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ARTICLE

Structural and Surface Characteristics of CuO and Pt/CuO Nanostructured Thin Films

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Abstract: The most prominent and utilizable platinum-coated copper Oxide nanostructured thin films are prepared using the SILAR method. Their structural properties have been studied using X-ray diffraction (XRD) and Raman spectroscopy. XRD pattern reveals the phase purity and crystallinity of CuO nanostructures. The average grain size estimated from XRD gives diameters in the range of 14 - 27 nm. Raman spectra explain the structural information of CuO and Pt/CuO nanostructured thin films, in which the peaks observed at 328 cm^{-1}, 609.32 cm^{-1} and 1141.77 cm^{-1} are the different phonon modes of CuO. The peak at 2136 cm^{-1} provides strong evidence for the formation of platinum on CuO nanostructures. The SEM micrograph confirms the floral morphology, which is composed of nano petals. From the observed morphology, it is observed that the deposited thin films such as CuO and Pt/CuO will give interesting applications to our society by being self-cleaning agents, photocatalysts, semiconductor devices, optical fibers, … etc.

Keywords: CuO, Pt/CuO, Structural analysis, SILAR, Crystallinity.

1. Introduction

Copper oxide, including cuprous oxide (copper (I) oxide) and cupric oxide (copper (II) oxide), is formed when copper is exposed to oxygen [1]. These semiconductor oxides have been investigated for various purposes, such as the inherent abundance of starting material (Cu), the ease of production by Cu oxidation, their non-toxic nature and the reasonably good electrical and optical properties exhibited by CuO [2]. Previous works showed that many of the growth methods for copper oxide resulted in a combined growth of copper (I) oxide (Cu_2O) and copper (II) oxide (CuO). However, CuO is a more widely used material than Cu_2O due to its stability. Cupric oxide (CuO) possesses a monoclinic crystal structure with a bandgap of 1.22–2.0 eV [3, 4]. Its high optical absorption coefficient in the visible range and reasonably good electrical properties constitute important advantages and render CuO as the most

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interesting phase of copper oxides. CuO has been employed as a heterogeneous catalyst for several environmental processes, solid-state gas sensor heterostructures and microwave dielectric materials.

In solution-phase deposition methods, various complexing agents have been added to the growth solution to enhance the physical properties of the thin films. CuO thin films exhibit an exceptional combination of multifunctional characteristics, including optical, electronic, optoelectronic, magnetic and semiconducting. SILAR is a simple solution-based method for the suitable formation of thin films with controlled thickness and deposition temperature [5, 6]. Novel morphology of CuO was obtained by SILAR method due to metal doping or presence of additives [7, 8, 9]. The chief purpose of this article is to study the CuO thin films and SILAR method as an alternative to standard coating methods, which are budgetary and easily suitable. In order to achieve this goal, CuO thin films were deposited on glass substrates using SILAR method without any additives or dopants. The structural and surface properties of the untreated sample and thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy [10, 11].Copper (II) oxide, CuO, is a p-type semiconductor with a narrow bandgap (1.2–1.7 eV) and high stability in harsh terms [12, 13]. The structural, morphological and optical properties of CuO thin films can be used in photovoltaic applications [14]. Nanostructures of CuO films have different forms, such as tetrapods, flowers, nanorods, nanoribbons, nanowires, nanobelts, nanosheets, micro-roses, woolen, lotus, nanowire, nanosheet and flower-like [15]. The monoclinic structured CuO thin films are appropriate for photovoltaic and optoelectronic applications, such as optical devices [16], super hydrophobic [17], photocatalysis [18], microwave dielectric materials [19], lithium-ion batteries [20] and gas sensors [21].Among different chemical methods, successive ionic layer adsorption and reaction (SILAR) is a facile, economically feasible and most versatile method in order to deposit material directly on the substrate. Moreover, the SILAR method holds a promise to develop different morphologies by controlling simple preparative parameters [16, 22, 23]. Hence, the present report focused on the synthesis of such CuO nanostructured thin films and structural properties of CuO thin films deposited by SILAR method.

2. Experimental Section

2.1 Substrate Preparation

Glass substrates were used to grow copper (II) oxide thin films. Before starting the growth, the substrates were cleaned using soap, acetone and distilled water for 10 minutes. Then, the substrates were air-dried.

