

Synthesis and Identification of 1-D CuO Nano Crystals

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Abstract: Design and development of large scale self assembly of meso, micro and nanostructure semiconductor assemblies had drawn significant interest because of their application in the development of economically viable solar cells, and also as a potential candidate in the field of photocatalytic system. In the present investigation we had synthesized one dimensional (1D) highly crystalline and elongated microstructures of CuO using simple hydrothermal process at 95 °C reacting Copper (I) acetate, NaOH and hexamethylenetetramine (HMTA). The resulting solution was aged in Teflon flask about 24 hours. The growth of 1D microstructures of CuO was probed by emission scanning electron microscopy (FE-SEM) and X-ray diffraction technique (XRD). The surface morphology reveals that growth of CuO rods were uniform, monodispersed throughout. The purity of CuO was also confirmed by elemental analysis using energy dispersive spectroscopy (EDS) technique. The possible growth mechanism for the formation of 1-D CuO microstructures was also explained.

Keywords: 1D microstructures of CuO, Nano particle, Nanostructure, CuO rods, CuO nanotubes, etc.

1. Introduction

In this dynamic and changing era, the design and development of large scale self assembly of meso; micro and nanostructure semiconductor assemblies had drawn significant interest because of their application in the development of economically viable solar cells, and photocatalytic system¹⁻⁵. A large number of 1D nanostructures have been synthesized over past decade. One dimensional nanobuilding blocks of transition metals oxides, hydroxides, sulfides, has been prepared via various process techniques⁶⁻⁷.

CuO is an important p-type transition-metal-oxide semiconductor, with a narrow band gap ($E_g = 1.2\text{eV}$) and exhibiting a versatile range of applications such as fabrication of electrical, optical, photovoltaic devices⁸⁻⁹; gas sensing¹⁰⁻¹¹, heterogeneous catalysis¹², and magnetic storage media. In addition, CuO is potentially useful component in the fabrication of solar cells, lithium ion electrode materials and photothermal and photoconductive applications¹³ and so forth. It also reveals complex magnetic phase and, thus form basis for several high temperature- T_c superconductors and materials with high magnetoresistance¹⁴⁻¹⁵. Moreover, it can be used to prepare a variety of organic-inorganic nanostructure composite with unique characteristics, which includes high thermal and electrical conductivities, high mechanical strength, high temperature durability and so on. Because of versatile properties and wide applications in various fields, the synthesis of nanostructure CuO has shown a potential need, however various kind of nanostructure CuO has been synthesized by using different techniques, which includes hydrothermal¹⁶, sol-gel¹⁷, gas-phase oxidation, micro emulsion and so forth. Usually the solution process is an easy and cost effective approach to obtain nanostructures with appreciable yield. Therefore, various classes of CuO nanostructures such as nanoparticles (zero dimensions), nanorods, nanowires,

nanoribbons have been reported in literature. Recently, Wang et al. have reported 1D CuO nanowhiskers using copper chloride, sodium hydroxide and ethylene glycol through wet chemical reaction method at relatively low temperature¹⁸. In addition to low temperature pathways, Wu and coworkers have synthesized CuO nanotube through template method at elevated temperature of 450-750 °C¹⁹. On the other hand Xu et al. have reported CuO nanoparticles (zero dimensions) by thermal deposition of copper acetate at 950 °C²⁰. Until now, there have been many papers based on the solution process reported in the literature. But there is still work need to be done to reach at general conclusion.

Herein, we are reporting the synthesis and characterization of highly crystalline and elongated CuO microstructures at low temperature. Moreover, there has been several experiments has been carried out to proposed growth mechanism of highly oriented and crystalline CuO microstructures.

