

Selected-Control Synthesis of PbO₂ and Pb₃O₄ Single-Crystalline Nanorods

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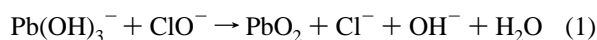
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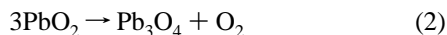
During the past decade, one-dimensional (1D) nanostructured materials have sparked a worldwide interest because of their unique electronic, optical, and mechanical properties and their potential applications in nanodevices and functional materials.^{1–5} As a consequence, highly anisotropic 1D nanostructures using various materials, such as elemental carbon, carbon-based substances, metals, oxides, sulfides, nitrides, etc.,^{6–14} have been fabricated through a variety of methods. Studies have shown that some of the physical properties exhibited by these nanostructures are different from those of the bulk crystals.^{15,16} Recently, considerable research efforts have been directed toward the preparation of binary oxides with 1D nanostructures. However, to the best of our knowledge, studies that describe the preparation of lead oxides with 1D nanostructures have been relatively few. Herein we report on a convenient and controllable approach for the synthesis of PbO₂ and Pb₃O₄ nanorods, which requires neither sophisticated techniques nor catalysts.

Lead oxides, which include four basic types (PbO, Pb₂O₃, PbO₂, and Pb₃O₄), have wide industrial applications due to their distinctive properties. In particular, Pb₃O₄ possesses interesting physical characteristics due to its mixed valence, resulting in its unique electronic structure.¹⁷ As we know, PbO₂ and Pb₃O₄ are commonly used as electrodes in batteries.¹⁸ Huynh et al.¹⁹ showed that the operating properties of batteries depend not only on the structure, but also on the morphology of the electrode components. In this case, it was shown that 1D nanostructures are more prone to charge transport than the bulk crystalline structures.¹⁹ Currently, because of limited studies on PbO₂ and Pb₃O₄ 1D nanostructures and their subsequent applications in nanoscale electronic devices, investigations on the size-dependent properties of lead oxides are significantly delayed. In this Communication, we will describe a novel method to afford two distinct lead oxides (black-brown PbO₂ and red Pb₃O₄) with rodlike morphologies. We believe that this synthetic methodology, which features the same reaction but under different conditions for each lead oxide, will be valuable toward research in the nanometer regime.

For PbO₂ nanorods, the redox reaction can be shown as follows:

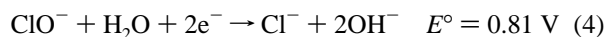
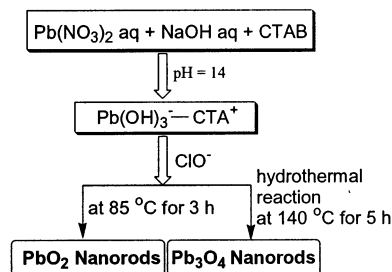


Furthermore, for Pb₃O₄ nanorods, the reaction was initially carried out under hydrothermal conditions, similar to that in eq 1. However, the resulting PbO₂ slowly decomposed to Pb₃O₄, as shown in the following:



Reaction 1 is comprised of two half reactions, as shown in the following:

Scheme 1. Selected-Control Strategy for PbO₂ and Pb₃O₄ Nanorods



The standard Gibbs free energy change $\Delta_r G_m^\circ$ of the redox reaction (reaction 1) was calculated to be $-108.6 \text{ kJ}\cdot\text{mol}^{-1}$ on the basis of standard reduction potential E° values, which implied a very strong tendency for the reaction to progress toward the products. In contrast, the subsequent reaction (reaction 2) was typically carried out at 390–420 °C. However, in our hydrothermal system, the reaction can be carried out at a remarkably lower reaction temperature (140 °C). This controllable synthesis route is shown in Scheme 1.

In a typical synthesis, cetyltrimethylammonium bromide (CTAB; 3 mmol) was added to 0.015 M Pb(OH)₃⁻ (70 mL) solution, which was formed by adjusting the pH of a lead nitrate solution with 1 M NaOH solution to pH 14. After the resulting solution was stirred for 30 min at 50 °C, which ensured the complete dissolution of CTAB, aqueous 1.5 M NaClO solution (1 mL) was added under constant stirring to the resulting clear solution to form a homogeneous solution. After the solution was maintained at 85 °C for 3 h, the resulting black-brown products (PbO₂ nanorods) were collected, washed several times using absolute ethanol and distilled water, centrifuged, and dried under vacuum at room temperature for 5 h. For the preparation of the red Pb₃O₄ nanorods, the above homogeneous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 140 °C for 5 h.

X-ray powder diffraction (XRD) patterns of the samples were collected on a Japan Rigaku D_{max} 2000 X-ray diffractometer with Cu K α radiation ($\lambda = 0.154178 \text{ nm}$). The XRD patterns of the newly prepared PbO₂ and Pb₃O₄ nanorods are shown in Figure 1. All diffraction peaks in Figure 1a can be perfectly indexed to the tetragonal PbO₂ [space group: *4/mmm*] with lattice constants $a = 4.9525 \text{ \AA}$ and $c = 3.3863 \text{ \AA}$ (JCPDS 25-447), while those in Figure 1b can be indexed to the tetragonal Pb₃O₄ [space group: *D*_{4h}¹² - *P4₂/MBC*] with lattice constants $a = 8.815 \text{ \AA}$ and $c = 6.565 \text{ \AA}$ (JCPDS 8-19); these results are consistent with those of PbO₂ and Pb₃O₄ bulk crystals, respectively. The XRD patterns indicate that the nanorods obtained via our current synthetic methods consist of pure phases.

