Materials Letters 146 (2015) 99–102

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Sheet, spherical and plate-like chromium sesquioxide (Cr_2O_3) nanostructures synthesized via ionic surfactants assisted facile precipitation method

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ARTICLE INFO

Article history:
Received 25 November 2014
Accepted 5 February 2015
Available online 11 February 2015

Keywords:
Chromium sesquioxide
Ionic surfactants
Morphological
Optical properties

ABSTRACT

Chromium sesquioxide (Cr_2O_3) nanostructures, assisted by various ionic surfactants such as sodium dodecyl sulfate (SDS), poly ethylene glycol (PEG) and cetyl trimethyl ammonium bromide (CTAB), were successfully achieved by the facile precipitation method with the average particle size of 35.05, 38.12 and 40.28 nm, respectively. The sheet, spherical and plate-like nanostructures were confirmed by SEM studies and a possible growth mechanism of the nanostructures were proposed. The increasing trends of the band gap energy confirm the quantum confinement effect for the prepared samples. The strong UV and weak visible emissions in photoluminescence indicate the high purity and perfect crystallinity of the prepared samples.

1. Introduction

One dimensional metal oxide nanostructures (sheets, rods, fibers, tubes, wires, ribbons) are of special interest due to their unique catalytic, electronic, optical, thermal and photonic properties, intrinsically associated with their low dimensionality and the quantum size confinement effect. Among the metal oxide materials, Cr_2O_3 has been recognized as one of the most important oxides with a wide band gap energy ($E_g = 3.4$ eV), in view of its numerous applications. Various techniques have been developed for the synthesis of Cr_2O_3 nanoparticles, such as hydrothermal, sol–gel, combustion, gel citrate, mechanochemical, urea assisted homogeneous precipitation, gas condensation, and microwave plasma. Among these methods, the precipitation method can control the grain size, crystalline phase, particles morphology and surface chemistry of the materials. By controlling the growth of the nanostructures, the various surfactants play an important role in the synthetic procedure, and lead to nanostructures with a controlled size and morphology [1–4].

Therefore, we present here the results of our study on the growth and optical properties of various ionic surfactants such as anionic-sodium dodecyl sulfate (SDS), nonionic-poly ethylene glycol (PEG) and cationic-cetyl trimethyl ammonium bromide (CTAB) assisted Cr_2O_3 nanostructures for application in the field of optoelectronic devices. Moreover, up to now, there has been no report on the synthesis of Cr_2O_3 nanostructures, by using different ionic surfactants via the facile precipitation method.

2. Experimental procedure

M of chromium nitrate and 1 g of SDS were dissolved in a 100 ml aqueous medium under vigorous stirring, and a precipitate was formed by the controlled addition of NaOH. The resultant precipitates were washed with distilled water and absolute ethanol, to remove the soluble impurities and dried at 120 °C for 12 h. Finally, greenish Cr_2O_3 nanopowders were formed, by calcining the dried precipitates at 400 °C for 2 h. The same procedure was followed for the preparation of the PEG and CTAB assisted Cr_2O_3 nanopowders.

The crystalline size and structures of the samples were characterized by X-ray diffraction on a rotating-target X-ray diffractometer (JSO-DEBYFLEX 2002). The surface morphologies were observed by using the Hitachi S-4500 scanning electron microscopy. The particle size and morphology were further confirmed by JEOL-3010 transmission electron microscopy. The optical absorption and photoluminescence emission spectra were obtained from a Varian Cary 5E spectrophotometer and Fluoromax-4 spectrofluorometer.

