



Frequency and temperature effects on dielectric and electrical characteristics of α -MnO₂ nanorods

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ABSTRACT

The α -MnO₂ nanorods were successfully prepared by hydrothermal methods at 160 °C for 48 h. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were employed to characterize the morphology and microstructure of the final product. The results show that the final product is the pure tetragonal α -MnO₂ phase with rod-like nanostructure in diameters 30 nm and lengths up to 0.5–1 μ m. The dielectric and the electrical properties of the α -MnO₂ nanorods were also analyzed and discussed at a range of the temperature from 223 K to 393 K. The dielectric constants and dielectric loss tangents both increase with the rising temperature and decrease with frequency. The electrical resistivity values also decrease with the rising temperature and frequency. It is also found that the dielectric loss of α -MnO₂ mainly results from the space polarization and the temperature dependence of resistivity follows the Arrhenius Equation.

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1. Introduction

In recent years, a considerable attention has been directed to nano-scale manganese dioxide materials, owing to their unique optical, electronic and electromagnetic properties compared with bulk materials [1,2]. Low dimensional manganese dioxide materials, such as nanowires, nanorods and nanobelts have been widely applied in catalysts, molecular-sieves and ion-sieves due to their ion-exchange, molecular adsorption, catalytic, electrochemical, and magnetic properties [3,4].

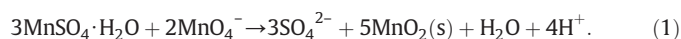
The basic unit of manganese dioxide is the octahedral [MnO₆] close-packed structure, which is built up by one manganese atom coordinated with six oxygen atoms. The [MnO₆] units are linked together in different ways so as to form various crystallographic and derivative structures. In nature, MnO₂ with different structural forms has been found, such as α -, β -, δ -, γ - and ϵ -MnO₂, and they all have their various properties [5].

Until now, numerous studies on manganese dioxide materials, including nanowires [6,7], nanorods [8,9], microspheres [10], and 3D or hierarchical structures [11–13] have been reported. Most of the recent publications are mainly focused on the formation mechanism and morphological characterizations of MnO₂ nanostructures and some magnetic or electromagnetic studies [6–16]. Liu and Yue et al. investigated the hysteresis loop characteristics of β -MnO₂ and α -MnO₂ nanorods at room temperatures, respectively, and found that they all exhibited ferromagnetic properties with high coercivity values [8,17]. Duan et al. [18] studied the dielectric and electromagnetic characteristics of

manganese dioxide materials with different crystalline and morphological structures prepared through hydrothermal methods. It is found that the real parts of dielectric permittivity values increase with the hydrothermal treating time, and the absorbing peak values shift to lower frequency bands due to the transformation of crystalline structures. They also found that the introduction of high magnetic field or doping with metal ions during the hydrothermal process could increase the electromagnetic performances of the final products [19–21]. Shi et al. [22,23] reported the high temperature dielectric properties of β -MnO₂ and β -MnO₂/SiO₂ core-shell structured nanorods, and found the enhanced temperature response attenuation at X frequency band. However, to our acknowledgments, the temperature dependent dielectric properties of MnO₂ materials at low temperature and lower frequency band are few reported. Our research work was focused on the temperature dependent dielectric properties of α -MnO₂ nanorods in this paper. The α -MnO₂ nanorods were synthesized by hydrothermal method at 160 °C for 48 h. The crystalline and morphological structures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The temperature dependent dielectric and electrical properties between 223 K and 393 K were discussed in the frequency range from 1 kHz to 1 MHz.

2. Experimental

The analytical grade chemicals were used to prepare the nanocrystalline MnO₂ by hydrothermal route through the following reaction:



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In a typical process, 3.16 g KMnO_4 and 5.07 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in 160 ml deionized water successively at room temperature and magnetically stirred for 30 min to form a homogeneous solution. Then the solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 48 h. After the reaction was completed, the autoclave was allowed to cool down to room temperature naturally. The resulting solid products were centrifuged and rinsed several times with deionized water and absolute ethanol, then finally dried at 100 °C for 8 h. The final black powder was collected for characterization.

The phase analysis was carried out by X-ray diffraction (XRD, DSC-2000; Cu-K α radiation, $\lambda = 1.54184 \text{ \AA}$) in the range of $2\theta = 10^\circ$ to 80° in steps of 0.02° . The particle morphologies and selected area electron diffraction (SAED) were observed employing field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and high-resolution transmission electron microscopy (HRTEM, Tecnai G² 20 S-Twin).

The temperature dependences of the complex permittivity and dielectric loss tangents were examined by an impedance analyzer (Agilent 4294A) and Test Chambers (ESPEC SU-261). The as-prepared MnO_2 powders were mixed uniformly with polyvinyl alcohol (PVA) with a filling ratio of 85 wt.% and molded into plate specimens with diameters of 15 mm and thicknesses 1–2 mm. After heated at 60 °C for 24 h, the specimens were collected for dielectric tests. The testing frequency ranges from 1 kHz to 1 MHz and the temperature is from 233 K to 393 K.

3. Results and discussion

Fig. 1 shows the XRD pattern of the sample synthesized at 160 °C for 48 h and subsequently dried at 100 °C for 8 h. The diffraction peaks of the as-prepared product can be easily indexed to pure tetragonal $\alpha\text{-MnO}_2$ phase (JCPDS 44-0141) with a space group $I4/m(87)$. The sharp diffraction peaks indicate that the product is well crystallized. In addition, no diffraction peaks for impurities are observed, which suggests the high purity of the product.

