STUDY OF SIZE CONTROLLED SYNTHESIS AND CHAACCTERISTIC OF MANGANESE (III) OXIDE NANOPARTICLE

Đến tòa soạn 31 – 3 – 2015

Thi Thu Ha Lai, Nguyen Bich Ngan, Van Thao Ta
Department of chemistry, Hanoi National University of Education, Vietnam

TÓM TẮT

TỔNG HỢP VÀ NGHIÊN CỨU TÍNH CHẤT CỦA HẠT MANGAN (III) OXIT Ở CÁC KÍCH THƯỚC NANO KHÁC NHAU

Bài báo trình bày nghiên cứu sử dụng phương pháp sol-gel có sử dụng các chất phụ gia hữu cơ để tổng hợp nano Mn_2O_3. Đã tiến hành nghiên cứu ảnh hưởng của nồng độ chất phụ gia hữu cơ (axit xitric và SDS (sodium dodecyl sulfate)) và nhiệt độ nung đến kích thước của sản phẩm nano tạo thành. Các sản phẩm tạo ra đều được xác định các tính chất vật lý dựa trên phổ XRD, EDS và hình ảnh SEM. Kết quả cho thấy, khi nồng độ của axit xitric tăng dần từ 0.5M đến 4.0M thì kích thước của nano Mn_2O_3 tạo thành giảm dần và đồng đều hơn, trong khi nồng độ của SDS (0.5M – 2.0M) gần như không ảnh hưởng đến kích thước của nano Mn_2O_3. Hình ảnh SEM cũng cho thấy ảnh hưởng của nhiệt độ nung đến kích thước hạt nano Mn_2O_3, trong đó sản phẩm nung ở 600^{o}C được xem là tối ưu hơn so với nung ở 500^{o}C hay 700^{o}C. Như vậy, việc tổng hợp nano Mn_2O_3 với các kích thước khác nhau (trong khoảng 50nm đến 400nm) có thực hiện dễ dàng dựa vào việc thay đổi nồng độ của axit xitric hay nhiệt độ nung. Do tính chất vật lý của các vật liệu nano thay đổi phụ thuộc vào kích thước hạt, nên việc tạo ra nano Mn_2O_3 ở các kích thước khác nhau có thể giúp mở rộng hơn các ứng dụng của vật liệu này trong công nghệ nano cũng như công nghệ vật liệu.

1. INTRODUCTION

Manganese oxides are important materials and have many applications in many fields such as catalysis, electrodes, high-density magnetic storage media, ion exchangers, sensors, molecular adsorption, and electronics [1-5]. Particularly Mn_2O_3 is a very important material extensively used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials and magnetic materials [6,7]. It has been widely used for the preparation of Li-Mn-O electrodes for rechargeable lithium batteries and for soft magnetic materials such as manganese zinc ferrite,

which is applicable as magnetic cores in transformers for power supplies [8].

Mn_2O_3 nanoparticles have prepared by various methods like surfactant-mediated synthesis, thermal decomposition, polymer-matrix assisted synthesis and spray-pyrolysis [9,10]. Some of the above methods suffer from the difficulty in size-homogeneity and well dispersion of Mn_2O_3 nanoparticles. Recently, the strategy of using organic templates or additives to control the nucleation, growth, and alignment of inorganic particles has been widely applied to the bio-mimetic morphogenesis of inorganic materials with complex forms [11]. In this method organic additives are used as emulsifiers. The main advantage of this method is lowering the calcination temperature [12]. Moreover, the rapid evolution of a large volume of gases during the annealing process of the method cools the product immediately, limits the occurrence of agglomeration due to the aggregation of small particles under high temperature, thus leading to nanocrystalline powders [13,14]. In spite of those advantages, an intensive study for the synthesis of Mn_2O_3 nanoparticle using this method has been not performed – for our best knowledge until now.

