Development of a microemulsion-based process for synthesis of cobalt (Co) and cobalt oxide (Co₃O₄) nanoparticles from submicrometer rods of cobalt oxalate

Jahangeer Ahmed [a], Tokeer Ahmad [a,1], Kandalam V. Ramanujachary [b], Samuel E. Lofland [b], Ashok K. Ganguli [a,*]

[a] Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India
[b] Department of Chemistry and Physics, Center for Materials Research and Education, Rowan University, 201 Mullica Hill Road, Glassboro, NJ 08028, USA

Abstract

Rod-shaped nanostructures of cobalt oxalate dihydrate were synthesized at room temperature by the microemulsion (reverse micellar) route. These rods are highly uniform in length and can be modified with temperature (from ∼6.5 µm at 50 °C to ∼2.5 µm at 150 °C) while keeping the diameter nearly constant (200–250 nm). Thermal decomposition of these rods in a controlled atmosphere (air and H₂) leads to nanoparticles of Co₃O₄ and Co, respectively, while in a helium atmosphere a mixture of Co and CoO nanoparticles is obtained. Co₃O₄ nanoparticles (∼35 nm) were slightly agglomerated, while Co nanoparticles were monodispersed and highly uniform (∼25 nm). The oxalate rods and Co₃O₄ nanoparticles show an antiferromagnetic ordering at 54 and 35 K, respectively.
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1. Introduction

Nanostructured wires and rods are expected to have interesting optical, electrical, magnetic, and mechanical properties as compared to micrometer-sized whiskers and fibers. The use of nanoscale structures as building blocks for self-assembled [1–3] structures could potentially eliminate conventional and costly fabrication lines, while still maintaining some concepts that have proven successful in microelectronics. There have been several studies on the synthesis of nanorods and nanowires in the last few years [4–14]. In our group we have been working on the controlled synthesis of metal-carboxylate rod-shaped structures for some time [15–17]. Our aim was to use these carboxylate nanorods (as precursors) to obtain metal oxide nanoparticles.

These transition metal oxides find many applications because of the interesting properties arising due to the variable oxidation state of the transition metals [18]. Co₃O₄ is an important transition metal oxide because of its application as gas sensors [19], catalysts [20], magnetic materials [21], electrochromic devices [22], electrochemical systems [23], and high-temperature solar selective absorbers [24]. CoO also shows interesting properties and has applications as gas sensors and as anodes of lithium-ion batteries [25,26]. Nanoparticles of cobalt metal are used in a variety of matrices to produce composite materials for high-density recording and other applications [27, 28]. Monodisperse and uniform cobalt nanocrystals (6–8 nm) were synthesized earlier by the reduction of cobalt(II)bis(2-ethylhexyl)sulfosuccinate (Co(AOT)₂) using NaBH₄ as the reducing agent [29]. Another report notes a broad distribution (8–200 nm) of cobalt nanoparticles [30] obtained by the thermal decomposition of cobalt acetate tetrahydrate.

There are very few reports in the literature on the synthesis of CoO nanoparticles and in most of these studies, CoO is obtained along with small amount of Co₃O₄ and Co parti-

* Corresponding author. Fax: +91 11 26854715.
  E-mail address: ashok@chemistry.iitd.ernet.in (A.K. Ganguli).
[1] Current address: Department of Chemistry, Jamia Millia Islamia University, New Delhi 110025, India.

cles [31]. Nanorods of cobalt oxide (CoO) with diameters of 10–80 nm and lengths ranging from 1 to 3 μm were earlier synthesized by calcining cobalt oxalate [32]. Seo et al. have reported the formation of CoO nanocrystals by thermal decomposition of a molecular precursor, $Co(acac)_3$ [33]. Pure CoO nanoparticles in the range of 5–18 nm were reported earlier by decomposition of the cupferronate in decalin under solvothermal conditions [34]. Several processes have been explored in the literature for the synthesis of nanomaterials. Apart from physical methods [35,36], several chemical methods such as hydrothermal [37], sol–gel synthesis [38], polymeric citrate [39,40], and the reverse micellar method [41] have been used to synthesize nanoparticles. Among these chemical methods the microemulsion process involving reverse micelles has been demonstrated as a versatile method for obtaining a wide variety of nanocrystalline oxides [42–46]. For example, we have reported a novel procedure to obtain monophasic nanoparticles of various metal oxides (MnO, Mn_2O_3, Mn_3O_4, CuO, ZnO, NiO) through the decomposition of metal oxalate nanorods obtained by the reverse-micellar route [15–17].