2.2 Preparation of CuO Nanostructured Thin Films

Initially, the glass substrate is dipped in copper ammonia complex $[(Cu\ (NH_3)_4)^{2+}]$ solution for 40 sec for the adsorption of the cationic solution. Next, the glass substrate is immersed in double distilled water for 20 sec for rinsing. Then, the substrate is dipped in the anionic solution (i.e., double distilled water at 80ºC) for 50 sec. Then, the substrate is immersed in double distilled water for 20 sec for rinsing. As the final step of the cycle, the substrate is dried in air for 20 secs. Thus, one SILAR cycle is completed. In order to obtain uniform deposition, cycles were repeated for 20 and 40 times.

2.3 Preparation of Pt/CuO Nanostructured Thin Films

20 ml of 1 mM aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ was added and stirring was performed for 15 min. The redox reaction was started by adding solid tri-sodium citrate. The reaction was carried out for 120 min. All experiments were performed at room temperature. CuO nanostructured thin films were immersed in platinum sol for 3h. After 3hr, Pt/CuO nanostructured thin films were dried in air and subjected to different characterization techniques to study their structural and surface properties.

3. Results and Discussion

3.1 Structural Analysis

The phase purity and crystallinity of the prepared CuO and Pt/CuO nanostructured thin films were identified by X-ray diffraction analysis. The XRD patterns of the CuO and Pt/CuO nanostructured thin films are shown in Fig. 1 (a and b). All the diffraction peaks of CuO nanostructured thin films can be readily indexed with the standard JCPDS (PDF#05-0661) file. The XRD patterns of CuO nanostructured thin films prepared by different deposition cycles consist of diffraction peaks derived from the monoclinic phase of crystalline CuO with ($\bar{1}11$) and (111) lattice planes. Conversely, no extra diffraction peaks are detected from the copper hydroxide or cuprous oxide, clearly showing that only CuO is formed in the substrate. The high intensity of peaks indicates that the prepared CuO thin films are highly crystalline in nature. Fig.2 (a and b) indicates the XRD pattern of Pt/CuO nanostructured thin films and shows the amorphous nature. The average crystallite size for the CuO thin films is estimated from Scherrer's formula and is varying from 14 to 27 nm.

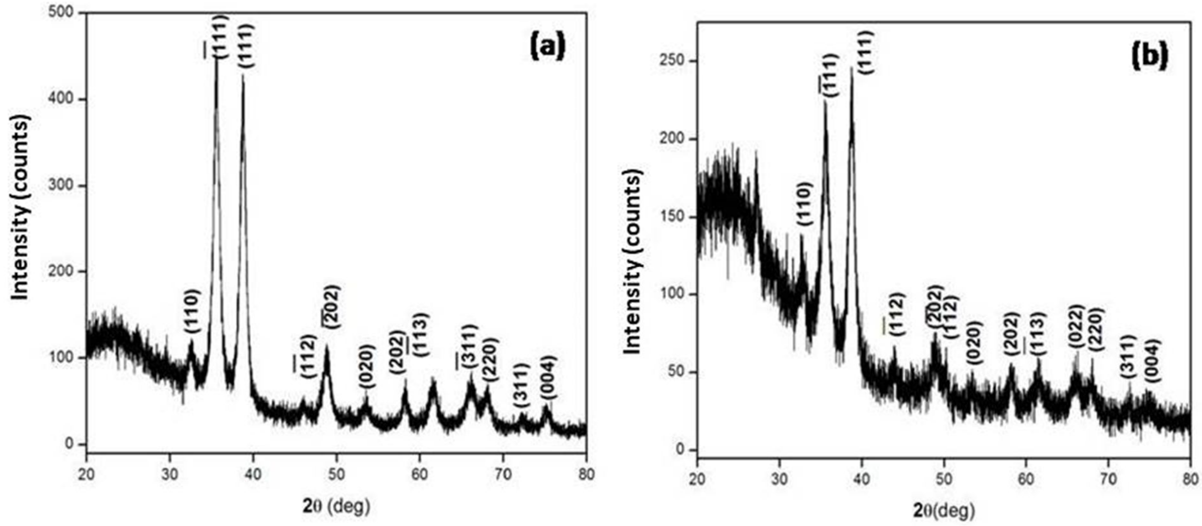

FIG. 1. XRD pattern of CuO nanostructured thin films prepared at a) 20 and b) 40 deposition cycles.

