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PbO networks composed of single crystalline nanosheets synthesized by a facile chemical precipitation method

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ABSTRACT

For the field of energy storage, nanostructured lead oxide (PbO) shows immense potential for increased specific energy and deep discharge for lead acid battery technologies. In this work, PbO networks composed of single crystalline nanosheets were synthesized utilizing a simple, low cost and rapid chemical precipitation method. The PbO networks were prepared in a single reaction vessel from starting reagents of lead acetate dehydrate, ammonium hydroxide and deionized water. Lead acetate dehydrate was chosen as a reagent, as opposed to lead nitrate, to eliminate the possibility of nitrate contamination of the final product. X-ray diffraction (XRD) analysis, high resolution scanning electron microscopy (HRSEM) and high resolution transmission electron microscopy (HRTEM) analysis were used to characterize the synthesized PbO networks. The reproducible method described herein synthesized pure β-PbO (massicot) powders, with no byproducts. A possible formation mechanism for these PbO networks is proposed. The growth is found to proceed predominately in the ⟨1 1 1⟩ and ⟨2 0 0⟩ directions while being limited in the ⟨0 1 1⟩ direction.

1. Introduction

Nanomaterial synthesis and characterization is an exceptionally active area of research. Current areas of interest for nanoparticle materials systems include drug delivery, bioactive coatings, energy storage and electronics; specific examples of recent applications are anisotropic gold nanowires for potential applications in biosensing [1], oriented Fe_2O_3 on silica for use in cancer theranostics [2], ZnO transparent conducting oxides for electronics [3] and synthesis studies of Co_3O_4 for lithium ion electrodes [4]. Thus, the interest in nanomaterials and nanotechnology arises not only from their unique chemical and physical properties, but also from their potential applications across many fields. Recently, several review articles related to nanoparticle synthesis have been published [5–9]. Additionally, researchers are looking into the optimization of nanoparticle synthesis through parameters such as temperature, reaction time, solvent effects and surfactant effects [10,11]. For the aforementioned reasons, researchers are working hard to find novel, cost effective synthesis methods for a variety of nanostructured materials [12–22]. One such material is divalent lead oxide (PbO), which has been commercially available since lead was first refined [23,24]. PbO exists as three polymorphs: orthorhombic massicot (β-PbO), rhombohedral litharge (α-PbO) and amorphous PbO, with each having unique applications.

While the initial applications of PbO were as pigments and additives in the ceramic, glass and paint industries [24], since 1859 PbO has been used extensively in the energy storage industry as electrodes in lead-acid battery technologies. Compared to their contemporary electrochemical competitors, these batteries are popular due to their advantageous low manufacturing cost, simplicity of design, reliability and safety. Additionally, the superior surge power capabilities of lead-acid batteries have led to their proliferation in starting, lighting and ignition (SLI) applications for combustion engines [24–27].

With the realization of potential health and environmental problems caused by petroleum-based fuels, there is now worldwide interest in the development of efficient electric and hybrid vehicles. Recently, new battery technologies have become widely used in the electric vehicle market, such as lithium ion technology. The use of lead-acid batteries for electric car applications has been limited by the need for improved deep discharge cycle life and specific energy. In addition, lead-acid batteries may account for up to 50% of an electric car's mass, thus effectively reducing the potential efficiency of the vehicle. Accordingly, the production of batteries with increased energy densities would allow for lighter, more efficient electric vehicles.

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Because of the advantages lead-acid batteries possess, significant interest is currently focused on improving both discharge capacity and cycle life while limiting battery mass [24–27]. While there are many different synthesis methods for producing both α-PbO and β-PbO, many of these growth methods are primarily used in the production of bulk PbO structures. However, very little advancement in battery technology is expected from new bulk PbO growth technologies. The development and optimization of PbO with varying nanostructural morphologies is one such potential solution for the advancement of battery technology.

Nanostructure and nanoparticle growth methods include; decomposition [28], sol–gel [29], electro-deposition [30], sonochemistry [31,32], chemical precipitation route [33–35], synthesis by coordination polymers [6,7,36–38], hydrothermal [39–44], microwave irradiation [12,14,16,19,45,46], pulsed current electrochemical methods [20] and even nanostructure synthesis via viruses [4]. However, many of these growth mechanisms possess undesirable growth conditions such as high temperature, high pH reaction environments or expensive growth technologies. Additionally, many synthesis methods are hindered by product impurity issues such as the production of α-PbO/β-PbO mixtures or contamination from hydroxide or nitrate compounds due to chemical precursors. In this work, we present the synthesis of orthorhombic PbO (massicot) networks composed of single crystalline nanosheets through a simple, rapid and low-cost chemical precipitation route. In this synthesis process, water is used as the reaction medium by which the massicot phase is reproducibly formed with no side products or contaminating phases. Phase identification of the synthesized powder was studied using X-ray diffraction. Powder morphologies and growth direction were characterized using a field emission scanning electron microscope and a field emission transmission electron microscope. A possible formation mechanism has been proposed for the grown PbO networks.

