

PII S0025-5408(97)00069-X

γ-RAY RADIATION PREPARATION AND CHARACTERIZATION OF NANOCRYSTALLINE MANGANESE DIOXIDE

Y.P. Liu¹*, Y.T. Qian², Y.H. Zhang², M.W. Zhang², C.S. Wang³ and L. Yang³

¹Department of Precision Engineering ²Department of Applied Chemistry ³Structure Research Laboratory University of Science and Technology of China Hefei, Anhui 230026, P.R. China

(Refereed) (Received September 20, 1996; Accepted March 6, 1997)

ABSTRACT

Nanocrystalline manganese dioxide (MnO₂) powders have been prepared by radiating potassium permanganate (KMnO₄) aqueous solution with γ -ray at ambient pressure and temperature. The influence of the experimental conditions on the results has been studied in detail. TEM and XRD show that the smallest mean particle size of the product is about 6 nm and the particle size distribution is very narrow. © 1997 Elsevier Science Ltd

KEYWORDS: A. nanostructures, A. oxides, B. chemical synthesis, C. photoelectron spectroscopy, C. X-ray diffraction

INTRODUCTION

The design, synthesis, and characterization of nanoscale materials characterized by a grain size of <100 nm have been the subject of much recent research. Experiments have shown that the properties of the nanoscale materials are significantly different and improved compared to their course-grained (micron-sized) counterpart [1-4]. Successful synthesis of nanoscale materials of powders has utilized inert gas condensation [5], hydrothermal method [6], and sol-gel method [7], among others. Despite the success of these methods, there are

^{*}To whom correspondence should be addressed.

some problems and limitations, such as complex technique, possible reaction between metal vapor and oven material, limited success with refractory metal for the gas condensation, high temperature and high pressure for the hydrothermal method, and expensive raw materials for the sol-gel method.

Recently, γ -ray radiation method has been applied to prepare nanocrystalline metals, alloys, and metal oxides [8–10]. In this paper, we first report the preparation of nanocrystalline manganese dioxides (MnO₂) powders by radiating potassium permanganate (KMnO₄) aqueous solutions with γ -ray at ambient pressure and temperature.

EXPERIMENTAL

Analytical-grade potassium permanganate powders were dissolved in distilled water to form a series of solutions. Polyvinyl alcohol (PVA) or sodium dodecyl sulfate (SDS) was chosen as a surfactant, and isopropanol as a scavenger for hydroxyl radicals. The pH of the solutions was adjusted by adding 1 M sodium hydroxide. The solutions were irradiated in the field of a 49,000Ci ⁶⁰Co source. After being separated, the precipitate was washed with distilled water and alcohol, then dried at 60°C in a vacuum drier. The products are black powders.

X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $0.05^{\circ}s^{-1}$ in the 2 θ range from 10° to 65° using a Rigaku Dmax γ_A diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). TEM images were taken with a Hitachi model H-800 transmission electron microscope, operating at 200 KV accelerating voltage. The particle sizes of powders were measured from microphotographs and calculated from XRD patterns according to the Scherrer formula:

$L = K\lambda/(\beta \cos \theta)$

where L is average particle size, K is the Scherrer constant related with the shape and index (*hkl*) of crystals [11], λ is the wavelength (=1.5418 Å) of X-ray, and β is obtained from the Warren and Biscoe equation [12],

$$\beta^2 = B^2 - b^2$$

where B and b are the angular half-widths for the sample under investigation and a standard sample, respectively. Analytically pure MnO_2 powders after being annealed 10 h at 350°C have been used as the standard sample.

X-ray photoelectron spectroscopy (XPS) patterns were measured on ESCALAB FISONS X-ray photoelectron spectrometer with exciting source Mg K α = 1253.6 eV in high vacuum (5 × 10⁻⁹ Pa). The constant analyzer energy of equipment is 20 eV.

RESULTS AND DISCUSSION

XPS and XRD Studies of the Products. XPS was used to analyze surface composition and content of 0.2–5 nm thickness. XPS patterns of sample 2 (Table 1) are given in Figure 1. The data of the XPS patterns are listed in Table 2.

There is an error of -0.4 eV for this set of instruments rectified with the standard binding energy, C ls binding energy 284.8 eV. From the Figure la, we can know the product contains

Sample	C _{KMnO4} (M)	C _{surfactant} (M SDS)	Radiation Dose	Average Particle Siz (nm)
1	0.005	0.005	$2.01 \times 10^{3} \text{ Gy}$	6
2	0.01	0.01	$2.01 \times 10^{3} \text{ Gy}$	8
3	0.015	0.015	$2.01 \times 10^{3} \text{ Gy}$	8
4	0.02	0.02	2.01×10^{3} Gy	9
5	0.01	0.005	$2.01 \times 10^{3} \text{ Gy}$	12
6	0.01	0.02	$2.01 \times 10^{3} \text{ Gy}$	10
7	0.01	0.03	$2.01 \times 10^{3} \text{ Gy}$	6
8	0.01	0.02	4.02×10^3 Gy	10
9	0.01	0.02	6.03×10^3 Gy	14

 TABLE 1

 The Relation Between Experimental Conditions and Results

only two elements, manganese and oxygen. The true value of Mn 2p3 binding energy should be 642.37 eV. It is very close to 642.3 ~ 642.4 eV of Mn⁴⁺ 2p3 binding energy and far from 641.5 ~ 641.75 eV of Mn³⁺ 2p3 binding energy. The results show that the valence of manganese of sample 2 (Table 1) is +4.

