SYNTHESIS OF COPPER OXIDE NANOTUBES BY KIRKENDALL EFFECT AND ITS ELECTROCHEMICAL ANALYSIS

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Abstract— CuO (Cupric Oxide) is one of the most important metal oxide in modern technologies. It is produced in large scale by pyrometallurgy used to extract copper from ores. This work presents the synthesis of copper oxide hollow nanotubes by kirkendall effect and its electrochemical performance. The Kirkendall effect is a simple, novel phenomenon that may be applied for the synthesis of hollow nanostructures with designed pore structures and chemical composition. We demonstrate the use of the Kirkendall effect for copper nanowires (NWs) and nanoparticles (NPs) via introduction kirkendall effect. Depending on the reaction time, Cu atoms gradually diffuse outward through the oxide layers, O2 diffuses inward. Due to unequal diffusion, void formation take place in the nanostructural cores. Through the Kirkendall effect, NWs and NPs were transformed into nanotubes (NTs) and hollow NPs, respectively. Characterization of these nanoparticles is done by XRD, SEM, TEM, EDX, SAED. Electrochemical performance that is Cyclic voltametry is studied and its capacitance is determined.

Keywords – Copper Oxide, Copper, Kirkendall effect, Cyclic voltametry.

I. INTRODUCTION

Nanoparticles have attracted steadily a growing interest because they have the potential to show superior and unique properties compared to those in bulk materials. It is essential to fabricate the nanoparticles with specific size and morphology for pursuing unique characteristics in nano-size level. The structural control of nanoparticles is one of the most important and interesting topics among the nanotechnologies. In particular, there is a deep interest in the methods used to fabricate hollow nanostructures, because their unique shapes bring about changes in chemical, optical and catalytic properties so as to be applicable to delivery vehicle so as to be applicable to delivery vehicle systems, fillers and catalysts.So far, various hollow spheres including carbons, polymers, metals and inorganic materials have been synthesized mainly through chemical reaction processes[1].

In the 1940s, it was a common belief that atomic diffusion took place via a direct exchange or ring mechanism that indicated the equality of diffusion of binary elements in metals and alloys. However, Ernest Kirkendall first observed inequality in the diffusion of copper and zinc in interdiffusion between brass and copper After the discovery of the Kirkendall effect in 1947,[2] which describes the consequences of different diffusivities for two solids in contact, much of the early research was conducted in order to find ways to minimize this effect macroscopic samples as it is disadvantageous in metallurgical applications. However, since the first published synthesis of hollow cobalt at al.,[3] the research regarding this so-called nanoscale Kirkendall effect has gained momentum due to possible tuning of physicochemical properties of the resulting hollow nanocrystals, as outlined in a recent review by Wang et al.[4] The reason why this effect is of particular interest is that the voids in the inside alter the electronic structure of the particle. Hence, different catalytic or optical properties can in turn be achieved in a controlled way. The nanoscale Kirkendall effect subsequently allowed for the preparation of hollow nanostructures for a wide variety of chemical systems using a large array of different techniques.

To meet the urgent need for environment-friendly, high efficiency energy storage and conversion devices for high-power electronic devices, backup power supplies, and electric vehicles, efforts have been made to develop batteries, fuel cells, and electrochemical capacitors (ECs) with the aim of replacing fossil fuel use[5]. ECs, also called supercapacitors or ultracapacitors, have received much attention because they can simultaneously achieve high power and energy densities.[6-9] Supercapacitors have shown great promise in applications such as high-power electronic devices, backup power supplies, and electric vehicles[7]. Based on their energy storage mechanisms, ECs are divided into two types, namely, electrical double layer capacitors (EDLCs) and pseudocapacitors[7]. EDLCs store energy by electrostatic charge separation,[8] whereas pseudocapacitors realize their energy storage function via fast, reversible redox reactions at the surface of the electrode materials. CuO (Cupric Oxide) is one of the most important metal oxide in modern technologies. It is produced in large scale by pyrometallurgy used to extract copper from ores. This work presents the synthesis of copper oxidehollow nanotubes by kirkendall effect and its electrochemical performance. The Kirkendall effect is a simple, novel phenomenon that may be applied for the synthesis of hollow nanostructures with designed pore structures and chemical composition. We demonstrate the use of the Kirkendall effect for copper nanowires (NWs) and nanoparticles (NPs) via introduction kirkendall effect. Depending on the reaction time, Cu atoms gradually diffuse outward through the oxide layers, O_2 diffuses inward. Due to unequal diffusion, void formation take place in the nanostructural cores. Through the Kirkendall effect, NWs and NPs were transformed into nanotubes (NTs) and hollow NPs, respectively. Characterization of these nanoparticles is done by XRD, SEM, TEM, EDX, SAED.

