

The formation of copper oxide nanorods in the presence of various surfactant micelles

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Abstract: Copper oxide nanorods with average diameters and lengths of *ca.* 8 nm and 400 nm, respectively, have been prepared by a simple one-step solid-state reaction in the presence of various surfactant micelles. The effect of three different surfactants viz., SDS, CTAB and Triton X-100 and their critical micellar concentration (CMC) on the formation of nanorods has been studied using XRD, TEM, DSC and XPS techniques. It is found that the formation of the nanorods in the presence of SDS micelles is better with higher thermal stability and possessing lower binding energy with regard to Cu_{2p} peak.

Keywords: nanostructures; X-ray diffraction topography; Differential scanning calorimetry (DSC), oxides

Introduction

Organized inorganic nanopore networks find potential use in catalysis (Tanev *et al.*, 1994; Burch *et al.*, 1996), separating technology (Barres, 1982) and biomaterials engineering (Ohgushi *et al.*, 1992; Guillemin *et al.*, 1987). One-dimensional (1D) nanoscale materials are currently of great interest due to their unique electronic, optical, and mechanical properties (Jiang *et al.*, 2000; Zhu *et al.*, 2002; Duan *et al.*, 2003). Owing to these reasons, many researchers worldwide have focused their attention to synthesize one-dimensional nano materials. The existing methods for synthesizing such nano particles are complex, energy intensive and require high temperatures and long durations (Lin & Mou, 1996; Liao *et al.*, 2001). Hence, the need arises to develop a simple way to synthesize these materials. Surfactant templates are generally employed in the synthesis of the same. Suspended single-walled carbon nanotubes and many nano materials formation in presence of surfactant and mixed surfactant systems have been reported (Hao *et al.*, 2004; Moore *et al.*, 2003). The effect of sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) on morphologies of gold nanoparticles in the presence of poly (amidoamine) dendrimers has been reported recently (Bakshi *et al.*, 2006). A novel and simple one-step solid-state reaction in the presence of a suitable polyethylene glycol viz. PEG-400 has been reported (Wang *et al.*, 2001) recently to

synthesize uniform copper oxide nanorods. The formation of a rod shape of copper oxide could be due to the surfactant assemblage, because PEG in water can form a chain structure (Sun *et al.*, 2000). However, to the best of our knowledge, low molecular weight PEG in aqueous solution does not form micelles. Therefore, in this investigation, we have used various surfactants viz. sodium dodecylsulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 as real micelle-forming agents for the first time in synthesizing copper oxide nano materials. The reason for using the above surfactants is also to understand the effect of different charges (anionic, cationic and neutral) and concentrations (below CMC and above CMC) of the surfactants on the formation of nanorods. In order to address the question of whether the micelles act as catalyst or template for the preparation of the nanorods, we have synthesized the above materials using surfactants below and above their critical micelle concentration (CMCs) with a view to stimulate further studies.

In this paper, copper oxide has been chosen owing to its varied technological applications (Berry *et al.*, 1988; Malandrino *et al.*, 1997a,b). It is the basis for several high-T_c superconductors. The CuO is a *p*-type semiconductor with a band gap of 1.2 eV commonly studied for its photoconductive properties and photothermal applications (Rakhshani, 1986; Wu *et al.*, 1987). Cu₂O and related materials are the subject of much current interest for use in high performance batteries (Poizot *et al.*, 2000).

Materials and methods

Materials

CuCl₂·2H₂O and NaOH of analytical grade purity were purchased from Ranbaxy Chemicals, India. Regarding grade, purity and characteristics of the surfactants, we have described in details in our earlier publications (Mandal *et al.*, 1980; Mandal, 1993; Mandal & Nair 1991; James *et al.*, 2005).

Methods

3.020 g of CuCl₂·2H₂O and 2 g of NaOH were ground for 5 min each before mixing together; 5 g of SDS (a) / CTAB (b) / Triton X-100 (c), was then added to the mixture. After 30 min grinding, the mixture was washed in an ultrasonic bath three

times with distilled water. Finally, it was air dried at 65°C for 2 h. In another set of experiments, the above procedure was followed using very small amount of surfactants so that the concentrations of the surfactants are below their CMCs. X-ray powder diffraction was carried out on a Shimadzu XD-D1 X-ray diffractometer with Cu-K α radiation

Fig. 1. XRD patterns of as-prepared copper oxide nanorod samples prepared using (a) SDS, (b) CTAB and (c) Triton X-100 micelles.

