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A synthesis technology of honeycomb-like structure MnO_2 from low grade manganese ore

Abstract

In this paper, the honeycomb-like structure MnO_2 was firstly prepared from low grade manganese ore with three main steps. Firstly, low grade manganese ore was reduced to be MnO by biomass at 400°C in 40min. Secondly, the soluble MnO from the reduced low grade MnO_2 ore was leached by dilute sulphuric acid to be $MnSO_4$ solution at 80°C in 30min, and lastly the honeycomb-like structure MnO2 can be prepared by the redox reaction of mixed $MnSO_4$ and $KMnO_4$ solution. The optimal experimental conditions were that the pH value of mixed solution was 5, the reaction temperature was 60°C, the mole ration of $KMnO_4$ and $MnSO_4$ was 2.5:3, the feed rate of $KMnO_4$ and $MnSO_4$ solution was 3ml/min until they were feed out, and then kept for 30min before filtrating. The final product was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM), demonstrating that its crystal structure was γ-MnO_2.

Keywords: mno$_2$, honeycomb-like structure, manganese ore, demonstrating, redox reaction, microstructure

Volume 2 Issue 1 - 2018

Yuna Zhao, Guocai Zhu
Tsinghua University, China

Correspondence: Yuna Zhao, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 102201, China, E-mail yunazhao@tsingua.edu.cn

Received: February 07, 2018 | **Published:** February 14, 2018

Abbreviations: SEM, scanning electron microscope; XRD, x-ray diffraction

Introduction

Manganese ore is important mineral resource, widely being used in various industries which include metallurgy, ceramics, pharmaceuticals etc. According to USGS statistics,[1] the base reserve of manganese ore in the world is about 5billion 700million ton, mainly in South Africa(71.8%), Ukraine(11.9%), Australia(3.8%), and China(2.5%). The total amount of China's manganese resource is abundant, but which have the characteristics of larger lean ore, little mine with rich grade and complicated ore type. Since the availability of high-grade manganese ore is limited, it is imperative to identify and process low-grade complex ores that don't adversely impact the environment.[2–4]

During the past few decades, controllable synthesis of specific microstructure materials has received considerable attention for their unique properties and potential applications in functional materials.[5–8] The growing interest has been focused on nanostructures MnO_2 because of their fundamental scientific significance and many technological applications.[9–11] These specific nanostructures with outstanding performance and unique chemical properties have been used extensively in various kinds of energy storage systems. The different structure MnO_2 were prepared successfully on the basis of the redox reactions of MnO_4^- and/or Mn^{2+}, such as hydrothermal Golden DC & Shen YF,[12–14] coprecipitation Lee HY & Staiti P,[15,16] thermal Muraoka Y,[17] sol-gel,[18–20] and electrochemical methods etc.[21,22]

Among these researches, few study have been done that the manganese ore as raw materials was used to prepare nanostructure manganese oxides. In this paper, the honeycomb-like structure MnO_2 has been successfully prepared from low grade manganese ore. Low grade manganese ore was firstly reduced to be dissolvable MnO by biomass at 400°C, the reduction product was leached with diluted sulfuric acid to be $MnSO_4$ solution. The obtained $MnSO_4$ solution was mixed with $KMnO_4$ solution to prepare honeycomb-like structure MnO_2. This technology offered a new way for the utilization of waste low grade manganese resource and decrease of environmental pollution.

Experimental section

Chemical analysis of low grade manganese ore and the final product

The low-grade manganese oxide ore was selected from Guangxi, South China. Its main chemical composition is shown in Table 1. In contrast to the raw ore, the Mn content of the prepared honeycomb-like MnO_2 was increased greatly to be 57.05%, and other impurity content is very low.

Table 1 Chemical composition of low grade manganese oxide ore and honeycomb-like MnO_2 (mass fraction)

Component	Mn	Zn	Ni	Pb	Co	Cu	Fe	Mg	Cr	Al	Si
Manganese ore /%	17.32	0.017	0.05	0.25	0.057	0.041	11.77	0.19	11.3	2.559	14.6
Honeycomb-like MnO_2/%	57.05	0.003	0.01	0.01	0.059	0.002	0.265	0.007	0	0.004	0

Experiment procedure

The preparation of $MnSO_4$ solution from low grade manganese: The mixture of manganese dioxide ore and sawdust were well-mixed and put into ceramic crucible, and then were roasted in muffle furnace (the sawdust dosage was 25% mass fraction of manganese ore, the roasting temperature was 400°C and roasting time was 30min) and hermetically cooled to room temperature before removing the cover. The reduced manganese ore was leached by 1mol/L sulfuric acid solution for 30min at 80°C, the ratio of sulfuric acid and reduced manganese ore is controlled at 10ml/g. The $MnSO_4$ solution can be obtained after filtrating the leached manganese ore and washing it by deionized water, using as raw liquid for preparing the honeycomb-like structure MnO_2, the content of $MnSO_4$ solution is 0.576mol/L.