2. Materials and Method

All the chemicals are analytical grade and used as without further purification. The typical reaction process for the synthesis of CuO microrods Copper (I) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$, 99.8% Sigma - Aldrich), Hexamethylenetetramine (HMTA; $\text{C}_6\text{H}_{12}\text{N}_4$, 99.8% Sigma - Aldrich), NaOH have been used. In the typical synthesis process, 0.05M copper acetate solution was prepared in distilled water while in a separate beaker 0.05M hexamethylenetetramine solution was prepared in deionized water under continuous stirring at ambient temperature. HMTA solution was added gradually into copper acetate under continuous stirring. Moreover, pH of solution was adjusted by adding NaOH solution. The resulting blue colour solution has been transferred into the Teflon flask at 95°C and system was aged for 24 hours. After completion of reaction black colour precipitate was obtained which was

further washed repeatedly with methanol and deionized water and dried at room temperature.

The structural properties of as grown microrods were examined by FE-SEM micrograph and X-ray energy dispersive spectroscopy (EDX). The crystal phase purity and crystallinity were examined by powder X-ray diffraction PXRD. The result shows the possible growth of highly crystalline CuO microrods.

3. Results and Discussion

The synthesized 1D rods of CuO microstructures crystal phase and compositions were identified by X-ray diffractometer (XRD, Rigaku, operating at 40 kV and 20 mA using Cu K α radiations, $\lambda = 1.54178 \text{ \AA}$ with scanning rate $4^\circ/\text{min}$) in the range of $20\text{--}80^\circ$. The typical X-ray diffraction pattern of CuO was fully matched with monoclinic phase of CuO crystals JCPDS-05-0661 as shown in Fig.1. CuO crystal having monoclinic space group $C2/c$ ($a = 4.68 \text{ \AA}$, $b = 3.42 \text{ \AA}$, $c = 5.1 \text{ \AA}$ and $\beta = 99.54^\circ$). The two major peaks at 34.95° and 38.36° were characteristic of pure monoclinic CuO crystal. There were no other peaks which could be responsible for presence of other oxides of copper (Cu_2O and $\text{Cu}(\text{OH})_2$). The purity of the compound was further supported by energy dispersive spectroscopy (EDX), as shown in fig 2. where Cu and O were found to be 55.29% and 44.71 % (1:1) respectively.

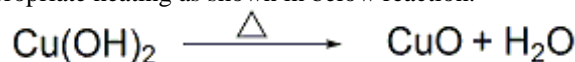
The FE-SEM micrograph of CuO crystal was depicted in Fig. 3. The low magnification images exhibit that the 1-D microstructures have centre of origin and grown in cluster. The diameter of rods was constant from base to the tip, i.e., CuO rods were grown uniformly and highly crystalline in nature. There were three different modes of attachment of rods, the short microstructures were attached to one another using their low Miller Indices crystal phase (100), (100) and (110) surfaces respectively. This type of crystalline growth has well been defined in the recent years and described to a cementing process or oriented attachment.²¹⁻²³ As the rods were grown in cluster, so they were connected to each other from base of origin. It was interesting to observe in the high resolution images where the growths of 1D rods were viewed as a separate cluster without using any template. In addition to this, the length of rods was remain almost constant throughout having similar diameter.

In our experiment, aqueous solution of 0.05M $\text{Cu}(\text{CH}_3\text{COO})_2$ was mixed with equivalent concentration of HMTA. It was important to note that there was no immediate precipitation, but the clear light blue colour of copper acetate turned into turbid. Moreover, pH of solution was maintained using NaOH solution, which not only adjusts pH of resultant solution but also plays an important part in the synthesis of microstructure of CuO. This observation suggested that in the initial stage $\text{Cu}(\text{CH}_3\text{COO})_2$ is converted to $\text{Cu}(\text{OH})_2$. The sequential reactions involving are given below.



The formation of $\text{Cu}(\text{OH})_2$ is very important for growth of CuO crystal which initially serve as building blocks for

synthesis of microstructure of pure CuO. The conversion of $\text{Cu}(\text{OH})_2$ to CuO crystals can be achieved by providing appropriate heating as shown in below reaction.



