

A technology of preparing MnO_2 nanowire from the low grade manganese ore

Abstract

Manganese dioxide nanowire was synthesized from the low grade manganese dioxide ore by hydrothermal method. Low grade manganese ore was firstly reduced to be dissolvable MnO by mixing reductant of the sawdust in ceramic crucible at 400°C , the reduced ore was leached with diluted sulfuric acid to be MnSO_4 solution at 80°C in 30min. The obtained MnSO_4 solution was mixed with KMnO_4 solid particle in homogeneous reactor to prepare MnO_2 nanowire, the optimized experimental conditions are that the mole ratio of $\text{MnSO}_4:\text{KMnO}_4$ is 3:1.5, pH value of the solution is 5, the reaction temperature is 180°C , the reaction time is 10h and the stirring speed is 5Hz. The MnO_2 nanowire with $\alpha\text{-MnO}_2$ crystal structure was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM).

Keywords: MnO_2 , manganese ore, nanowire, hydrothermal synthesis

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Introduction

Manganese dioxide has received considerable attention among transition metal oxides because of its outstanding structural flexibility. It is well known that MnO_2 is of high theoretical specific capacitance (1370F g^{-1}), natural abundance, environmental friendliness and low cost.¹⁻³ MnO_2 exhibits different electrochemical properties at very low loadings (about a few mg cm^{-2}) on the current collector because of its extremely low electrical conductivity (10^{-5} to 10^{-6}Scm^{-1}).⁴⁻⁷ Functional nanomaterials have been found wide applications in diverse areas due to their intrinsically different properties compared with bulk materials. Except for the excellent electrochemical property of MnO_2 bulk materials, nanostructured manganese dioxide exhibits its efficient electrolyte/cation interfacial charge transports which enables improved pseudo capacitive performance, a good rate capability and reversibility. As a promising PC material among transition metal oxides, nano- MnO_2 is of outstanding structural flexibility and exists in tunnel, spinel and layered crystallographic forms.^{8,9} To improve the performance, various MnO_2 nanostructures with different morphologies, including nanoflowers,^{11,12} nanosheets,¹³⁻¹⁵ nanotubes¹⁶ and nanowires¹⁷⁻¹⁹ have been synthesized. One-dimensional nanorods

and nanowires are able to enhance electronic/ionic conductivity and shorten ion transport pathway for faradaic reactions.²⁰⁻²⁴

In China, the resources of low grade manganese ore is very rich, and it is not exploited and utilized due to the low content of manganese and high cost. In this paper, MnO_2 nanowire was prepared successfully from the manganese dioxide by hydrothermal method. Low grade manganese ore was firstly reduced to be dissolvable MnO by sawdust at 400°C , the reduced ore was leached with diluted sulfuric acid to be MnSO_4 solution. The obtained MnSO_4 solution was mixed with KMnO_4 solid particle in homogeneous reactor to prepare MnO_2 nanowire. This technology provided a new way for the exploitation and utilization of waste low grade manganese resource in China.

Experimental section

Chemical analysis of low grade manganese ore from Hunan, China

The original materials of the low-grade manganese oxide ore was selected from Hunan, South China, its main chemical composition is shown in Table 1.

Table 1 Chemical composition of low grade manganese oxide ore (mass fraction)

Component	Mn	Fe	Al	Ni	Pb	Co	Mg	Cr	Cu
Manganese ore /%	19.39	11.865	1.714	0.106	0.014	0.038	0.115	0.010	0.014

Experiment procedure

The preparation procedure of MnSO_4 solution from low grade manganese from Hunan, China was carried as follows: the low grade MnO_2 ore and sawdust according to the proportion of 4:1 (weight ratio) were well-mixed and hermetically put into ceramic crucible, and then were roasted in muffle furnace at the roasting temperature of 400°C and roasting time of 30min. The reduced manganese ore in ceramic crucible was cooled to room temperature before removing the cover. The reductant was leached by 1mol/L sulfuric acid solution for 30min at 80°C , the ratio of sulfuric acid and the reductant was controlled at 10ml/g. The MnSO_4 solution could be obtained after filtrating the leached manganese ore and washing it by deionized water, using as raw liquid for preparing MnO_2 nanowire, the content of MnSO_4 solution is about 0.64mol/L. MnO_2 nanowire was synthesized by the following experimental procedure. The pH value

of the obtained MnSO_4 solution was adjusted to be 5 with sodium hydroxide, and then a certain amount of KMnO_4 solid particle and the MnSO_4 solution was mixed the in homogeneous reactor according to its ratio of 3:2, the chemical reaction was carried out at the reaction temperature of 180°C , the reaction time of 10h and the stirring speed of 5Hz. The crystal structure and the morphology of MnO_2 nanowire were characterized by X-ray diffraction and Scanning Electron Microscopy.