The preparation of the honeycomb-like structure MnO_2: A certain amount of $KMnO_4$ solution and the $MnSO_4$ solution were feed into three necks flask by a peristaltic bump, and the flask was put in a 80°C water bath. The honeycomb-like structure MnO_2 product was obtained by washing, filtrating and drying at 80°C in drying oven. The crystal structure and the morphology was characterized by X-ray diffraction and Scanning Electron Microscopy. The Schematic diagram of the preparing process for honeycomb-like MnO is shown in Figure 1.

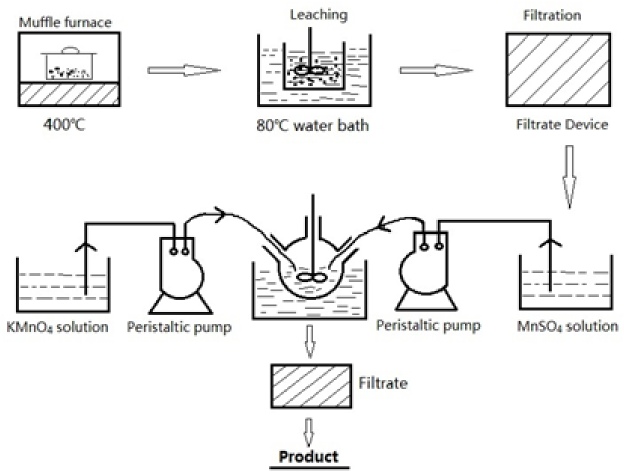

Figure 1 Schematic diagram of the preparing process for honeycomb-like MnO

Result and discussion

The effect of pH value

The flask with three necks was put into water bath with 60°C constant temperature. $MnSO_4$ solution was adjusted to the different pH value of 3, 4,5,6,7 by adding NaOH particle, and then $MnSO_4$ and $KMnO_4$ solution with the mole ratio of 3:2 were added into flask at the same speed of 3ml/min. The MnO_2 content of the precipitate was shown in Figure 2. When the pH value of $MnSO_4$ solution was increased to be 5, MnO_2 content of the product can be reached to be 94.24%. When the reduced MnO_2 ore was leached by dilute sulfuric acid to be $MnSO_4$, other impurity ions such as Fe^{2+}, Al^{3+} and Zn^{2+} was solved. Some ions was precipitated if pH value of $MnSO_4$ solution was increased to be 5, so the purity MnO_2 product was improved. When pH value of $MnSO_4$ solution was improved to be over 6, the precipitated $Al(OH)_3$ was dissolved again in the $MnSO_4$ solution, resulting in the decrease of the purity MnO_2 product.

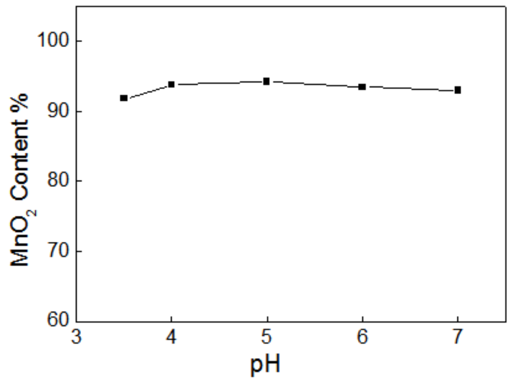

Figure 2 The pH effect on the purity of MnO_2 product

The effect of reaction temperature

The pH value of $MnSO_4$ solution was adjusted to be 5 by adding NaOH particle. The flask with three necks was put into water bath with the different temperature and then $MnSO_4$ and $KMnO_4$ solution with the mole ratio of 3:2 were added into flask at the same speed of 3ml/min. The MnO_2 content of the precipitate was shown in Figure 3. With the increase of water bath temperature, the purity of the MnO_2 product was improved gradually. When the reaction temperature ranged from 60°C to 90°C, the purity of MnO_2 product was increased from 94.24% to be 94.3%. At the relative high reaction temperature, the rate of chemical reaction was accelerated. However, in consideration of water evaporation at 90°C, the temperature of water bath was controlled at 60°C.

