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2-pyrrolidone - Capped Mn₃O₄ Nanocrystals

Research Article

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Abstract: Water-soluble Mn₃O₄ nanocrystals have been prepared through thermal decomposition in a high temperature boiling solvent, 2-pyrrolidone. The final product was characterized with XRD, SEM, TEM, FTIR and Zeta Potential measurements. Average crystallite size was calculated as ~15 nm using XRD peak broadening. TEM analysis revealed spherical nanoparticles with an average diameter of 14±0.4 nm. FTIR analysis indicated that 2-pyrrolidone coordinates with the Mn₃O₄ nanocrystals only via 0 from the carbonyl group, thus confining their growth and protecting their surfaces from interaction with neighboring particles.

Keywords: Spinels • Nanocrystalline Materials • Thermal Decomposition • Mn_3O_4 • Transmission Electron Microscopy (TEM)

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1. Introduction

Magnetic nanoparticles have attracted increasing interest among researchers of various fields due to their promising applications in high density magnetic recording media and biomedical field such as magnetic resonance imaging (MRI), cell and DNA separation, drug delivery, gene cloning and hyperthermia for cancer therapy [1].

Among magnetic nanoparticles, manganese oxide (Mn_3O_4) as a magnetic transition metal oxide, is an important material due to its wide range applications in high density magnetic storage medium, catalyst, ion-exchange, molecular adsorption, electrochemical materials and varistors [2-7]. Mn₃O₄ had been widely used as the main source of ferrite materials which have extensive applications in electronic and information technologies. The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Mn₃O₄ is known to be an active catalyst for the decomposition of waste gas NOx, selective reduction of nitrobenzene and so on [8-10]. It has been shown to be a corrosion-inhibiting pigment for epoxy-polyamide- and epoxy-ester-based primers and top coating [11,12]. It is

also a starting material for manufacturing soft magnetic materials such as manganese zinc ferrite, which is useful for dioxy-magnetic cores in transformers for power supplies [13]. Much research work has focused on the lithiation of Mn_3O_4 for synthesis of intercalation compounds such as lithium manganese oxides as electrode materials for rechargeable lithium batteries [14-17].

Various methods have been employed to prepare nanocrystalline transition metal oxides including co-precipitation [18,19], micro-emulsion [20,21], electrochemical synthesis [22], pyrolysis [23,24], hydrothermal synthesis [25,26], and low-temperature synthesis [27].

It is essential to coat the nanoparticles with a capping molecule during chemical synthesis in order to prepare well-dispersed colloids. The advent of new methods to prepare semiconductor and metal nanocrystals, specifically the injection of molecular precursors into hot organic surfactants, has yield markedly improved samples with good size control, narrow size distributions, and good crystallinity of individual and dispersable nanocrystals [28-35]. Recently, the possibility of producing water-soluble magnetite nanocrystals by a thermal decomposition method using strong polar 2-pyrrolidone as a coordinating solvent was achieved by many scientists and also the mechanism leading to magnetite in 2-pyrrolidone was discussed [28,29,36]. These studies have attempted to mass produce 2-pyrrolidone coated high quality magnetite nanocrystals. 2-pyrrolidone was chosen as a solvent and stabilizer due to its strong polarity, high boiling point, and coordination capacity with transition metal ions [28,29,36].

In this work, we report thermal decomposition reaction of Mn(acac)3 in 2-pyrrolidone to achieve surface capped manganese oxide, Mn_3O_4 , nanocrystals for the first time.

2. Experimental Procedures

X-ray powder diffraction analysis, XRD, was used for the characterization of the crystalline product. Philips diffractometer with PW 3020 goniometer (Cu K_a).For FTIR measurements, Mattson Satellite Infrared Spectrometer FTIR was used in the region 400-4000 cm⁻¹. Spectra of solid samples were obtained from KBr pellets using KBr / sample weight ratio of 100/3 mg.

Scanning Electron Microscopy (SEM) analysis was performed, in order to investigate the microstructure of the sample, using FEI XL40 Sirion FEG Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to SEM analysis.

Transmission Electron Microscopy, TEM, analysis was performed using a FEI Tecnai G2 Sphera Microscope. A drop of diluted sample in ethanol was deposited on a TEM grid and alcohol was evaporated. Particle size distribution was obtained from several micrographs, counting a minimum of 150 particles.

Zeta potential measurements were performed using a Zetasizer Nano (Malvern Instruments) in folded capillary zeta potential cells, and pH titrations were performed using 0.25 M NaOH and 0.25 M HCl solutions in the auto-titrator unit.