Result and discussion

The effect of mole ratio of MnSO_4 and KMnO_4 on the micro-morphology of MnO_2 nanowire

The experiments of preparing MnO_2 nanowire were carried out under the conditions that the reaction time and temperature was 12h

and 180°C the pH of MnSO_4 solution was 5 and the stirring rate was 5Hz, the obtained MnO_2 microstructure was not nanowire when the mole ratio of MnSO_4 and KMnO_4 were 3:1.5, 3:2, 3:2.5, 3:3. From Figure 1, MnO_2 nanowire couldn't be prepared under the above mentioned experimental conditions. According the stoichiometric ratio of KMnO_4 and MnSO_4 , the mole ratio of 3:2 was chosen for the consequent experiments.

The effect of the reaction temperature on the microstructure of MnO_2 nanowire

The mole ratio of MnSO_4 and KMnO_4 was 3: 2, the reaction time was 6h, the pH of MnSO_4 solution was 5 and the stirring rate was 5Hz, the effects of reaction temperature on the morphology of MnO_2 nanowire were shown in Figure 2. When the temperature was 120°C a little amount of MnO_2 nanowire could be found, as shown in Figure 2A. If the reaction temperature raised to be 180, a great deal of MnO_2 nanowire was formed, as could be seen in Figure 2D. Because

of the high reaction temperature, the rate of chemical reaction was accelerated, resulting in the crystal growth of MnO_2 nanowire. The temperature of 180°C was chosen for the consequent experiments.

The effect of the pH of MnSO_4 solution on the microstructure of MnO_2 nanowire

The mole ratio of MnSO_4 and KMnO_4 was 3: 2, the reaction time was 12h, the reaction temperature was 180°C and the stirring rate was 5Hz, the effects of the pH value of MnSO_4 solution on the morphology of MnO_2 nanowire were shown in Figure 3. When the pH value of the MnSO_4 solution was 3, the prepared product was not nanowire structure, but the accumulated MnO_2 bulk particle. With the increase of the pH of the MnSO_4 solution, the obvious nanowire structure was formed, and the MnO_2 nanowire morphology was clear when the pH of the MnSO_4 solution was raised to be 5. Therefore it was optimal condition that the pH value of MnSO_4 solution was controlled at 5.

