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Synthesis and characterization of metal oxide nanorod brushes

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Abstract. **Nanorod brushes of α-Al_2O_3, MoO_3 and ZnO have been synthesized using amorphous carbon nanotube (*a*-CNT) brushes as the starting material. The brushes of α-Al_2O_3 and MoO_3 are made up of single crystalline nanorods. In the case of ZnO brushes, the nanorod bristles are made by the fusion of 15–25 nm size nanoparticles and are porous in nature. Metal oxide nanorod brushes thus obtained have been characterized by XRD, FESEM, TEM and Raman spectroscopy. Single crystalline ruby nanorods were obtained by introducing chromium ions during the synthesis of alumina rods.**

Keywords. **Metal oxide nanorods; nanorod brushes; alumina nanorods; MoO_3 nanorods; ZnO nanorods; ruby nanorods.**

1. Introduction

Synthesis of one-dimensional metal oxide nanostructures is getting enormous attention in recent years due to their potential applications in nanoelectronics, photonics, data recording media, gas sensing and gas storage (Rao and Govindaraj 2005). Though several transition metal oxides in the form of wires, tubes and rods were reported using various chemical and physical methods, synthesis of Al_2O_3 and MoO_3 nanorods has generated a great deal of interest owing to their improved mechanical and catalytic behaviour, nonlinear optical characteristics and unusual optical luminescence properties. For example, alumina nanorods for its excellent high temperature stability and high surface area find extensive applications in catalysis. Molybdenum trioxide, on the other hand, is being used as an oxidation catalyst and as a lubricant. Various approaches to synthesize these metal oxide nanorods involve vapour–liquid–solid growth, vapour–solid growth, laser ablation, solvothermal, electrochemical and carbothermal methods (Rao and Govindaraj 2005; Rao *et al* 2007). Al_2O_3 nanowires were obtained by vapour–liquid–solid growth in presence of SiO_2 and Fe acts as a catalyst (Valcarcel *et al* 1998; Tang *et al* 2001; Zhou *et al* 2002; Peng *et al* 2003). Satishkumar *et al* (1997, 2002) synthesized crystalline γ-Al_2O_3 and MoO_3 nanotubes through carbothermal route by coating the functionalized carbon nanotubes with aluminum isopropoxide. In a similar approach, Li *et al* (2005) reported the formation of single crystalline alumina using mesoporous carbon aerogels as substrate and aluminum nitrate as the source. Short alumina naotubes have also been fabricated by controlling anodization process of aluminum in dilute sulfuric acid (Pu *et al* 2001; Zou *et al* 2002). Xiao *et al* (2002) electrodeposited alumina inside the pores of alumina membrane and finally etched out the membrane using aqueous NaOH solution to obtain alumina nanotubes and nanowires. Lee *et al* (2003) synthesized alumina nanowires by hydrothermal method in presence of surfactants. α-Al_2O_3 nanobelts and nanosheets with different morphologies and size have been prepared by a chemical route from H_2O and Al in argon atmosphere at high temperatures (Fang *et al* 2003). Hwang and coworkers (2004) synthesized amorphous Al_2O_3 nanotubes by atomic layer deposition of alumina on ZnO core followed by etching the ZnO. Indeed, similar methods were adopted for the preparation of MoO_3 nanowires and nanotubes by several researchers (Niederberger *et al* 2001; Lou and Zeng 2002; Song *et al* 2005; Xia *et al* 2006). In all these cases, the one-dimensional morphologies obtained for Al_2O_3 and MoO_3 was mostly restricted to tubular and fibrous structures and no formation of aligned, single-crystalline nanorods were reported so far by any chemical route. In this report, we have synthesized crystalline Al_2O_3, MoO_3 and ZnO nanorod brushes using amorphous carbon nanotube (*a*-CNT) brushes as the starting materials. Amorphous carbon nanotube brushes (Dinesh *et al* 2007) were derived from the carbonization of glucose within the polycarbonate membranes. In our earlier studies we have shown that these *a*-carbon nanotubes can be successfully utilized to create gallium nitride (Dinesh *et al* 2007) and BC_4N nanotube brushes (Raidongia *et al* 2008). By introducing chromium during the synthesis, we also obtained single crystalline ruby nanorod brushes.

