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EFFECT OF ELECTRON BEAM IRRADIATION ON STRUCTURAL, MORPHOLOGICAL AND ELECTRICAL PROPERTIES OF CuO ELECTRODES

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ABSTRACT

CuO nanostructures with various nanostructures were obtained by irradiating chemically deposited thin films. This study reports the effect of irradiation of 10 MeV electron beam on the X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical properties of CuO nanostructures thin films. The crystal size was found to decrease upon electron beam irradiation and the materials exhibit poor crystallization. Electrochemical supercapacitive properties show that CuO electrode exhibits high specific capacitance after electron beam irradiation. Moreover, impedance analysis shows lower ESR value, high power performance, excellent rate as well as frequency response of CuO electrode. The wonderful electrochemical properties of the CuO electrode involve that it has immense reasonable potential applications for high performance supercapacitors.

Keywords: CuO thin films, XRD, SEM, irradiation, electrochemical properties etc

INTRODUCTION:

It is well known with the aim of rechargeable supercapacitors have established powerful importance and have extensive applications in transportable electronic devices, uninterruptible power provisions, hybrid electrical vehicle systems, and renewable energies due to their high command density, time-consuming cycle life, low cost, and rapid charge–discharge processes, compared to lithium-ion batteries and traditional capacitors [1, 2]. The electrode material is the key factor that determines the performance of supercapacitors. In general, supercapacitors can be divided into two types, and redox pseudocapacitors and electrochemical double-layer capacitors, depending upon the available electrochemical mechanisms of energy storage. It is significant for pseudocapacitors to attain high specific surface area, high electrical conductivity, and a fast cation diffusion process to achieve high power densities and energy densities. Ruthenium oxides and hydroxides have been previously demonstrated to show very high pseudo-charge capacitance [3, 4]. However, the high cost limits their applications. Other transition metal oxides [5] such as NiO, Co_3O_4, MnO_2 and VO_x, were later considered and well studied. Among these metal oxides, CuO can be a promising material due to its low cost, and it is chemically stable and environmental friendly [6]. However, to our most excellent comprehension, little work has been carried out on the application of CuO as supercapacitor/pseudo capacitor electrodes because of their low electrical conductivity and unstable cycling performances [7]. Due to its low cost, chemical stability and being environmentally friendly, nanostructured copper oxides (CuO) have been synthesized using various methods such as electrodeposition [8], template-free growth [9], precipitation method [10], and chemical bath deposition [7], for supercapacitor applications. Nanostructure CuO with large surface area will improve specific capacitance of this material. For instances, cauliflower-like CuO exhibited a higher specific capacitance of 116.9 F g^{-1} compared with 26 F g^{-1} of globular CuO as found by Zhang et al. [10]. Mean while, Hsu et al. synthesized lotus-like CuO/$Cu(OH)_2$ array electrode which produced excellent specific capacitance of 278 F g^{-1} with capacitance loss of 15% over 5000 cycles [11]. Among different chemical methods, chemical bath deposition method is very simple, inexpensive and attractive method. CBD method has its own advantages such as ion-by-ion growing mode, excellent material utilization efficiency, and good control over the deposition process along with the film thickness and large-scale deposition capability on any type of substrate.

In this investigation, the nanosheets-like CuO thin films have been successfully synthesized by simple CBD method and applied as supercapacitor electrode material. The CuO films were characterized by different physico-chemical characterizations. CuO nanosheets with excellent energy and power densities in 0.5M KOH electrolyte. These results show that after electron beam irradiation CuO nanosheets is promising material for electrochemical supercapacitors application.

Synthesis of CuO thin films

CuO thin films have been deposited using CBD as reported elsewhere [7]. We have used the similar methodology to obtain moderately films. The source of copper used was 0.1 M $CuSO_4$, and to make it alkaline, aqueous ammonia was added. The flexible copper foil (FCF) were used as the substrates, which was cleaned with detergent, followed by rinsing with double-distilled water and finally treated with ultrasonic waves for 25 min. These cleaned flexible copper foil (FCF) were immersed in the above bath and the bath was heated. When the bath attained the temperature of 343 K, the precipitation was started in the bath. During the precipitation, heterogeneous reaction occurred on the foil and deposition of copper oxide took place on the foil. The foil coated with copper oxide thin films were removed after 45 min. from the bath, washed with double-distilled water, dried in air and preserved in an airtight container.