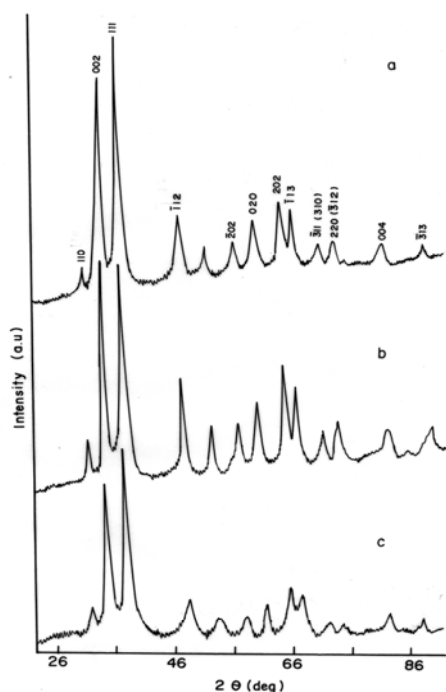
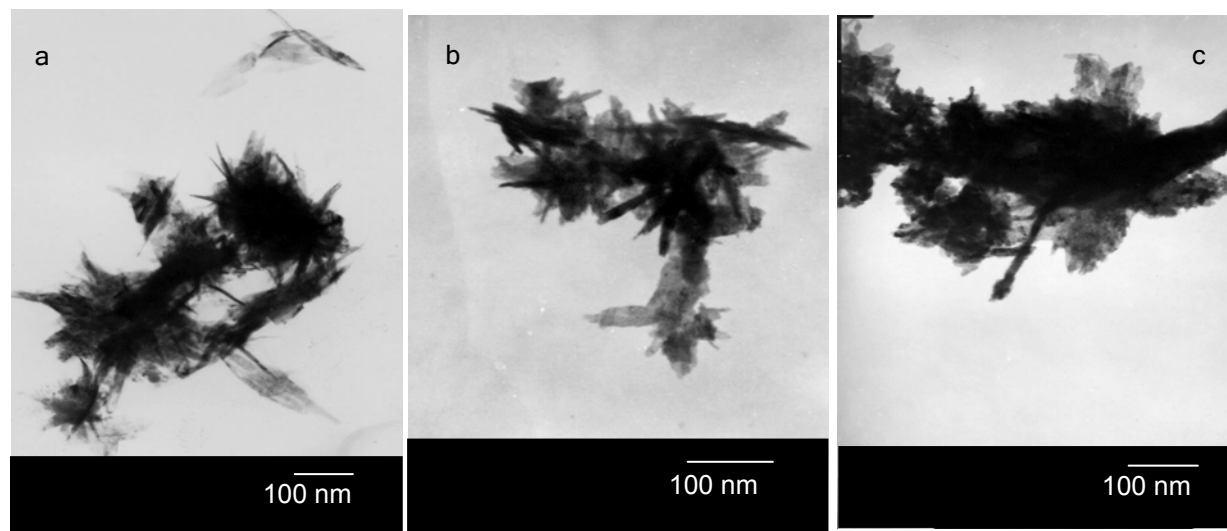


Fig. 2. TEM images of as-prepared copper oxide nanorod samples prepared using a) SDS, (b) CTAB and (c) Triton X-100 micelles.



($\lambda=1.5405 \text{ \AA}$). Transmission electron microscopy (TEM) micrographs were taken using a JEOL EM1200 Ex II transmission electron microscope, with an accelerating voltage of 80 kV. The samples were fused in a differential scanning calorimetric cell of a Mettler Toledo Star system differential scanning calorimeter (DSC). The temperature was calibrated effectively using indium as standard. The heating rate was 10°C/min and temperature was varied from 30 to 600°C under N₂ atmosphere. The XPS measurements were conducted with a Kratos XPS Axis 165 spectrometer equipped with hemispherical energy analyzer. The non-monochromatized AlK α X-ray source was operated at pass energy of 160 eV with an increment of 0.1 eV. The binding energy of C 1s core level (binding energy = 284.6 eV) of adventitious hydrocarbon was used as a standard. The XPS spectra were fitted using a non-linear least square method with the convolution of Lorentzian and Gaussian functions after a polynomial background was subtracted from the raw spectra.

