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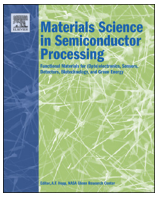

Iron mediated cathodic electrosynthesis of hausmannite nanoparticles

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ABSTRACT

A novel synthetic route has been proposed to prepare hausmannite nanoparticles. The synthetic route comprises an iron mediated constant current cathodic electrodeposition of manganite and heat treatment of the latter to obtain hausmannite. The obtained nanostructures have been characterized using X-ray Diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and Fourier transform Infrared Spectrometry (FTIR). The role of iron in the formation of manganite precursor has been studied by cyclic voltammetry (CV) and differential thermal analysis (DTA). A formation mechanism based on iron mediated formation of Mn^{3+} and subsequent cathodic reduction of the disproportionated products has been proposed accordingly. The prepared nanoparticles exhibited specific capacitance of 143 F g^{-1} in 0.5 M Na_2SO_4 solution. The retained specific capacity was 87% after 2000 cycles.

1. Introduction

Metal oxide nanocrystals are widely applied in catalysis, energy storage, magnetic data storage, sensors, and ferrofluids [1]. Due to oxidation states of manganese (Mn^{2+}, Mn^{3+}, and Mn^{4+}) manganese oxide crystals mainly exist in MnO, Mn_3O_4, Mn_2O_3 and MnO_2 forms. Among these, hausmannite (Mn_3O_4) is one of the most stable forms having a variety of important applications. It has a normal spinel structure with Mn^{3+} and Mn^{2+} ions occupying the octahedral and tetrahedral positions of the structure, respectively. It is particularly used as the main source for large scale production of soft magnetic materials such as manganese zinc ferrite. Moreover, it is an efficient and inexpensive catalyst for the decomposition of air pollutants. Along with other oxides of manganese, it has recently attracted considerable attention as an electrode material for supercapacitors. Small particles in the nanometer range display different chemical and physical properties compared with bulk materials. A widely accepted definition of a nanostructure is a system where at least one of dimensions is smaller or equal to 100 nm. Some typical examples include layer-like, wire-like, and particle-like structures. Due to the size confinement in nanostructures, quantum effects occur when the characteristic size of the object is comparable with the critical length (typically 1–10 nm) of the corresponding physical processes, such as mean free path of electrons, the coherence length, or the screening. Nanometer-sized manganese oxides with remarkably increased surface area and greatly reduced size are expected to display a better performance in their applications [2–4]. The electrical and magnetic properties of manganese oxide are completely different from those of

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their bulk counterparts [5,6]. Changes in dielectric properties were attributed to changes in particle size, shape, and boundaries. The classical synthetic route for the preparation of Mn_3O_4 is the heating of manganese oxides over 1000 °C [7]. High temperature processes are less favorable from practical and economical standpoints. Hence, many researches have been conducted to develop low temperature synthetic routes for Mn_3O_4 [8–10]. In the last decade, Mn_3O_4 nanocrystals of different shapes and sizes have been synthesized via various techniques such as chemical bath deposition [11], microwave-assisted solution-based methods [12], chemical spray pyrolysis [13], sono-chemical synthesis [14] and electrochemical methods [15].

In this study, we have developed a novel mild route for the synthesis of Mn_3O_4 nanoparticles. The synthetic route has two steps. In the first step, the MnOOH precursor is cathodically electrodeposited from solutions containing 10^{-2} M manganese(II) nitrate and minor amounts of iron (III). In these circumstances, Mn^{2+} undergoes an anodic iron mediated oxidation to Mn^{3+}, as evidenced by cyclic voltametric study. The latter diffuses to the cathode where the local increase of pH causes a disproportionation of Mn^{3+} to Mn^{2+} and MnO_2. With prolongation of the cathodic process, the obtained MnO_2 is reduced to MnOOH. In the second step, the obtained oxyhydroxide precursor is subjected to heat treatment at 300 °C for 2 h to obtain Mn_3O_4.