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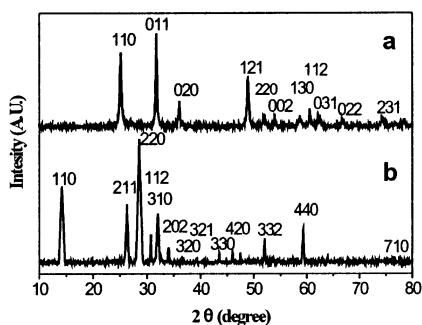


Figure 1. XRD patterns of (a) PbO_2 and (b) Pb_3O_4 .

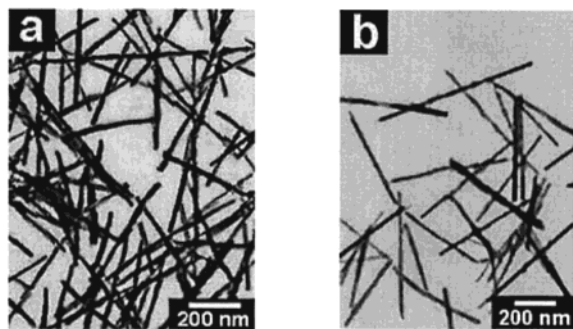


Figure 2. TEM images of (a) PbO_2 and (b) Pb_3O_4 nanorods.

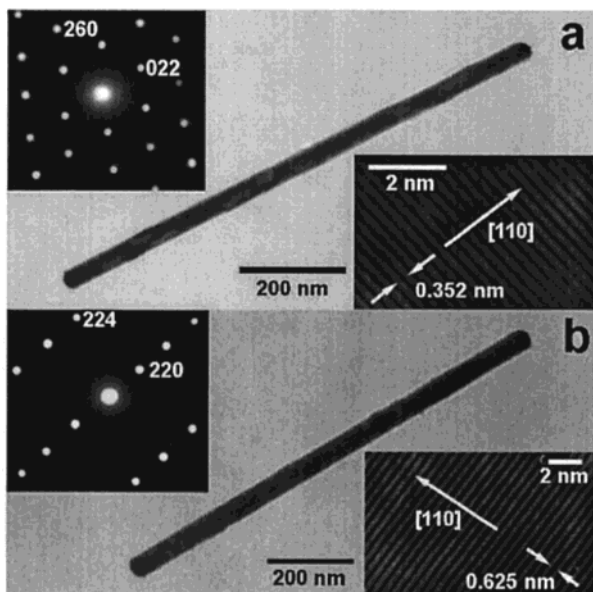


Figure 3. (a) TEM image of a single PbO_2 nanorod with a diameter of 40 nm. Left inset: SAED pattern of the same nanorod. Right inset: a HRTEM image of the same nanorod. (b) TEM image of a single Pb_3O_4 nanorod with a diameter of 50 nm. Left inset: SAED pattern of the same nanorod. Right inset: a HRTEM image of the same nanorod.

The morphology and microstructure of the prepared PbO_2 and Pb_3O_4 were further investigated with transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution TEM (HRTEM). Typical TEM images (Figure 2) showed that samples of both PbO_2 and Pb_3O_4 display rodlike shapes and that these nanorods are straight with uniform diameters in the range 10–60 nm, and lengths ranging from 500 nm to 1 μm . The SAED patterns of PbO_2 and Pb_3O_4 (insets in Figure 3a and 3b, respectively), which were taken from (single rods), showed that the nanorods are single crystalline. Representative HRTEM images of respective nanorods (Figure 3) showed clear lattice fringes, without defects or dislocations, thus providing additional confirmation that

these nanorods are single crystalline. For PbO_2 and Pb_3O_4 nanorods, interplanar spacings were about 0.352 and 0.625 nm, respectively, both corresponding to the (110) crystal planes, whereas the angle between the (110) planes and the long axes of the rods was both about 45° .

The synthesis of PbO_2 and Pb_3O_4 nanorods, somewhat similar to shape-controlled synthesis of spheroidal and rodlike gold nanoparticles,²⁰ was carried out via oxidation of $\text{Pb}(\text{OH})_3^-$ using ClO^- in a rod-shaped micelle environment.²¹ In this case, the surfactant CTAB played an important role in determining the morphology of the products. Because only PbO_2 and Pb_3O_4 particles were obtained in the absence of CTAB, it is reasonable to suggest that nanorod growth is due to specific interactions between the cationic surfactant CTAB and the anionic $\text{Pb}(\text{OH})_3^-$.²² Our results indicate that PbO_2 slowly decomposed to Pb_3O_4 under hydrothermal conditions, while retaining the morphology of PbO_2 . In addition, it was shown that reaction temperatures affect the growth of Pb_3O_4 nanorods. When the reaction was carried out at temperatures above 160 $^\circ\text{C}$, only bulk Pb_3O_4 was observed. This may be attributable to the instability of the micelles under the higher temperature conditions, resulting in the failure of the template.²³ If the reaction temperature was below 120 $^\circ\text{C}$, a mixture of PbO_2 and Pb_3O_4 was obtained; this indicated that the decomposition process of PbO_2 to Pb_3O_4 might be kinetically slow. Currently, we are extending our synthetic methodology toward the preparation of other oxides with 1D nanostructures.

In summary, a novel and simple approach was successfully utilized in the syntheses of PbO_2 and Pb_3O_4 nanorods. According to the SAED and HRTEM patterns, PbO_2 and Pb_3O_4 nanorods are single crystalline. It is our hope that this simple aqueous solution synthetic route can be applied as a general method for the preparation of other oxides with 1D nanostructures.

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