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Synthesis of Micron-sized Hexagonal and Flower-like Nanostructures of Lead Oxide (PbO_2) by Anodic Oxidation of Lead

Dinesh Pratap Singh, Onkar Nath Srivastava

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Abstract: Micron sized hexagon- and flower-like nanostructures of lead oxide (α-PbO_2) have been synthesized by very simple and cost effective route of anodic oxidation of lead sheet. These structures were easily obtained by the simple variation of applied voltage from 2-6 V between the electrodes. Lead sheet was used as an anode and platinum sheet served as a cathode. Anodic oxidation at 2 V resulted in the variable edge sized (1-2 μm) hexagon-like structures in the electrolyte. When the applied potential was increased to 4 V a structure of distorted hexagons consisting of some flower-like structures were obtained. Further increment of potential up to 6 V resulted in flower like structures of α-PbO_2 having six petals. The diameter of the flower-like structures was ∼200-500 nm and the size of a petal was ∼100-200 nm.
Keywords: Lead oxide nanostructures; Anodic oxidation; Hexagon-like structures; Flower-like nanostructures

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Introduction

The fabrication of micrometer and submicrometer-sized materials are of great scientific and technological importance in applications such as photonic materials, microchip reactor, miniaturized sensor, separation technologies, and non-linear optical apparatus [1-6]. Lead monoxide nanostructures and its composites [7] have been synthesized by various methods such as spray pyrolysis [8], porous alumina template based method [9], sonochemical method [10] and sol gel method, [11] etc. PbO_2 electrodes are applied in the industrial processes such as energy conversion, synthesis, process recycling and environmental treatment [12-17]. It is well known that PbO_2 exhibits excellent chemical stability in an acid medium and nanostructured lead dioxide are reported as a novel stationary phase for solid phase microextraction [18]. PbO_2 can be obtained easily as anodic deposits from solutions of the low-valence lead ions [19]. The properties of lead dioxide are highly dependent on its method of synthesis, which affects the structure, morphology and phase composition. PbO_2 sub micrometer-sized hollow spheres and microtubes [20], lead oxide nanotubes [21], porous PbO_2 electrodes [22], lead oxide nanobelts [23], and lead dioxide films [24] have been synthesized by applying different synthesis routes. Liang Shi et al. reported lead oxide nanosheets, scrolled nanotubes, and nanorods in a controlled way [25].

PbO_2 nano-powders were synthesized by the ultrasonic irradiation of an aqueous suspension of dispersed. β-PbO, as a precursor, in the presence of ammonium

[1]Avenida Ecuador 3493, Estación Central, Departamento de Física, Universidad de Santiago de Chile Santiago-9170124, Chile
E-mail: singh.dinesh@usach.cl; dineshpsingh@gmail.com
[2]Department of Physics, Banaras Hindu University, Varanasi- 221005 INDIA
E-mail: hepons@yahoo.com

peroxydisulfate as an oxidant [26]. Recently a sonochemical method was used for the synthesis of pure lead (II) oxide nanoparticles or nanobelts by utilizing mixed nano lead (II) two-dimensional coordination polymer as precursor [27-29].

Moreover, the electrocatalytic properties of PbO_2 may be enhanced by the incorporation of ions such as F^-. In this context, fluorine-doped PbO_2 has been synthesized in the presence of some additives of fluorine-containing compounds (F^-, potassium salt of nonafluoro-1-butanesulfonic acid $C_4F_9O_3SK$ and Nafion) [30]. Due to the limited studies on PbO_2 morphology and their subsequent application in nanoscale and microscale electronic devices, investigation on the synthesis and size dependent properties of lead oxide are significantly delayed. Micron sized hexagons and flower-like structures of α-PbO_2 have been synthesized by a very simple route of anodic oxidation of lead sheet. These structures can be easily obtained by the simple variation of voltage from 2 to 6 V between the platinum and lead electrodes. Synthesis of these structures is very simple and no costly chemicals, catalysts and surfactants are required.

Experimental Method

The experiment was performed in an electrochemical bath of Perspex with two electrodes set up. High purity lead sheet (alfa ascar, 99.9%) was utilized as a working electrode (the anode). A platinum sheet served as the counter electrode (the cathode) for anodization. The distance between the electrodes was kept 1 cm. A constant voltage of 2 V, 4 V or 6 V was applied between the electrodes using a potentiostat for a time span of one hour in every case. The volume of the electrochemical bath was $4 \times 3 \times 3$ cm^3 and the surface area of each electrode was 2×1 cm^2. 5 ml distilled water (with very low ionic conductivity $\sim$ 6-10 μS/m and pH=6.5) was used as the electrolyte. After every electrolysis run the synthesized material (settled down on the bottom of the electrolytic cell) was dried on the formvar coated copper grid and further characterized by transmission electron microscopy (TEM, Tecnai 20 G^2), and x-ray diffraction technique (XRD, X Pert Pro Panalytical).