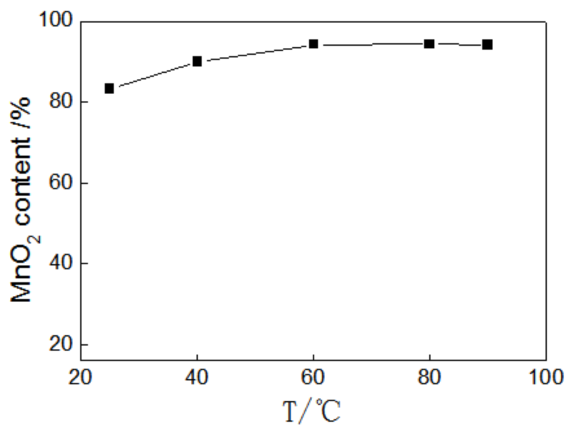

Figure 3 The effect of reaction temperature on the purity of MnO_2

The effect of the molar ratio of $KMnO_4$ and $MnSO_4$

The pH value of $MnSO_4$ solution was adjusted to be 5 by adding NaOH particle. The flask with three necks was put into water bath with 60°C and then $MnSO_4$ and $KMnO_4$ solution with the different mole ratio were separately added into flask at the same speed of 3ml/min. The MnO_2 content of the precipitate was shown in Figure 4. With the decrease of mole ratio of $KMnO_4$ and $MnSO_4$, the content of the product raised at first and then descended. The optimal mole ratio of $KMnO_4$ and $MnSO_4$ is 2.5:3, and the purity of MnO_2 is 95.01%.

The effect of the flux velocity of $KMnO_4$ and $MnSO_4$

The pH value of $MnSO_4$ solution was adjusted to be 5 by adding

DOI: 10.15406/mojabb.2018.02.00045

NaOH particle. The flask with three necks was put into water bath with 60 °C and then $KMnO_4$ and $MnSO_4$ solution with the mole ratio of 2.5:3 were added into flask at the different speed of 2,3,4,5,6ml/min. The MnO_2 content of the precipitate was shown in Figure 5. With the increase of $MnSO_4$ and $KMnO_4$ solution feed rate, the purity of MnO_2 product was decreased. When the feed rate was improved to be over 5, the purity of MnO_2 product was decreased slowly. When the feed rate was relative fast, partial solution of $MnSO_4$ and $KMnO_4$ did not occur redox reaction which causing the decrease of MnO_2 precipitation and the content of the impurity in product was relative high. So the feed rate 3ml/min of $MnSO_4$ and $KMnO_4$ solution was recommended.

