Growth of copper oxide nanorods

Nanoforms of materials have drawn considerable interest in the recent years because of their wide range of applications in semiconductors for band tailoring, magnetic nanoparticles for giant magneto-resistance materials and CoO nanoparticles in Li batteries[1]. In the nanoform, optical and electronic properties get modified compared to its bulk counterpart, because of large surface-to-volume ratio. The transition-metal oxides find applications in many fields like magnetic storage media, electronics, catalysis[2] and solar-energy transformation. Amongst them, copper oxide (CuO) finds a place in several high-temperature superconductors[3,4] and in photoconductive[5] and photothermal[6] applications. There are several routes

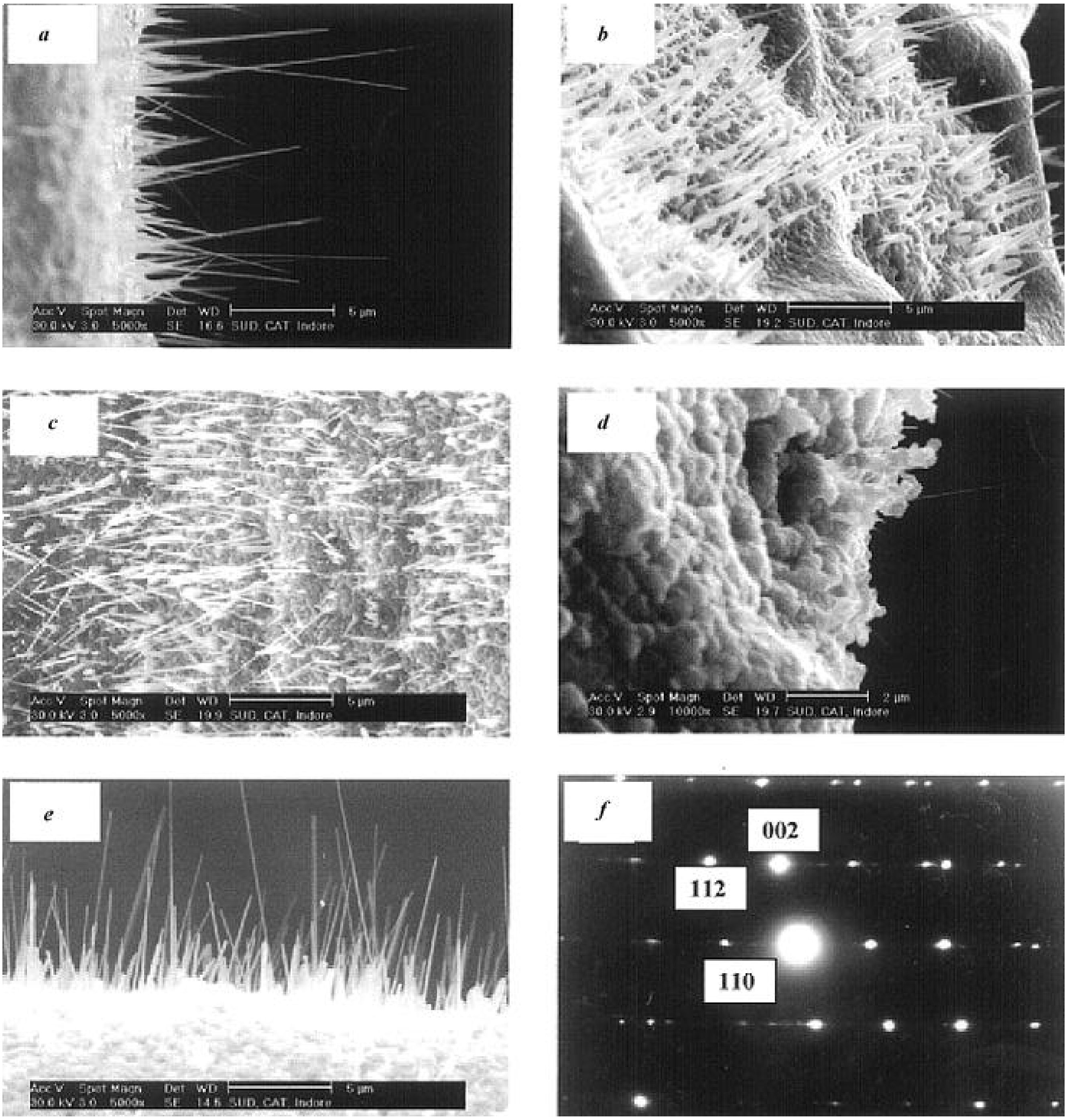

Figure 1. Formation of CuO nanorods at oxygen flow rate of (***a***) 35 ml/min, (***b***) 150 ml/min, (***c***) 300 ml/min, (***d***) 500 ml/min, (***e***) in air. *f* Selected area electron diffraction pattern of a single CuO nanorod.

through which CuO nanoparticles can be formed, like microwave irradiations[7], alcothermal route[8], sol-gel[9] technique, one-step solid-state reaction method at room temperature[10], electrochemical methods[11], etc. However, studies on the synthesis of CuO nanorods are sparse. CuO nanofibres have been fabricated by thermal evaporation[12], thermal decomposition of precursor[13] of $Cu_2C_2O_4$ or by combination of electro deposition and self-catalytic mechanism.