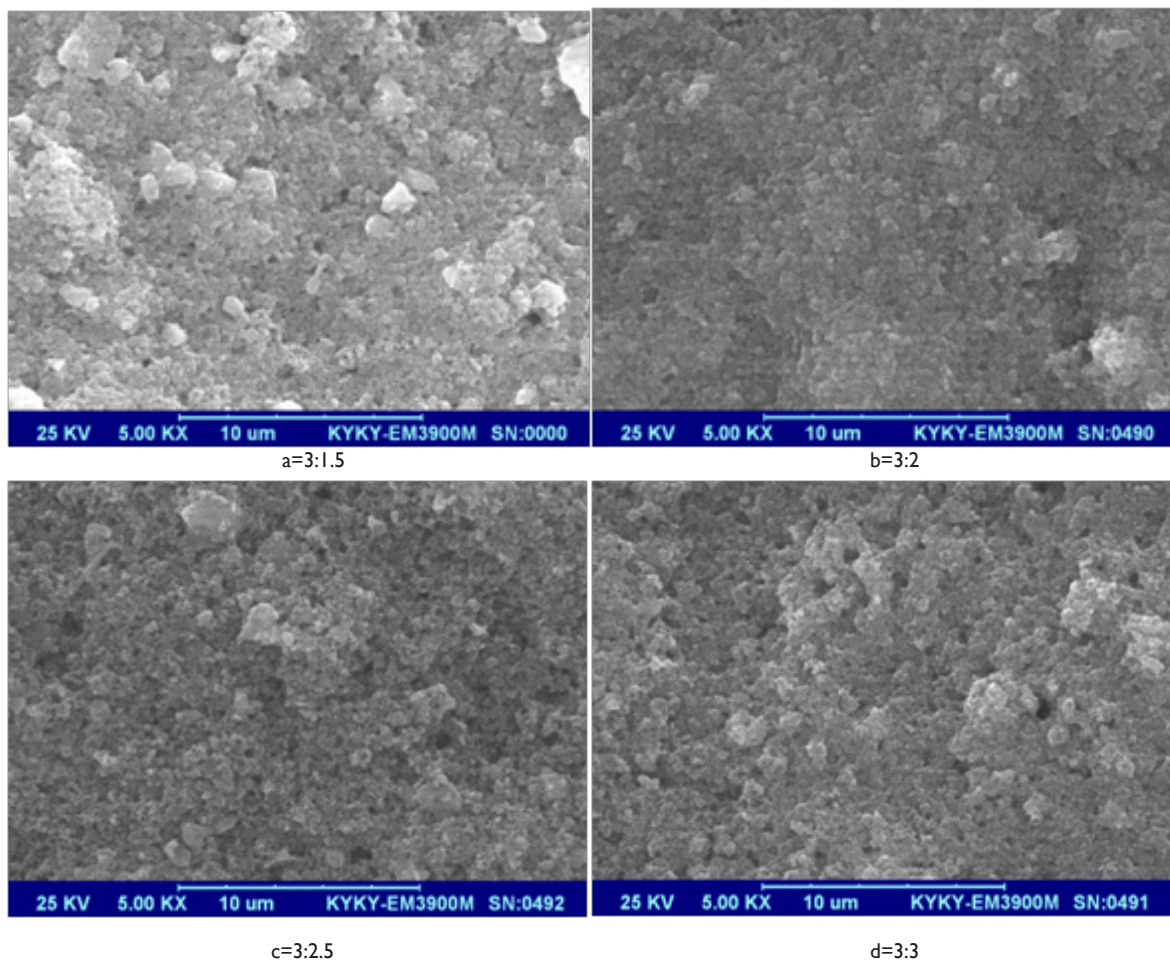


Figure 1 The effect of the mole ratio of MnO_2 and KMnO_4 on the prepared MnO_2 microstructure.

The effect of the reaction time on the microstructure of MnO_2 nanowire

The mole ratio of MnSO_4 and KMnO_4 was 3: 2, the pH value of MnSO_4 solution was 5, the reaction temperature was 180°C and the stirring rate was 5Hz, the effects of the different reaction time

on the morphology of MnO_2 nanowire were shown in Figure 4. With the extension of reaction time, the MnO_2 nanowire structure became to be clearer when the reaction time was increased to be 10h. When the reaction time was 4h, nanowire had not formed because of inadequate reaction time. The reaction time of 10h was suggested for the consequent experimental conditions.