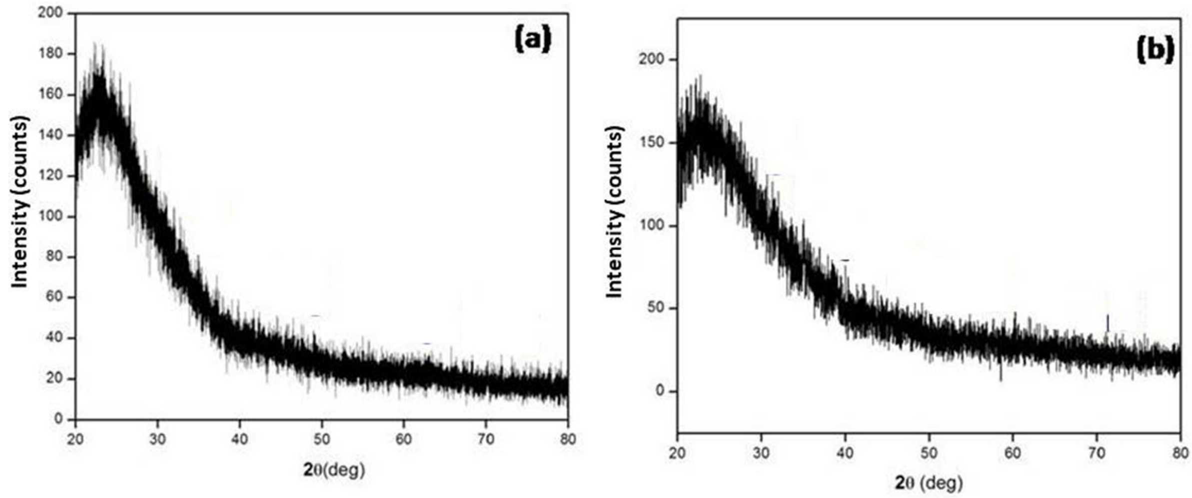

FIG. 2. XRD pattern of platinum-coated CuO nanostructured thin films.

3.2 Raman Spectra of CuO and Pt/CuO Nanostructured Thin Films

Raman spectroscopy, which is a sensitive probe to the local atomic arrangements and vibrations of the materials, has been also widely used to investigate the microstructural nature of the nanosized materials in general and CuO nanomaterial in particular. Raman scattering also provides useful information about the structures and bonds of materials. Raman scattering could help detect the existence of unintended phases, such as Cu_2O or Cu $(OH)_2$ or show the crystallinity of the product. Raman active normal modes of CuO are ΓRA = 4Au + 5Bu + Ag + 2Bg. Among these vibration modes, there are three acoustic modes (Au + 2Bu), six infrared active modes (3Au + 3Bg) and three Raman active modes (Ag + 2Bg). Three well known bands of CuO are Ag (278.81 cm^{-1}), Bg 1 (326 cm^{-1}) and Bg 2 (614.85 cm^{-1}) [5]. Fig.3 shows Raman spectra of CuO nanostructures prepared by SILAR method with different deposition cycles. When increasing the deposition cycles to 40, the red shifts occur due to the phonon confinement effect in nanometer size materials. Multiphonon band of CuO nanostructures appears at a wave number of 1130 cm^{-1}. Fig. 4 shows the Raman spectra of platinum-coated CuO nanostructured thin films. The peaks observed at 328 cm^{-1}, 609.32 cm^{-1} and 1141.77 cm^{-1} are the different phonon modes of CuO. The peak at 2136 cm^{-1} provides strong evidence for the formation of platinum on CuO nanostructures.