Here we report a simple route for the synthesis of CuO nanorods by annealing a copper foil. This method of synthesis of CuO nanorods was found to be convenient and fast. Annealing of copper foil leads to the formation of CuO nanorods spread in a large area. In order to study the effect of oxygen flow rate on the growth of nanorods, we have carried out the synthesis process in different oxygen flow-rate conditions. Samples prepared under similar conditions of growth gave nanorods of similar diameter and length, indicating that this method of synthesis of nanorods is reproducible.

Synthesis of CuO nanorods was carried out on a copper foil. The commercial-grade copper foil (0.1 mm thickness) was cleaned by dipping once in dilute hydrochloric acid. Then the foil was thoroughly washed in de-ionized water and finally ultrasonically cleaned in methanol for 15 min. The cleaned copper foil was loaded in a silica tube and the tube was put in a resistive-heating horizontal furnace at 500°C for 30 min. Different samples were prepared by annealing at 500°C in 35, 150, 300 and 500 ml/min of oxygen flow. Annealing of foil was also carried out in air to know the effect of a mixture of gases on the growth of CuO nanorods. Samples were characterized in Philips XL30CP scanning electron microscope (SEM), operated at 30 kV. Transmission electron microscopy was carried out on Philips CM200 microscope operated at 200 kV. The microscope was used both in imaging and diffraction mode. Energy-dispersive X-ray analysis was also carried out to confirm the elemental composition of nanorods.

In order to study the influence of oxygen flow rate on the growth of CuO nanorods, different samples have been prepared under oxygen flow of 35, 150, 300 and 500 ml/min and in air. Figure 1 *a* shows the SEM image of the sample prepared at a flow rate of 35 ml/min. The image shows the growth of nanorods perpendicular to the surface of the substrate (copper foil). The length of the nanorods is found to be in the range 5–10 μm and the diameter, 100–150 mm. The growth of these nanorods has been seen through the pores formed on the oxide film grown on the copper foil. Figure 1 *b* shows the SEM image of the sample prepared at a flow rate of 150 ml/min. The density of the nanorods has been found to be much more compared with the sample prepared at an oxygen flow rate of 35 ml/min. The length of the nanorods in this sample ranges from 10 to 15 μm and the diameter ranges from 70 to 100 mm. The growth of nanorods in this condition is found to be in the form of bundles. These bundles originate from all the pores formed on the oxide film. The porosity of the film has also increased drastically. At this flow rate, hill- and valley-type of structures have been observed and the growth of nanorods preferentially occurs in the valley regions.

Further increasing the oxygen flow rate to 300 ml/min reduces the density of nanorods and the length of nanorods reduces to < 5 μm (Figure 1 *c*). The diameter of the nanorods remains more or less same as in the previous case. Though the hill- and valley-type structures have still been observed, the porosity of the oxide film reduces to a large extent. Oxygen flow rate of 500 ml/min produces few nanorods (Figure 1 *d*). This indicates that flow rate of oxygen influences the growth of CuO nanorods. In order to study the effect of a mixture of gases on the formation of nanorods, we have annealed the copper foil in air at 500°C for 30 min. Figure 1 *e* shows the SEM image of the sample prepared at 500°C in air. As is evident from Figure 1 *e*, nanorods have been formed. The length of the nanorods is found to be 5–10 μm and diameter, 100–125 nm. Air annealing also forms porous oxide film on the substrate. In order to confirm the phase of nanorods, i.e. CuO or Cu_2O type, we have performed electron-diffraction studies. Figure 1 *f* shows a representative electron diffraction pattern taken from a single nanorod. The diffraction pattern was indexed with lattice parameters: $a = 0.4684$ nm, $b = 0.3425$ nm, $c = 0.5129$ nm and $b = 99.47°$. The zone axis of the pattern has been found to be [– 110]. In the diffraction pattern we have observed some superlattice spots along the 110 direction, with some streaks. This shows that some disorder is present in the nanorods. Detailed studies are underway and the results will be forthcoming. Analysis of diffraction patterns reveals that the nanorods are of CuO. Energy-dispersive analysis also shows the presence Cu and O, which confirms that nanorods are of CuO and not of Cu.

From the present study it can be concluded that the proposed method for the growth of nanorods is quite effective. The growth of nanorods in all samples is nearly perpendicular to the substrate. Nanorods can also be formed by annealing the copper-foil in air at 500°C for 30 min. The optimum rate of flow of oxygen was found to be 150 ml/min. At this flow rate, largest lengths of nanorods have been observed.

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