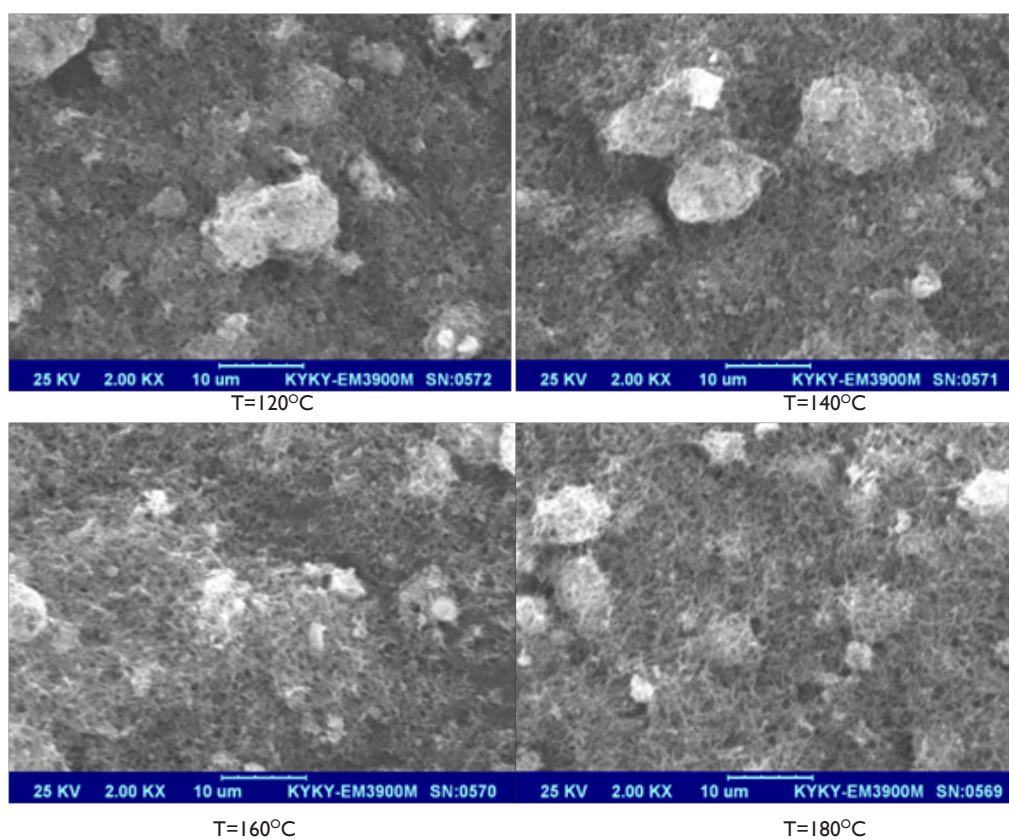


Figure 2 The effect of reaction temperature on the prepared MnO_2 microstructure.

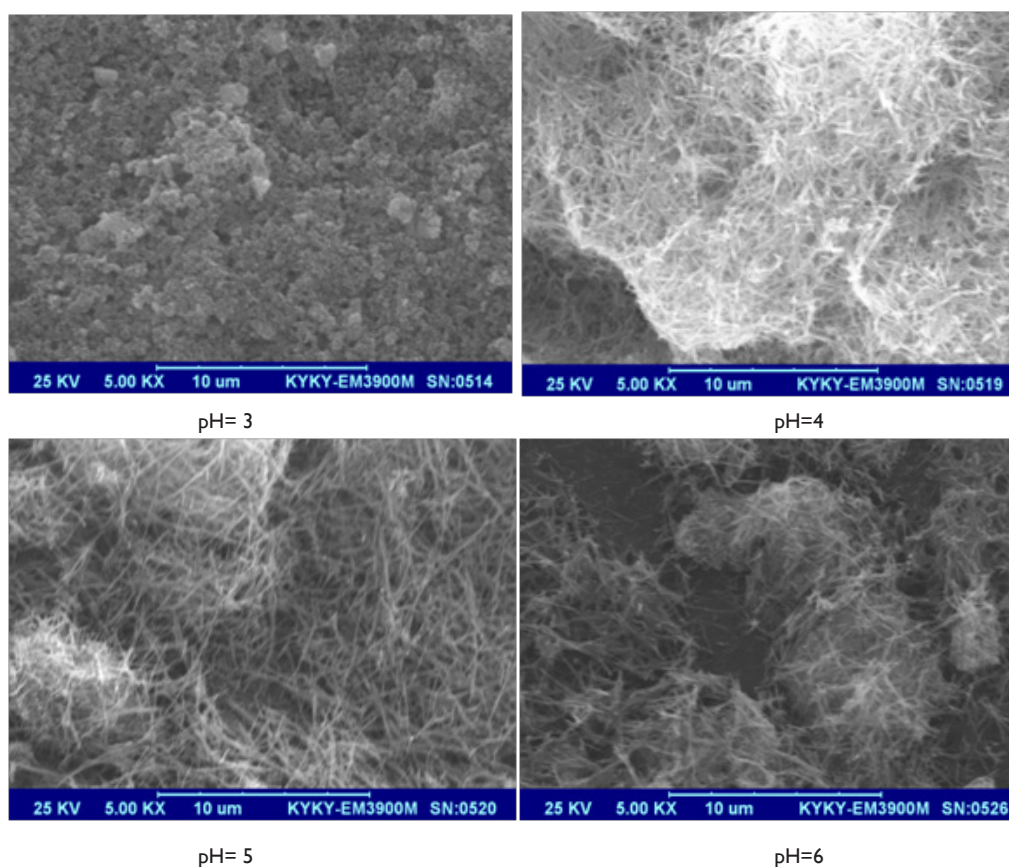


Figure 3 The effect of the pH value of the MnSO_4 on the prepared MnO_2 microstructure.