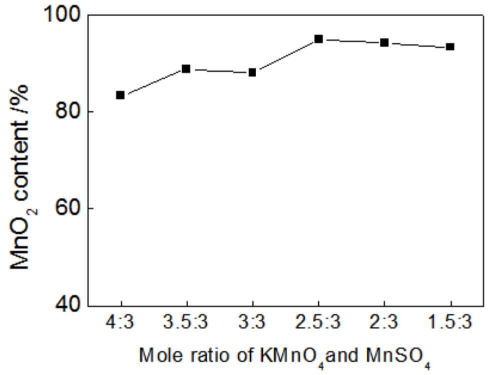

Figure 4 The effect of mole ratio of $KMnO_4$ and $MnSO_4$

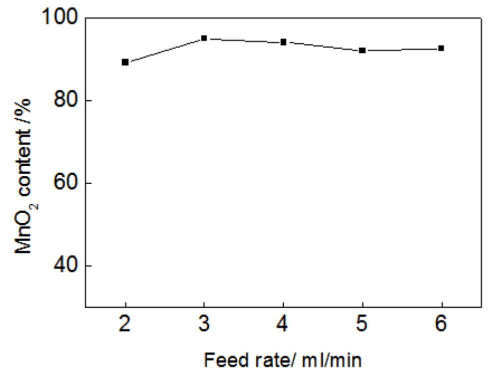

Figure 5 The effect of feed rate on the purity of MnO_2

The effect of stand time

The pH value of $MnSO_4$ solution was adjusted to be 5 by adding NaOH particle. The flask with three necks was put into water bath with 60°C and then $MnSO_4$ and $KMnO_4$ solution with the different mole ratio of 3:2.5 were added into flask at the speed of 3ml/min. When the feed of $MnSO_4$ and $KMnO_4$ solution was finished, the mixed solution in the flask with three necks was standed for 0, 10, 20, 30, 40, 50min. The MnO_2 content of the precipitate was shown in Figure 6. The effect of the stand time on the purity of the product is negligible; the redox reaction of $MnSO_4$ and $KMnO_4$ was finished with the completion of feed. So the stand time of 30min is enough.

XRD analysis of the honeycomb-like structure MnO_2

The crystal phase of the honeycomb-like structure MnO_2 was analyzed by powder X-ray diffraction. The XRD patterns of the representative a product was shown in Figure 7, it corresponded to the formation of γ-MnO_2 (ICDD-JCPDS No. 14-0644). Meanwhile, the broadened diffraction peaks indicated that the crystalline sizes of the samples was small, further verifying the high crystallinity of the MnO product.

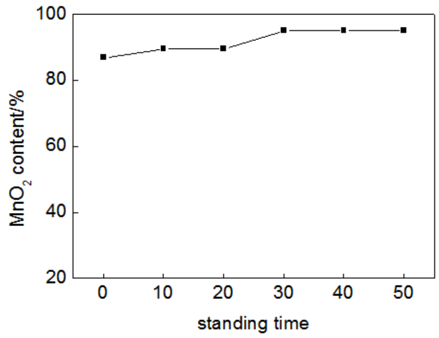

Figure 6 The effect of stand time on the purity of MnO_2

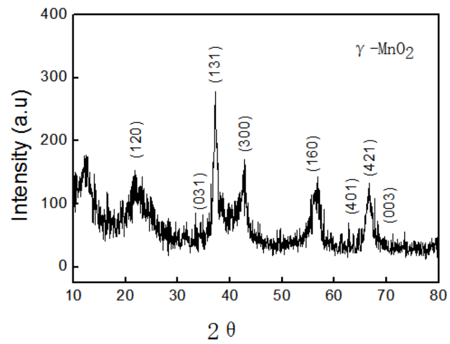

Figure 7 XRD patterns of the representative products

SEM characterization of the honeycomb-like structure MnO_2

The morphology of the prepared sample is characterized by SEM. Figure 8A shows the characteristic SEM images of honeycomb-like structure MnO, demonstrating that the prepared product consists of honeycomb-like structure MnO. Figure 8B shows the magnified image of honeycomb-like structure MnO and many holes can be seen clearly on the MnO product surface.

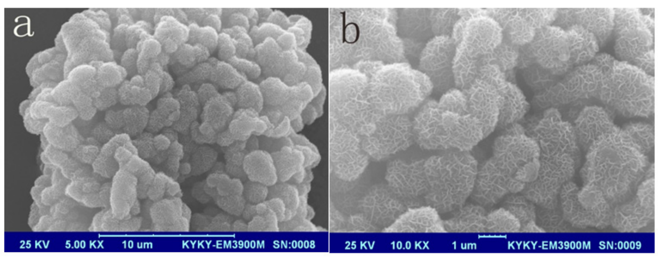

Figure 8(A) SEM image of MnO product.

Figure 8(B) SEM image of magnified honeycomb-like MnO

Conclusion

Honeycomb-like structure γ-MnO is prepared from low grade manganese ore by a technology including three main procedures: reduction of low grade manganese, leaching process of the reduced manganese ore, oxidation-reduction process of $MnSO_4$ and $KMnO_4$ solution. The reduction process of manganese ore is finished in 40min at 400°C, the leaching process is carried out in 80°C water bath in

Citation: Zhao Y, Zhu G. A synthesis technology of honeycomb-like structure MnO_2 from low grade manganese ore. *MOJ App Bio Biomech.* 2018;2(1):57–60. DOI: 10.15406/mojabb.2018.02.00045

30min, and honeycomb-like structure MnO_2 product is eventually prepared by oxidation-reduction process of $MnSO_4$ and $KMnO_4$ solution with the experimental conditions of the solution pH5, reaction temperature of 60°C, flux velocity of 3ml/min, the mole ratio of 2.5:3 and the standing time of 30min.