Earlier researches have shown that in the preparation of MnO_2 materials, the concentrations of K^+ ions are one of the key factors to control the phases and structures [24,25]. Different structures can be obtained with different K^+ ions and a higher KMnO_4 concentration is beneficial to develop 2×2 tunnels, which leads to the formation of $\alpha\text{-MnO}_2$ phases [26,27]. The present XRD result corresponds well with this point of view.

Fig. 2 presents the typical SEM and TEM images of the as-synthesized sample. It can be seen that the product is in nanorods with uniform diameters from Fig. 2(a). The nanorods are straight, smooth and have flat surfaces with the diameters of 30 nm and lengths up to 0.5–1 μm , which also can be seen from Fig. 2(b). The SAED pattern

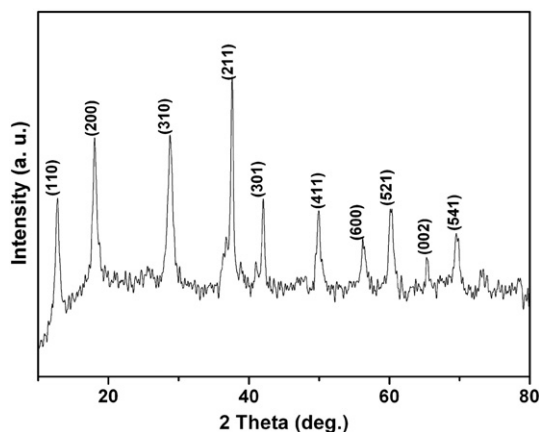


Fig. 1. The XRD pattern of the as-synthesized product.

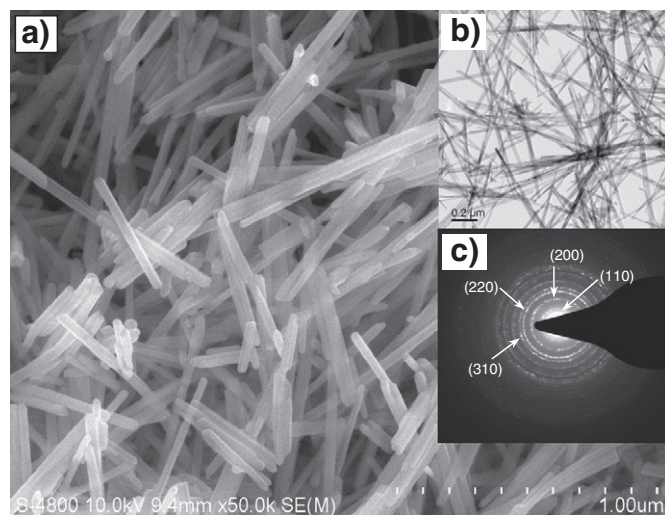


Fig. 2. The typical SEM (a), TEM (b) images and SAED patterns (c) of as-synthesized product.

in Fig. 2(c) indicates that the $\alpha\text{-MnO}_2$ nanorods are of high crystallization degree, which also agrees with the XRD patterns in Fig. 1.

For a dielectric loss material, the complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and the loss tangent ($\tan \delta_e = \epsilon''/\epsilon'$) are the quantified responses of molecules to an external electromagnetic field. The complex permittivity is related with the electromagnetic losses due to the friction accompanying polarization and orientation of electric dipoles [28]. It represents and determines the dielectric properties of an absorbing material.

According to Debye dipolar relaxation expression [29], the permittivity of a dielectric loss material can be represented as following:

$$\epsilon_r = \epsilon'(f) - j\epsilon''(f) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau_0} \quad (2)$$

where ω , τ_0 , ϵ_s and ϵ_∞ are the angular frequency, macroscopic relaxation time, static dielectric constant and optical dielectric constant, respectively. From Eq. (2), the real and imaginary parts of the complex dielectric permittivity can be deduced as:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s + \epsilon_\infty}{1 + \omega^2\tau_0^2}, \quad \epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau_0}{1 + \omega^2\tau_0^2} \quad (3)$$

From the above Eqs. (2) and (3), one can see that dielectric permittivity is a complex function of both the frequency and temperature, apart from the dependence of other parameters such as pressure, etc.

Fig. 3 illustrates the changes in dielectric constants of $\alpha\text{-MnO}_2$ nanorods with frequency at different temperatures from 233 K to 393 K. In Fig. 3(a), the real permittivity ϵ' shows a clear trend of the increasing with rising temperature and of the decreasing with increasing frequency. At the fixed temperature of 233 K, the dielectric constant changes from 45.2 to 7.3 when frequency increases from 1 kHz to 1 MHz. However the dielectric constant turns from 133.6 to 78.6 with the frequency increasing from 1 kHz to 1 MHz when the temperature rises to 393 K. Shi et al. [22] examined the temperature dependent dielectric properties of $\beta\text{-MnO}_2$ nanorods in X band at the temperature range from 293 to 773 K and found a decrease of the permittivity values with the frequency and the temperature.

The dielectric properties of MnO_2 material can be come down to the interaction of electromagnetic radiation with charge multipoles at the interface. As has known, $\alpha\text{-MnO}_2$ has aberrant octahedron structures with tunnels and cavities. The tunnels and cavities can take in other charge carriers such as atoms and molecules to enter the interior of manganese dioxide structures, which results in a local displacement

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