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Cuprous Oxide Nanowires Prepared by an Additive-Free Polyol Process

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ABSTRACT: The polyol method was employed for the first time to synthesize cuprous oxide nanowires using only a precursor of Cu(II) acetate monohydrate and diethylene glycol (DEG). With careful control of the reaction temperature (190 °C), the precursor concentration (0.01–0.1 mol/L), and the reaction time (6 h), we prepared Cu₂O nanowires with a diameter of approximately 20 nm and a length up to 5 μm. The nanowires were characterized by SEM, TEM, XRD, and IR spectroscopy.

Introduction

Cuprous oxide (Cu₂O) is a reddish nonstoichiometric p-type semiconductor with a direct forbidden band gap of 2 eV and a high optical absorption coefficient. Crystalline Cu₂O has a cubic structure, with the space group $O_{4h} = Pn-3m$ and two molecules in the unit cell.¹ It represents a promising material for the conversion of solar energy into electrical or chemical energy,² for lithium batteries as the negative electrode materials,^{3,4} and in the photocatalytic degradation of organic pollutants using visible light.⁵ Cuprous oxide-based materials are also mentioned in the literature for use in optoelectronic or light-emitting devices.²

Semiconductors in the nanometer size range are interesting because they may possess physical and chemical properties that are not only characteristic of atoms or their bulk counterpart but show unique properties due to the large surface-area-to-volume ratio. Special attention has been focused recently on one-dimensional nanostructured materials. Research in this field currently represents a great challenge for scientists, as witnessed by the many reports on the preparation of nanorods and nanowires of various metals and metallic oxides.^{6–8} Cu₂O nanowires can be prepared by various methods.^{2–8} Wang et al.² synthesized crystalline Cu₂O nanowires by a route using hydrazine hydrate as the reducing agent in the presence of a surfactant. Liu et al. prepared Cu₂O nanowires by an electrochemical method with an alumina membrane as a template.⁹ One-dimensional nanowhiskers of Cu₂O were obtained from a liquid deposition procedure by the addition of a surfactant, cetyltrimethylammonium bromide, as a template.¹⁰ Wang et al.¹¹ used polycrystalline Cu(OH)₂ nanowires as a precursor for the growth of Cu₂O nanowires. The Cu(OH)₂ also served as a template controlling the size and shape of the Cu₂O nanowires. Recently, Yu et al.¹² prepared Cu₂O nanoparticles on single-wall and multiwall carbon nanotubes using a polyol process at 200 °C.

In the polyol process, the polyol has multiple functions: it acts as a solvent, stabilizer, and reducing agent; limits particle growth; and prevents agglomeration. However, the reaction mechanism for particle formation is not yet entirely clear. This well-known method has been used for the preparation of metallic and metallic-oxide particles.^{13–17} Only in recent reports has it been pointed out that it can also be useful for the preparation

of metallic and metallic-oxide nanowires.^{18–21} In the work of Piquemal et al., a one step preparation of single-crystal silver nanowires using mesoporous silica as a host was presented. Reduction was performed using a polyol process, without any subsequent thermal treatment.¹⁹ Sun et al.²⁰ demonstrated that the polyol process could be used for the large-scale synthesis of silver nanowires. The chemicals employed were silver nitrate and ethylene glycol in the presence of poly(vinylpyrrolidone) with or without the presence of Pt.^{19,20} Zhao et al.²¹ prepared Cu, Cu₂O, and CuO of different morphologies using a microwave-induced polyol process. Different morphologies were also obtained by changing the water/ethylene glycol ratio. A whiskerlike morphology was observed for CuO and cubic Cu₂O. Jiang et al.²² also utilized the polyol method for the preparation of nanowires based on different metallic oxides (TiO₂, SnO₂, In₂O₃, and PbO), but so far, there have been no reports on the preparation of Cu₂O nanowires using the polyol process.