Here, we demonstrates a sol-gel method using the various concentration of SDS or citric acid as organic additives for size controlled Mn_2O_3 nanoparticle preparation. Annealing temperature was also investigated at 500 to 700 ^oC. The characterization of final samples by XRD and EDS revealed high purity, had cubic phase structure and chemical formular is Mn_2O_3 as expected. Significantly, results show clearly the effect of citric acid concentration on Mn_2O_3 nanoparticle size, the increase of citric acid concentration leads to the decrease of nanoparticle size. Whereas, it was not found any influence of SDS concentration on the size of prepared Mn_2O_3 nanoparticle products. Furthermore, 600^oC was found to be the best annealing temperature in this study. Altering the citric acid concentration or annealing temperature allows us to achieve Mn_2O_3 nanoparticles with different sizes, this might open new applications of obtained matterials in nanotechnology field.

2. EXPERIMENTAL AND MATERIALS

Manganese nitrate, citric acid, sodium dodecyl sulfate (SDS), were purchased from Sigma-Aldrich supplier. Double distilled (DD) water was used as the solvent throughout the experiment.

2.1. Characterization Methods

The crystal structure of Mn_2O_3 nanoparticles was analyzed by a Rich Siefert 3000 diffractometer with Cu-Kα1 radiation (λ = 1.5406 Å). The morphology of the materials was analyzed by SEM HITACHI SU6600 scanning electron microscopy respectively.

2.2. Synthesis of Mn_2O_3 Nanoparticles

Mn_2O_3 was prepared by thermal decomposition of manganese citrate/manganese dodecyl sulfate. The manganese citrate/manganese dodecyl sulfate was prepared by reacting aqueous solutions of 1 M manganese nitrate with citric acid (0.5 - 4 M)/sodium dodecyl sulfate (SDS) (0.5 – 2 M). The obtained suspension was firstly incubated at 60 ^oC

for overnight, then 200 °C for 3 h and then finally calcined at high temperature (500 – 700 °C) for 5 h. The obtained manganese oxide nanoparticles are characterized by XRD, EDS and SEM.

3. RESULTS AND DISCUSSIONS

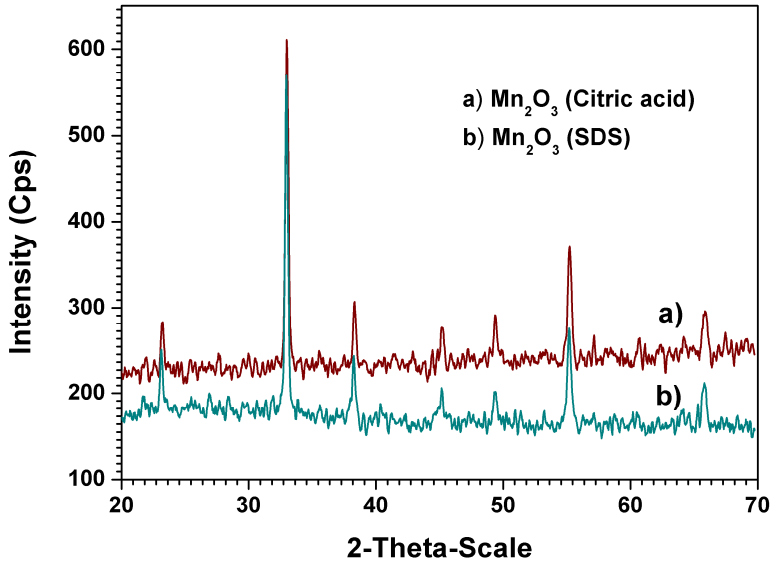

Figure 1: XRD pattern of the Mn_2O_3 nanoparticles prepared at 600 °C.

Figure 1 shows the XRD patterns of Mn_2O_3 nanoparticles prepared by using (**a**) 1M citric acid and (**b**) 1M SDS as organic additive at 600 °C . The XRD parttens clearly indicate that manganese oxides have cubic phase structure in the both preparation methods, the peak positions (2θ = 23.14°, 32.96 °, 38.24 °, 45.17 °, 49.36 °, 55.19 ° and 65.80 °) and relative intensities obtained for the Mn_2O_3 are entirely consistent with the previous reports [8], identifying it as Mn_2O_3 with a cubic structure and cell constant a = 9.4146 A. The XRD results also implies the sol-gel method using either citric acid or SDS as organic additives is suitable for preparing Mn_2O_3 nanoparticle.