All the chemicals are analytical grade and used without further purification. In a typical procedure for the preparation of Mn_3O_4 nanoparticles, a 20 ml portion of 2-pyrrolidone containing 2 mmol (0.50632 g) Mn(acac)2 was heated with vigorous stirring at 250°C. After being refluxed for 12 h, the reaction system was cooled to room temperature. Addition of methanol, CH_3OH , into 2-pyrrolidone solution resulted in a dark-brown precipitate which was washed with acetone several times and then dried. The final brown powder was proven to be soluble in water and 2-pyrrolidone.



Scheme 1. Reaction scheme for the synthesis of 2-pyrrolidone capped Mn₃O₄ nanoparticles.



Figure 1. X-ray powder diffraction pattern of as-prepared capped Mn₂O₄ nanoparticles.

3. Results and Discussion

Reaction scheme is presented in Scheme 1, where acetyl acetone complex of Mn^{3+} and 2-pyrrolidone is refluxed at elevated temperatures, resulting in capped Mn_3O_4 particles.

The presence of alcohol is very important to initiate the particle formation. The rate of addition of alcohol affects the distribution of particle size. A stepwise addition results in a larger size and a wider size distribution, while a very fast addition results in a larger number of nuclei formed simultaneously thus yielding a narrower size distribution and better control over size. Refluxing the solution for extended periods before the addition of alcohol is effective in controlling the distribution of particle size.

The X-ray powder diffraction pattern of the product is given in Fig. 1. The XRD peaks attest to the formation of Mn_3O_4 as the major phase. All the experimental XRD peaks are in agreement with those reported in the literature for Mn_3O_4 (JCPDS card no 24-0734). Crystallite size was calculated from XRD peak broadening (*i.e.* full width at half maximum, FWHM) using the Scherrer equation as ~15 nm (based on 2 1 1 peak).

Observed Bands (cm ⁻¹)		Bond Assimment
2-Pyrrolidone	Product	Band Assignment
3300-3250	3410, 3460	N-H strech
	3570-3200	hydroxy group, H-bonded OH stretch
2962	2921	asymmetric CH ₂ stretch
2892	2853	symmetric CH ₂ stretch
1680	1637	C=O strech
1457, 1427	1383	C-H deformation
1286	1294	C-C-N streching
1168, 1064	1111	C-N streching
991	860	ring breathing
684		N-H out of plane bending
628	611	C=O out of plane bending
476		C-N-C bending

Table 1. Infrared Transmission Frequencies of 2-Pyrrolidone and the final product.



Figure 2. FTIR spectra of (a) pure 2-pyrrolidone, and (b) 2-pyrrolidone capped Mn₃O₄ nanocrystals.

FTIR measurements were carried out on the pure 2-pyrrolidone and Mn_3O_4 nanoparticles capped with 2-pyrrolidone respectively: results are presented in Fig. 2 and summarized in Table 1. A broad peak observed in the region 3000-3500 cm⁻¹ originates from the overlap

of amine groups and the stretching of the H bonded OH groups [37]. Hydrogen bonding is due to the conjugation of C=O group on 2-pyrrolidone with the OH bearing NH nanoparticles. The split of the peak into two is due to the N-H stretching vibrations of the unsubstituted amide groups on 2-pyrrolidone [38]. The broadness of the FTIR peak at around 3500 cm⁻¹ also proves the existence of H-bonding among pyrrolidone molecules. The surfactant molecules in the adsorbed state were subject to the field of solid state nanoparticle surface. As a result the characteristic bands shifted to a lower frequency region and indicate that the surfactant surrounding the Mn₃O₄ nanoparticles are in a close-packed, crystalline state. It is worth noting that the C=O stretch band of pure 2-pyrrolidone which is present at 1679 cm⁻¹ shifts to 1629 cm⁻¹ for the current magnetic nanocrystals, which indicates the O that is coordinated in C=O presents a lower stretching frequency due to the attachment to the nanoparticles' surface. The asymmetric CH₂ stretch



Figure 3. a) SEM micrograph, b) TEM micrograph, and c) calculated histogram of 2-pyrrolidone capped Mn₃O₄ nanocrystals.



Figure 4. Surface potential measurement of a clear suspension of 2-pyrrolidone capped Mn₃O₄ nanoparticles.

(2952 cm⁻¹) and symmetric CH₂ stretch (2892 cm⁻¹) shifted to 2922 and 2852 cm⁻¹, respectively. In addition, FTIR spectra of the particles exhibit characteristic peaks of Mn_3O_4 at around _1 = 613 cm⁻¹ and _2 = 503 cm⁻¹ respectively. The band at 1384 cm⁻¹ can be assigned _1 vibrations of CO₂ molecules that are present in the sample chamber [39].