II. EXPERIMENTAL DETAILS

Materials and methods

Sodium hydroxide, Cupric nitrate, Ethylenediamine, 80% Conc Hydrazine, Distilled Water, Carbon black, Ethyl cellulose extrapure lauric acid, terpinol. With analytical grade were choosen as a raw material. The hydrazine ($N_2H_4.H_2O$) was selected as the reducing agent and all the synthetic proceeses were carried out within a water bath at atmospheric conditions.

A] For synthesis of copper nanowires

In each synthesis, 20-30 mL of NaOH (3.5-15 M) and 0.5-1.0 mL of $Cu(NO_3)_2$ (0.10 M) aqueous solution were added to a glass reactor (capacity 50 mL). Varying amounts of ethylenediamine (EDA; 0.050-2.0 mL; 99 wt %) and hydrazine (0.020-1.0 mL; 35 wt %) were also added sequentially, followed by a thorough mixing of all reagents. The reactor was then placed in a water bath with temperature control over 25-100ºC (optimized at 60ºC) for 15 min to 15 h; copper products were washed and stored in a water-hydrazine solution to prevent oxidation. The formation of metallic copper in this work is based on the following redox reaction under the basic condition.

$$2Cu^{2+} + N_2H_4 + 4OH \longrightarrow 2Cu^{\circ} + N_2 + 4H_2O$$

The reductive conversion of Cu^{2+} to metallic copper in this process is 100%, which was indicated in total disappearance of the light blue color. Interestingly, the as-prepared nanowire cake is lifted up to the top of solution due to the high density of solution

B] For synthesis of CuO nanotubes by kirkendall effect

The synthesized Cuº nanowires is transformed to hollow Cu nanotubes by heating the prepared nanowires in air at desired temperature (200ºc-, 500ºc) in oven or in furnace at different time variation. Colour of copper is changed to black which indicates formation of copper oxide. The annealing is done in electric furnace and in spray pyrolysis.

$$2Cu^{\circ} \xrightarrow[\text{air}]{\Delta} \text{hollow Cu}$$

C] Characterization

The crystallographic structure of products was determined with X-ray diffraction (XRD) The spatial, morphological, and compositional investigations were carried out with scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDX), transmission electron microscopy and selected area electron diffraction

D] Electrochemical Measurements

The process of fabricating working electrodes specifically involved mixing the as prepared composites, carbon black, and Ethyl cellulose extrapure lauric acid in a mass ratio of 80:15:5, respectively, and then was pressed onto docter blade. After drying for almost 12hrs. electrochemical measurements were performed in 1 M KOH aqueous electrolyte at room temperature in a three-electrode setup, which included the as-prepared working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetry (CV) were used to evaluate the electrochemical performance of the composites on an electrochemical workstation CV tests were conducted within the potential window between 0.0 and 1.0 V at different scan rates of 1, 5, 10, 30, 50, and 100 mVs−1 III]

III. RESULT AND DISSCUSION

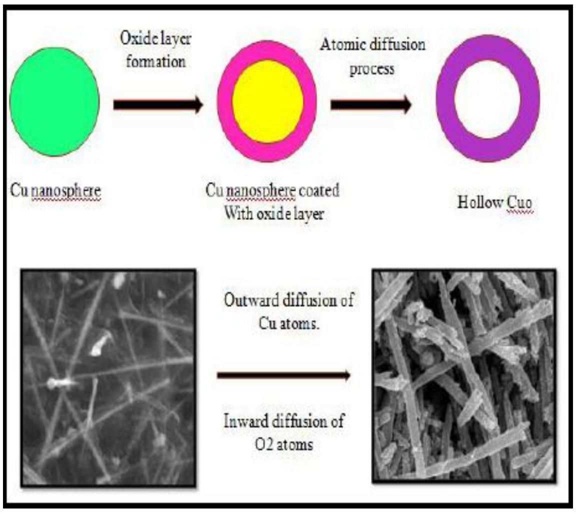

Figure 1: Transformation of Cu nanowires to CuO nanotubes

Cu nanowires are annealed to achieve kirkendall effect at temperature of 400ºC for 6 hrs in the furnace such that Cu nanowires is oxidized and reactes to form CuO. In this process the Cu diffuses outwards and O_2 diffues inwards hence, there is unequal diffusion takes places. So due to which there is gaps left inside that is nothing but formation of voids (pore formation occurs). So due to which, inner core starts becaming hollow, resulting to CuO nanotubes formation. This phenomenon is known as Kirkendall effect