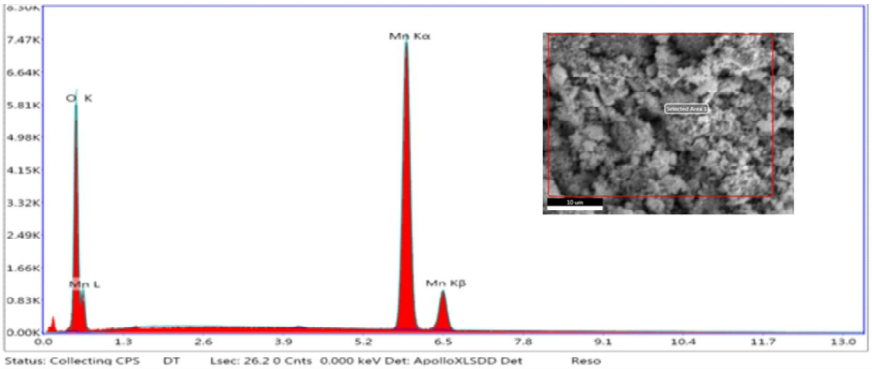

Figure 2: EDS spectrum of Mn_2O_3 nanoparticle calcinated at 600 °C in 1M citric acid

EDS spectrum of Mn_2O_3 nanoparticle calcinated at 600 ^oC in 1M citric acid was also investigated in the area (the red box of SEM) shown with the spectrum in **Figure 2**. The EDS spectrum indicates both manganese and oxygen signatures. By the integrating area of Mn and O peaks, the atomic ratio of Mn:O is ca. 2:3, consistent with the previous result of the XRD partten in the **Figure 1** for the chemical formular of Mn_2O_3. In addition, there was no impurities were found in EDS spectrum of mentioned sample. The EDS spectrum of Mn_2O_3 nanoparticle synthesized by using 1M SDS as organic additive also exposed the exact same partten with that of sample prepared by using 1M citric acid.

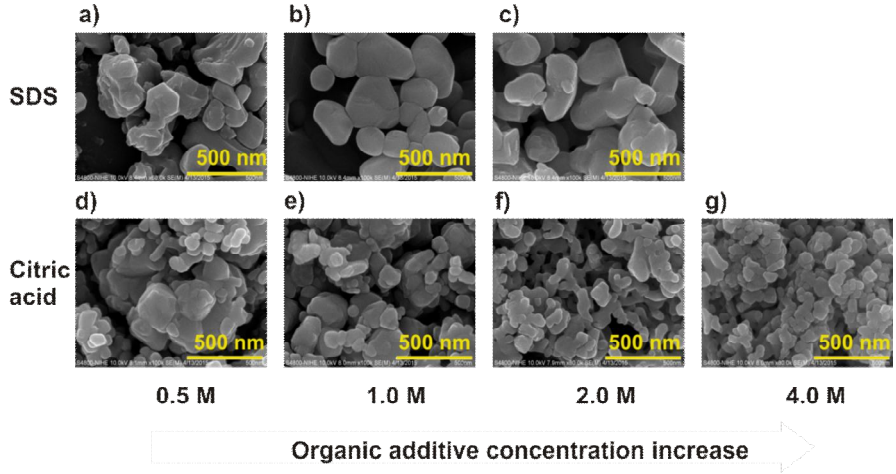

Figure 3: SEM image of Mn_2O_3 nanoparticles prepared in the various concentrations of organic additives: a) 0.5 M SDS; b) 1.0 M SDS; c) 2.0 M SDS; d) 0.5 M citric acid; e) 1.0 M citric acid; f) 2.0 M citric acid; and g) 4.0 M citric acid, calcinated at 600 ^oC.