In this paper, we present the results of the synthesis of Cu₂O nanowires by the polyol method using Cu(II) acetate monohydrate (CuAc₂) and diethylene glycol (DEG) without any additives. For the first time, we demonstrate that it is possible to prepare Cu₂O nanowires consisting of crystalline Cu₂O, some amorphous Cu₂O, and a small amount of carbon using the polyol method by carefully controlling the precursor's concentration, the reaction temperature, and the reaction time.

Experimental Section

The preparation of the Cu(I) oxide in the form of nanowires begins with the mixing and sonicating (20 min) of Cu(II) acetate monohydrate (CuAc₂) in DEG to achieve complete dissolution. The concentration of CuAc₂ ranged from 0.01 to 0.1 mol/L; in the present work, the CuAc₂ concentration was 0.01 mol/L. The solution was transferred into a 250 mL reactor equipped with mixer, reflux condenser, and a temperature controller with a thermocouple sensor. The reaction mixture was heated to 190 °C at a rate of 7–8 °C/min. The color of the mixture changed from green to brown in approximately 5 h. After 6 h, the reaction was stopped by cooling the reaction mixture, which was left overnight to allow the precipitate to settle. The solvent was removed by suction and the precipitate was washed twice with ethanol and dried in an oven at 85 °C. To make an initial determination of the particle size, we took SEM micrographs of gold-sputtered and unsputtered samples on a Zeiss Supra 35 VP at an acceleration voltage of 3.37 kV.

X-ray diffraction (XRD) spectra were recorded on a Siemens D-5000 diffractometer with a Cu anode as the X-ray source. The step size was 0.004°, and the step time was 1 s. For the transmission electron micrographs, powdered samples were mixed with ethanol and a drop of the suspension was placed on a holey-carbon coated Cu grid. The samples were examined with a JEOL 2000FX at low resolution and a

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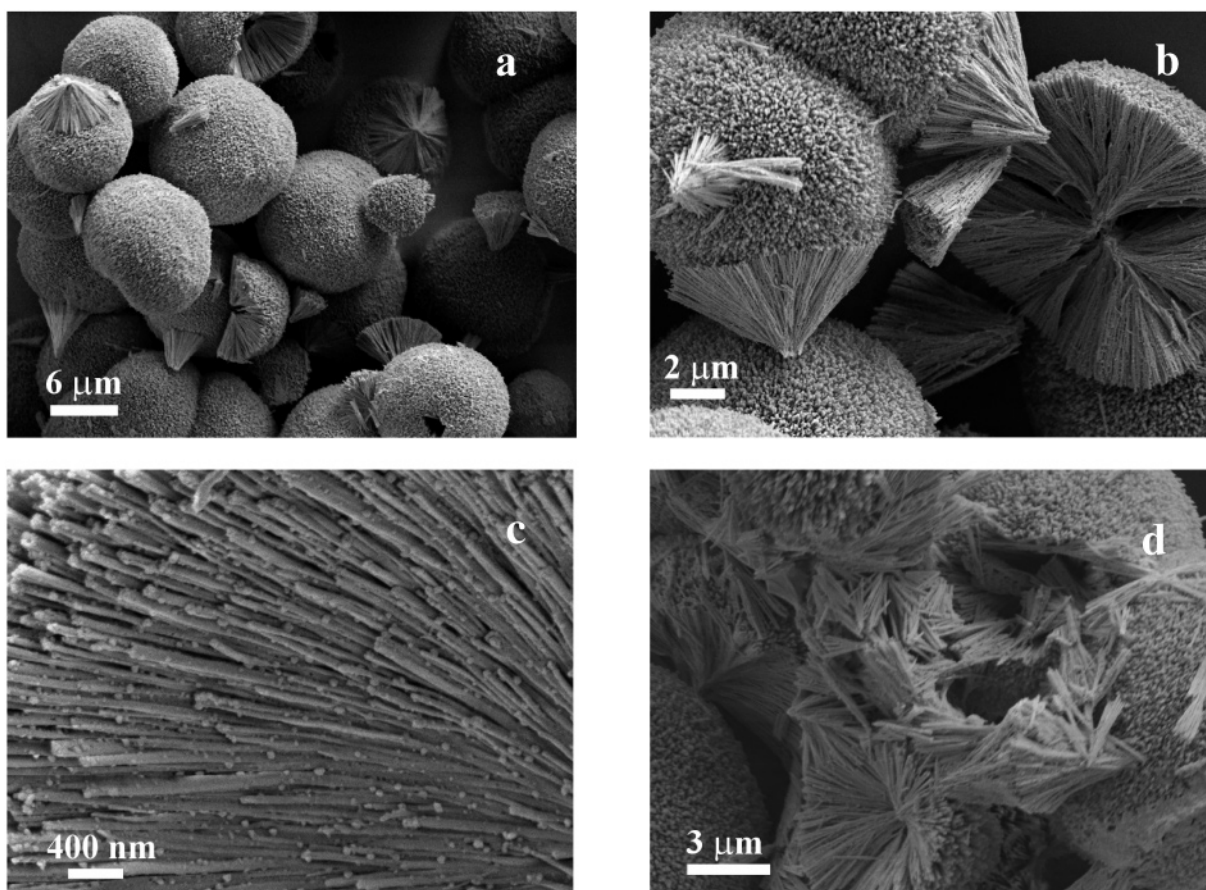