Results and Discussion

The obtained powders were characterized by X-ray powder diffraction (XRD) (Fig. 1 a, b, c). Powder XRD peaks of the copper oxide are consistent with the data of the JCPDS file (*JCPDS International center for Diffraction Data*, 1991). The peaks at 2θ values of 32.53, 35.41, 38.73, 45.20, 48.86, 53.53, 58.63, 60.27, 67.98, 74.94 and 81.27° correspond to the crystal planes of 110, 002, 111, $\bar{1}12$, $\bar{2}02$, 020, 202, $\bar{1}13$, 220($\bar{3}12$), 004, $\bar{3}13$ of crystalline copper oxide, respectively, which are in good agreement with the recent observations (Wang *et al.*, 2001). It could be seen

that the XRD patterns for all the three samples are same except for varying intensity and broadness of some of the peaks. The nano particles so obtained have rod like structure according to transmission electron microscopy studies with diameter of *ca.* 8 nm and length of *ca.* 400 nm (Fig. 2 a, b, c). The TEM picture for the copper oxide nanorods in the presence of SDS micelles is sharp compared to the other two (i.e., in CTAB and Triton-X-100 micelles). The XRD pattern correlates with respect to the fact that in nanoparticles since there are not many atomic layers, the pattern can be somewhat diffuse (Fig. 1a), which is however, less than that for a thicker crystal where it can be very sharp (Fig. 1b). Crystals have not formed well with Triton X-100. The TEM and XRD pattern show less crystallinity and presence of more amorphous

Fig. 3. DSC thermograms of as-prepared copper oxide nanorod samples prepared using (a) SDS, (b) CTAB and (c) Triton X-100 micelles.

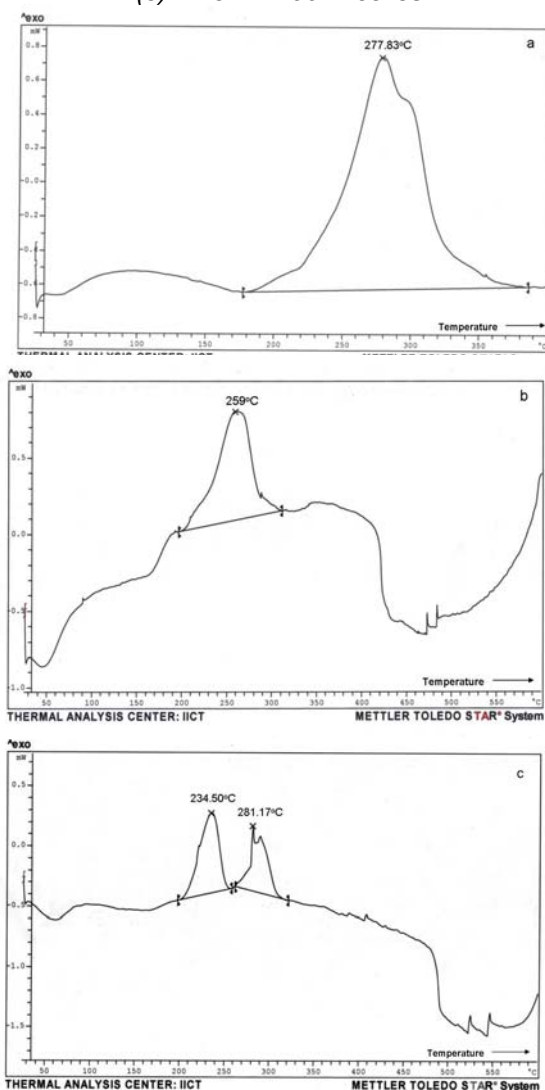


Table 1. Exothermic peaks of as-prepared samples in the presence of three different surfactants with concentration below and above CMC from DSC studies

Surfactant	Peak temperature (°C) Above CMC	Peak temperature (°C) Below CMC
SDS	278	275
CTAB	259	258
Triton X-100	234	230

compound (Hwang *et al.*, 2001). The low molecular weight anionic surfactant viz. SDS gives better nanoparticles compared to CTAB and Triton X-100. Our results are in good agreement with the recent results obtained by Bakshi *et al.* (2006).