2. Experimental procedure

Due to possible nitrate contamination of PbO products when using lead nitrate as a reagent, lead acetate was used as the Pb source. Synthesis was carried out at room temperature using lead acetate dehydrate [$Pb(CH_3COO)_2\cdot 3H_2O$], ammonium hydroxide (NH_4OH) and deionized water as the primary reagents. All reagents were used as received without further purification and were purchased from Sigma–Aldrich (St. Louis, MO) and Fisher Scientific (Pittseburgh, PA).

First, analytical grade $Pb(CH_3COO)_2\cdot 3H_2O$ (2 g) was dissolved in 50 ml of deionized water while stirring at room temperature. This initial solution was colorless and had a pH of 6.2. Next, 75 ml of 30% (by weight) ammonium hydroxide (NH_4OH) aqueous solution was gradually added to the above colorless solution at room temperature under continuous agitation (stirring), which yielded a milky-like, yellow solution with a pH of 11.2. This solution was then centrifuged for 5 min with speed of 3000 rpm to separate the phases. The resulting light yellow precipitate pellets were washed with acetone five times and dried in an oven at 85 °C for 12 h. Phase identification was carried out with X-ray diffraction analysis (XRD, Rigaku SmartLab Diffractometer) with Germanium filtered Cu-K_{α} radiation ($\lambda = 1.54178$ Å). Powder morphologies and growth direction were characterized with a field emission scanning electron microscope (FESEM, JEOL 7100F), and a 200 kV field emission transmission electron microscope (FEG-HRTEM, Philips-CM200). ImageJ software was used for diameter and thickness measurements.

3. Results and discussion

The X-Ray powder diffraction pattern of the synthesized powder was recorded in the 2θ range of 20–90° (Fig. 1a) with a scanning speed of 2.00°/min. All the diffraction peaks were well matched with the JCPDS card No. 38-1477, which corresponded to massicot, or pure β-PbO. It was clearly observed that the peak with strongest intensity was (1 1 1), which was the strongest one according to the JCPDS card sheet. No other peaks related to impurities or intermediate materials, such as lead (II) oxide hydrates ($3PbO\cdot H_2O$), were observed. The synthesis procedure of β-PbO phase was repeated three times, which confirmed the reproducibility of the chemical precipitation method. In the β-PbO unit cell, two oxygen sub-layers are located between two lead sub-layers; the layers formed calliope (staggered) Pb–O chains with the Pb exhibiting asymmetric square pyramidal coordination (Fig. 1b). It is known that massicot is one of the natural mineral forms of lead (II) oxide and that this dimorph of PbO has an orthogonal lattice structure with lattice parameters of $a = 5.492159$ Å, $b = 5.893166$ Å and $c = 4.755345$ Å. Accordingly, the mean distance of the Pb–O bonds between and within the chains of the β-PbO is about 0.2358 nm, with the oxygen atoms found in the interior of the sheets in an asymmetric coordination [47]. The Debby–Scherer equation ($d = K\lambda/B\cos\theta$) was used to calculate the average crystallite size of the synthesized PbO nanostructures, which was ascertained to be 62.5 nm.

Fig. 2a–e shows the synthesized massicot, or β-PbO powder nanostructures and was obtained with a high-resolution SEM. As can be seen in the micrographs, the PbO networks were well-formed and consisted of PbO nanosheets. Each network had an average diameter of approximately 1–3 μm, and the individual PbO nanosheets had an average thickness of approximately 60–85 nm. Fig. 2a and b depicts good representations of the morphology of the nanosheet PbO networks. Fig. 2c and d shows

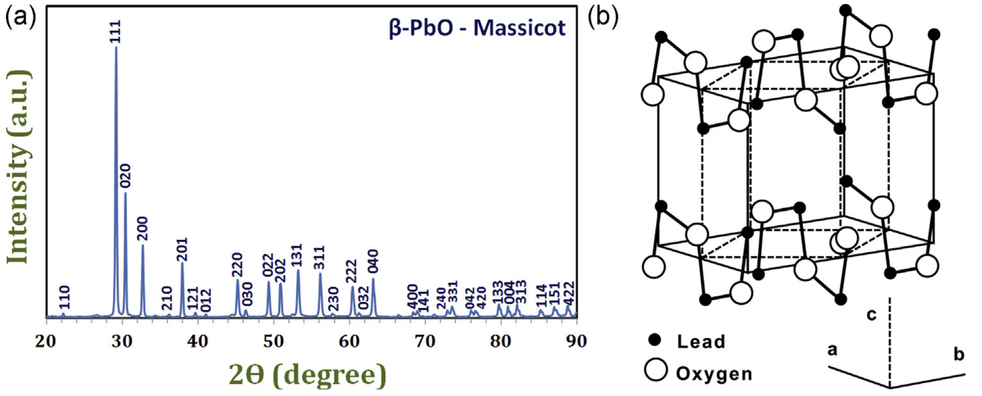

Fig. 1. (a) XRD pattern acquired from as-synthesized β-PbO powders, and (b) Massicot, or β-PbO, unit cell showing lead and oxygen positions [48].