Figure 1. SEM micrographs of Cu₂O nanowires organized as (a) spherical structures, or (b) cone-shaped bundles, (c) insert of the organization of nanowires, (d) conical structures of disassembled nanowires.

JEOL 2010F transmission electron microscope equipped with a field-emission gun at high resolution. Both microscopes were operated at 200 kV. An energy-dispersive X-ray spectrometer (LINK ISIS-300, with a UTW Si–Li detector) was employed for the chemical analyses. The SAED pattern simulations were FT-performed using an electron microscopy simulation (EMS) program developed by Stadelmann.²³

IR spectra of the samples (KBr pellets) were obtained using a spectrometer Perkin-Elmer 1725 X in the spectral range between 4000 and 400 cm^{−1} (resolution of 4 cm^{−1}).

The ¹³C (75 MHz) NMR spectrum was recorded on a Varian Unity Inova 300 MHz NMR spectrometer using deuterated ethanol as the solvent and tetramethylsilane (TMS) as the internal reference.

Results and Discussion

The samples prepared after 6 h of heating are presented in Figure 1a. Spherically organized particles of about 10 μm in size consisting of self-assembled individual nanowires are clearly visible in Figure 1b. The spherical particles may also disassemble into cone-shaped bundles made of nanowires (Figure 1c) or into individual nanowires (Figure 1d).

A typical X-ray diffraction (XRD) spectrum of these samples is presented in Figure 2: four peaks, with 2θ values of 36, 42, 61, and 73°, correspond to the crystal planes 111, 200, 220, and 311 of the crystalline Cu₂O. From XRD pattern, the crystallite size using Scherrer formula was calculated to be 25 nm. The unit-cell parameter for cubic cell was calculated with CelRef, which is a crystal cell parameter refinement program for powder XRD, using a least-squares method. The obtained values are $a = b = c = 4.2706$ Å, which are in good agreement with reported values for cuprite with the reference code: 00-005-0667 ($a = b = c = 4.2696$ Å).

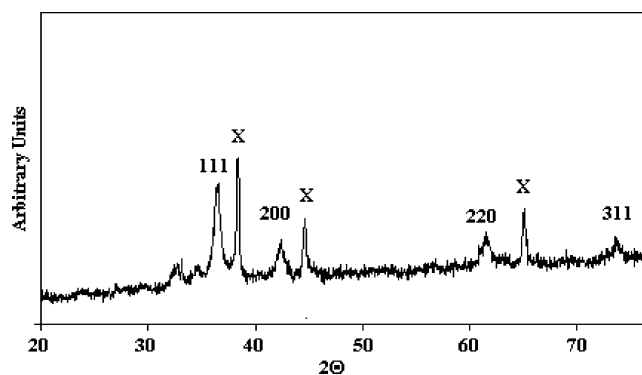


Figure 2. XRD spectrum of Cu₂O nanowires (X–Al holder).