Here we report the room temperature synthesis of cobalt oxalate rods (submicrometer in two dimensions) using reverse micelles. These rods were decomposed under a controlled environment to obtain monophasic nanoparticles of Co_3O_4 and cobalt. These nanoparticles were characterized in detail using powder X-ray diffraction, TGA/DTA, and TEM. The magnetic properties of the rods and nanoparticles have also been investigated.

2. Materials and methods

Commercially available $(CH_3COO)_2Co\cdot4H_2O$ (CDH, AR, 99%), $(NH_4)_2C_2O_4\cdot H_2O$ (S.D. Finechemicals, LR, 99%), cetyltrimethylammonium bromide (CTAB) (Spectrochem, AR, 99%), 1-butanol (SLR, AR, 99.5%), and isooctane (Spectrochem, 99%) were used for the synthesis of the cobalt oxalate rods.

The synthesis of cobalt oxalate utilized two microemulsions. Microemulsion **I** composed of cetyltrimethylammonium bromide as the surfactant, *n*-butanol as the cosurfactant, isooctane as the hydrocarbon phase, and 0.1 M cobalt acetate solution as the aqueous phase. Microemulsion **II** had the same constituents as Microemulsion **I** except that the aqueous phase was a solution of ammonium oxalate (0.1 M) instead of cobalt acetate. The weight fractions of various constituents in these microemulsions were as follows: 16.76% of CTAB, 13.90% of *n*-butanol, 59.29% of isooctane, and 10.05% of the aqueous phase [15]. These two microemulsions were mixed slowly and stirred overnight on a magnetic stirrer. The resulting precipitate was separated from the apolar solvent and surfactant by centrifugation and subsequent washing with a 1:1 mixture of methanol and chloroform. The washing process was repeated three times to remove the surfactant and solvent. The precipitate was dried in air and then heated under different conditions to obtain cobalt and cobalt oxide nanoparticles.

Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer with Ni-filtered Cu*K*α

radiation using a scan speed of 1 s and scan step of 0.05°. The cell parameters were determined using a least-squares fitting procedure using quartz as the external standard. Thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out using a Perkin–Elmer system in flowing nitrogen atmosphere, with a heating rate of 5 °C/min. Dynamic light scattering (DLS) experiments were performed using a particle-size analyzer (Model Nano ZS90, Malvern Instruments, UK). All the measurements were carried out at a scattering angle of 90° and a temperature of 25 °C, which was controlled by means of a thermostat.

Transmission electron microscopic (TEM) studies were carried out using a JEOL JEM 200CX electron microscope operated at 200 kV. The TEM specimens were prepared as noted below. After dispersion of the powder in acetone by ultrasonic treatment, a few drops were put onto a porous carbon film supported on a copper grid, and then dried in air. The magnetization studies were carried out at temperatures ranging from 5 to 300 K, in applied fields of up to 10 kOe with a Quantum Design Physical Properties Measurement System.

3. Results and discussion

On mixing the two microemulsions containing Co^{2+} and oxalate ions a light pink powder of cobalt oxalate dihydrate was obtained. The powder X-ray diffraction pattern (Fig. 1) of cobalt oxalate dihydrate matches well to that reported earlier (JCPDS No. 25-0250). The unit cell parameters ('**a**' = 11.826(2) Å, '**b**' = 5.416(7) Å, and '**c**' = 15.714(5) Å) are close to the reported cell parameters of $CoC_2O_4\cdot2H_2O$. Cobalt oxalate dihydrate was heated at different temperatures of 50, 100, 150, and 185 °C to see the effect of temperature on the structure and morphology of the oxalate precursor. The intensity of the X-ray reflections increases with temperature up to 150 °C (Fig. 2a) and anhydrous cobalt oxalate (monoclinic form) is obtained at 185 °C (Fig. 2b). From the X-ray patterns, it appears that the crystallinity of the cobalt oxalate precursor improves with increasing temperature.

TGA studies show two weight losses for cobalt oxalate dihydrate (Fig. 3). The first weight loss (17.21%) occurs at 170 °C and corresponds to the loss of two water molecules. Note that the X-ray diffraction studies show an increase in amorphous nature (broad reflections) between 150 and 185 °C which is understandable due to the structural transition of the orthorhombic form of dihydrate to the monoclinic form of anhydrous cobalt oxalate. The second weight loss at 380 °C was found to be ~40.60% which corresponds to the loss of two carbon dioxide molecules to form the cobalt oxide. DTA studies (Fig. 3) also showed two endotherms corresponding to the two weight losses. There are several reports in the literature related to thermal decomposition of oxalates where both endothermic and exothermic processes have been suggested during the thermal decomposition of metal oxalate [47–49]. It may be noted that decomposition in a nitrogen atmosphere leads to an endothermic transition [49] as also seen in our studies. In the presence of oxygen or air the decomposition becomes exothermic due to formation of CO_2 from CO (formed during decomposition).