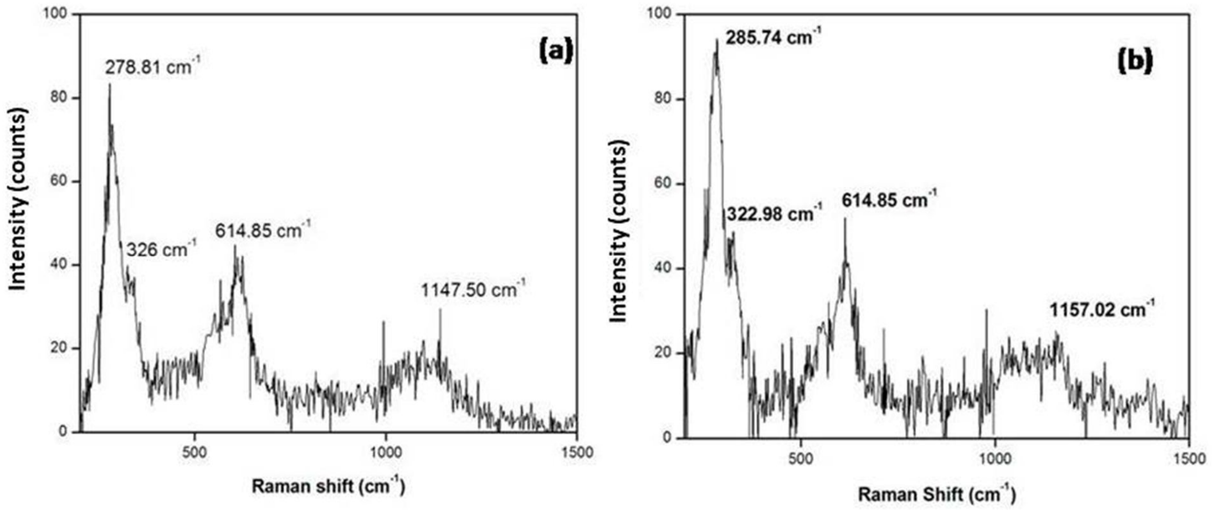

FIG. 3. Raman spectra of CuO nanostructured thin films prepared at a) 20 and b) 40 deposition cycles.

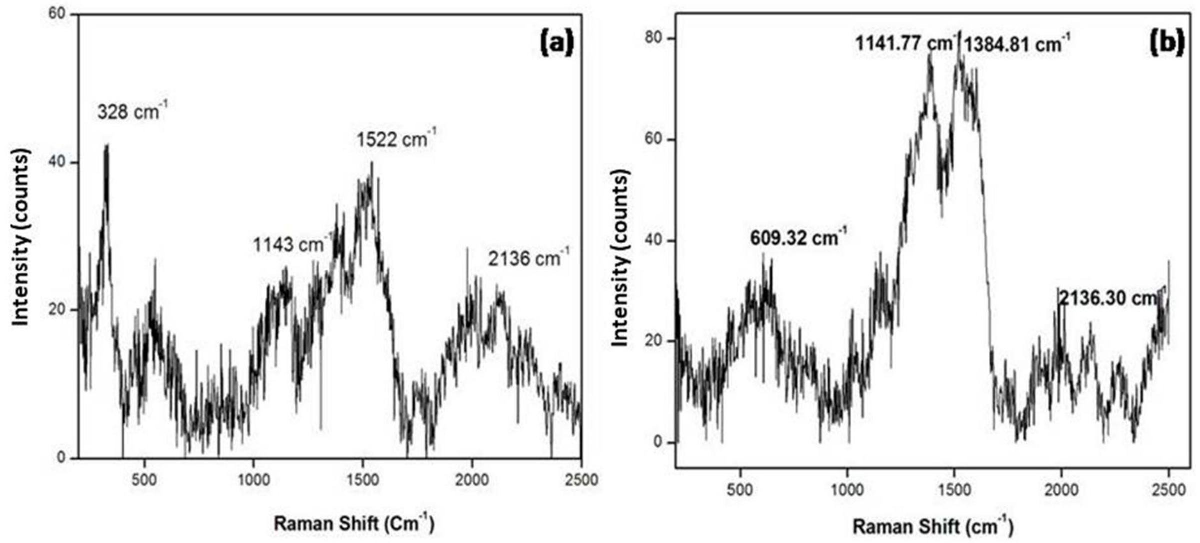

FIG. 4. Raman spectra of platinum-coated CuO nanostructured thin films.

3.3 Morphological Analysis

The morphology of designed CuO and Pt/CuO nanostructured thin films was determined by SEM and the prepared films are investigated in terms of shape, size and self-assembly of nanostructures. The morphology of CuO and Pt/CuO thin films for different cycles is shown in Fig. 5 and Fig. 6. All the micrographic images reveal that the nanostructures basically possess the petal shape and the petals are assembled together to form the floral structure. Initially, the floral structure is aggregated when platinum is coated over the CuO thin films. Grown nanopetals have been divided over the entire area of the film without any blowholes and assembled together to form a floral nanostructure, as shown in Fig. 5 and Fig. 6. The size of the flowers is around 200 nm. The self-assembled floral structure is due to the weak interaction by Van der Waals force.

