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Direct ultrasonic-assisted synthesis of sphere-like nanocrystals of spinel Co_3O_4 and Mn_3O_4

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ABSTRACT

A simple sonochemical method was developed to synthesize uniform sphere-like or cubic Co_3O_4 and Mn_3O_4 nanocrystals by using acetate salts and sodium hydroxide or tetramethylammonium hydroxide (TMAH) as precursors. Influence of some parameters such as time of reaction, alkali salts, and power of the ultrasound and the molar ratio of the starting materials on the size, morphology and degree of crystallinity of the products was studied. Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), FTIR spectroscopy, Thermal gravimetry analysis and differential thermal analysis (TGA/DTA) were used to characterize the nanocrystals.

1. Introduction

Despite several years of investigation and numerous studies, the interest has been focused on nanoscale or micro-sized materials, which stems from the facts that new properties are required at the length scale and these properties were changed with their size and morphology. The development of metal oxide nanocrystals has been intensively pursued because of their useful applications in catalysis, energy storage, magnetic data storage, sensors and ferrofluids [1–4]. A spinel structure formed by a nearly closepacked fcc array of anions with holes partly filled by the cations can be represented by the formula AB_2O_4 [5], where A represents metallic ions located in A interstitial (tetrahedral) sites and B metallic ions located in B (octahedral) sites. Due to the large electronegativity of oxygen, the ionic type of bonds prevails in almost all oxide spinels [6]. Spinel cobalt oxide (Co_3O_4) is considered to be an important functional material, and has been widely used in electrochemistry, magnetism, catalysis and energy storage [7–15]. Cobalt oxide, with excellent cycle reversibility and high specific capacity, has received a considerable amount of attention over the last few years as one of the promising potential electrode materials for lithium-ion batteries [16]. Owing to the origin of the poor durability and their rapid degradation on cycling, many methods have been attempted to prepare nanoscale cobalt oxide, including solid state reaction [17], hydrothermal reaction [18], sodium nitrate-mediated synthesis [19,20], and microwave irradiation [21].

Manganese oxide (Mn_3O_4, trimanganese tetroxide, Hausmannite) is currently used in many industrial application domains as catalysis, magnetism, electrochemistry or air decontamination. For example, Mn_3O_4 is a common catalyst for the oxidation of methane and carbon monoxide [22], the selective reduction of nitrobenzene [23], the decomposition of nitrogen oxides [24–26] and the oxydehydrogenation of alcohols [27]. In magnetic applications, Mn_3O_4 enables to produce soft magnetic materials such as manganese zinc ferrite which is used for magnetic cores in transformers for power supplies [28]. Trimanganese tetroxide is also used in electrochemistry as a precursor in the synthesis of Li–Mn–O electrode materials for rechargeable lithium batteries [29–33]. Finally, in air-purification applications, Hausmannite powder is able to combust organic compounds in the 100–500 °C temperature range [34,35]. In order to offer better performances due to its size and/or its morphology toward these applications, Mn_3O_4 is prepared by following various methods: (i) calcination of manganese oxides (MnO_2, Mn_2O_3, etc.), oxyhydroxide (g-MnOOH), carbonate ($MnCO_3$) and nitrate ($Mn(NO_3)_2$) at high temperature (1000 °C) [36–38], (ii) solvothermal treatment of manganite (MnOOH) [39–44], (iii) sol–gel process with a post-treatment at higher temperature [45,46], (iv) precipitation coupled with oxidation of manganese hydroxide ($Mn(OH)_2$) [47], (v) electrospinning technique [48,49] and (vi) gas condensation [50]. More recently, other Mn_3O_4 synthetic processes are investigated: (vii) chemical bath deposition to prepare thin films [51], (viii) gamma-ray

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Table 1
Experimental conditions for the preparation of Co_3O_4 and Mn_3O_4 nanocrystals

Sample	$Co(OAc)_2$ or $Mn(OAc)_2$	Base	Sonicating time	Ultrasound power (W)
1	50 ml (0.1 M)	100 ml (NaOH 0.1 M)	1 h	6–9
2	25 ml (0.1 M)	100 ml (NaOH 0.1 M)	1 h	6–9
3	25 ml (0.1 M)	50 ml (TMAH 0.2 M)	1 h	6–9
4	25 ml (0.1 M)	50 ml (TMAH 0.2 M)	2 h	6–9
5	25 ml (0.1 M)	50 ml (TMAH 0.2 M)	30 min	6–9
6	25 ml (0.1 M) + 1 g $NaNO_3$	50 ml (TMAH 0.2 M)	1 h	6–9
7	25 ml (0.1 M)	50 ml (TMAH 0.2 M)	1 h	15–18

irradiation of manganese sulfate ($MnSO_4$ _H_2O) [52] and finally (ix) precipitation method from manganese nitrate ($Mn(NO_3)_2$) at moderate temperature [53].