There are two peaks for O ls binding energy (Fig. 1c). The peak 532.71 eV marks O ls binding energy of OH, which can be caused by O atoms in water molecules adsorbed on the surface of nanocrystalline particles. Because MnO_2 particles are very small, specific surface of the samples is large, so the adsorption to water in air is very strong although 1×10^{-9} Pa high vacuum in XPS measurement cannot let them off. The peak 530.41 eV marks O ls binding energy of oxides. The difference of 112.3 eV between this value and that for Mn^{4+} 2p3 binding energy agrees with the difference between Mn 2p3 binding energy and O ls binding energy in manganese dioxide. Based on the above discussion, the product is a kind of manganese dioxide. But it is difficult to distinguish a composition and a phase from many kinds of manganese oxides according to the XPS pattern.

The data of Table 2 show that the atom number ratio Mn : O = 17.5 : 33.5 = 1 : 1.91, slightly lower than Mn : O = 1 : 2 in MnO_2 , which may come from the oxygen atom defects in nanoparticles of MnO_2 .

An XPS pattern of analytically pure MnO_2 powders consisting of coarse grains is given in Figure 2, for comparison with the nanocrystalline sample. There is no error for this experiment rectified with the standard binding energy, C 1s binding energy 284.8eV. This pattern shows good agreement with that of the analytically pure sample. Only a peak for O 1s binding energy marking the O atom in OH is much lower than that of nanocrystalline MnO_2 . The reason for this is that analytically pure MnO_2 powders consist of coarse grains; the surface fraction is very low, so the adsorption content to H₂O molecules is small, and, as a result, this peak is low in the XPS pattern.

Figure 3 shows a typical XRD pattern of the product (sample 2 in Table 1). Because the particle sizes of the product are very small, strong diffraction peaks widen greatly and weak ones disappear; only three diffraction peaks exist in the pattern. Based on the conclusion resulting from the XPS pattern and data of the sample, only a tetragonal phase MnO₂, its exact formula MnO_{1.88}, is in accord with the XRD pattern; therefore, we conclude that the



XPS patterns of sample 2 in Table 1. (a) Scanning spectrum of binding energy from 0–1000 eV, (b) Mn 2p3 binding energy, and (c) O 1s binding energy.

Peak	SF	[AT]%	Peak Center	Peak Arca
O ls	2.85	33.3	530.41	7138.7
Mn 2p3	8.99	17.5	642.76	11977.7

 TABLE 2

 Data of XPS Quantitative Analysis of Sample 2 in Table 1

crystalline product is a tetragonal phase of MnO₂, the exact formula of which is MnO_{1.88}. Compared with the XPS data, oxygen content of the surface composition is slightly higher than that of the crystal; this is caused by disorder and adsorption of nanoparticles to oxygen. The three peaks in the pattern are well indexed with 100, 003, and 005, respectively. The rationale for this conclusion is that e_{aq} with a standard reduction potential of -2.97 V [13] can reduce Mn⁷⁺ to Mn⁵⁺, whereas only a weak reductant can reduce Mn⁷⁺ to Mn⁴⁺. From this indexed pattern, the values of *a* and *c* axes can be calculated: a = 6.99 and b = 7.12. The values of *a* and *c* are very close to those reported in JCPDS.

Average particle sizes of the samples were calculated by the following method: three average particle sizes are separately calculated according to three peaks in the XRD patterns and then the average value for these three average particle sizes is calculated as the average particle size of the sample. The largest difference between the three values for the same sample is ≤ 1 nm.

TEM Study of Nanocrystalline Manganese Dioxide Powders. Figure 4 shows a TEM image of nanocrystalline manganese dioxide powders (sample 2 in Table 1). The image displays spherical particles of the product. The particles are very small and narrowly distributed. All the particles are <15 nm, and some of them are too small to be clearly distinguished from this image.

Influence of Experimental Conditions on Particle Size. Detailed experiments show that the concentration of KMnO₄, the concentration of surfactant, and the γ -ray radiation dose have influence on the average particle size of nanocrystalline MnO₂ powders, but the pH of the solutions and the concentration of (CH₃)₂CHOH have not. The relation between experimental conditions and results is listed in Table 1.