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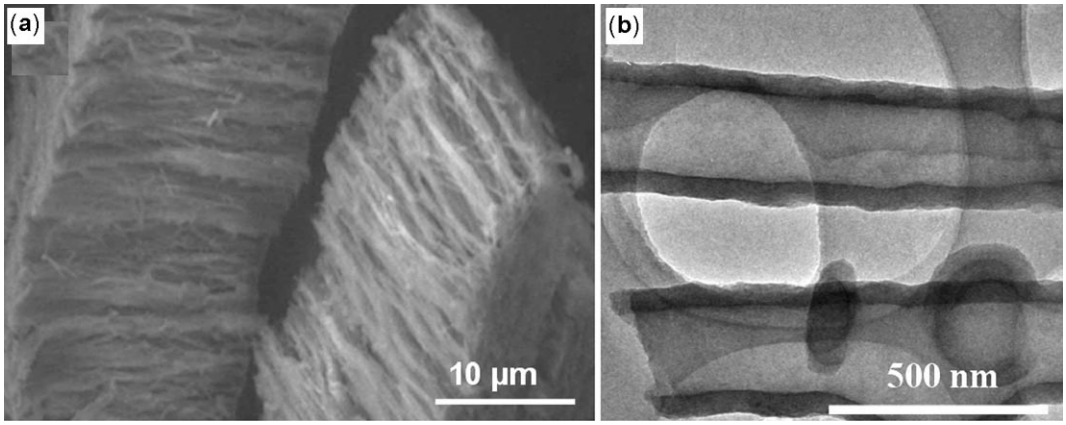


Figure 1. (**a**) FESEM image of *a*-CNTs and (**b**) TEM image of *a*-CNTs.