At initial stage of the reaction the appropriate amount of heat is evolved when NaOH dissolved in the water. In addition to this, HMTA get hydrolyzed and thus hydroxyl ions were generated.



Hence, the described reactions explain the proper growth of CuO. Therefore, it is expected that electrostatic attraction also play pivotal role in the uniform growth.

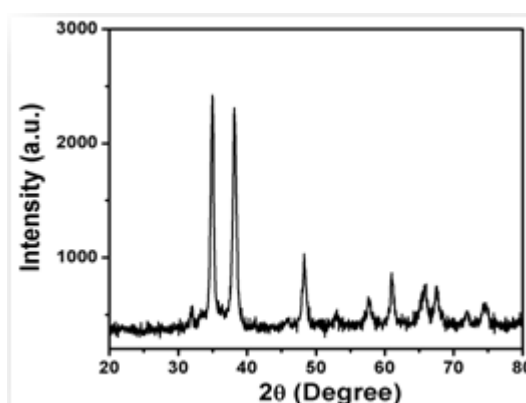


Figure 1: X- ray diffraction pattern of as synthesized CuO microstructure

Elements	Element (%)	Atomic (%)
O	16.92	44.71
Cu	83.08	55.29
Total	100	100

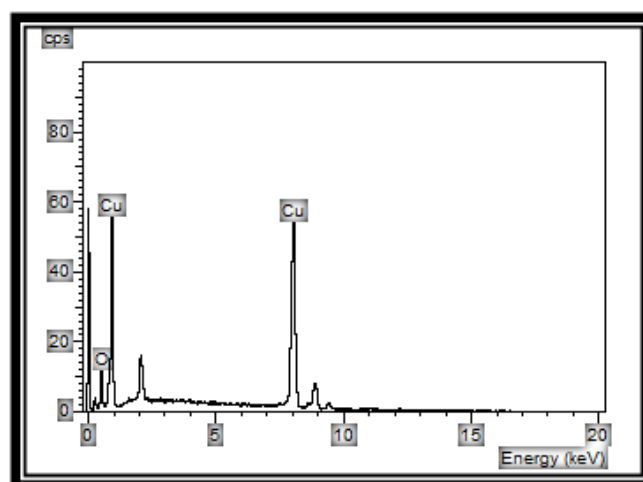


Figure 2: Energy dispersive X-ray spectrum of CuO microstructure

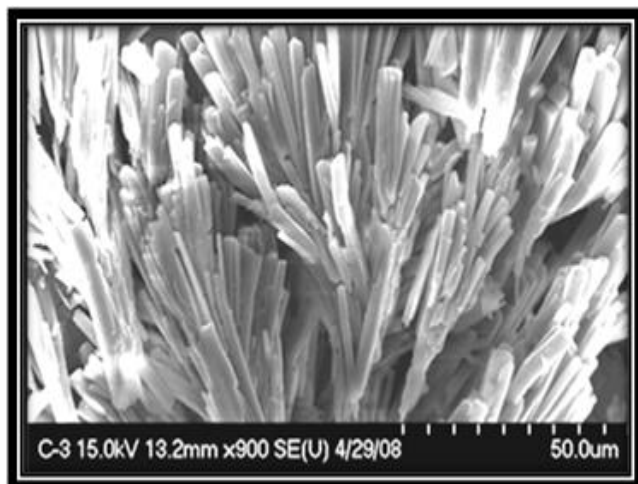


Figure 3: FE-SEM low magnification images

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4. Conclusion

In summary, we successfully synthesized one dimensional CuO microstructures via simple hydrothermal process at 95°C using copper acetate, hexamethylenetetramine and NaOH in water solvent. The detailed structural investigation reveals that the growth of microstructures were uniform and centre oriented, as the rods were grown in cluster so they were connected to each other from base of origin. One dimensional CuO exhibiting high surface area and hence providing an opportunity to use them for fabrication of efficient devices in near future.

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