Results and discussions

Structural analysis

Fig. 1 demonstrated the typical X-ray diffraction patterns (XRD) of pristine (Fig.1a) and 10 MeV electron irradiated CuO films with dose 20 kGy (Fig. 1 (b). Fig. 1 revealed that the pristine and irradiated CuO thin films exhibit monoclinic phase CuO (JCPD card no. 080-0076) [12]. The observed diffraction peaks of monoclinic phase CuO films are found at 2θ values of angles 35.20°, 38.25°, 46.53°, 50.19°, 62.45°, 66.40 and 74.11° corresponding to the lattice planes (002), (11-1), (20-2), (112), (11-3), (31-1) and (004) respectively. All the peaks intensities identified clearly shows that from CuO and hence no additional lines matching to Cu, O and $Cu(OH)_2$ are present in Fig. 1. The intensity of (002) plane is found higher than all other peaks in the diffraction patterns, represents that the crystallites are preferentially oriented along (002) plane. This result strongly suggests that high-energy electron beam irradiation has not changed single phase monoclinic structure of CuO films. These results indicate reduction in the crystallinity of the films that is attributed to the localized temperature increase within the film during irradiation. This is likely to result in a rearrangement of atoms. The average crystallite size is calculated using the well known Scherer relation (1.10). The decrease in crystallite size may be credited to a higher nucleation rate as compared to the growth rate or atomic rearrangement of CuO elements. This behavior matches with the results obtained by Hsu et al [13-15].

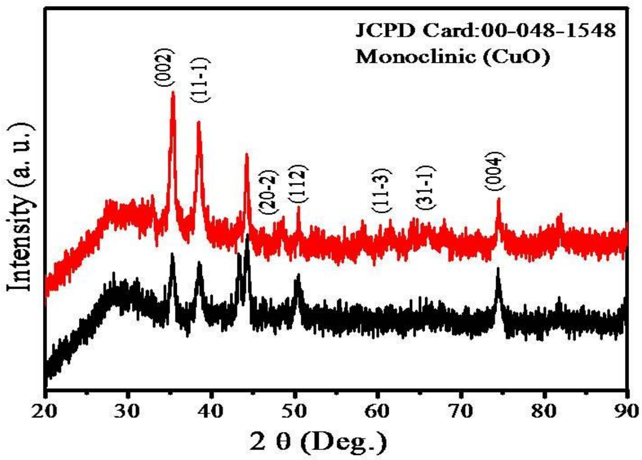

Fig. 1 X-ray diffraction patterns (a) pristine and electron irradiated 10 MeV at 20 kGy on CuO thin films on flexible copper foil

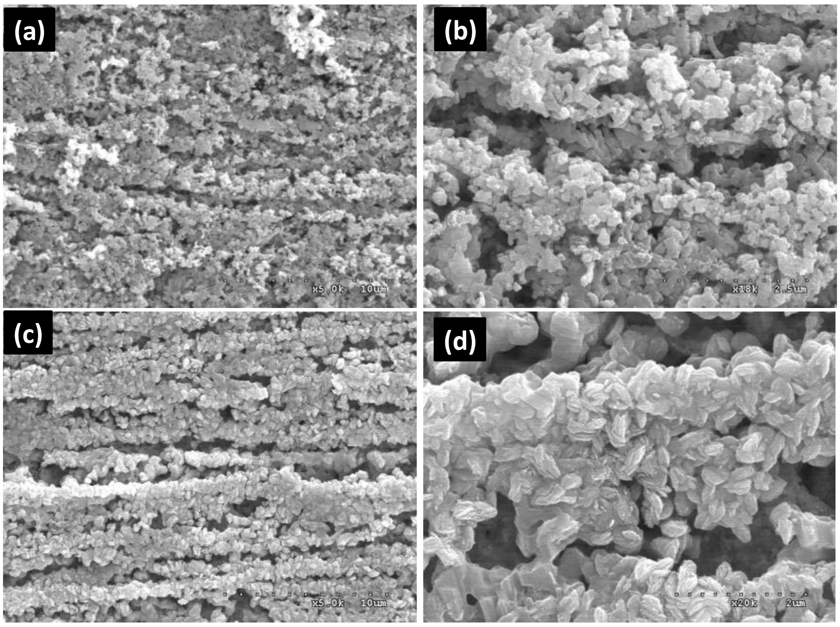

Fig. 2 (a-d) SEM images at different magnifications of pristine and electron irradiated 10 MeV at 20 kGy on CuO thin films

