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Physical and electrochemical study of cobalt oxide nano- and microparticles

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ABSTRACT

Cobalt oxide nanocrystals of size 17–21 nm were synthesized by a simple reaction between cobalt acetate (II) and dodecylamine. On the other hand, micrometric Co_3O_4 was prepared using the ceramic method. The structural examination of these materials was performed using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM and HRTEM). XRD studies showed that the oxides were pure, well-crystallized, spinel cubic phases with a-cell parameter of 0.8049 nm and 0.8069 nm for the nano and micro-oxide, respectively. The average particle size was 19 nm (nano-oxide) and 1250 μm (micro-oxide). Morphological studies carried out by SEM and TEM analyses have shown the presence of octahedral particles in both cases. Bulk and surface properties investigated by X-ray photoelectron spectroscopy (XPS), point zero charge (pzc), FTIR and cyclic voltammetry indicated that there were no significant differences in the composition on both materials. The magnetic behavior of the samples was determined using a vibrating sample magnetometer. The compounds showed paramagnetic character and no coercivity and remanence in all cases. Galvanostatic measurements of electrodes formed with nanocrystals showed better performance than those built with micrometric particles.

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1. Introduction

Currently, studies on transition metal oxides presenting nanostructures have increased because of their particular properties in comparison with the bulk materials. Among these oxides, Co_3O_4 belonging to the normal spinel crystal structure $A_8B_{16}O_{32}$ in which Co(II) ions occupy the tetrahedral 8a sites and Co(III) ions occupy the octahedral 16d sites is an interesting material, because of its semiconducting [1], magnetic [2], optical [3], electrochemical [4], photocatalytic [5] and electrocatalytic properties [6]. It is also a promising material for applications such as electrochromic [7], solar [8], sensors [9] and Li-ion batteries devices [10,11].

Several methods have been reported for the synthesis of Co_3O_4 nanoparticles, the most common being thermal decomposition of precursors [12–20] and hydrothermal techniques [21–26]. Various other methods have also been used for the synthesis of spinel cobaltite nanocrystals including mechanochemical, combustion method, polyol process, microemulsion route, aerosol, solvothermal synthesis, mesopores, reflux synthesis,

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electrospining, ultrasonic assisted synthesis, oxidation–reduction method, coprecipitation method, sol–gel and template techniques [27–40].

These complicated routes with different precursors, surfactants, or extreme conditions of pressure and temperature often give rise to a broad distribution of particle sizes. In this paper, we present a simple synthetic method which uses cobalt acetate as the cobalt precursor and dodecylamine as a surfactant to produce Co_3O_4 nanoparticles having a narrow particle size range (17–21 nm). In order to compare the properties of nanoparticulate Co_3O_4 produced with this novel method with those shown by micrometric (1000–1500 μm) Co_3O_4 particles, the synthesis of this material was also carried out using a conventional ceramic preparation method. The synthesized oxides were characterized according to its crystal chemistry, morphology, magnetic and electrochemical properties.

2. Experimental Section

2.1. Sample Preparation

All the reagents (Sigma Aldrich p.a.) were used as received without further purification. In a typical synthesis, 0.2 g of cobalt acetate $Co(CH_3COO)_2 \cdot 4H_2O$ was dissolved into 6.3 g of dodecylamine $CH_3(CH_2)_{11}NH_2$ at 85 °C under magnetic stirring. After continuous stirring at room temperature for 0.5 h, the solution was heated at 220 °C for 10 h in an oven and then cooled to 25 °C. A. brown precipitate was recovered by centrifugation, followed by washing with n-hexane several times, and then sintering at 500 °C at heating rate of 10 °C/min for 6 h in air. Co_3O_4 microsized was prepared from cobalt nitrate salt $Co(NO_3)_2$ $6H_2O$ using the conventional ceramic method. The precursor was heated at 400 °C in air and then calcined at 500 °C (10 °C/min) for 10 h. In both cases a black solid was obtained and stored in vacuum.