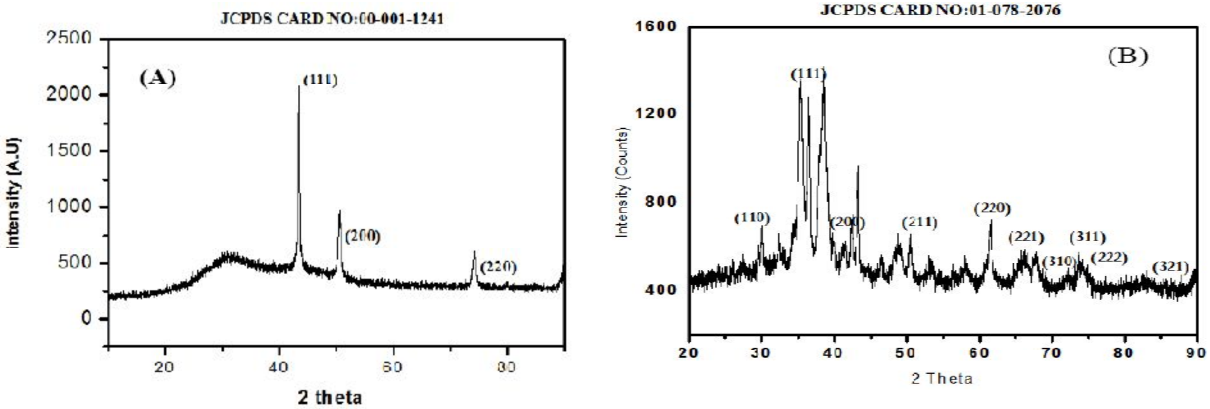

Figure 2: (A) XRD plot of pure Cu nanowires , (B) XRD plot of CuO nanotubes

Figure 2 shows a representative XRD pattern of the pristine Cu nanowires and CuO nanotubes. The peaks of Cu (JCPDS 00-001-1241) are observable for Cu. Moreover, the intensity of the peaks at 42°, 46°, 67° and 77° for pure nanowire. The peaks of CuO (JCPDS 01-078-2076) are observable for CuO. Moreover, the intensity of the peaks at 30°, 35°, 37°,50º, 62°, 68º, 75º for CuO nanotubes peaks are observable

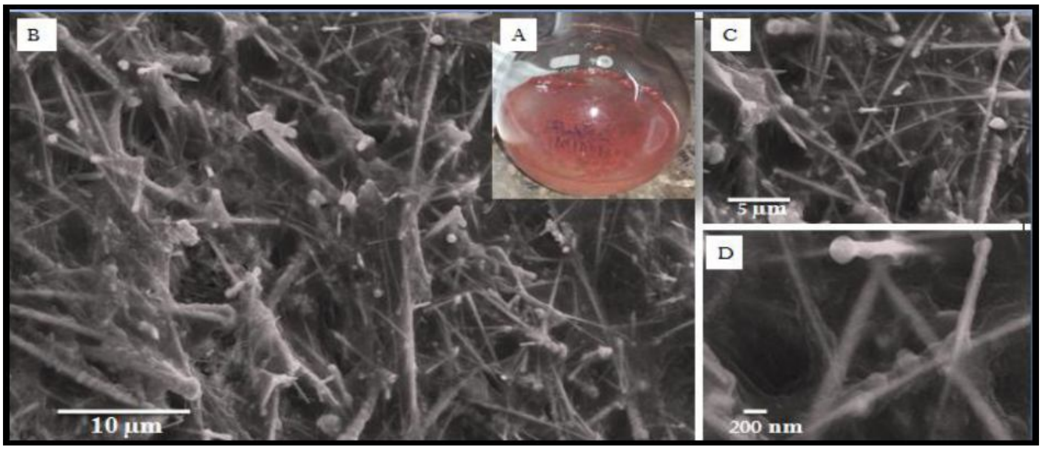

Figure 3: (A) As prepared Cu nanowires in mother liquor.(B,C,D) SEM images of general and detailed Cu nanowires.

