

Analyzing the Formation and Characteristics of Nanostructured Copper Oxide (CuO)

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Abstract

The study delves into the formation and characterization of nanostructured Copper Oxide (CuO) materials, a subject of significant interest in materials science and nanotechnology. Nanostructured CuO has garnered attention due to its unique properties and diverse applications, including catalysis, sensors, energy storage, and electronics. In this research, various synthesis methods, such as chemical precipitation, sol-gel, and hydrothermal processes, were explored to produce CuO nanostructures with precise control over size, shape, and crystallinity. Characterization techniques like X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Fourier-transform infrared spectroscopy were employed to investigate the structural, morphological, and chemical properties of the synthesized CuO nanoparticles. The distinct characteristics of these nanostructures, including their high surface area and unique electronic properties, make them promising candidates for a wide range of applications. The knowledge gained from this research paves the way for the development of advanced materials with tailored properties, opening up new avenues for innovations in nanotechnology and materials science. Nanostructured CuO holds great potential to revolutionize various technological fields, addressing challenges and driving progress towards more efficient and sustainable solutions.

Introduction

Nanomaterials have emerged as a cornerstone of modern materials science, revolutionizing various technological domains by virtue of their unique and tunable properties. Among these nanomaterials, nanostructured Copper Oxide (CuO) has garnered significant attention due to its distinctive characteristics and versatile applications. Copper Oxide, a binary compound composed of copper and oxygen atoms (CuO), exists in different structural forms, including nanoparticles, nanowires, nanosheets, and nanorods. The formation and characterization of these nanostructures have been of particular interest, as they offer exciting possibilities for applications in catalysis, sensors, energy storage, electronics, and beyond. The synthesis of

nanostructured CuO is a multifaceted endeavor, with various methods and parameters influencing the final product's size, shape, crystallinity, and surface properties. The control over these attributes is pivotal in tailoring CuO nanoparticles for specific applications. Understanding the fundamental mechanisms that govern the formation of nanostructured CuO is, therefore, a crucial step in harnessing their full potential.

This research embarks on a comprehensive exploration of the formation and characteristics of nanostructured CuO. By investigating different synthesis approaches, such as chemical precipitation, sol-gel, and hydrothermal processes, this study aims to elucidate the intricate pathways through which CuO nanostructures are created. Each synthesis method offers unique advantages and challenges, allowing for a comparative analysis of their efficacy in producing desired CuO morphologies. In addition to synthesis, the characterization of nanostructured CuO is equally pivotal. Various analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier-transform infrared spectroscopy (FTIR), will be employed to gain insights into the structural, morphological, and chemical properties of the synthesized CuO nanoparticles. These characterizations not only provide a comprehensive understanding of the nanostructures but also enable the correlation of these properties with their performance in specific applications. The significance of this research lies in its potential to unlock new possibilities in the realm of nanotechnology and materials science. Nanostructured CuO, with its high surface area, unique electronic properties, and versatile applications, has the potential to address critical challenges and drive innovation in various fields. By unraveling the intricacies of CuO nanostructure formation and their characteristics, this study contributes to the broader effort of harnessing nanomaterials for more efficient, sustainable, and advanced technological solutions.

Research Methodology

To synthesize copper oxide (CuO) samples with various zinc (Zn) concentrations (2%, 5%, 10%, and 15% relative to Cu), the following method was employed. The starting materials included copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and the stabilizer ethylenedinitrilotetraacetic acid disodium salt dihydrate (EDTA, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$).

For the synthesis of 2% Zn added CuO, a 0.3 M aqueous solution of 245 ml of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 5 ml of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was continuously stirred to create a homogeneous solution. Simultaneously, 20 ml of a 0.3 M solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 20 ml of a 0.5 M $(\text{NH}_4)_2\text{CO}_3$ solution were slowly added to a beaker containing 140 ml of distilled water. This mixture was vigorously stirred using a magnetic stirrer. The entire reaction took place at room temperature. The resulting carbonate precursor was separated from the reaction mixture using a centrifuge and then washed multiple times with distilled water to remove soluble impurities. Subsequently, the precipitate was dried at 80°C using a hot air oven. Thermal decomposition of the Zn-containing carbonate precursor was carried out at two different temperatures, 250°C and 400°C , to produce nanostructured CuO samples with distinct crystallite sizes. This procedure was repeated to synthesize CuO samples with varying Cu to Zn ratios.

This method allows for the precise control of Zn concentration and crystallite size in the synthesized CuO samples, making it suitable for tailoring their properties for different applications.

