. After one hour, only the nanorod diameter increases. Hereafter, flower-like structures appear on the surface of nanorods. However, it is worth mentioning that their number increases with time. It can be seen that even after 24 hours of reaction, we did not observe significant changes in surface morphology. It can be said that low

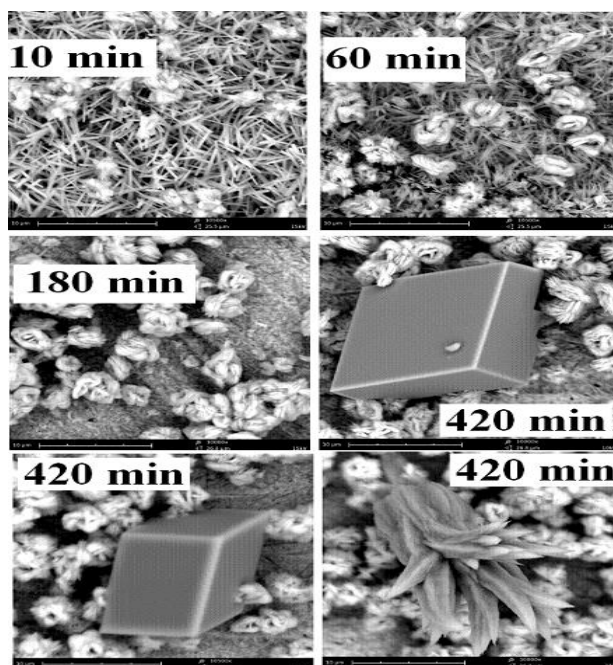
temperature, hinder the rapid growth of crystals and prevents large changes in morphology.

Figures 2 and 3 show morphologies of the copper oxide films grown on copper foils along with reaction time at room temperature. The results show that after 10 min, CuO nanostructures with uniform nanorods morphology were formed on copper. The diameter of CuO nanorods is about 40-90 nm. The height of CuO nanorods is about 1-2 micrometer. By increasing the reaction time to 60 min, CuO flower-like were formed on the substrate. A CuO micro flower consists of dense CuO nanosheets (petals) with a typical thickness about 40-80 nm that can be seen on the surface of samples. The size of a single flower was about 4-5  $\mu\text{m}$ . The nanosheets were connected together on the bases, rooted in one center and assembled into the beautiful flower-like morphology. Significantly, the nanorods arrays are formed under

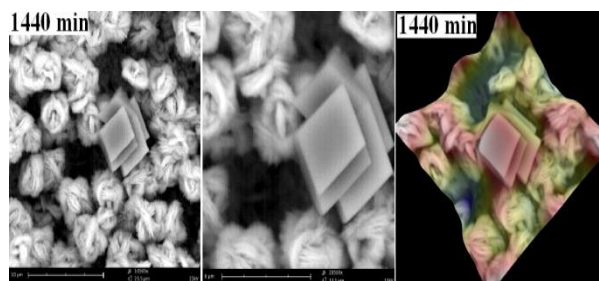
the microflowers and the diameter of the nanorods is approximately 100 nm. The SEM image of the CuO sample obtained within 3 h reaction time shows that the substrates are fully covered by CuO nanoplates. Here also microflowers with larger size are standing on the nanoplates arrays. It can be seen that the number of microflowers were increased. SEM image of the CuO sample obtained after 7 h shows that particular structures were observed on the surface. It can be seen that the greater part of the surface is covered with microflowers. Cubic shaped (square and rectangular) and tulip flower-shaped structures were also seen on the surface. As shown in Figure 3, after 24 h, several square pages are located on each other and have created a special form. We can conclude that by increasing reaction time, we can observe that copper oxide is grown and various structures with larger dimensions appears on the surface.



**Figure 1.** SEM images of thin films grown on Cu foils by wet chemical method at 0 °C for 10 min, 30 min, 60 min, 180 min, 420 min and 1440 min



**Figure 2.** SEM images of thin films grown on Cu foils by wet chemical method at room temperature for 10 min, 60 min, 180 min and 420 min



**Figure 3.** SEM images of thin films grown on Cu foils by wet chemical method at room temperature for 24 h with different magnifications and a three-dimensional image of the surface

#### Structure of the CuO nanostructures

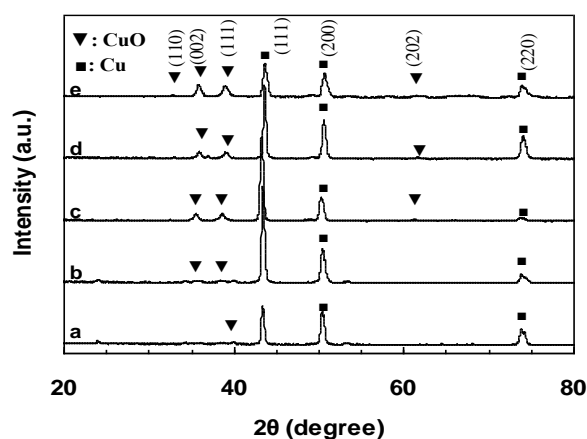
The crystal phases of the CuO nanostructures films grown on copper foils were examined by X-ray diffraction (XRD). Figure 4 shows the XRD patterns of the products grown on Cu foil at room temperature during the various periods of time. The major diffractions peaks found in the XRD pattern are related to Cu substrate such as Cu(111), Cu(200) and Cu(220) respectively [21]. It also shows the presence of peaks due to the formation of CuO on Cu foils. The major diffraction peaks corresponding to the

CuO are located at  $2\theta=32.58, 35.68, 38.88$  and  $61.48$ , moreover, they confirm the formation of monoclinic phase of CuO nanostructures [21]. There is no peak related to other impurities in the XRD pattern. This suggests how the high quality CuO hierarchical nanostructures are obtained.