3. Results and discussion

The XRD patterns of the different surfactants assisted Cr_2O_3 are shown in Fig. 1. All the reflection peaks were indexed to the rhombohedral structure of Cr_2O_3, and matched well with the reported data in JCPDS card no. 70-3766 [5]. The presence of the surfactants in the preparation of Cr_2O_3 improves the crystallinity, and enhances the growth of crystallites along certain preferred directions. The strong and sharp reflection peaks suggest that the samples prepared are well

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http://dx.doi.org/10.1016/j.matlet.2015.02.014
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crystallized. By using the Debye–Scherrer's formula, the average crystallite sizes of the SDS, PEG and CTAB assisted Cr_2O_3 were found to be 35.05, 38.12 and 40.28 nm, respectively.

The SEM images reveal a distinctive difference in the morphology of the samples, as shown in Fig. 2(a–c). The aggregated and slightly aggregated nanospherical and nanoplate-like morphology was observed for the samples assisted by the PEG and CTAB surfactants, as shown in Fig. 2(b and c), whereas a well-dispersed nanosheets was observed in the case of the SDS assisted sample, as seen in Fig. 2(a). Since a possible interaction exists in a surfactants and a precursor, it is imaginable that the morphology and size of the product are influenced by the surfactants [6]. It is clear that the surfactants play an important role in controlling the morphology of the products. Further, the TEM image of the SDS assisted Cr_2O_3 nanosheets is shown in Fig. 2(d); it can be seen from the image, that the prepared sample consists mainly of sheet-like nanostructures, with an average particle size of about ~35 nm, and the particle size obtained from the TEM pattern is quite comparable to the size calculated from Scherrer's equation. The selected area electron diffraction (SAED) pattern in the inset of Fig. 2(d) reveals that the nanosheets are polycrystalline in nature and well crystallized. Moreover, a possible growth mechanism of Cr_2O_3 nanosheets, nanosphericals and nanoplates via the precipitation method is proposed in Scheme 1.

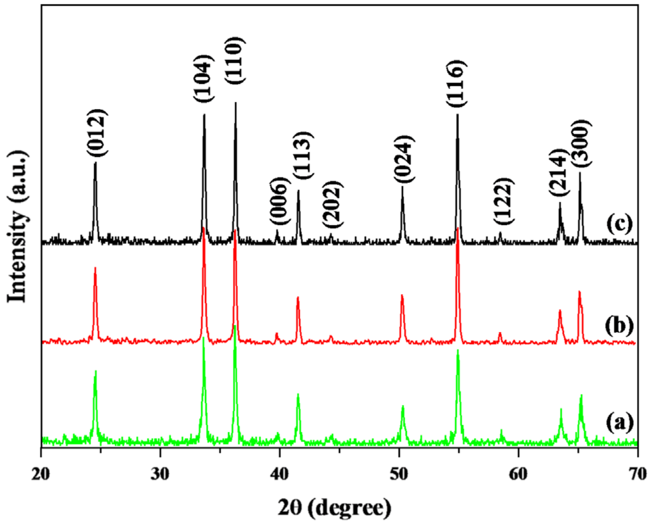

Fig. 1. XRD patterns of (a) SDS, (b) PEG and (c) CTAB assisted Cr_2O_3 nanostructures.

Fig. 3(a–c) shows the UV–vis absorption spectra of the SDS, PEG and CTAB assisted Cr_2O_3 nanostructures, respectively. The absorption peak at ~360 nm can be assigned to the band gap transition of the Cr^{4+} ions. The other two peaks centered at ~450 and 600 nm correspond to the intrinsic $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ d^3 electronic transitions of the Cr^{3+} ions, situated in the six coordinate geometry and octahedral symmetry, respectively, based on the crystal field theory [7]. The optical band gap (E_g) of the products can be obtained by plots of $(\alpha h\nu)^2$ versus photon energy, as shown in the inset of Fig. 3. The measured band gap energies of the Cr_2O_3 are found to be 3.78, 3.72 and 3.67 eV, respectively, which are higher than that of the bulk Cr_2O_3. Hence, the increase in the band gap values than that of bulk material was attributed to the blue shift, which indicates that the quantum confinement effect was observed for the prepared samples.