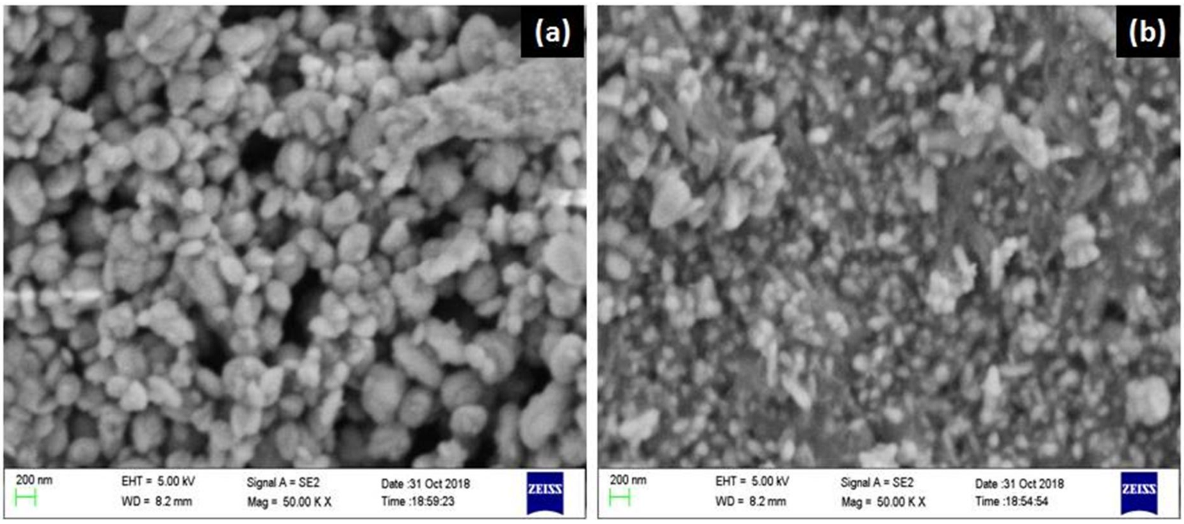

FIG. 5. SEM image of CuO nanostructured thin films prepared at a) 20 and b) 40 deposition cycles.

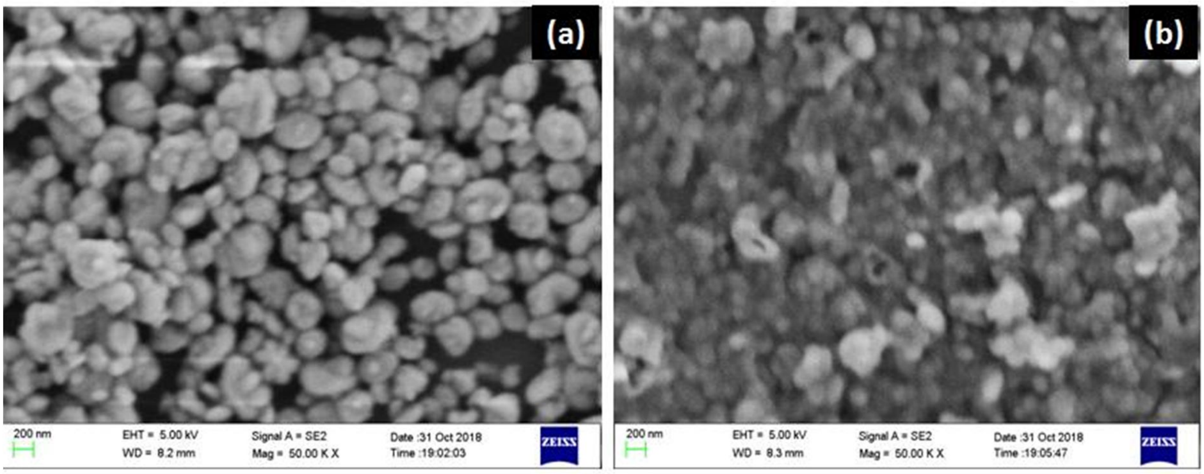

FIG. 6. SEM image of platinum-coated CuO nanostructured thin films prepared at a) 20 and b) 40 deposition cycles.

4. Conclusion

Copper oxide and platinum-coated copper oxide nanostructured thin films were prepared using the simple chemical method. Their structural properties have been studied using XRD and Raman spectroscopy. In XRD, the dominating intensity of the diffracted peaks (-111) and (111) reveals the improved crystallinity of CuO nanostructures. The average grain size estimated from XRD gives diameters in the range of 14 - 27 nm. Raman spectra explain the structural information of CuO and Pt/CuO nanostructured thin films, in which the peaks observed at 328 cm^{-1}, 609.32 cm^{-1} and 1141.77 cm^{-1} are the different phonon modes of CuO. The peak at 2136 cm^{-1} provides strong evidence for the formation of platinum on CuO nanostructures. Being more crystalline, CuO deposited thin films may be used in semiconductor devices and in optical fiber communication systems. The SEM micrograph confirms the floral morphology, which is basically composed of nano petals. From the observed morphology, it is observed that the deposited thin films, such as CuO and Pt/CuO, will give interesting applications to our society by being self-cleaning agents, photocatalysts, semiconductor devices, optical fibers, … etc.

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