The effect of the stirring speed on the microstructure of MnO_2 nanowire

The mole ratio of MnSO_4 and KMnO_4 was 3: 2, the pH value of MnSO_4 solution was 5, the reaction temperature was 180°C and the reaction time was 10h. The effects of the different stirring rate on the

morphology of MnO_2 nanowire were shown in Figure 5. When the stirring rate was 3Hz, only a few nanowire was formed. Due to relative low stirring rate, the crystal growth velocity of MnO_2 nanowire was low, resulting in accumulation of MnO_2 nanoparticles. If the stirring rate was increased to be 5Hz, a great amount of MnO_2 nanowire was prepared successfully.

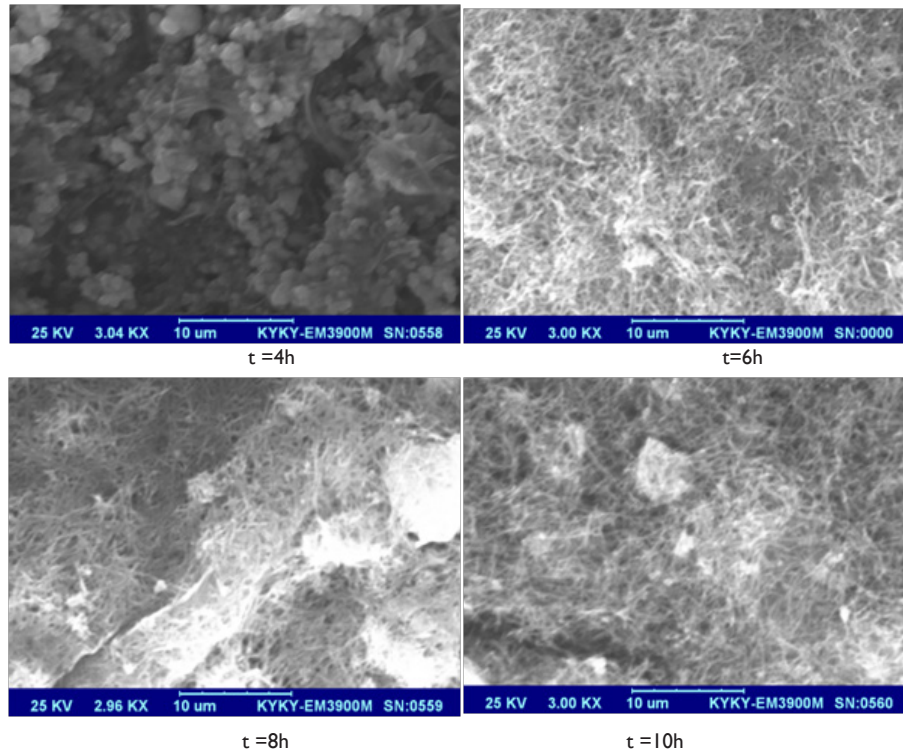


Figure 4 The effect of reaction time on the prepared MnO_2 microstructure.