2.2. Characterization Techniques

Crystallographic information was obtained using the powder X-ray diffraction (XRD) method on a Philips X-Pert diffractometer employing Cu-Kα radiation (λ = 0.15406 nm) over the range 2θ = 10° to 80°. The diffractometer was operated at 40 KV and 30 mA using a scanning rate of 2° min^{-1}. Nanocrystal size was measured by transmission electron microscopy (TEM) (JEOL 100 CXII) at 120 KeV and the micromorphology was examined by scanning electron microscopy (SEM) (Zeiss MA 3 nm resolution). The particle size distributions were obtained by image analysis [41]. The coherent domain size of the nanocrystallites was estimated from the Debye–Scherrer formula [42]. The oxide surface composition was examined by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained with a Phoibos 150 electron analyzer (Specs) under ultrahigh vacuum (1 × 10^{-9} mbar) using Al Kα radiation (1486.6 eV) and a constant pass energy of 20 eV. All binding energies (BE ±0.2 eV) were charge-corrected to the adventitious C1s signal (284.6 eV). The absorption properties of the as-synthesized Co_3O_4 nanocrystals were investigated at room temperature by Fourier transform infrared spectroscopy (FTIR Bruker IFS-66 V) from 4000 to 400 cm^{-1}. Specific surface measurements were carried out by using the Brunauer–Emmett–Teller (BET) method (Micromeritics 2010) and the nitrogen adsorption isotherm at −73 K determined volumetrically after outgassing at 1 × 10^{-5} Torr for 4 h at 120 °C.

Magnetization was measured at 5 and 300 K using a vibrating sample magnetometer (VSM Cryogenic) applying an external field ranging between −5 and +5 Tesla.

The acid–base surface character was determined using a zeta-meter electrophoresis apparatus (cell No. 3080 K: 67), with pH calibration (PZC measurements). Cyclic voltammetry was performed in 1 M KOH at room temperature using a three-electrode single compartment cell with an oxide pellet as the working electrode (10 mm diameter, 2 mm thickness) prepared by mixing Co_3O_4 (80%), acetylene black (10%) and Teflon (10%). A platinum plate was used as the counter electrode and Hg/HgO/KOH as the reference electrode. For the galvanostatic measurements, current steps of j = 1 × 10^{-4} A/cm^2 (or 1 × 10^{-3} A/g) were applied and a thin oxide pellet was also used as electrode. The electrodes were prepared by mixing active material, carbon super P and Teflon that were pelletized and dried at 90 °C in vacuum. Swagelok cells were laboratory-assembled using lithium metal as the counter electrode, Celgard 2400 membrane as the separator and 1 M $LiPF_6$ in EC:DMC 1:1 *w/w* as electrolyte. The electrochemical measurements were carried out using voltalab PGZ 301, Radiometer (Copenhagen).

3. Results and Discussion

3.1. Oxide Characterization

The X-ray diffraction patterns showed good crystallinity and were indexed according to JCPDS file no. 01-074-1656 for Co_3O_4 (Fig. 1). No impurity peaks were observed. The calculated interplanar distances of 0.284, 0.243, 0.201, 0.155 and 0.143 are in good agreement with the (220), (311), (400), (511) and (440) diffraction planes of cubic Co_3O_4 for both samples. From Fig. 1 it is clear that the samples have cubic face centered structure (space group Fd3m). The experimentally determined lattice constants *a* = 0.8049 ± 0.004 nm and *a* = 0.8069 ± 0.003 nm for

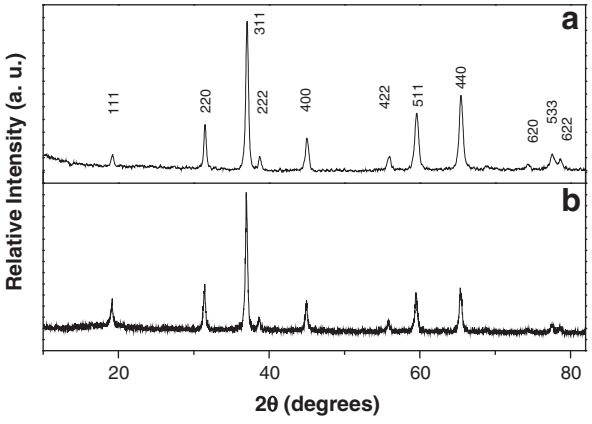

Fig. 1 – X-ray diffractogram of the Co_3O_4 oxide prepared at 500 °C (a) nanometric size and (b) micrometric size.

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