In Figure 3a, the bright-field TEM image of a bundle of Cu₂O nanowires on the holey carbon film is shown. Larger crystals (up to 20 nm) were attached to individual wires (Figure 3b). From the high-resolution TEM image (images a and b of Figure 4), it was clear that the wires were composed of 2–5 nm crystallites, embedded in an amorphous matrix. The crystallites were randomly oriented in the nanowire; this was concluded from the selected-area electron diffraction (SAED) patterns, where uniform and continuous circles were observed (Figure 5). From the comparison of the experimental and calculated (simulated) SAED patterns it was found that, apart from cubic $Pn\bar{3}mS$ Cu₂O, no other crystalline phase was present. Using EDXS, it was determined that the amorphous phase contains, in addition to Cu and oxygen, a minor amount of carbon.

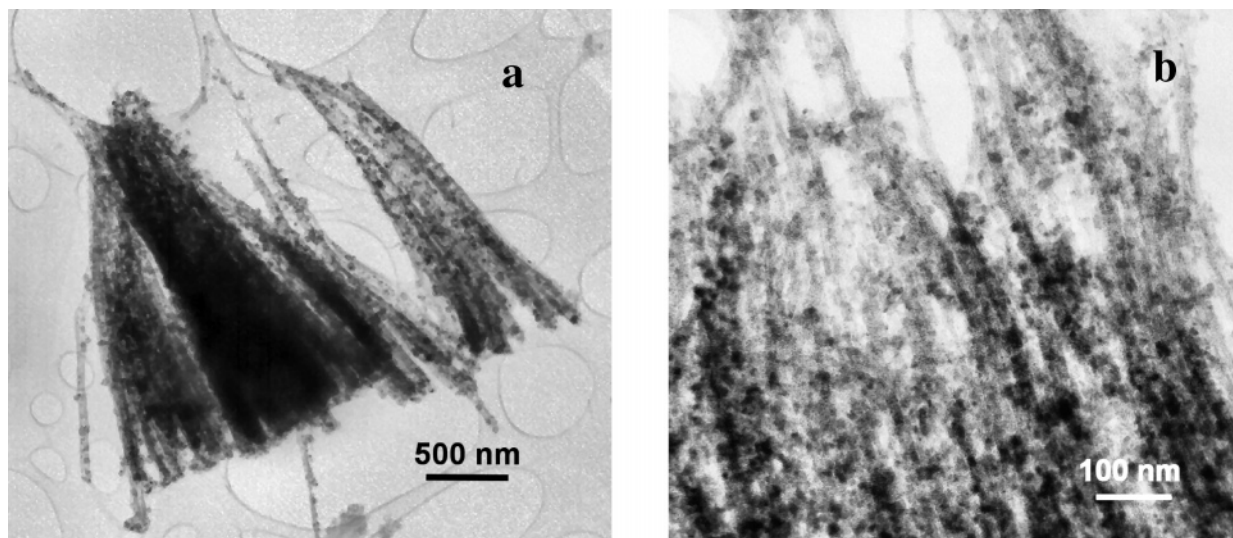


Figure 3. Bright-field TEM micrograph of (a) a bundle of Cu₂O nanowires, and (b) Cu₂O particles attached to nanowires.