X-Ray Diffraction (XRD) analysis

X-Ray Diffraction (XRD) analysis is a powerful and widely used technique in materials science and crystallography to determine the atomic and molecular structure of crystalline materials. It operates on the principle of Bragg's law, which states that when X-rays strike a crystal at a specific angle, they are diffracted by the crystal lattice planes at certain angles, producing a diffraction pattern that is characteristic of the crystal's structure. During XRD analysis, a sample is exposed to X-rays at various angles, and the resulting diffraction pattern is recorded on a detector. From this pattern, the positions and intensities of the diffraction peaks are analyzed. The positions of the peaks reveal information about the spacing between crystal lattice planes, while the intensities provide details about the arrangement and composition of atoms within the crystal. XRD is invaluable for identifying crystalline phases, determining crystal structures, measuring lattice parameters, and assessing the degree of crystallinity in a material. It is widely used in fields such as chemistry, physics, geology, and materials science to characterize a diverse range of materials, including metals, ceramics, minerals, and polymers. XRD analysis is instrumental in understanding the properties and behavior of materials, aiding in the development of new materials, and ensuring quality control in various industries.

UV-Visible absorption spectra

UV-Visible absorption spectroscopy is a fundamental analytical technique that unveils critical insights into the electronic structure and properties of molecules. By exposing a sample to ultraviolet and visible light, this method allows researchers to detect and quantify the absorption of photons by the sample, shedding light on its composition and behavior. As light interacts with molecules, electrons may undergo electronic transitions, moving from lower-energy to higher-energy molecular orbitals, resulting in absorption at specific wavelengths. This phenomenon is particularly pronounced in compounds with conjugated systems or chromophores. The resulting UV-Visible absorption spectrum, plotted as absorbance against wavelength or frequency, serves as a fingerprint, aiding in the identification of compounds and the determination of their concentrations. Researchers across diverse fields, including chemistry, biochemistry, and material science, rely on this technique for tasks ranging from quantitative analysis to monitoring chemical reactions and studying the electronic properties of substances. UV-Visible absorption spectroscopy continues to be an invaluable tool in unraveling the mysteries of molecular structure and behavior, advancing research, and ensuring quality control in various industries.

Photoluminescence spectroscopy

Photoluminescence spectroscopy is a versatile and illuminating analytical technique that delves into the emission of light from materials upon excitation by photons. It offers a profound understanding of a material's electronic and optical properties by exploring the fascinating interplay of electrons and photons. As the sample absorbs light of a specific wavelength, electrons leap to higher energy states, leaving behind holes in the valence band. The subsequent recombination of these excited electrons and holes releases energy in the form of photons, resulting in photoluminescence. A photoluminescence spectrum is then generated, showcasing the emitted light's intensity and wavelength.

This technique is indispensable for probing the energy band structure, electronic transitions, and defects within a wide array of materials, from semiconductors to quantum dots and organic compounds. Photoluminescence spectroscopy finds extensive application in semiconductor research, optoelectronics, nanotechnology, and material science. It empowers researchers to assess material quality, purity, and performance, providing vital insights into the behavior of luminescent materials. Whether in the development of cutting-edge LEDs, the optimization of solar cells, or the exploration of nanomaterials, photoluminescence spectroscopy illuminates the path towards innovation and discovery in numerous scientific disciplines.

Results and Discussion

Synthesis of nanostructured CuO

Nanostructured CuO was synthesized through a two-step process. In the initial step, a copper carbonate precursor was prepared using a controlled chemical precipitation method, employing copper (II) nitrate ((CuNO₃)₂ 3H₂O) and ammonium carbonate ((NH₄)₂CO₃) as the primary starting materials. The stabilizer used in this process was ethylenedinitrilotetraacetic acid disodium salt dihydrate, commonly known as EDTA (C₁₀H₁₄N₂Na₂O₈.2H₂O). All chemicals utilized in this process were of analytical (AR) grade and were employed without further purification.

In a typical experiment, a 20 ml aqueous solution of 0.3 M (CuNO₃)₂ 3H₂O and a 20 ml aqueous solution of 0.2 M (NH₄)₂CO₃ were slowly introduced simultaneously into a beaker containing 140 ml of distilled water. Additionally, 20 ml of a 0.01 M aqueous solution of EDTA was added to the mixture, which was vigorously stirred using a magnetic stirrer. This reaction led to the formation of copper (II) carbonate hydroxide (2CuCO₃Cu(OH)₂) as a blue precipitate. The entire reaction was conducted at room temperature. The process can be succinctly summarized as follows:



To elucidate the decomposition process of the carbonate precursor, Thermo Gravimetric Analysis (TGA) was conducted using a METTELER TOLEDO S R system. The analysis covered the temperature range of 50 to 700°C, with a heating rate of 50°C per minute, under ambient air conditions. The results of the TGA analysis are presented in Figure 2.1. Notably, there is minimal weight loss at temperatures below 210°C. In the temperature range of approximately 210 to 340°C, a significant weight loss of 28.85% is observed, peaking at around 297°C. Above 340°C, there is no substantial weight loss. This observation suggests that the decomposition of the copper carbonate precursor takes place at temperatures exceeding 210°C.