SEM and TEM analysis of as-prepared Mn3O4 samples was performed in order to study the material's microstructure and morphology; micrographs are presented in Fig. 3. SEM micrograph shows particles with spherical morphology with a wide range of sizes. Nanoparticles around 300 nm and 40 nm were measured. Resolution of SEM micrographs did not allow us to make a comprehensive particle size evaluation. Therefore TEM analysis was performed and particles were shown to be spherical, and their distribution is represented by a histogram in Fig 3(c). In order to analyze the size distribution quantitatively, the particle size distribution was fitted using a log-normal function [40].

$$P(D) = \frac{A}{D\sigma_D \sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma_D^2} \ln^2(\frac{D}{D_0})\right)$$

where σ_D is the standard deviation of the diameter and D0 is the mean diameter. A mean diameter of D0, as determined from Eq. (1), is about 14±0.4 nm. Size obtained from TEM analysis agrees well with the crystallite size obtained from XRD measurements using the peak broadening. Features observed in SEM are mainly secondary particles that are formed as a result of aggregation/clustering of smaller ones. This is most probably due to the magnetization within the nanoparticles causing them to cluster. Detailed magnetic investigations are undertaken and results are to be reported elsewhere.

The extent of surface coverage of nanoparticles with 2-pyrrolidone molecules was also analyzed using zeta potential mesaurements. Changes in the surface charge is directly based on the chemistry at the nanoparticles' surface. Figure 4 shows the results of analysis performed on a prepared sample dispersed in DI water. Surface of nanoparticles are positively charged at low pH values. Amide groups on 2-pyrrolidone are difficult to protonate. The surface of nanoparticles is not covered very densely due to the sterically bulky 2-pyrrolidone groups. So, the nanoparticles' surface still have some OH groups exposed, which are protonated at low pH values that render the surface charge positive. The increase in pH removes the positive charge and negatively charges the accesible OH groups on the nanoparticles' surface, thus reversing the initially observed charge. The transition from positive charge to negative takes place at pH 4.8, which corresponds to the range where the isoelectric point for Mn₃O₄ particles is expected. Based on this analysis it is clear that the

 ${\rm Mn_3O_4}$ nanoparticles' surface is not fully covered and the surface originating OH groups are accessible to the solution around.

4. Conclusion

In summary, we have shown that it is possible to prepare water soluble nanocrystals of Mn₃O₄ in the absence of water or air by thermal decomposition of manganese acetylacetonate in a high boiling solvent of 2-pyrrolidone as a novel synthetic approach. The experimental results reveal that 2-pyyrolidone not only serves as a media for high temperature decomposition reaction, but also involves surface coordination which renders the manganese nanocrystals water-soluble and the colloidal solution stable. TEM analysis revealed the size of nanoparticles as ~14±0.4 nm, in agreement with the size calculated from XRD peak broadening as 15 nm. Particles are readily dispersed in aqueous solution; however they cluster due to their inherent magnetization. Zeta potential analysis revealed surface OH groups are still present, most likely due to sterically bulky 2-pyrrolidone groups, and are exposed to the surrounding solution.