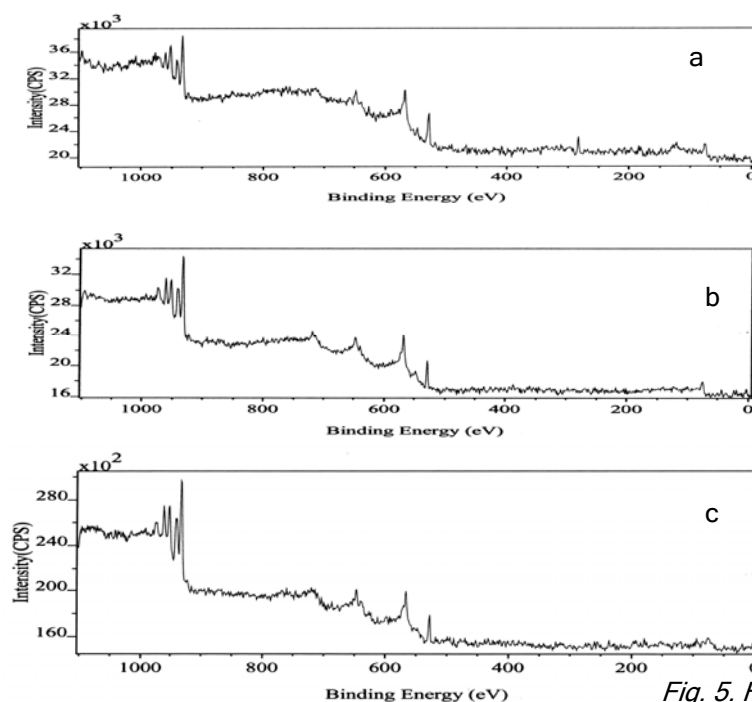
We have chosen Triton X-100 because the hydrophilic head group of Triton X-100 containing 9 oxyethylene units (Mandal *et al.*, 1980), which is equivalent to PEG-400. Controlled aging of TiO₂ nanoparticles blended with diblock copolymers and processed into dip-coated thin films led to ordered nanostructures with cubic and hexagonal symmetries that can be transformed into mesoporous TiO₂ by using some steps has recently been reported (Hwang *et al.*, 2001). Monodispersed nanocrystalline CeO₂ powders of size *ca* 2 nm displaying quantum size effects have recently been prepared (Liao *et al.*, 2001) by microwave irradiation in aqueous solution containing (NH₄)₂Ce(NO₃)₆, PEG and NaAc.

In order to better understand the components and thermal behavior of the as-synthesized product, we carried out DSC of the copper oxide nanorods. The DSC thermograms of the as-synthesized nanorods in the presence of SDS, CTAB and Triton X-100 show an exothermic peak centered at 278, 259 and 234°C, respectively (Fig. 3). It is interesting to note that there is another peak obtained at 281°C for the nanorod sample made in the presence of Triton X-100 (*cf.* Fig.3c). This may be due to the polydisperse nature of Triton X-100 surfactant micelles. It is seen that nanorods with SDS have more thermal stability compared to those based on other surfactants. The

Table 2. Binding energies peaks of Cu_{2p} for the as-prepared samples in the presence of three different surfactants with concentration below and above CMC

Surfactant	Binding energy (eV) Above CMC	Binding energy (eV) Below CMC
SDS	933.38	934.08
CTAB	933.64	934.26
Triton X-100	933.55	933.14

Fig. 4. Wide scan X-ray photoelectron spectra of the as-prepared CuO nanorod samples using (a) SDS, (b) CTAB and (c) Triton X-100 micelles.



exothermic peaks for as-synthesized nanorods in the presence of SDS, CTAB and Triton X-100 below and above CMCs are shown in Table 1. It can be seen that the thermal stability of nanorods prepared above CMC is more when compared to that synthesized below CMC.