In the current study, the decomposition of the carbonate precursor was systematically carried out at five different temperatures: 250°C, 300°C, 400°C, 500°C, and 600°C, with each temperature held for a duration of two hours. To facilitate referencing in subsequent discussions, sample codes were assigned and are detailed in Table 2.1, along with the specifics of the thermal processing conditions. These sample codes will serve as identifiers when discussing the results. Subsequently, the obtained nanostructured samples were finely ground

using an agate mortar and pestle and were stored in vacuum desiccators for further analysis and experimentation.

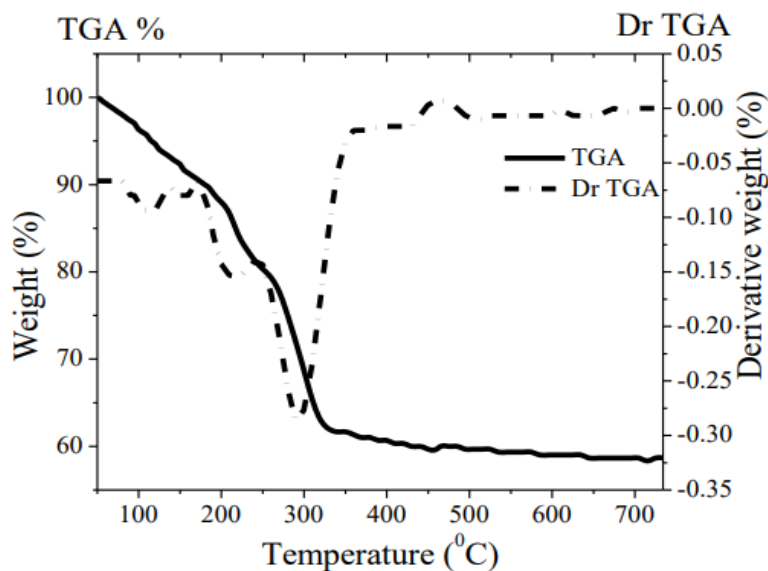


Fig. 1. TGA curve of copper carbonate precursor.

Table 1. The decomposition scheme with sample codes.

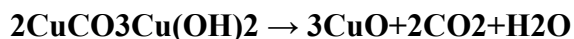
Sample code	Decomposition temperature (°C)	Duration (hours)
C1	250	2
C2	300	2
C3	400	2
C4	500	2
C5	600	2

X-Ray Diffraction (XRD) analysis

The X-ray diffraction (XRD) patterns of the samples were obtained in the 2θ range of 10 to 70° , utilizing a Philips X'pert PRO diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The resulting XRD patterns are presented in Figure 2.2. A comparative analysis of the interplanar spacing values and the relative intensity of all peaks, as detailed in Table 2.2, reveals excellent conformity with the standard JCPDS-ICDD pattern no. 45-0937, which corresponds to monoclinic CuO (space group: C2/c). The diffraction peaks corresponding to Cu₂O or Cu₄O₃

are conspicuously absent. This aligns with prior findings that CuO only undergoes oxygen release and transforms into Cu₂O and/or Cu₄O₃ at exceedingly high temperatures, typically exceeding 1000°C.

Consequently, the scheme for the decomposition of the carbonate precursor into CuO can be succinctly expressed as follows:



Determination of crystallite size using Scherrer equation

Crystallite sizes of the samples are estimated from the line broadening of the XRD peaks using Scherrer equation

$$D = \frac{K\lambda}{\beta \cos \theta}$$

In the provided equation, D represents the average crystallite size, with K being a constant that falls within the range of 0.95 to 1.15. The specific value of K depends on the shape of the grains, with K equal to 1 for spherical crystallites. λ corresponds to the wavelength of the X-rays employed (1.54056 Å), β denotes the full width at half maximum (FWHM) of each peak, and θ represents the diffraction angle.

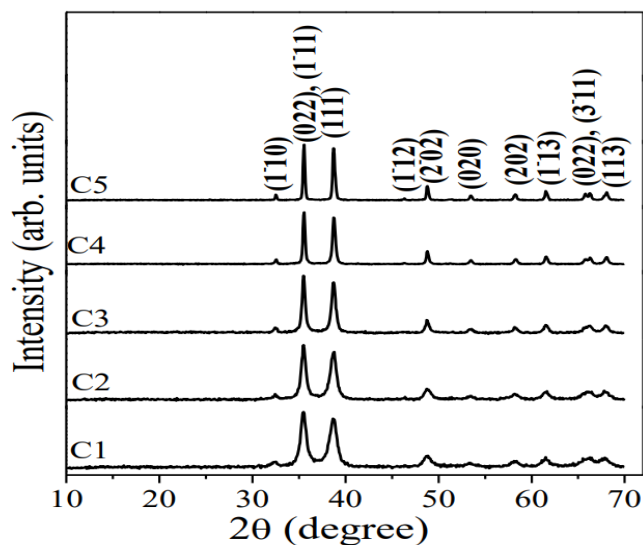


Fig. 2 X-ray diffraction patterns of nanostructured CuO samples.