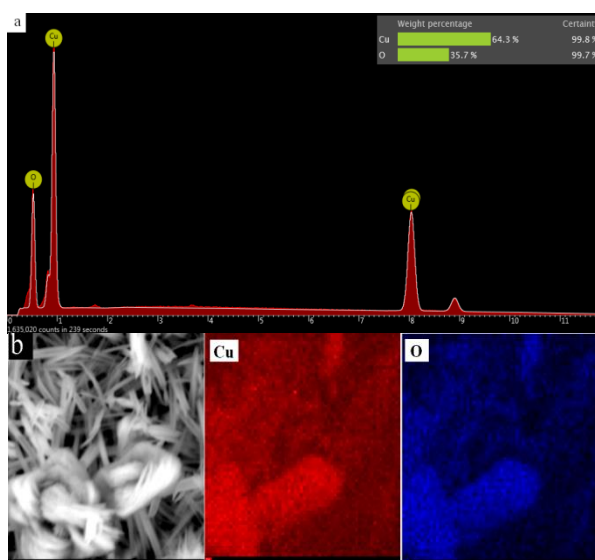
Copper oxide films which were grown on copper foils and were analyzed by energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of copper and oxygen atoms, exclusively and no impurities are



present in sample (Figure 5a). According to elemental mapping analysis (Figure 5b), the dispersion of copper and oxygen is uniformly homogenous in the sample.



**Figure 4.** X-ray diffraction pattern of CuO nanostructures grown on copper foil at room temperature for (a) 10 min, (b) 30 min, (c) 1 h, (d) 3 h and (e) 7 h



**Figure 5.** (a) Energy-dispersive X-ray spectroscopy (EDS) analysis of CuO films grown on Cu foils (b) Elemental mapping spectra of CuO films containing of elements map of copper distribution and elements map of oxygen distribution

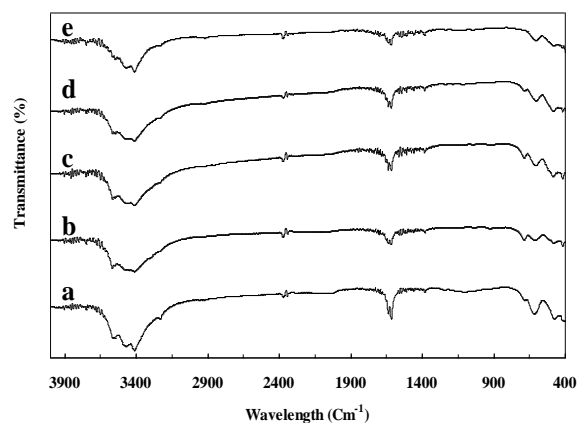
### FT-IR spectra

To investigate the composition of as-obtained CuO samples, analysis is done through infrared spectroscopy. FT-IR spectra are powerful tool to provide information on the nature of metal oxides. A metal oxide generally gives absorption bands below  $1000\text{ cm}^{-1}$  that arises from inter-atomic vibrations. Figure. 6 shows the FT-IR spectrum of

CuO nanostructures grown on Cu foil at room temperature at different periods of time. As indicated in the spectrum, the absorption bands between  $1300$  and  $3500\text{ cm}^{-1}$  are mainly assigned to the chemisorbed and/or physisorbed  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules on the surface of nanostructured CuO crystals [22]. The broad peaks in the range  $3100\text{-}3800\text{ cm}^{-1}$  which can be attributed to O-H

stretching vibration are assigned to small amount of H<sub>2</sub>O existing (during pellet formation) in the nanostructured CuO. Peaks around 400-900 cm<sup>-1</sup> are attributed to the metal-oxygen stretching of CuO. It must be mentioned that a metal oxide generally gives absorption bands below 1000 cm<sup>-1</sup>

which arises from inter-atomic vibrations. More precisely, the absorption bands observed at 690, 611, 485 and 402 cm<sup>-1</sup> correspond to CuO [23]. The FT-IR results are also in good agreement with the XRD analysis results.



**Figure 6.** FT-IR spectrum of thin film grown on Cu foil by wet chemical method at room temperature for (a) 10 min, (b) 30 min, (c) 1 h, (d) 3 h and (e) 7 h

### Conclusion

In this study, for the first time, CuO nanostructures samples with a variety of novel morphologies were successfully grown on the Cu copper foil *via* a solution route. Compared with the other methods which require high temperature and expensive equipment, this procedure does not need pressure and temperature controlling. XRD, SEM, and FT-IR techniques have been used to characterize the CuO nanostructures. The results showed that the size and structure of the final products could be effectively affected by both temperature and reaction time. Increasing the reaction time leads to larger grain size. Depending on different applications, with the changes in temperature and reaction time, appropriate nanostructures can be prepared.

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