

SYNTHESIS AND CHARACTERIZATION OF ZNMN₂O₄ NANOPARTICLE BY A REVERSE MICELLE PROCESS

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Abstract

The preparation of ZnMn₂O₄ nanoparticles in Igepal CO-520-cyclohexane-water reverse micelle solutions has been studied. Transmission electron microscopy (TEM) and X-ray diffraction pattern analyses revealed the resultant particles to be ZnMn₂O₄. The average size and distribution of synthesized particles calcined at 400°C for 2 hours were in the range of 20 nm and narrow, respectively. The phase of synthesized particles was crystalline. The magnetic behavior of the synthesized particles was ferromagnetism. The effects of synthesis parameters, such as the molar ratio of water to surfactant and calcination temperature, are discussed.

1 Introduction

Nanocrystalline materials are showing great promise in industry and technology [1,2]. This is chiefly because they have some unique properties which are not shown by the bulk crystalline materials [3,4]. The spinels are complex oxides and represented by the general formula of A²⁺B³⁺O₄ [5]. Zinc manganese oxide (ZnMn₂O₄) was one of the important blended transition-metal oxides with spinel structure [6-14]. It was well known that zinc manganese oxide spinel is a promising technological material for the negative temperature coefficient (NTC) thermistors [10], or the cathode material of the secondary batteries [14] because of their excellent electrochemical properties.

Many different methods of producing nanosized spinel powders were reported such as hydrothermal processing, glycolthermal processing, Sol-Gel processing and ion exchange resin manufacture methods [15-19]. Compared to other methods, the reverse micelle method is one of the most promising wet chemistry syntheses. This method provides a favorable microenvironment for controlling the chemical reaction. The reaction rates are easily controlled in reverse micelle method, so that nanoparticles made by this reverse micelle method show narrow size distribution [20].

Reverse micelle solutions are transparent, isotropic, thermodynamically stable water-in-oil microemulsion where the aqueous phase is dispersed as nanosized droplets. The droplets are surrounded by a monolayer of molecules in the continuous polar organic phase [21, 22]. The surfactant stabilized water pools provide a microenvironment for the preparation of ultrafine particles by exchanging their contents via the fusion redispersion process and by preventing the excess aggregation of particles [23, 24]. Therefore, the particles obtained in such a medium are very fine and monodispersed.

The objectives of this work are to prepare the nanosized ZnMn_2O_4 powders with superparamagnetic property by reverse micelle method and to investigate the effects of the processing conditions such as water to surfactant rate, on the formation, morphology and phase of the powders.

2 Experimental

Fig 1. shows the schematic illustration of the reverse micelle method. Micro-emulsions were prepared from cyclohexane (Sigma-Aldrich, HPLC grades), generally known as Igepal CO-520 (Aldrich Chemical, 98% used without further purification), aqueous solutions of 0.1M $\text{Zn}(\text{NO}_3)_2$, 0.2M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Microemulsion having a total volume 100ml was prepared at ambient temperature in a 250ml vial with rapid stirring. The microemulsions were comprised of 20.05g of Igepal CO 520, 50ml of cyclohexane, 1.625-3.25ml $\text{Zn}(\text{NO}_3)_2$ and 1.625-3.25ml $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ mixed aqueous solution, deionized water and 2.5-5ml NH_4OH . The average size of the synthesized powders was controlled by the $R = [\text{water}]/[\text{surfactant}]$ ratio. The microemulsion was mixed rapidly, and after 5min of equilibration. Reverse micelles were prepared from a nonionic surfactant Igepal CO-520. The microemulsion was then centrifuged to extract the particles, which were subsequently washed by ethanol to remove any residual surfactant and water.

The recovered powders were analyzed for phase composition using X-ray diffraction (XRD, Philips X'pert MPD PW3040, Holland) over the 2θ range from 20° to 80° at the scan speed of 2° min^{-1} . The morphology of the synthesized particles was observed using transmission electron microscope (TEM, Jeol 2000FXII, Japan). For TEM studies, samples were prepared by adding drops of freshly prepared cluster solution on a carbon film supported on a Cu grid.