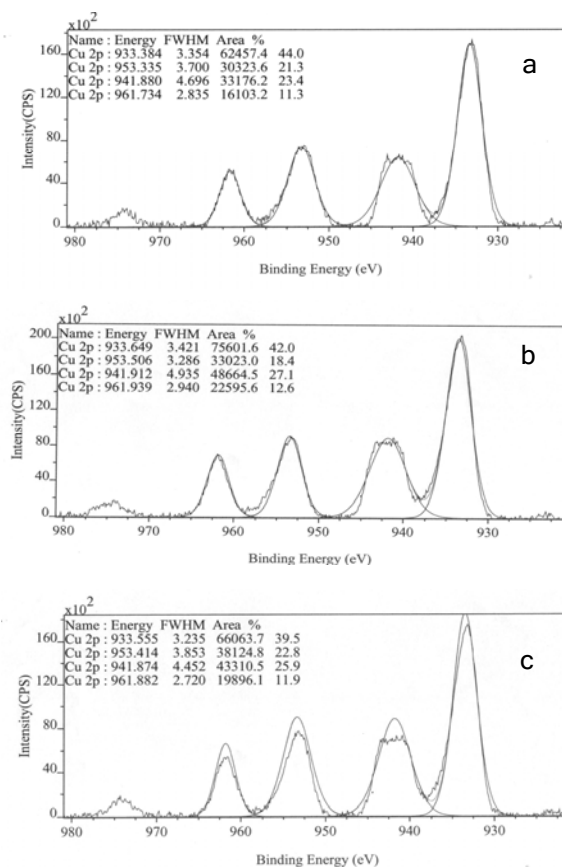
The binding energies of the metals in the as-synthesized samples were probed by XPS. The wide scan XPS spectra of the as-synthesized samples in the presence of different surfactant micelles are shown in Fig. 4. It can be seen that no other peaks except those corresponding to C, Cu and O are present in the spectra indicating the purity of the samples. The high resolution XPS spectra of the copper oxide nanorods in the presence of SDS, CTAB and Triton X-100 micellar concentrations are shown in Fig. 5. The Cu_{2p} peak lies at 933.38, 933.64 and 933.55 eV for nanorods in the presence of SDS, CTAB and Triton X-100, respectively with a satellite feature located at a higher binding energy by about 8.5 eV. These results are in agreement with those cited in the literature (Wang *et al.*, 2002). In order to find the effect of concentration of surfactant on the binding energies, XPS analysis for nanorods prepared in the presence of surfactants below CMC was also carried out. The graphical representations of XPS measurements carried out for samples prepared below CMCs are not shown here to save journal space. However, the data are presented in Table 2. It can be seen that for SDS and CTAB based CuO

nanorods samples, the binding energies for below CMC concentrations are 0.70 and 0.62 eV, respectively and are higher than that for above CMC samples, whereas for Triton X-100 based nanorods, a reverse trend is observed (*cf.* Table 2). It is well established that CuO and Cu₂O decompose at 1026 and 1235°C, respectively. However, in the present investigation of Cu-oxide nanorods formation, it is possible to prepare them even at lower temperatures. Therefore, the catalytic role of the surfactants can not be ignored in addition to template.

Conclusion

In conclusion, a simple method for synthesizing nanorods using various surfactants has been successfully developed. Although the nanorod formation of copper oxide in the presence of polyethylene glycol

Fig. 5. High resolution XPS spectra taken for Cu_{2p} of the as-prepared CuO nanorod samples using (a) SDS, (b) CTAB and (c) Triton X-100 micelles.



has been reported in the recent past, the above nanorod formation in presence of SDS surfactant micelles in our present investigation is superior to the reported one. The advantage of this process is that it is fast, simple and efficient with potential varied applications. The role of charge and concentrations of the surfactants in the preparation of the nanorods has been proved. It has been found that the formation of the Cu-oxide nanorods in the presence of anionic SDS micelles is better with higher thermal stability and possessing lower binding energy with regard to Cu_{2p} peak. This is due to the interaction between oppositely charged ions viz. anionic SDS micelles and cationic Cu metal. However, in CTAB micelles, repulsions are normally observed. The principles used in this work are simple and can be easily adapted to other metal oxide systems.

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