Acknowledgements

The author thanks National Natural Science Foundation (Grant No. 51504141) for providing the research grant.

Conflict of interest

The author declares that there is no conflict of interest.

References

1. http://minerals.usgs.gov/minerals/pubs/,2009-04-15
2. Figueira BAM, Angelica RS, Costa ML, et al. Conversion of different Brazilian manganese ores and residues into birnessite-like phyllomanganate. *Appl Clay Sci*. 2013;86:54–58.
3. Faria GL, Ten JAS, Jannotti N, et al. Disintegration on heating of a Brazilian manganese lump ore. *Int J Miner Process*. 2013;124:132–137.
4. Tang Q, Zhong H, Wang S, et al. *Metal Soc*. 2013;24:861–867.
5. Zinchenko AA, Yoshikawa K, Baigl D. DNA-templated silver nanorings. *Adv Mater*. 2005;17(23):2820–2823.
6. Alemán B, Ortega Y, García JÁ, et al. Fe solubility, growth mechanism, and luminescence of Fe doped ZnO nanowires and nanorods grown by evaporation-deposition. *J Appl Phys*. 2011;110(1):1–5.
7. Zhang LC, Liu ZH, Tang XH, et al. Synthesis and characterization of β-MnO_2 single crystals with novel tetragonous morphology. *Materials Research Bulletin*. 2007;42(8):1432–1439.
8. Zhang DE, Wu W, Li SZ, et al. A novel chemical reduction route toward fabrication of Fe_3O_4 octahedrons and Fe tubes. *J Mater Sci*. 2010;45(1):34–38.
9. Li ZQ, Ding Y, Xiong YJ, et al. Rational Growth of Various α-MnO_2 Hierarchical Structures and β-MnO_2 nanorods via a Homogeneous Catalytic Route. *Cryst Growth Des*. 2005;5(5):1953–1958.
10. Guo LW, Peng DL, Makino H, et al. Structural characteristics and magnetic properties of λ-MnO2 films grown by plasma-assisted molecular beam epitaxy. *J Appl Phys*. 2001;90:351–354.
11. Duan YP, Ma H, Li XG, et al. The Microwave Electromagnetic Characteristics of Manganese Dioxide with Different Crystallographic Structures. *Physica B*. 2010;405(7):1826–1831.
12. Golden DC, Chen CC, Dixon J. Synthesis of Todorokite. *Science*. 1986;231(4739):717–719.
13. DeGuzman RN, Shen YF, Neth EJ, et al. Synthesis and Characterization of Octahedral Molecular Sieves (OMS-2) Having the Hollandite Structure. *Chem Mater*. 1994;6(6):815–821.
14. Shen YF, Zerger RP, Suib SL, et al. Manganese oxide octahedral molecular sieves preparation characterization and applications. *Science*. 1993;5(260):511–515.
15. Lee HY, Kim SW, Lee HY. Expansion of Active Site Area and Improvement of Kinetic Reversibility in Electrochemical Pseudo capacitor Electrode. *Electrochemical and Solid-State Letters*. 2001;4:19–22.
16. Staiti P, Lufrano F. Study and optimisation of manganese oxide-based electrodes for electrochemical supercapacitors. *Journal of Power Sources*. 2009;187(1):284–289.
17. Muraoka Y, Chiba H, Atou T, et al. Preparation of α-MnO2 with an Open Tunnel. *J Solid State Chem*. 1999;144(1):136–142.
18. Ching S, Petrovay DJ, Jorgensen ML. Sol-gel synthesis of layered birnessite-type manganese oxides. *Inorg Chem*. 1997;36(5):883–890.
19. Ching S, Roark JL, Duan NG, et al. Sol−Gel route to the tunneled manganese oxide cryptomelane. *Chem Mater*. 1997;9(3):750–754.
20. Reddy RN, Reddy RG. Synthesis and electrochemical characterization of amorphous MnO2 electrochemical capacitor electrode material. *Journal of Power Sources*. 2004;132(1):315–319.
21. Devaraj S, Munichandraiah N. High Capacitance of Electrodeposited MnO2 by the Effect of a Surface-Active Agent. *Electrochemical and Solid-State Letters*. 2005;8(7):373–377.
22. Hu CC, Tsou TW. Ideal capacitive behavior of hydrous manganese oxide prepared by anodic deposition. *Electrochemistry Communications*. 2002;4(2):105–109.