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References

- [1] Sun S. Murray C.B., Weller D., Folks L., and Mosser A., Science, 287, 2000 (1989)
- [2] A. R. Armstrong, P.G. Bruce, Nature 381, 499 (1996)
- [3] Y.F. Shen , R.P. Zerger, R.N. Deguzman , S.I. Suib, L. Mccurb, D.I. Potter, L.L. Oyoung, Science 260, 511 (1993)
- [4] M.C. Bernard, H.L. Goff, B.V. Thi, J. Electrochem. Soc. 140, 3065 (1993)
- [5] A.H. De Vries , L. Hozoi, R.Broer , Phys. Rev. B 66, 35108 (2002)
- [6] Y. Yamashita, K. Mukai, J.Yoshinobu, M. Lippmaa, T. Kinoshita, M. Kawasaki, Surf. Sci. 514, 54 (2002)
- [7] Y. Q. Chang, X.Y. Xu, X.H. Luo, C.P.Chen. D.P.Yu, J. Cryst. Growth 264, 232 (2004)
- [8] T. Yamashita and A. Vannice. J. Catal. 163, 158 (1996)
- [9] W.M. Wang, Y.N. Yang and J.Y. Zhang. Appl. Catal. A 133, 81 (1995)
- [10] A. Maltha, H.F. Kist, B. Brunet, J. Ziolkowski, H. Onishi, Y. Iwasawa and V. Ponec. J. Catal. 149, 356 (1995)
- [11] I. Metil. Mod. Paint Coat. 72, 49 (1982)
- [12] C.H. Hare and M.G. Fernald. Mod. Paint Coat. 74, 40 (1984)
- [13] V.V. Pankov. Ceram. Int. 14, 87 (1988)
- [14] L. Sanchez, J. Farcy, J.-P. Pereira-Ramos, L. Hernan, J. Morales and J.L. Tirado. J. Mater. Chem. 6, 37 (1996)
- [15] L. Sanchez and J.-P. Pereira-Ramos. Electrochim. Acta 42, 531 (1997)
- [16] T. Kanasaku, K. Amezawa and N. Yamamoto. Solid State Ion. 133, 51 (2000)
- [17] W. Zhang et al. I Journal of Crystal Growth 263, 394 (2004)
- [18] Y.H. Zhu and Q.F. Wu, J. Nanopart. Res. 1, 393 (1999)
- [19] Y. Konishi, T. Nomura and K. Mizoe, Hydrometallurgy 74, 57 (2004)
- [20] C.J. O'Connor, C.T. Seip, E.E. Carpenter, S. Li and V.T. John, Nanostruct. Mater. 12, 65 (1999)
- [21] Z.L. Liu, X. Wang, K.L. Yao, G.H. Du, Q.H. Lu, Z.H. Ding, J. Tao, Q. Ning, X.P. Luo, D.Y. Tian and D. Xi, J. Mater. Sci. 39, 2633 (2004)
- [22] S. Franger, P. Berthet and J. Berthon, J. Solid State Electrochem. 8, 218 (2004)

- [23] H. Hofmeister, F. Huisken, B. Kohn, R. Alexandrescu, S. Cojocaru, A. Crunteanu, I. Morjan and L. Diamandescu, Appl. Phys., A 72, 7 (2001)
- [24] Y.K. Gun'ko, S.C. Pillai and D. Mcinerney, J. Mater. Sci., Mater. Electron. 12, 299 (2001)
- [25] M.Z. Wu, Y. Xing, Y.S. Jia, H.L. Niu, N.P. Qi, J. Ye and Q.W. Chen, Chem. Phys. Lett. 401, 374 (2005)
- [26] Y.B. Khollam, S.R. Dhage, H.S. Potdar, S.B. Deshpande, P.P. Bakare, S.D. Kulkarni and S.K. Date, Mater. Lett. 56, 571 (2002)
- [27] A.Baykal, Y.Köseoglu, M.Senel, Central European Journal of Chemistry, 5(1), 169 (2007)
- [28] Z.Li, Q.Sun and M.Gao, Angew.Chem.Int. Ed., 44, 123 (2005)
- [29] Z.Li, H. Chen, H.Bao and M.Gao, Chem.Mater., 16(8), 1391 (2004)
- [30] J.Rockenberger, E.C.Scher, and A.P.Alivisatos, J.Am.Chem.Soc., 121, 11595 (1999)
- [31] S.Sun, H.Zeng, D.B. Robinson, S.Riaoux, P.M.Rice, S.X.Wang, and G. Li, J.Am.Chem.Soc., 126, 273 (2004)
- [32] S.Sun, and H.Zeng, J.Am.Chem.Soc., 124, 8204 (2002)
- [33] N.Wu, L.Fu, M.Su, M.Aslam, Ka C. Wong, and V.P.Dravid, Nanoletters, 4(2), 383 (2004)
- [34] S.Xuan, L.hao, W.Jiang, X.Gong, Y.Hu, and Z.Chen, JMMM, 308, 210 (2007)
- [35] T.Hyeon, Su S.Lee, J.Park, Y.Chung, and H.Bin Na, J.Am.Chem.Soc., 123, 12798 (2001)
- [36] P.R.Shukla, J. Bhargava, J.Indian Chem.Soc., 60, 788 (1983)
- [37] R.A. Meyers, Interpretation of Infrared Spectra, A Practical Approach. J. Coates (Ed.), in Encyclopedia of Analytical Chemistry (John Wiley& Sons Ltd, Chichester, 2000) 10815-10837
- [38] R.M. Silverstein, G.C. Bassler, and T.C. Morrill, Spectrometric Identification of Organic Compounds, 4th ed. (John Wiley and Sons, New York, 1981)
- [39] K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Wiley, New York, 1986)
- [40] T.Kim and M.Shima, J.Appl.Phys. 101, 09M516 (2007)