Figure 3 shows the SEM images of Mn_2O_3 nanoparticles synthesized in the various concentrations of either SDS (**Fig. 3a-c**) or citric acid (**Fig. 3d-g**) as organic additives and calcinated at 600 ^oC. As the concentration of SDS was varied from 0.5 M to 2.0 M, the size of Mn_2O_3 nanoparticles was not observed any alteration (~ 350 nm) (**Fig. 3a-c**). The limited solubility of SDS prevented us performing experiment with the higher concentration of SDS, thus it was imposible to obtain the nanoparticle product of 4.0 M SDS, this was also another limitation of SDS for using as organic additive. **Figure 3d-g** shows the effect of citric acid concentration on the size of Mn_2O_3 nanoparticles. Since the concentration of citric acid increases in the range of 0.5 M and 4.0 M, Mn_2O_3 nanoparticle size decreases significantly (from ~250 nm to ~50 nm), and much smaller than Mn_2O_3 nanoparticles synthesized by using SDS as organic additive. Moreover, shape and size of nanoparticle product prepared with high concentration of citric acid (4 M) appears to be more uniform and fine spherical particles. This might account for the formation of citriate complexes with metalic cations which effectively keeps the constituent metalic cations dispersed homogeneously and thus makes the

formation of nanoparticles type easier [11, 12]. We also tried to increase citric acid up to saturated concentration (~ 5 M at 60 ^{o}C), the nanoparticle size of Mn_2O_3, however, appeared not to decrease any more. Thus, 4 M citric acid concentration could be the optimal concentration of an organic additive for preparing Mn_2O_3 nanoparticle with the size of ~ 50 nm.

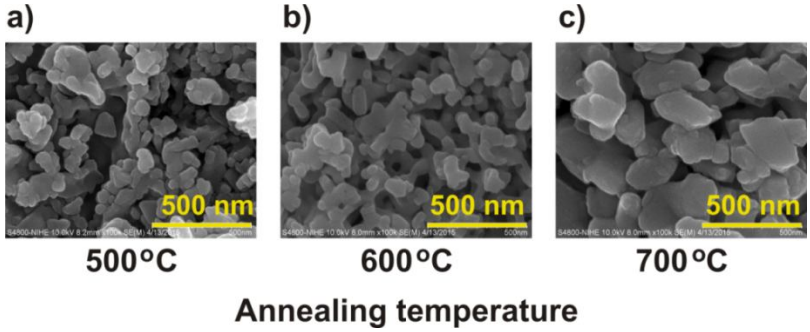

Figure 4: SEM images of Mn_2O_3 nanoparticle prepared at various annealing temperature (500-700 ^{o}C).

The effect of annealing temperature was also investigated, the results are showed in the Figure 4. In this experiment, Mn_2O_3 nanoparticle was prepared at three different annealing temperatures (500, 600 and 700 ^{o}C) with 4.0 M citric acid as organic additive. When annealing temperature changes, the size and morphology of obtained nanoparticle products also vary significantly. Particularly, the best result was achieved at the annealing temperature of 600 ^{o}C, while product obtained at 700^{o}C shows the biggest size. The shape of product obtained at 500 ^{o}C shows less uniform than that at 600 ^{o}C. This would be accounted for the different rate of oxidation reaction and gasses release. While, the biggest size of nanoparticle at 700 ^{o}C could resulted in the agglomeration of small particles under high temperature [13,14]. Thus, 600 ^{o}C could be considered as an optimal temperature for the preparation of Mn_2O_3 nanoparticle via sol-gel method.

In conclusion, we demonstred conditions for the size-controlled synthesis of Mn_2O_3 nanoparticle. The experiments exploited either SDS or citric acid with various concentration as organic additives, the effect of annealing temperatures was investigated as well. Products was then characterized by XRD, EDS and SEM. The result clearly showed the effect of citric acid concentration on the size of obtained Mn_2O_3 nanoparticle, while this was not found as changing concentration of SDS. The result also indicated that 600^{o}C seemed to be best temperature for annealing comparing with 500^{o}C and 700^{o}C. The method allowed us to synthesis Mn_2O_3 nanoparticle with size of ca. 50 nm and also the bigger sizes. For nanomatterials, the size could determine properties of the matterial, this might promise various applications of Mn_2O_3 nanoparticles in the field of nanotechnology.