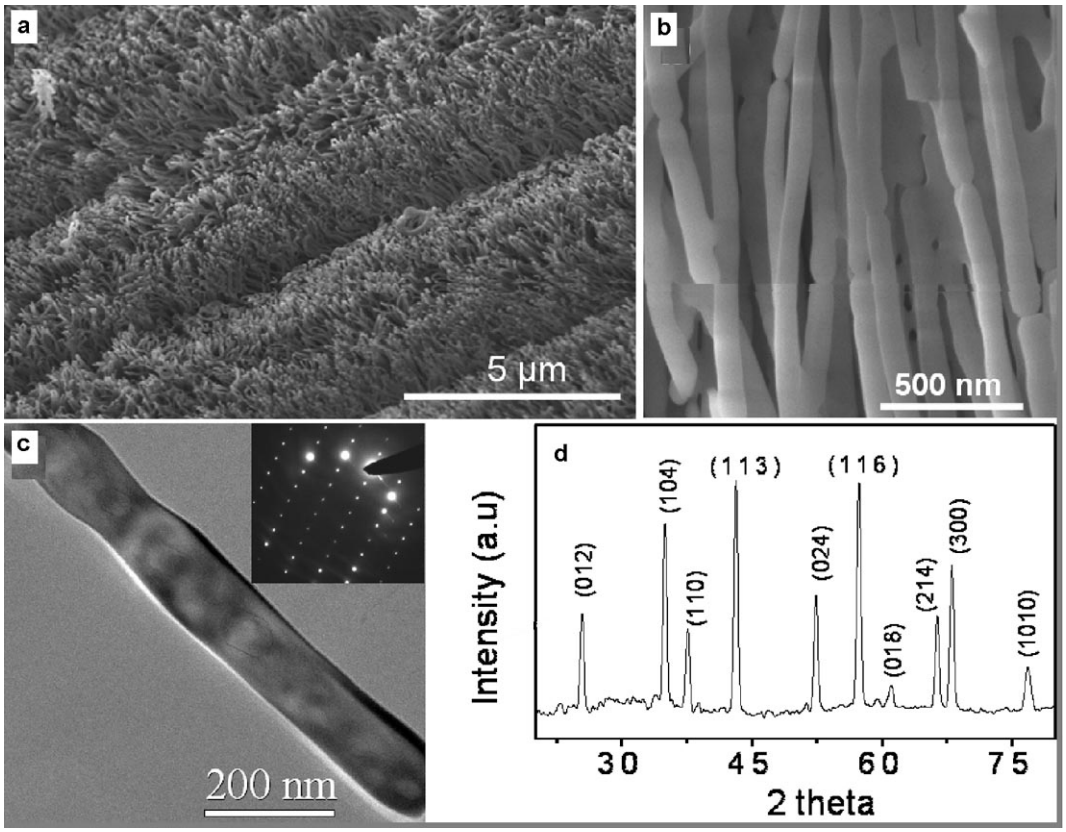


Figure 2. (**a**) FESEM image of α-Al_2O_3 nanorods, (**b**) higher magnification FESEM image of α-Al_2O_3 nanorods, (**c**) TEM image of a individual α-Al_2O_3 nanorods and (**d**) XRD of α-Al_2O_3 nanorods.

2. Experimental

Amorphous carbon nanotube (*a*-CNT) brushes were prepared by the following procedure (Dinesh *et al* 2007). Polycarbonate membranes with a pore diameter of 220 nm were soaked in 22 mL of 0·5 M aqueous solution of glucose in a 25 mL Teflon-lined autoclave. The temperature of the autoclave was maintained at 180°C for 6 h after which it was allowed to cool to room temperature. The brownish liquid, rich in carbon spheres was discarded. The membranes that had turned brown were washed with deionized water and ethanol several times and dried at 40°C for 1 h.

To obtain Al_2O_3 nanorods, the brown coloured membrane was first soaked in 0·5 M solution of aluminum nitrate nanohydrate for 12 h and then dried at 45°C for 5 h. The composite was further heated at 1100°C for 3 h to give white-coloured Al_2O_3 nanorods. Pink coloured ruby

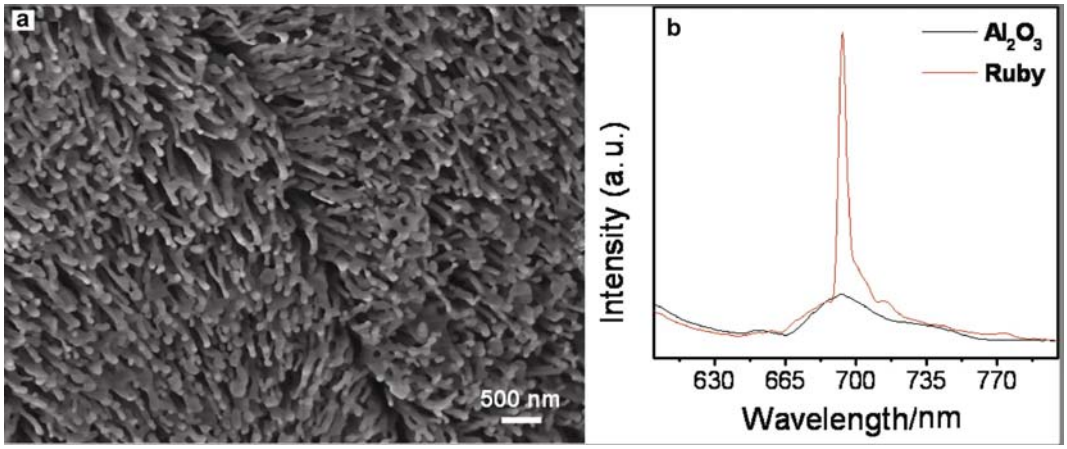


Figure 3. (**a**) FESEM image of ruby nanorods and (**b**) PL spectra of ruby and alumina nanorods.