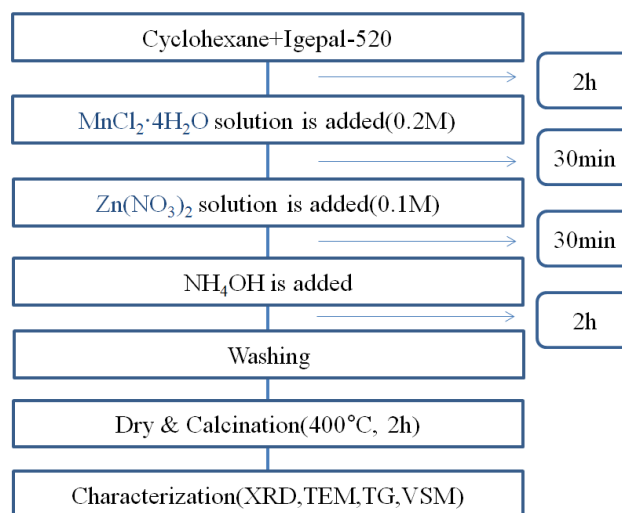


Fig 1. Experimental flow chart of synthesized Zinc manganese oxide (ZnMn_2O_4) powders by reverse micelle processing.

3 Results

Ternary systems of Cyclohexane/Igepal CO-520/water offer certain advantages: they are spheroidal and monodisperse aggregates where water is readily solubilized in the polar core, forming a 'water pool' characterized by the ratio of water to surfactant concentration. Another important property of reverse micelles is their dynamics character; the water pools can exchange their contents by a collision process. The aggregation and self-assembly of the silver/surfactant/water species is complex, and very little is known about the cluster growth and final nano-structure as a function of synthesis conditions. The molar ratio of water to surfactant can determine the size of the micro-emulsion water core [25]. Therefore, the

diameter of the nanoparticles in the micro-emulsion can be controlled by the water/surfactants molar ratio(R) value.

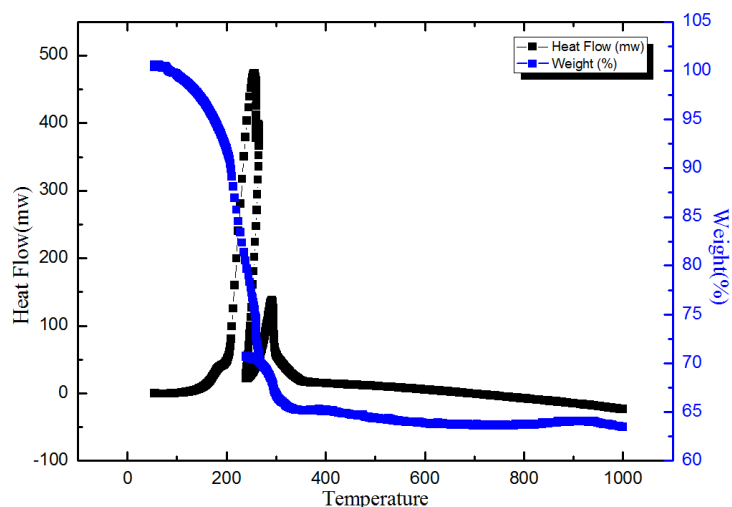


Fig 2. TG-DSC curves of the ZnMn₂O₄ powders at R=8

Fig. 2 shows the typical thermal behavior of the ZnMn₂O₄ nanoparticles. The TG curve shows a total weight loss of 35% at 400°C. The two exothermic peaks at 260°C and 290°C are the burning of organics and correspond to the crystallization of the ZnMn₂O₄ spinel.