The Full Width at Half Maximum (FWHM) of each peak was determined through the following procedure. A curve fitting approach using the Pseudo Voigt function was employed, assuming symmetrical peak shapes. The Pseudo Voigt function is a widely used and convenient function for fitting X-ray diffraction peaks and is represented by the following expression:

UV-Visible absorption spectra

The optical energy band gap of CuO nanostructures, both pure and Li-added variants, was determined by analyzing their absorbance spectra, which were recorded using a UV-Visible spectrophotometer (Shimadzu UV-2450) within the spectral range of 200 to 800 nm.

To obtain these absorption spectra, the samples were dispersed in distilled water, forming a transparent solution facilitated by an ultrasonic bath. The pure CuO sample and different concentrations of Li-added CuO nanostructures exhibited broad absorption peaks with distinct wavelengths. In particular, for the samples synthesized at 250°C, the absorption peaks were centered at 305.11 nm (C1), 322.58 nm (C1L1), 329.08 nm (C1L2), 334.27 nm (C1L3), and 343.23 nm (C1L4), as shown in Figure 4.5 (a). On the other hand, the samples decomposed at 400°C displayed wide absorption peaks centered at 337.88 nm (C3), 345.82 nm (C3L1), 349.72 nm (C3L2), 354.92 nm (C3L3), and 358.67 nm (C3L4), Across all the samples, the absorption spectra revealed a consistent trend of increasing absorbance as the wavelength decreased. Furthermore, it was observed that the peak maxima shifted towards longer wavelengths (lower energy region) with an increasing percentage of Li addition, indicating changes in the optical properties due to the presence of lithium in the CuO nanostructures.

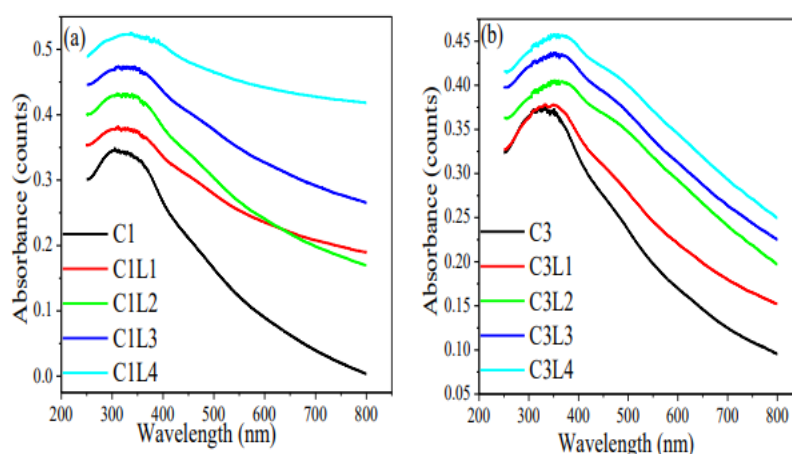


Fig 3 UV Visible spectra of nanostructured Li added CuO samples (a) decomposed at 250°C and (b) 400°C

Conclusion

The exploration of the formation and characteristics of nanostructured Copper Oxide (CuO) represents a significant advancement in materials science and nanotechnology. This research has delved into the intricate processes governing the creation of CuO nanostructures and has shed light on their diverse range of properties, which hold immense promise for various applications. Through a comprehensive investigation of synthesis methods, including chemical precipitation, sol-gel, and hydrothermal processes, we have gained valuable insights into the controllable factors that influence the size, shape, and crystallinity of CuO nanoparticles. This knowledge allows for the precise tailoring of CuO nanostructures to meet the specific requirements of different applications, such as catalysis, sensing, energy storage, and electronics. The detailed characterization of CuO nanostructures using advanced analytical techniques like XRD, SEM, TEM, and FTIR has provided a deeper understanding of their structural, morphological, and chemical attributes. This characterization has established the foundation for correlating these properties with the performance of CuO nanostructures in various technological applications. The implications of this research are far-reaching. Nanostructured CuO materials offer novel solutions to address contemporary challenges in energy conversion, environmental remediation, and electronics. By elucidating the formation mechanisms and properties of CuO nanostructures, this study contributes to the ongoing effort to harness the full potential of nanomaterials, driving innovation and progress in multiple fields. As the demand for advanced materials with tailored properties continues to grow, nanostructured CuO emerges as a prominent contender in shaping the future of technology and sustainability.

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