REFERENCES

[1] Seo, W. S.; Jo, H. H.; Lee, K.; Kim, B.; Oh, S. J.; Park, J. T. (2004) *Angew. Chem., Int. Ed*, 43, 1115-1117.

[2] Armstrong, A. R.; Bruce, P. G. (1996) *Nature*, 381, 499-500.
[3] Shen, Y. F.; Zerger, R. P.; DeGuzman, R. N.; Suib, S. L.; McCurdy, L.; Potter, D. I.; O'Young, C. L. (1993) *Science*, 260, 511-515.
[4] Anilkumar, M.; Ravi, V. (2005) *Mater. Res. Bull.*, 40, 605-609.
[5] Yang, L.-X.; Zhu, Y.-J.; Tong, H.; Wang, W.-W.; Cheng, G.-F. (2006) *J. Solid State Chem*, 179, 1225-1229.
[6] M.I. Shiloms, A.F. Pshenichnikov, K.I. Morozov, and I. Yu. Shurubor, (1990) *J. Magn. Magn. Mater.,* 85, 40–46.
[7] C. Bergemann, D. Muller-Schulte, J. Oster, L.A. Brassard, and A.S. Lubbe, (1999) *J. Magn. Magn. Mater.,* 194, 45–52.
[8] R. Manigandan, R. Suresh, K. Giribabu, L. Vijayalakshmi, A. Stephen, V. Narayanan, (2014) *Optoelectronic Materials and Thin Films*, 1576, 125-127.
[9] C. Gruttner, and J. Teller, (1999) *J. Magn. Magn. Mater.,* 194, 8–15.
[10] L. Guo, J. Huang, X.Y. Li, and S.H. Yang, (2001) *Phys. Chem. Chem. Phys.* 3, 1661–65.
[11] M. Ghiasi, A. Malekzadeh, (2012) *Cryst. Res. Technol.* 47, No. 4, 471 – 478.
[12] M. Khazaei, A. Malekzadeh, F. Amini, Y. Mortazavi, and A. Khodadadi, (2010) *Cryst. Res. Technol.* 45, 1064.
[13] P. Courty, H. Ajot, C. Marcilly, and B. Delmon, (1973) *Powder Technol.* 7, 21.
[14] H. M. Zhang, Y. Teraoka, and N. Yamazoe, (1987) Chem. Lett. 16, 665.

XÁC ĐỊNH ĐỒNG THỜI As (III), As(V), MONOMETHYLARSONIC …… *(tiếp theo tr. 324)*

[3], P, Niedzielski, (2005) *The new concept of hyphenated analytical system: Simultaneous determination of inorganic arsenic(III), arsenic(V), selenium(IV) and selenium(VI) by high performance liquid chromatography–hydride generation–(fast sequential) atomic absorption spectrometry during single analysis, Analytica Chimica Acta,* ***551*** *199-206.*
[4], T,Guerin, M,Astruc, A,Batel, M,Borsier, (1997) *Multielement specsiation of As, Se,Sb and Te by HPLC-ICP-MS, Talanta* ***44*** *2201-2208.*
[5], M,Kotrebai, J,F,Tyson, E,Block, P,C,Uden, (2000) *High-performance liquid chromatography of selenium compounds utilizing perfluorinated carboxylic acid ion pairing agent and inductively coupled plasma and electrospay ionization mass spectrometric detection, Journal of chromatography A,* ***866*** *51-63.*
[6], Van Anh Nguyen, Sunbaek Bang, Pham Hung Viet, Kyoung-Woong Kim (2009) *Contamination of groundwater and risk assessment for arsenic exposure in Ha Nam province, Vietnam, Environment International 35 466-472.*
[7], Phạm Hải Long, Vũ Văn Tú, Hoàng Nam, Nguyễn Thị Huệ. (2012) *Xác định đồng thời As III, AsV, MMA và DMA trong nước ngầm và nước mặt bằng HPLC-ICP-MS, Tạp chí Khoa học và Công nghệ, Tập 50, số 2B, 270-277.*