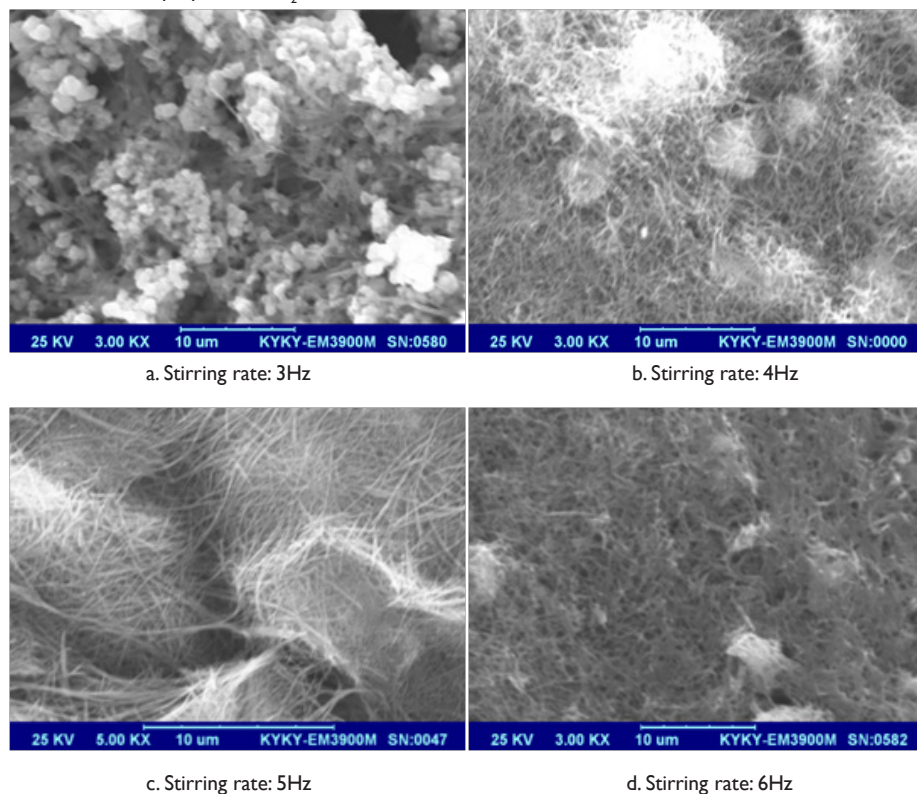


Figure 5 The effect of stirring rate on the prepared MnO_2 microstructure.

The SEM characterization and X-ray of MnO_2 nanowire

Figure 6A showed the characteristic SEM images of MnO_2 nanowire, demonstrating that the prepared product consisted of clear

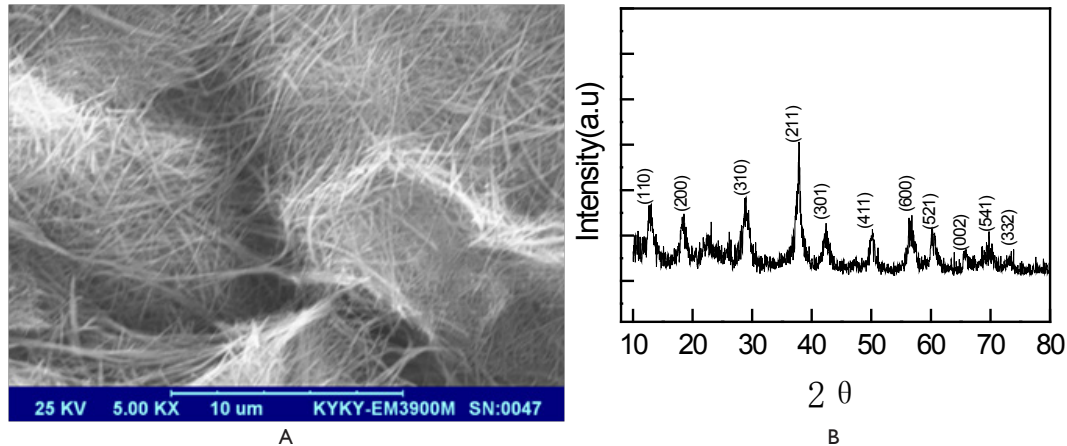


Figure 6 A: SEM image of MnO_2 nanowire, B: X-ray pattern of MnO_2 nanowire.

Conclusion

The MnO_2 nanowire is prepared from low grade manganese ore by a hydrothermal method technology. After low grade manganese was reduced by the biomass to be MnO , the roasted slag was leached by dilute sulphuric acid to be MnSO_4 solution. Lastly, KMnO_4 particle was added in the MnSO_4 solution to finish the oxidation-reduction process. The reduction process of manganese ore is finished in 30min at 400°C , the leaching process is carried out in 80°C water bath in 30min, and MnO_2 nanowire is eventually prepared by oxidation-reduction process of MnSO_4 and KMnO_4 solution with the experimental conditions of the mole ratio of MnSO_4 : KMnO_4 is 3:1.5, pH value of the solution is 5, the reaction temperature is 180°C , the reaction time is 10h and the stirring speed is 5Hz. The characterization results of X-ray diffraction (XRD) and scanning electron microscope (SEM) show that the MnO_2 nanowire is α - MnO_2 crystal structure.

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Conflicts of interest

Authors declare that there is no conflict of interest.

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