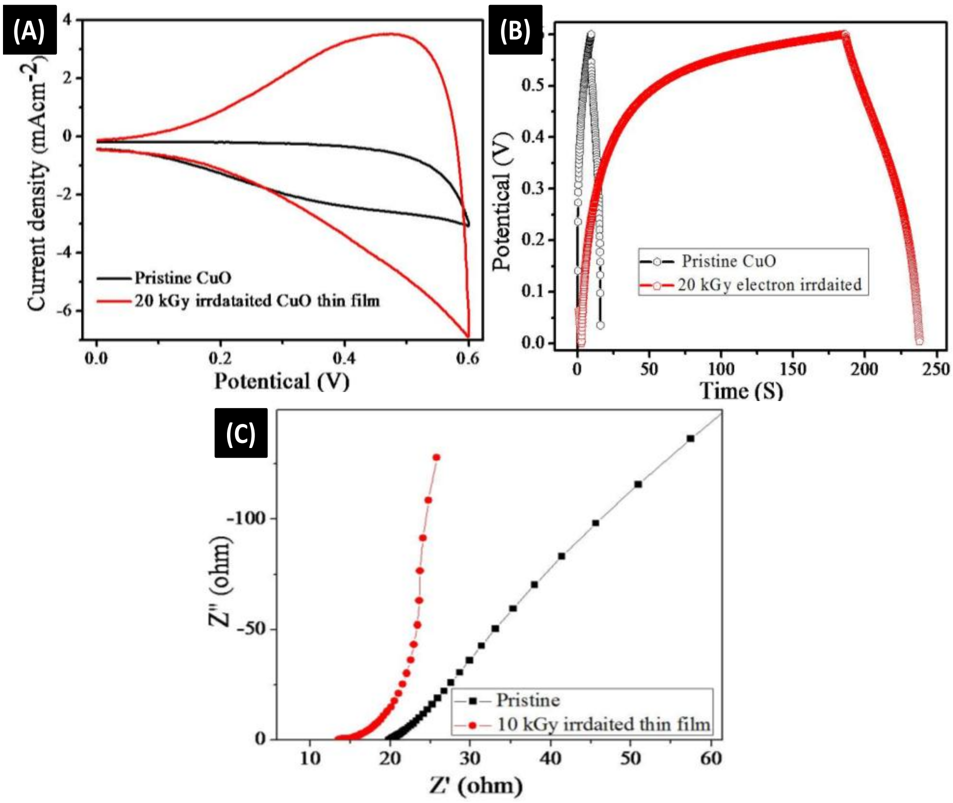

Fig.3 (A) Cyclic voltammogram, (B) Galvanostatic charge–discharge, and (C) Nyquist plots of pristine and electron irradiated 10 MeV at 20 kGy on CuO thin films

Surface morphology analysis

Fig. 2 (a-d) shows the FE-SEM images of the pristine and 10 MeV electron irradiated CuO films with 20 kGy doses and different magnifications. The pristine sample shows the very nicely grown interconnected nanoparticle. Fig. 2 (a-d) the substrate surface is well covered by the CuO thin film layer. Outstanding observation is noticed as deposited CuO thin films are processed with 20 KGy doses of electron beam irradiation with respect to formation of innovative nanostructures nanosheets like morphologies all over the substrate having grains size about 3 5nm to 20 nm respectively.

Fig. 2 (d) is of the nanosheets image which shows that the nanopetals structures are well adherent and horizontal grown on flexible copper foil. More meticulous morphologies of the sheets-like nanostructures with porous nanopetals are shown in Fig. 2d. These nanopetals are interconnected with each other, which provided a high volumetric specific surface area and good mass transport property [16, 17] and generate pores and crevices which allow large surface area for easy diffusion of the electrolyte onto the nanopetals surface [18,19].

Super capacitive studies

Cyclic voltammetry (CV)

CV measurement of specific capacitance in the double layer supercapacitor, for after and before irradiation of CuO thin films. Fig. 3A shows the CVs of CuO electrode scanned in the double layer region of 0.0 to 0.6 V vs. SCE at 5 mVs^{-1} scan rates in KOH electrolyte. It can be seen that the CVs show no observable peak development, but has a large current separation between forward and reverse scans. The CVs possess almost rectangular shape, especially at higher scan rates indicating capacitive behavior. The capacitance values are determined by measuring the integrated charge from the CV. It is felt that there may be a substantial pseudocapacitance contribution to the overall measured capacitance of the nanosheets of copper oxides electrode.

Galvanostatic discharge study

Galvanostatic discharge at different current density of 3 $mAcm^{-2}$ were evaluated to realize the rate capability of the obtained CuO electrodes after and before irradiation and presented in Fig. 3B. A current density is used in present investigation to allow for the complete reaction between the KOH electrolyte and the NPs, NSs CuO electrodes. These charge–discharge studies were carried out within potential window 0.0V to + 0.6V. The shape of discharging curves is ideal line, suggesting the contribution of a faradic reaction direction. The reductions in discharging times are clearly seen as due to its nanostructure of copper oxide electrode. As the NSs offer a highest surface area and an easy path for intercalation and deintercalation of ions, which effectively reduces the internal resistance of the material. As seen in Fig. 3B, the discharge curves are linear in the total range of potential with constant slopes, showing nearly perfect capacitive behavior.

Electrochemical impedance spectroscopy (EIS)

EIS of the after and before CuO electrode was measured at open circuit potential in KOH electrolyte and the Nyquist plot is shown in Fig. 3C. The spectrum exhibits one partially intercrossed and low semicircles at the high frequency region, which can be attributed to the redox reactions between Cu(I) and Cu(II) species. The depression of the semicircles is an implication of surface roughness of the electrode. The EIS results show the pseudo-capacitance characteristics and the porous structure feature of the NSs-CuO electrode.

Conclusions

In summary, a as-deposited and irradiated CuO films as a electrodes for supercapacitors has been prepared by using a easy, fast and helpful chemical bath deposition method. X-ray studies showed that as deposited and irradiated CuO films are monoclinic structure. There is a radical variation in surface morphology with electron beam irradiation. These outcome imply that chemical bath deposition and electron beam irradiation techniques was simplistic and appropriate for the different materials for miscellaneous applications.

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