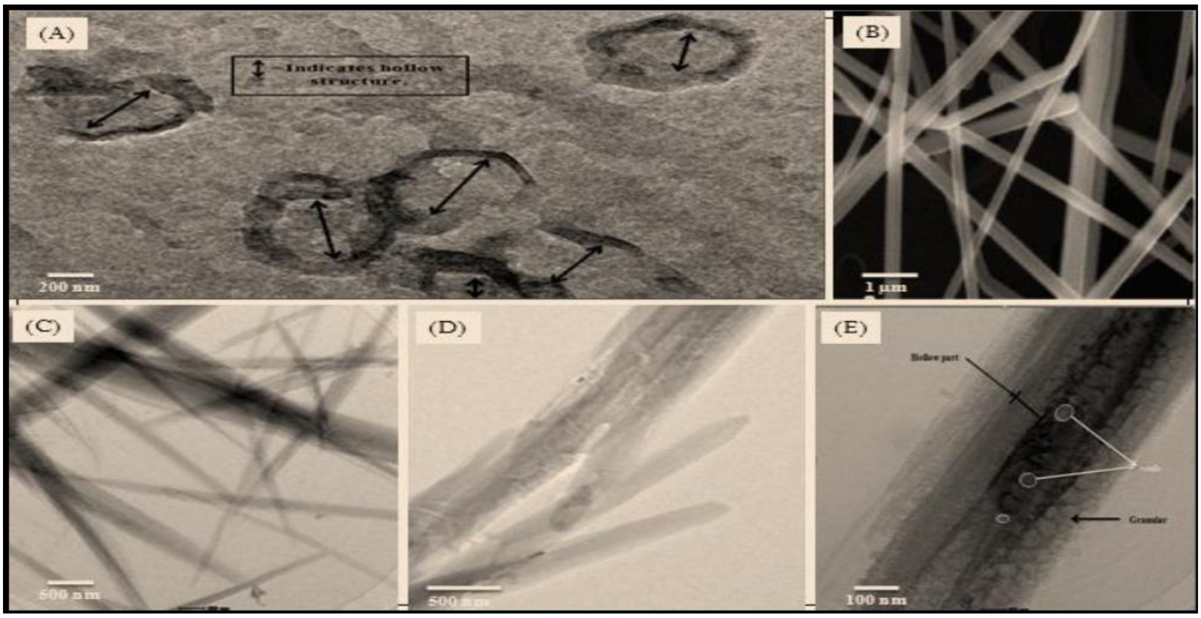

Figure 4 : (A) TEM image showing hollow nanosphere. (B,C,D) TEM image of polycrystalline CuO nanotubes formed at 400ºC for 6 hr. (E) Single nanotube showing formation of voids and granular pores on the surface.

Figure 3 shows some SEM images of copper nanowires. Interestingly, the as-prepared nanowire cake is lifted up to the top of solution, due to the high density of solution and entrapping of nitrogen bubbles among the nanowires after magnetic stirring. Our experiments indicate that a high concentration of NaOH is essential to prevent the copper ions from forming copper hydroxide precipitates. On the other hand, a certain amount of EDA is also indispensable to control product morphology. The interplay between NaOH and EDA had been recognized in this work. For example, with a high concentration of NaOH, the needed amount of EDA is small, while for a lower concentration of NaOH, the amount of EDA has to be increased accordingly in order. With a moderate amount of EDA, both wire and disk like morphologies could be obtained.

To obtain high regularity for the 1D product As shown in these images, the prepared nanowires are straight, with constant diameters in the range of 60-160 nm (mostly in 90-120 nm). The wires are ultralong, having lengths of more than 40μm.

Nonetheless, this surface oxidation can be prevented by storing the nanowires in dilute hydrazine solution. Apart from their electric conductor applications, thecopper nanowires prepared can also be used as a solid precursor for fabrication of other nanostructures. straight polycrystalline CuO nanotubes, which retain the original shape of Cu nanowires, have been fabricated from kirkendall effect . A significant fraction of pristine Cu could be converted to CuO after heating in air at 300ºC in just 10 min It is thought that the preformed surface CuO may provide good starting points for metal out-diffusion, during which copper moves preferentially toward the surface region while oxygen anions on the surface are relatively immobile. The hollowing mechanism of copper can also be explained with the Kirkendall effect Taking advantage of their interior space, the polycrystalline CuO (p-type semiconducting oxide) nanotubes may find new applications in photocatalytic reactions such as water splitting with visible lights. In summary, using low-cost starting chemicals, largescale synthesis of high-quality ultralong copper nanowires can be achieved under mild conditions. The prepared copper nanowires can also be used as starting solid precursor for fabrication of polycrystalline oxide nanotubes via kirkendall effect.