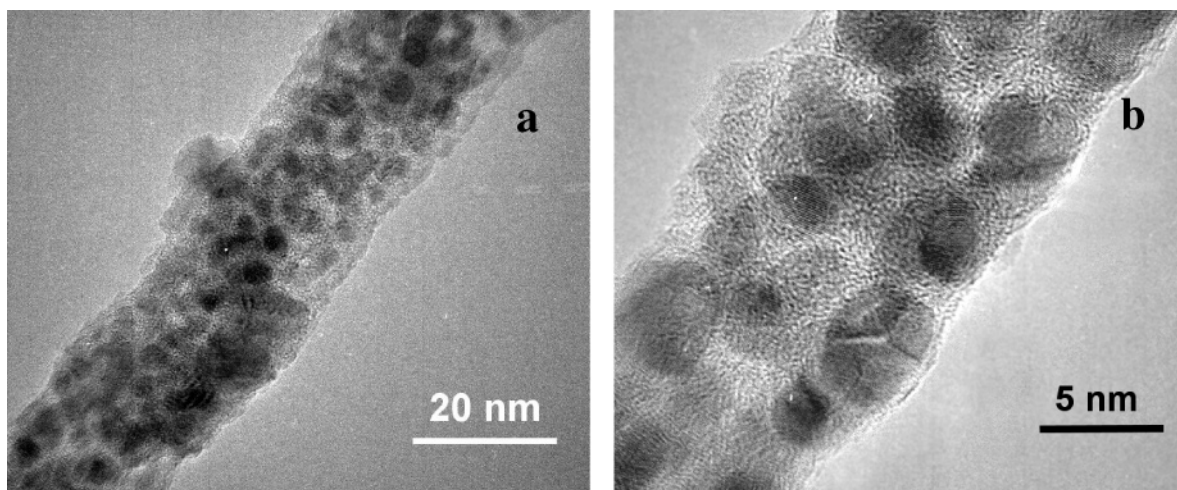


Figure 4. HRTEM images of Cu₂O nanowire with 2–5 nm crystallites embedded in an amorphous matrix: scale (a) 20 and (b) 5 nm.

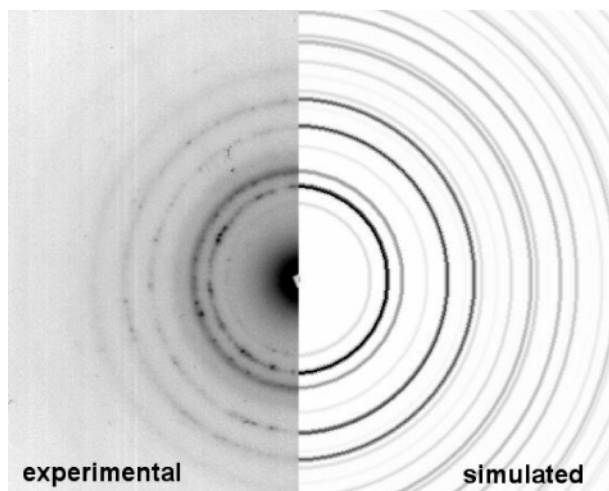


Figure 5. Comparison of experimental and simulated SAED patterns of Cu₂O nanowire.

This finding is corroborated by IR analysis, which revealed that copper oxide in the final state is present only as Cu₂O (crystalline and amorphous). The IR spectrum of this sample (Figure 6) shows a characteristic band at 634 cm⁻¹ correspond-

ing to Cu₂O (optically active lattice vibration in the oxide),²⁴ with the presence of some bands that originate from the adsorption of the media. The mentioned adsorption phenomenon of polyols has already been observed for metallic and metallic-oxide particles synthesized by the polyol method. By using chemical analysis, it was determined that the carbon content of such samples was about 5%.¹⁵

It is known that the polyol used for the reduction of a precursor,^{13–16} in our case DEG, is both a solvent and a reducing agent and that it evidently plays a critical role in the nucleation and growth of the crystalline Cu₂O nanowires. The influence of the amount of water on the growth mechanism of Cu₂O in DEG and the concentration of the CuAc₂ precursor are the other two important parameters. As has already been reported, water in the Cu(II) acetate monohydrate precursor¹⁶ makes the concentration of the product lower, which is essential for reduction efficiency. Namely, the formation of metallic oxide in the polyol medium results from a hydrolysis reaction with the participation of water present in the precursor salt. Thus, in our case, the presence of water in the CuAc₂, as well as the concentration of the starting CuAc₂ in the DEG, are the key parameters in the process of the formation of nanowires. As was reported by Chen et al.,²⁵ Cu₂O was not formed under hydrothermal conditions when Cu(NO₃)₂, CuSO₄, or CuCl₂ were