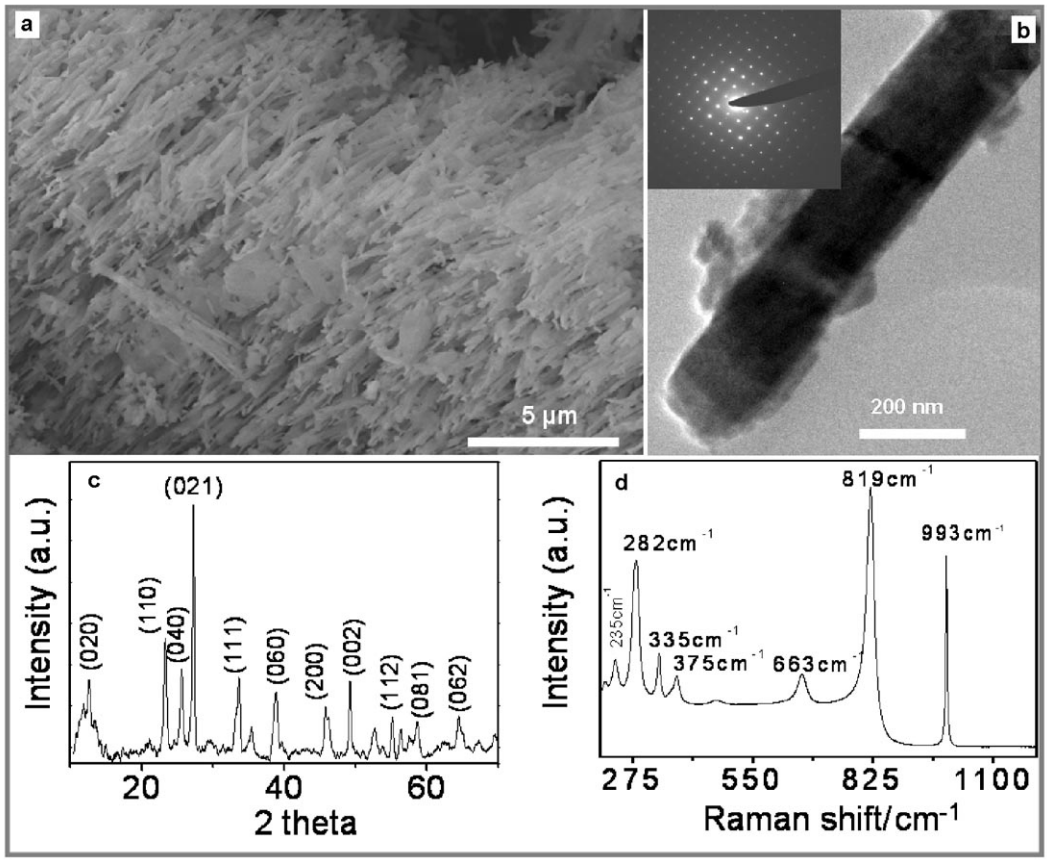


Figure 4. (**a**) FESEM image of MoO_3 nanorods, (**b**) TEM image of a individual MoO_3 nanorod, (**c**) XRD pattern of MoO_3 nanorods and (**d**) Raman spectra of MoO_3 nanorods.

nanorods were prepared by introducing 0·25 g (Cr/Al = 0·025) chromium nitrate nanohydrate along with the aluminum nitrate precursor during the synthesis. For MoO_3 rods, the membrane was soaked in the 0·028 M solution of ammonium heptamolybdate tetrahydrate for 12 h followed by drying at 45°C for 5 h. In the case of ZnO nanorods, 0·5 M solution of zinc nitrate was used. The Zn and Mo precursor loaded composite membranes were thermally treated at 430°C for 3 h to obtain bluish-coloured MoO_3 and white coloured ZnO nanorod brushes. The products were investigated by electron microscopy and other physical techniques.