Fig. 4(a–c) shows the PL emission spectra of the SDS, PEG and CTAB assisted Cr_2O_3 nanostructures, respectively. The spectra show a strong and broad UV with weak visible emission peaks at ~396 and

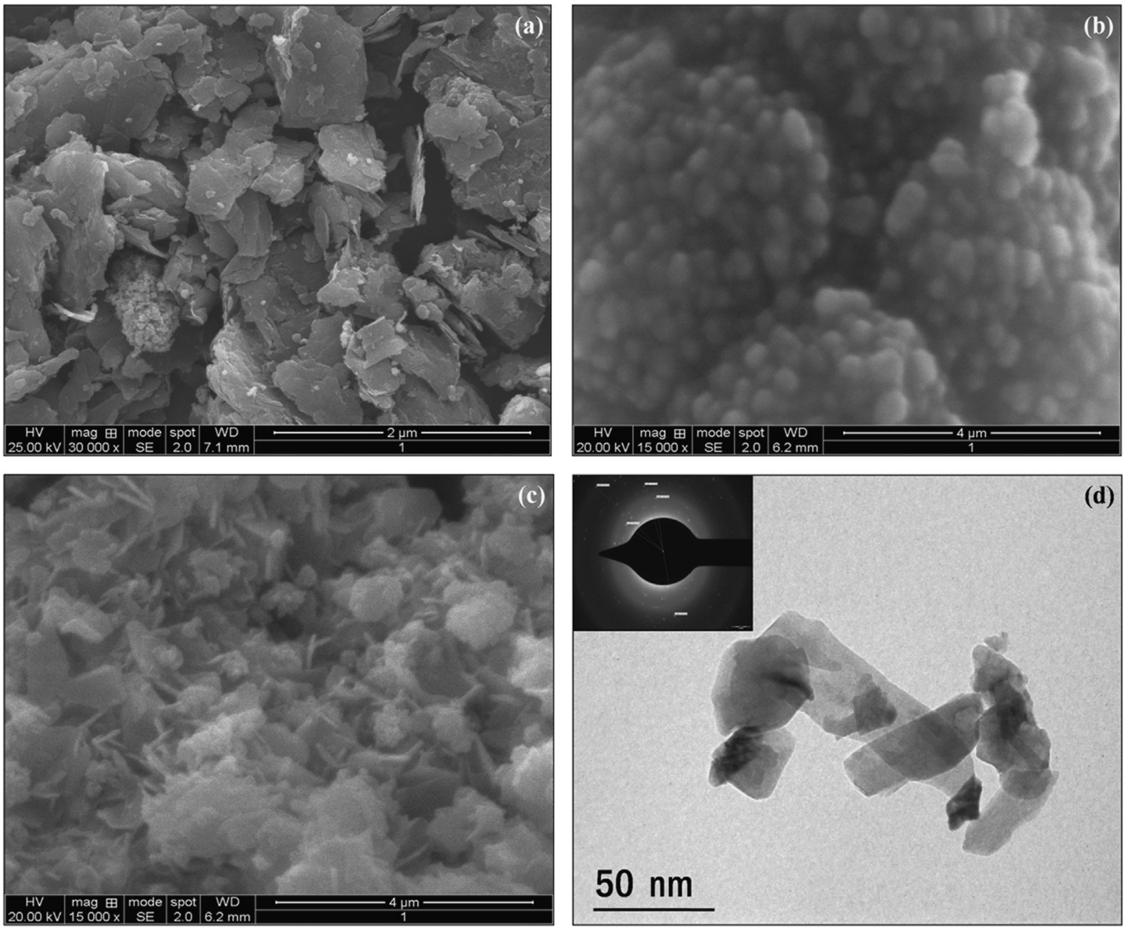

Fig. 2. SEM images of (a) SDS-sheets, (b) PEG-sphericals and (c) CTAB-plates assisted Cr_2O_3 nanostructures; (d) TEM image of SDS assisted Cr_2O_3 nanosheets.