2. Experimental

2.1. Materials

Analytical grade $Mn(NO_3)_2 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were purchased from Merck (Darmstadt, Germany). Deionized water was obtained through a Millipore water purification system (Milford, MA, USA). The graphite anodes were purchased from local suppliers.

2.2. Preparation of Mn_3O_4

A solution of Mn^{2+} at a concentration of 10^{-2} M was prepared by dissolving appropriate amounts of $Mn(NO_3)_2 \cdot 4H_2O$ in deionized water. Different amounts of iron (as $Fe(NO_3)_3 \cdot 9H_2O$) were added to the solution to obtain Fe/Mn ratio of 0, 2.5, 5, and7.5%. Electrodeposition reactions were carried out at a constant current density of 0.5 mA cm^{-2}. The cathode was a steel 316L planar electrode with 100 × 100 × 0.5 mm dimensions. Two parallel planar graphite electrodes of the same dimensions were placed in the solution working as counter anodes. The steel electrode with the electrodeposited layer was removed from the solution after 45 min (total charge passage of 3.5 C per square centimeter of electrode area) and washed immediately with deionized water. The deposited hydrous $Mn(OH)_x$ layer was scrapped after 12 h and subjected to heat treatment. The annealing step was done between 25 °C to 300 °C at a heating rate of 10 °C min^{-1}.

2.3. Characterization

The crystal structure of the samples was studied by powder X-ray diffraction (XRD) measurements using CuK_α radiation ($\lambda = 1.5406$ nm) from a STOE XD-3A X-ray diffractometer. A TESCAN VEGA3 SB field-emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX) detector was used to investigate the surface morphology and elemental composition of the samples. The Infra Red spectra of the samples were recorded by means of a BOMEM MB-series FTIR spectrometer within the wave number range of 250 to 4000 cm^{-1} after pelleting with KBr.

2.4. Electrochemical measurements

Electrochemical studies were performed using an Autolab 302 N potentiostat. Cyclic voltammetric measurements were carried out by means of a standard three electrode cell configuration with a platinum wire, an Ag/AgCl and a glassy carbon (with 0.071 cm^2 area) as counter, reference, and working electrodes, respectively. In order to investigate the storage ability of the samples, cyclic voltammetry was performed in a Na_2SO_4 (0.5 M) aqueous solution within a potential range of −0.1 to +0.9 V vs. Ag/AgCl at different scan rates ranging from 1 to 100 mV S^{-1}. The Specific Capacitance (SC) was then calculated by integration of the current over the whole range of applied cyclic potential according to Eq. (1):

$$SC = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V)dV \quad (1)$$

where I is the measured current (A), $(V_a - V_c)$ is the sweep potential range (V), m is the mass of electrochemically active material (g) and v is the sweep rate (V S^{-1}).

3. Results and discussion

3.1. XRD study

The cathodic base generation from manganese nitrate baths has been widely studied. As reported in the literature, the annealed final product is pure α-MnO_2 [16] or a combination of α-MnO_2 and γ-MnO_2 [17,18] crystalline forms depending on experimental parameters. Interestingly, the addition of iron to the initial solution had a product rendering effect in this work. Fig. 1 shows the XRD patterns of samples as prepared from solutions containing different amounts of iron. As can be seen, in the case of (a), the dominants peaks can be attributed to Mn_3O_4 in Hausmannite crystalline form as depicted on the top of the figure (JCPDS 24-0734). The pattern also comprised four minor peaks at $2\theta = 21.50$ (R110), 37.12 (P101), 42.83 (P111) and 47.72° (R131) corresponding to manganese dioxide in Ramsdelite and Pyrolusite crystalline forms. The increasing of the Fe/Mn ratio (5 and 7.5% respectively) resulted in decreasing (b) or even fading (c) of Ramsdelite/Pyrolusite related peaks in favor of Hausmannite characteristic peaks. Higher amounts of iron (10%) resulted in a significant decrease in crystallinity of the annealed sample (the results are not shown). Hence, a Fe/Mn ratio of 7.5% was selected as optimized value due to the crystalline purity of the product.