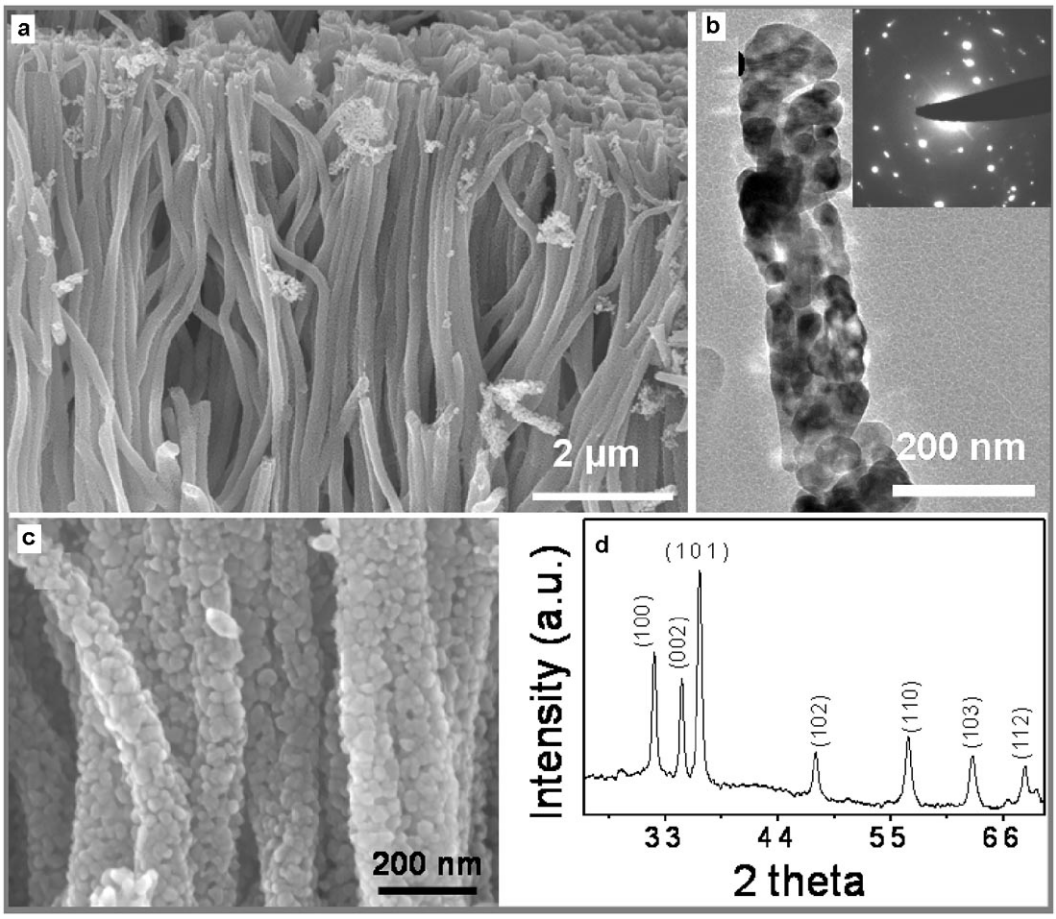


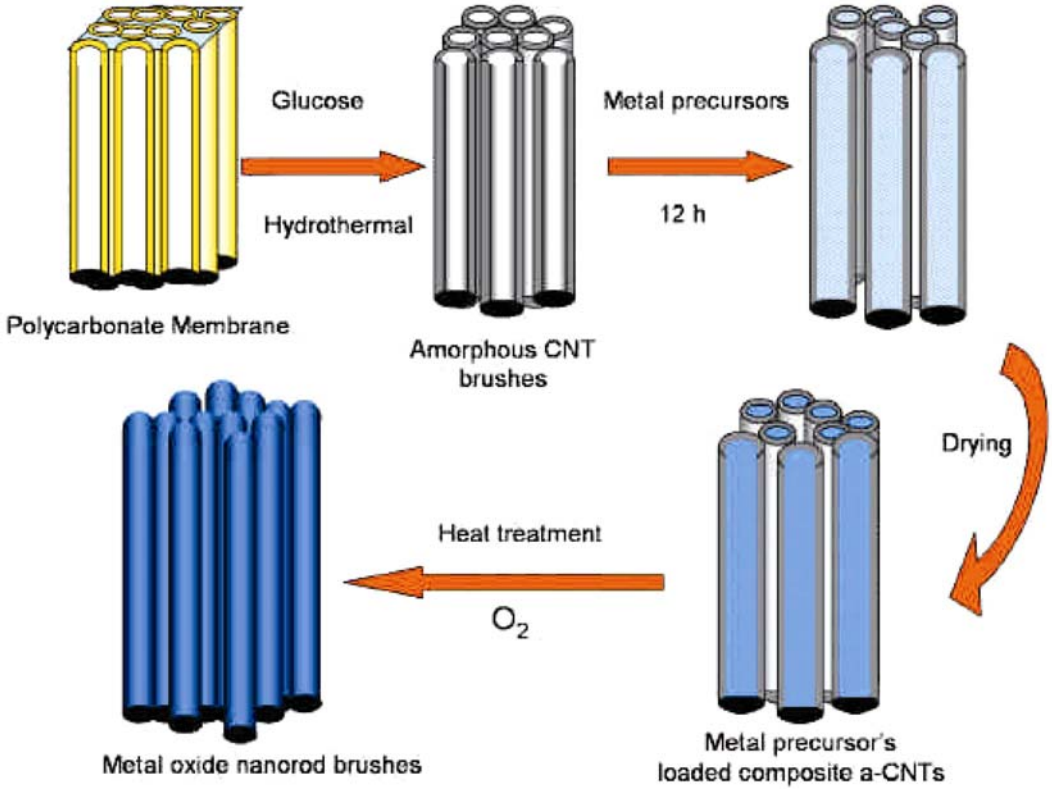
Figure 5. (**a**) FESEM image of ZnO nanorods, (**b**) higher magnification FESEM image of ZnO nanorods, (**c**) TEM image of a individual ZnO nanorod (inset ED pattern on the nanorod) and (**d**) XRD pattern of ZnO nanorods.

3. Characterization

X-ray diffraction (XRD) patterns were recorded at 25°C with a Rich-Siefert 3000-TT diffractometer employing CuKα radiation. The morphology of the nanotubes was examined by a field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, Netherlands), and scanning electron microscope (SEM) Leica S-440I instrument (UK). TEM images were recorded with a JEOL JEM 3010 instrument (Japan) operated at an accelerating voltage of 300 kV. Raman spectra were recorded with a LabRAM HR with 633 nm line from HeNe laser. Photoluminescence studies were done by using Perkin Elmer LS 50B instrument using a Xe lamp source.

4. Results and discussion

In figure 1a we show a FESEM image of *a*-CNTs, after dissolution of polycarbonate membrane using dichloromethane. All the nanotubes are well aligned and packed together as brushes. The length of the nanotube is around 15 μm. The outer diameter of the nanotube is around 250 nm with a wall thickness of 45 nm (figure 1b). Calcination of amorphous carbon membrane filled with aluminum precursor at high temperature (1100°C) yields crystalline alumina nanorods with brush-like morphology analogous to *a*-CNT brushes. Figure 2a shows a low magnification FESEM image of α-Al_2O_3 nanorods in which all the nanorods are well aligned and packed together covering a large area. The high magnification FESEM image of the rods in figure 2b, viewed perpendicular to the rod axis, shows a smooth surface with occasional joints all along their length indicating the end to end fusion of alumina nanorods of 1 μm length. A TEM image of an individual nanorod shown in figure 2c reveals that the diameter of the tube is around 150 nm. Inset of figure 2c is the corresponding electron diffraction pattern revealing single crystalline nature of the nanorods. The XRD pattern of the Al_2O_3 nanorods shows all the reflections indexed to pure α-Al_2O_3 corundum structures with cell parameters, a = 4·758 Å and b = 12·99 Å (JCPDF card No: 461212). The sharp peaks in the XRD pattern reflect the crystalline nature of the nanorods, supporting the electron diffraction pattern.