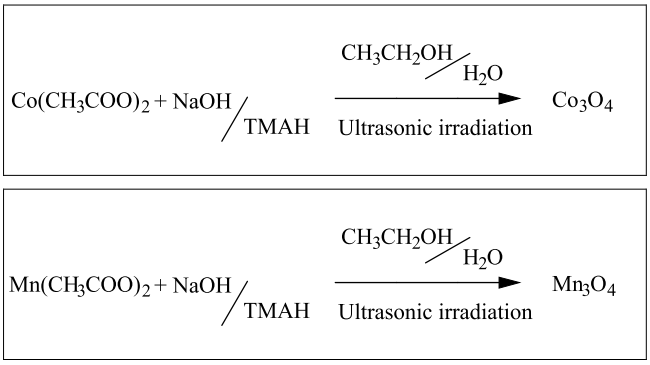
The properties of the metal oxides are influenced by the structure and morphologies including crystallite sizes, orientations, stacking manners and aspect ratios, which are sensitive to the preparation methodology used in their synthesis [54].

Recently, sonochemical synthesis, an alternative means to the general synthetic methods, has been used in the preparation of many materials. Ultrasound induces chemical changes due to cavitation phenomena involving the formation, growth, and instantaneously implosive collapse of bubbles in liquid, which can generate local hot spots having a temperature of roughly 5000 °C, pressures of about 500 atm, and a lifetime of a few microseconds [55]. These extreme conditions can drive chemical reactions such as oxidation, reduction, dissolution, and decomposition, which have been developed to fabricate a variety of metal, oxide, sulfide, and carbide nanoparticles [56–60].

In this study, nano-crystalline transition metal oxide (Co_3O_4, Mn_3O_4) powders are prepared via a one-step sonochemical method. Metal oxide particles with different crystallite sizes, morphologies and degree of crystallinity are obtained at various conditions. The powders were characterized by XRD, TGA/DTA, SEM, TEM and FTIR spectroscopy.

2. Experimental

Co_3O_4 and Mn_3O_4 nanocrystals were prepared by the reaction of $Co(CH_3COO)_2$ and $Mn(CH_3COO)_2$ precursors with NaOH or tetramethylammonium hydroxide (TMAH) bases in ethanol and water as solvents. The reaction was performed under ultrasound power. The molar ratio of initial materials, the time of sonicating, the power of the ultrasound and the titrated base were the parameters which were changed for reaching the optimized conditions. To investigate the role of alkali salts on the size and morphology of nanoparticles, we used 1 g of $NaNO_3$ in the reaction number 6.



Scheme 1. The reactions of Co_3O_4 and Mn_3O_4 formation.

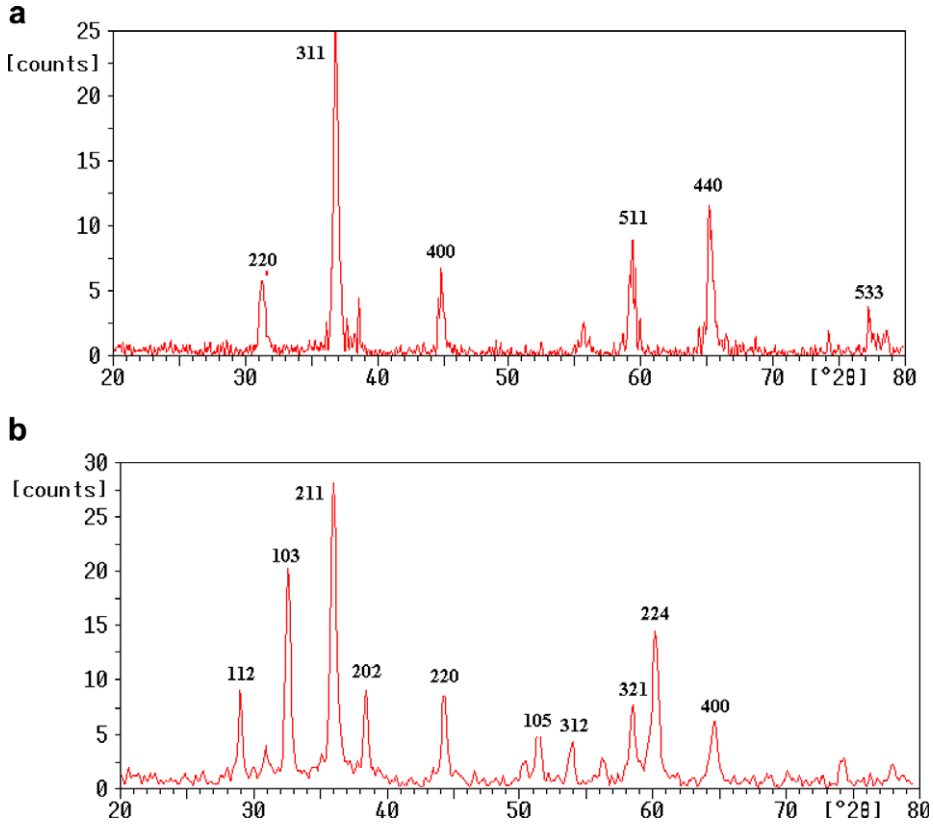


Fig. 1. X-ray powder diffraction pattern of (a) Co_3O_4 (sample No. 7) and (b) Mn_3O_4 (sample No. 7).