The experimental data (Table 2) reveal that concentration of surfactant has the greatest influence on precipitation rate and particle size of manganese dioxide powders. Increase in surfactant concentration results in increasing precipitation rate. When the SDS concentration was 0.005 M (sample 1), the time for complete precipitation was a half hour; but when the SDS concentration was 0.03 M (sample 7), it was 12 hours. For both samples, the average particle size was 6 nm.

To get enough product, it is necessary to use a high concentration of KMnO₄ (≥ 0.01 M). But a concentration of SDS as high or higher than the concentration of KMnO₄ solution results in finer particles. Keeping a constant ratio of SDS to KMnO₄ (=1), the average particle size of the products increases gradually as both concentrations are increased: average particle size for sample 1 is 6 nm while that of sample 4 is 9 nm. An increasingly higher ratio of SDS to KMnO₄ results in reducing average particle size: average particle size of sample 6 is 8 nm while that of sample 7 is 6 nm. However, it is difficult to wash out SDS particles from products. If SDS concentration is three times that of KMnO₄, the product contains a small amount of SDS and the yield is lower because the product must be washed many more times to remove SDS.



XPS patterns of analytically pure sample. (a) Scanning spectrum of binding energy from 0-1000 eV, (b) Mn 2p3 binding energy, and (c) O 1s binding energy.



FIG. 3 XRD patterns of sample 2 in Table 1.

As shown in Table 1, when the radiation dose increases from 2.01×10^3 Gy (sample 2) to 6.03×10^3 Gy (sample 9), average particle size correspondingly increases from 8 nm to 14 nm. In addition, the radiation dose affects the purity of the products. The radiation dose of 1.0×10^4 Gy results in a little Mn³⁺ compound mixed in nanocrystalline MnO₂ powders.

The pH of the solutions practically has no influence on particle size. There is a suitable pH range for the preparation of nanocrystalline MnO_2 powders: $6.5 \le pH \le 8.5$. If the pH of the solutions is above 9.5, Mn^{3+} may be detected via XPS patterns.

In order to avoid the reaction of $(CH_3)_2CHOH$ and $KMnO_4$, the concentration of $(CH_3)_2CHOH$ cannot be above 0.5 M.

CONCLUSION

 γ -ray radiation method is successful for the preparation of nanocrystalline MnO₂ powders. The exact molecular formula of crystalline part should be MnO_{1.88}, and the composition of particle surface is MnO_{1.91}, slightly higher than that of the crystalline part. Suitable preparation conditions have been determined: the SDS concentration should be one to two



FIG. 4 TEM image of sample 2 in Table 1.

times that of KMnO₄, the pH of the solutions should be in the range of 6.5–8.5, the scavenger concentration should be below 0.5 M, and the radiation dose may be from 2.0×10^3 to 4.0×10^3 Gy. Adopting these experimental conditions, we have produced nanocrystalline MnO₂ powders with no impurity and high yield, besides narrow distribution of particle size and average particle size in the range 6–10 nm.

ACKNOWLEDGMENT

This paper was performed under the auspices of Chinese National Science Research Foundation and the Doctoral Foundation of Chinese Education Commission. Authors would like to thank Mr. Tingheng Sun and Yucai Quan for their help in γ -irradiation experiments.

REFERENCES

- 1. H. Hahn and R.S. Averback, J. Am. Ceram. Soc. 74, 2918 (1991).
- 2. G.W. Nieman, J.R. Weertman and R.W. Siegel, J. Mater. Res. 6, 1012 (1991).
- 3. Y.C. Zhou and M.N. Rahaman, J. Mater. Res. 8, 1680 (1993).
- J.K. Vassiliou, V. Mehrota, M.W. Russell, R.D. McMichael, R.D. Shull and R.F. Ziolo, J. Appl. Phys. 73, 5109 (1993).
- 5. R. Birringer, H. Gleiter, H-P. Klein and P. Marquardt, Phys. Lett. 102A, 365 (1984).
- 6. W.J. Dawson, Am. Ceram. Soc. Bull. 67, 1673 (1988).
- 7. S. Roy, A.Chatterjee and D.Chakravorty, J. Mater. Res. 8, 689 (1993).
- 8. Z. Chen, B. Chen, Y. Qian, M. Zhang, L. Yang and C. Fan, Acta Metall. Sinica B 5 (1992).
- 9. Y. Liu, Y. Qian, M. Zhang, Z. Chen and C. Wang, Mater. Res. Bull. 31, 1029 (1996).
- 10. Y. Liu, Y. Qian, M. Zhang, Z. Chen and C. Wang, Mater. Lett. 26, 81 (1996).
- 11. J.A. Langford and A.J.C. Wilson, J. Appl. Cryst. 11, 102 (1978).
- 12. C.N.J. Wagner and X. Aqua, Adv. X-ray Anal. 7, 46 (1964).
- 13. M. Zhang, Introduction to Radiation Chemistry, p. 81 Press of University of Science and Technology of China (1994).