Scheme 1. Scheme showing the synthesis of metal oxide nanorod brushes.

Cr-doped single crystalline α-Al_2O_3 (ruby) is the first solid state laser invented in 1960 (Mayman 1960). Ruby is still used in a number of applications where short pulse of red light is required. Ruby produces a pulse of visible light with a wavelength of 694 nm. Nanorods of ruby were not reported hitherto. We have obtained single crystalline ruby nanorods by introducing chromium ions during the synthesis of single crystalline alumina rods. A FESEM image of well-aligned ruby nanorods is shown in figure 3a. In figure 3b the photoluminescence properties of the ruby nanorods is compared with the α-Al_2O_3 nanorods. The intense PL peak of ruby nanorods at 693·5 nm is several times stronger than the α-Al_2O_3 nanorods. In addition, it shows a very sharp emission peak, with narrow bandwidth as against the broad emission peak for alumina. The characteristic $R1$ and $R2$ peaks of ruby merge to a single peak due to temperature broadening and low-resolution power of the instrument.

In figure 4a we show a FESEM image of MoO_3 nanorods exhibiting brush like morphology similar to that of a-CNTs brush template. The average diameter of the nanorods is around 190 nm. The length of the nanorods is <2 μm and is not up to the thickness of the membrane suggesting the discontinuity in the structure. TEM image shown in figure 4b confirms the rod-like morphology of MoO_3. The electron diffraction pattern shown in the inset of figure 4b indicates that the nanorods were single crystalline. Figure 4c shows the XRD pattern of MoO_3, the strong intensity of the peaks indicates high crystallinity of the nanorods. All the peaks can be indexed to the pure phase of α-MoO_3 with orthorhombic structure and lattice parameters, a = 3·96 Å, b = 13·86 Å and c = 3·7 Å (JCPDS card number 05-0508). The nanorods show the characteristics Raman bands for the MoO_3 crystal (figure 4d) at 235 (B_{3g}), 282 (B_{2g}, B_{3g}), 335 (B_{1g}, A_g), 375 (B_{1g}), 663 (B_{2g}, B_{3g}), 819 (A_g, B_{1g}) and 993 (A_g, B_{1g}) cm^{-1}.

Figure 5a shows a FESEM image of aligned ZnO nanorods obtained through the a-CNT template. In contrast to Al_2O_3 and MoO_3, ZnO nanorods are made up of small nanoparticles of around 15–25 nm diameter. The diameter of the nanorods is in the range of 150–180 nm with lengths of about 15 μm. TEM image shows that nanoparticles are fused randomly to form a nanoporous rod. The electron diffraction pattern shown in the inset of figure 5b confirms the polycrystalline nature of the nanorods. The broad peaks observed in the XRD pattern further support our observation that the nanorods are composed of ZnO nanoparticles. These porous nanostructures might have high surface area with good potential applications.

5. Conclusions

In conclusion, we have utilized the amorphous carbon nanotube brushes as template to prepare single crystalline

nanorod brushes of Al_2O_3 and MoO_3 and polycrystalline brushes of ZnO. We believe that the presence of carboxylic and phenolic functional groups present on the surface of *a*-CNT helps to hydrolyze the metal precursors within the voids of the membrane which would subsequently form a polymer network (scheme 1). Further calcination at high temperatures, coupled with the exothermic heat generated by the combustion of carbon facilitates the formation of crystalline nanorods of metal oxides.

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