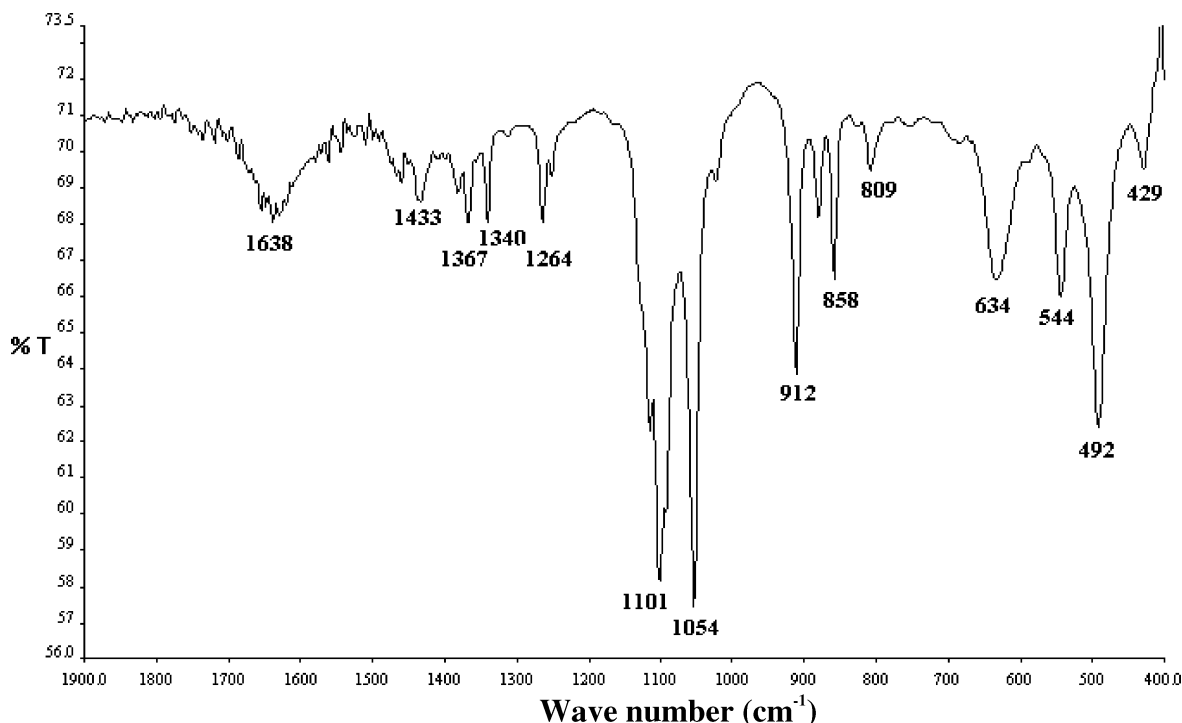


Figure 6. FTIR spectrum of Cu_2O nanowires showing a characteristic Cu_2O absorption band at 634 cm^{-1} .