In figure (4A) indicates formation of hollow nanospheres and where as in (B,C,D) TEM images shows polycrystalline CuO nanotubes formed at 400ºC for 10 hr. Figure (4E) shows single hollow CuO nanotubes. Figure5 shows the SAED pattern which shows crystalline and polycrystalline behaviour .EDX graph shows the presence of Cu.

Hence, samples prepared for use as the electrode in supercapacitors were tested and compared. CV tests were conducted in a three-electrode system using 1 M KOH as electrolyte. The CV curves of the samples at scan rates ranging from 1 to 100 mV s−1 in 1 M KOH aqueous electrolyte are shown in Figures (6A,B). The quasi-rectangular curves of the sample at low scan rate (10 mVs−1) suggest the excellent pseudocapacitive nature . The capacitance of 12 mF g−1. Capacitance decreases as scan rate increases as shown in figure (6C).

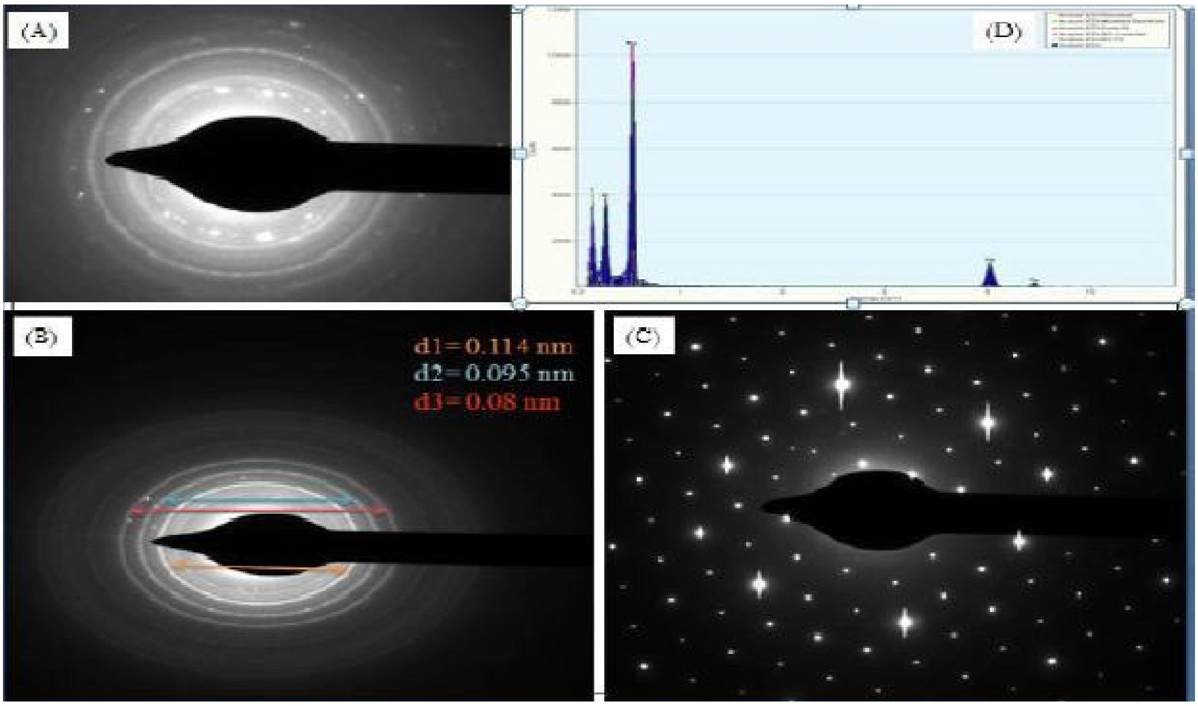

Figure 5: (A,B,C) SEAD pattern of CuO nanotubes formed in air at 400ºC for 6 hr (D) EDX plot showing Cu peak.

The capacitance of different clusters was estimated according to the following equation:

$$Csp = \frac{\int Imax\, dv}{A \times scan\ rate \times PD}$$

where Csp is the capacitance, (scan rate×PD) is the potential scan rate (mV/s-1), A is the selected area and Imax is the current response (mA)[6].