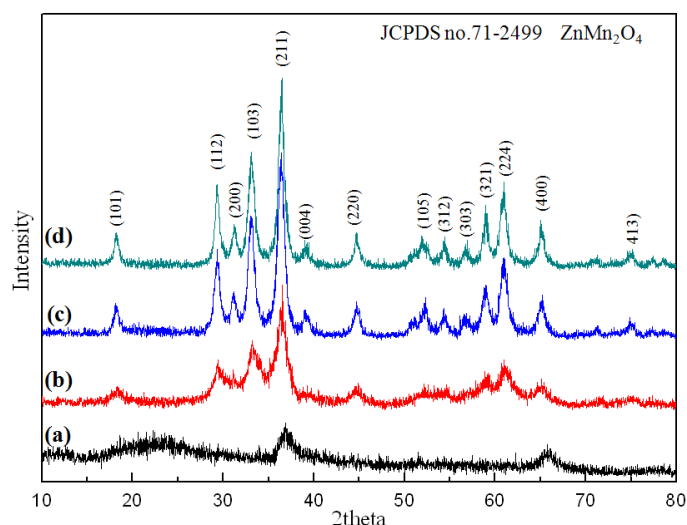


Fig 3. X-ray diffraction patterns of the synthesized ZnMn₂O₄ powders (a) without calcinations R=4 and calcinations at 400°C for 2hour as a function of R (water /surfactants molar ratio): (b) before calcinations, R=4, (c) R=6, (d) R=8.

Fig 3. shows the X-ray diffraction pattern of the ZnMn₂O₄ particles with calcined at 400°C for 2hour as a function of water/surfactants molar ratio. The X-ray powder diffraction patterns have shown that the synthesized magnetic particles have a single spinel phase of ZnMn₂O₄ (JCPDS no.71-2499). No other crystalline phases are found in the calcined samples. The XRD peaks increases as the water to surfactant ratio is increased for the preparation of powder. The crystallite size of powders obtained using different water to surfactant ratio is given in Table 1. The average size and distribution of synthesized particles calcined at 400°C for 2hours were in the range of 20nm and narrow, respectively. The average crystallite size of the powders increases as the water to surfactant ratio (R) is increased from 4 to 8 during the preparation of powder.

Water to surfactant molar ratio	Crystallite size (XRD, nm)	Particle size (TEM, nm)
4	11	9
6	19	15
8	23	20

Table 1. Crystallite size, particle size and saturation magnetization of ZnMn₂O₄.

Fig 4. shows the transmission electron microscopy of the synthesized ZnMn₂O₄ particles with calcined at 400°C for 2hours as a function of water/surfactants molar ratio. It has been shown that the average sizes of the synthesized ZnMn₂O₄ powder are about 20nm. The particle sizes are increased from 9 to 20nm as the R value increases from 4 to 8. The morphology is nearly spherical with narrow particle size distribution. The nucleation and growth are controlled by interaction between micelles, phase behavior and solubility, average occupancy of the reacting species in the aqueous medium, dynamic behavior of the reverse micellar solution and so on [26].

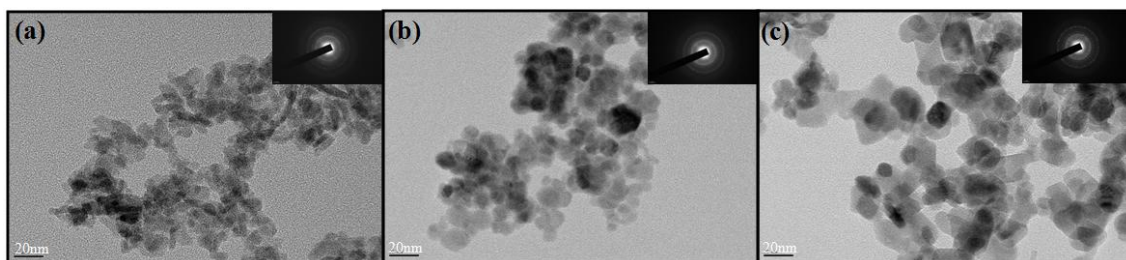


Fig 4. TEM images of the ZnMn₂O₄ powders prepared at X=1 after calcinations (400°C, 2h) : (a) R=4, (b) R=6, (c) R=8.

4 Conclusions

Nanosized ZnMn₂O₄ powders have been prepared using a reverse micelle process. The water/surfactant molar ratio influenced the average size and distribution of the synthesized particles. The average size of the synthesized particles increased with increasing R. The average size and size distribution of the synthesized particles was about 20nm and narrow, respectively.

It is possible to the application of magnetic nanoparticles for drug delivery using nanoparticulate magnetic carrier. If the water/surfactant molar ratio and mixture ratio of the aqueous solutions is carefully controlled, it is possible to control the average size, crystalline phase and magnetic property of the synthesized powders.

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