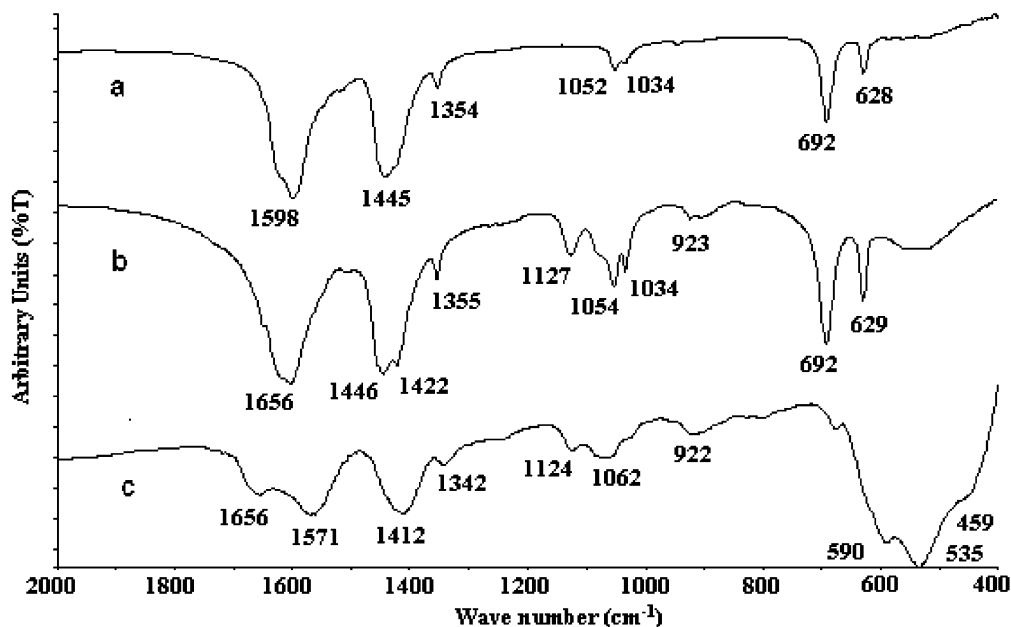


Figure 7. FTIR spectra of samples taken after (a) 5, (b) 20, and (c) 25 min at $190\text{ }^\circ\text{C}$.

used as the precursors, but was formed when CuAc_2 was added to $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 . The organic acid evolved in the reaction in this case acts not only as an acid but also as a reducing agent.²⁵ Additional parameters that are very important, not only for the formation of Cu_2O but also for the final morphology, are the temperature of the reaction and the reaction time. However, the type of polyol, in our case DEG, also plays an important role in the formation of Cu_2O nanowires. Namely, uniform Cu_2O particles were obtained by heating a CuAc_2 solution in ethylene glycol ($120\text{ }^\circ\text{C}$) or tetraethylene glycol (up to $300\text{ }^\circ\text{C}$).²⁶

Among the research topics related to the preparation of nanowires, a special emphasis has been given to the organization

of building units and the mechanism of nanowire growth in the form of some aggregative structure.

Different research methods, such as IR, NMR, and mass spectroscopy, as well as XRD diffraction and electron microscopy, have been used to elucidate the formation mechanism. Several authors report on the oligomerization of Ti, Sn, Pb, and In glycolates as the mechanism responsible for the formation of nanowires.^{22,27} In analogy to these systems, acetate groups of CuAc_2 can be replaced by DEG units in the initial stage of refluxing through the formation of $\text{Cu}-\text{O}$ covalent and (and/or) $\text{Cu}-\text{OH}$ coordination bands.

The mechanism responsible for the formation of Cu_2O nanowires is a complex one and consists of a few simultaneous

processes, as indicated from SEM and IR spectroscopy and supported by NMR and TEM. An intermediate step in the process of solid-state formation is the creation of spheres composed of nanowires that grow from the center. In the beginning, the nanowires are amorphous, but with time, Cu₂O crystallites start to grow, as can be seen from images a and b of Figure 3. At the end of the formation process, nanowires are mostly composed of Cu₂O nanocrystalites and some amorphous phase.

