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 40 min. Secondly, the soluble MnO from the reduced low grade MnO ore was leached by dilute sulphuric acid to be MnSO$_4$ solution at 80 °C in 30 min, and lastly the honeycomb-like structure MnO$_2$ 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 3 ml/min until they were feed out, and then kept for 30 min 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$_2$.

Keyword: MnO$_2$; Honeycomb-like structure; Manganese ore; Demonstrating; Redox reaction; Microstructure

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 5 billion 700 million 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 studies 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$_2$ 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).

<table>
<thead>
<tr>
<th>Component</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Pb</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Cr</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese Ore /%</td>
<td>17.32</td>
<td>0.017</td>
<td>0.05</td>
<td>0.25</td>
<td>0.057</td>
<td>0.041</td>
<td>11.77</td>
<td>0.19</td>
<td>11.3</td>
<td>2.559</td>
<td>14.6</td>
</tr>
<tr>
<td>Honeycomb-Like MnO$_2$/%</td>
<td>57.05</td>
<td>0.003</td>
<td>0.01</td>
<td>0.01</td>
<td>0.059</td>
<td>0.002</td>
<td>0.265</td>
<td>0.007</td>
<td>0</td>
<td>0.004</td>
<td>0</td>
</tr>
</tbody>
</table>
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 30 min) and hermetically cooled to room temperature before removing the cover. The reduced manganese ore was leached by 1mol/L sulfuric acid solution for 30 min 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 filtering 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 pump, and the flask was put in 80 °C water bath. The honeycomb-like structure MnO$_2$ product was obtained by washing, filtering and drying at 80 °C in drying oven. The crystal structure and the morphology were 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.

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 were 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.

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.

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 3 ml/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 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, 6 ml/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 3 ml/min of MnSO$_4$ and KMnO$_4$ solution was recommended.

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.

SEM characterization of the honeycomb-like structure MnO$_2$

The morphology of the prepared sample is characterized 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 3 ml/min. When the feed of MnSO$_4$ and KMnO$_4$ solution was finished, the mixed solution in the flask with three necks was stood for 0, 10, 20, 30, 40, 50 min. 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 30 min is enough.
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 MnSO₄ and KMnO₄ 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 30min, and honeycomb-like structure MnO₂ product is eventually prepared by oxidation-reduction process of MnSO₄ and KMnO₄ solution with the experimental conditions of solution pH 5, reaction temperature of 60 °C, flux velocity of 3ml/min, the mole ratio of 2.5:3 and the standing time of 30min.

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Conflict of Interest

The authors declare, that there is no conflict of interest.

References