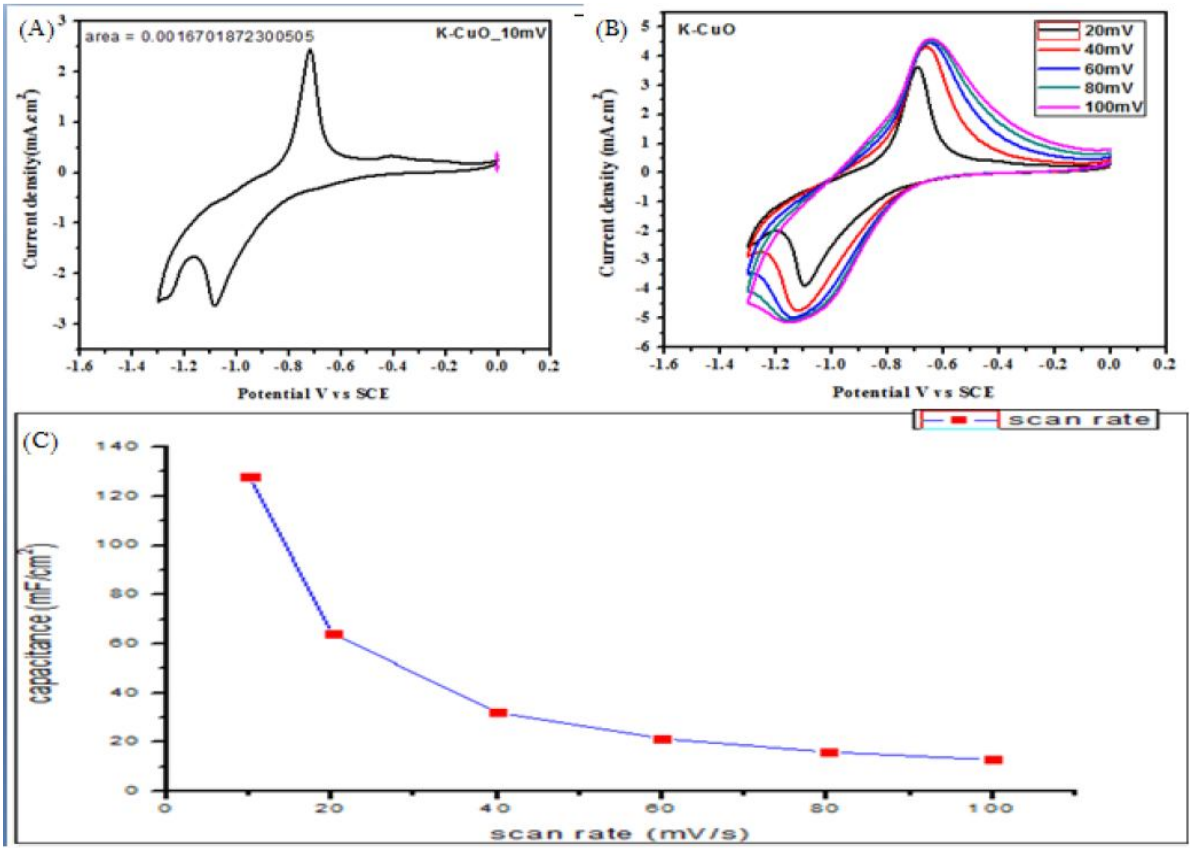

Figure 6: (A) The CV curves of CuO sample at 10 mV scan rates (B) The CV curves of CuO sample at all scan rates. (C) Plot of capacitance and scan rate

CONCLUSION

The Kirkendall effect has been considerably developed and used as a powerful process to synthesize hollow nanostructure of different shapes. A conceptual extension for the formation of hollow nanostructure initiated by the kirkendall effect is proposed, suggesting that surface diffusion processes might be dominant mass flow mechanism responsible for the enlargement of the interior pores after initial nucleation and formation induced by Kirkendall effect. In this work Cu nanowires are produced of diameter 100 to 200 nm with length upto 40µm. CuO nanotubes are report, of diameter 400nm to 500nm with hollow diameter between 300-400 nm. Another perspective which deserves to be pointed out is the TEM 3D tomography of Kirkendall nanospheres and nanotubes. This would allow better comprehension of the hollowing mechanism similar to some other process such as the galvanic replacement, which has already been monitoring using TEM tomography[10]. One of the important perspective of this research is the understanding of the Kirkendall-induced hollowing process at the atomic levels using computer modelling.

ACKNOWLEDGMENT

This work was done in physics department shivaji university Kolhapur. I thank Prof (Dr).P.S.Patil and Prof Dr.K.K.Sharma for constant guidances, support & suggestion throughtout this project.

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