IR spectra of samples taken after 5 and up to 25 min are presented in Figure 7. In the IR spectra obtained after 5 and 20 min, the presence of a carboxylate group, $\nu_{\text{as}}(\text{COO}^-)$ (asym. stretching) at $\sim 1600\text{ cm}^{-1}$ and $\nu_{\text{s}}\text{COO}^-$ (sym. stretching) at about 1450 cm^{-1} , is observed. The separation of $\Delta(\nu)$ between $\nu_{\text{s}}(\text{COO}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$ bands indicates the type of coordination of the carboxylate group.^{29,30} The difference between the stretching $\Delta = \nu_{\text{as}} - \nu_{\text{s}}$ is used as a criterion for determining the mode of binding the carboxylate. A value of about 150 cm^{-1} ³⁰ corresponds to an ionic structure, which means that the carboxylate group in Cu(II) acetate does not interact strongly with the metal ion. The bands at 692 and 628 cm^{-1} also confirm the presence of a carboxylate group, because the observed bands correspond to the deformation of COO^- .

The IR spectra taken during the second stage of the reaction (e.g., the IR spectrum after 25 min of heating in Figure 7c) show a few new bands. Two bands appearing at 1570 and 1412 cm^{-1} were previously observed in copper glycolate complexes and were assigned by Nakamoto et al.^{30,32,33} Larsson studied infrared spectra of metal glycolate complexes in aqueous solution to elucidate the structure of the complex ion in equilibrium by means of the C—OH stretching band that appears near 1060 cm^{-1} ³¹ and is also observed in our spectrum at 1062 cm^{-1} (Figure 7c). In the range from 700 to 400 cm^{-1} , a very broad band appears consisting of a few overlapping bands that can be assigned to the in-plane and out-of-plane C=O bending modes of the Cu—glycolate complex.³⁰ The band at 535 cm^{-1} can be assigned to a ring-deformation mode³² and may prove that CuO is formed.³⁴

A few parallel processes are responsible for the formation of the final product. As presented in the IR spectra (Figure 7), in the initial stage of refluxing, acetate groups of CuAc₂ were gradually replaced by DEG units forming (di)glycolates through Cu—O covalent and/or Cu—OH coordination bonds.²² It seems clear that after additional heating, the glycolate complex decomposed and the Cu(II) was reduced by DEG in Cu₂O, which preserved the wirelike morphology even after 6 h of heating. This morphology is presented in Figures 3–5 where Cu₂O nanowires with crystallites of 2–5 nm are formed with an amorphous phase. During reduction of Cu(II) to Cu(I) species, DEG decomposes to ethylene glycol, which is then oxidized to aldehydes and ketones as reported earlier.²⁸

The chemical interaction between precursor and DEG leading to a chainlike structure was supported by NMR spectroscopy. The chemical shift for the carbon atom in the β -position to copper and DEG—ether bond is shifted from 61.8 to 64.3 ppm, whereas the chemical shift for the carbon atom in the γ -position to copper and α -position to the DEG—ether bond shifted from 73.2 to 69.8 ppm. The chemical shifts of EG carbon atoms in polymeric structures were observed in the same region.²²

A similar mechanism for the formation of TiO₂, SnO₂, In₂O₃, and PbO nanowires by the polyol process was described in the work of Jiang.²² Chainlike precursors, most probably glycolates, were obtained by refluxing metal salts in ethylene glycol, which connected during heating into a wirelike morphology. In our

case, it was not necessary to additionally thermally treat the obtained samples, because Cu₂O nanowires were formed after 6 h of refluxing in a one step-reaction, as presented in the SEM and TEM micrographs and the IR and XRD spectra.

Conclusion

In conclusion, we have demonstrated for the first time that Cu₂O nanowires can be prepared by using the very well-known polyol process but without the addition of surfactant or stabilizer. It has to be pointed out that the final morphology of the Cu₂O nanowires is highly dependent on the concentration of the starting CuAc₂. This type of structure was obtained only with CuAc₂ in the concentration range 0.01–0.1 mol/L. The reaction temperature and time were also found to play an important role in obtaining Cu₂O nanowires: at temperatures above $190\text{ }^{\circ}\text{C}$ and times longer than 8 h, pure Cu nanoparticles were formed instead of Cu₂O nanowires. The advantage of the presented method is that Cu₂O nanowires are produced using a simple one-step synthetic route, without the addition of a surfactant or any other additive, under controlled heating by using just the CuAc₂ precursor and DEG.

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