Results and discussion

Figure 1(a) and (b) show the transmission electron microscopy image and selected area electron diffraction (SAD) of the materials synthesized by electrolysis at 2 V for one hour. Micron sized hexagon like structures having different edge size were observed throughout the whole sample. These structures were perfect hexagons with an edge size variation from 1 to 2 μm. Figure 1(b) is the magnified TEM micrograph of the hexagon-like structures. These structures were highly crystalline in nature. The contrast present in the images, mainly the extinction contours, indicates the presence of some sort of defects. The inset in Fig. 1(b) is the selected area electron diffraction (SAED) pattern from the hexagon structures, indicating that these structures are of crystalline PbO_2.

Figure 2(a) and Figure 2(b) are the TEM micrographs of the material as obtained after the electrolysis at 4 V for one hour. The TEM micrographs reveal the distorted hexagon-like structures consisting of some different nanomaterials. Figure 2(b) is the magnified TEM image of such a distorted hexagon. Interestingly, it can be seen that the hexagons still have maintained its boundary; whereas the region inside the boundary of the hexagons have changed into small particle-like structures. The further magnified TEM micrograph as shown in Fig. 2(c) reveals that these particles are in the form of small circular and flower-like structures. Circular and flower-like particles have been indicated by white arrow in the Fig. 2(c). Figure 2(d) is the SAED pattern from these structures.

As we increased the applied potential to 6 V, the hexagon-like structures disappeared and only flower-like structures (which were also previously observed inside the hexagons) were observed in the sample as can be seen from Fig. 3(a) and 3(b). Figure 3(c) is a magnified TEM image of the flower-like structures having

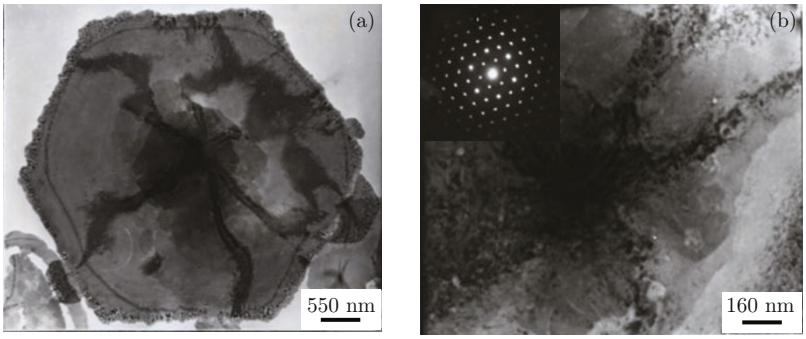

Fig. 1 (a) TEM micrograph of the Hexagon-like structures synthesized at 2 V. (b) Magnified TEM micrograph of the hexagon and inset is the SAED pattern of the hexagon revealing the structures of α-PbO_2.

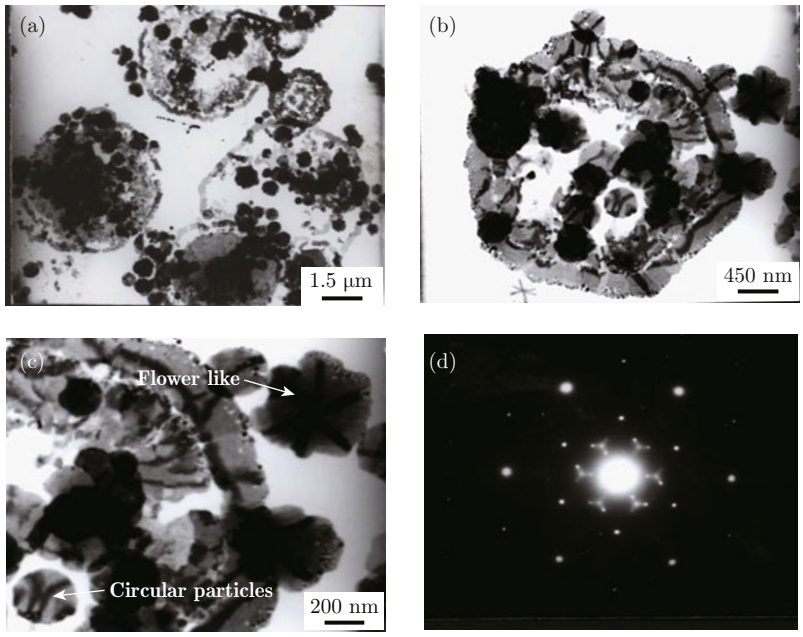

Fig. 2 (a) Distorted hexagons at higher applied voltage of 4 V. (b) TEM micrograph of a single hexagon where only the boundary of the hexagon is visible. (c) Magnified TEM micrograph revealed the circular- and flower-like structures. (d) The SAED pattern from these structures.

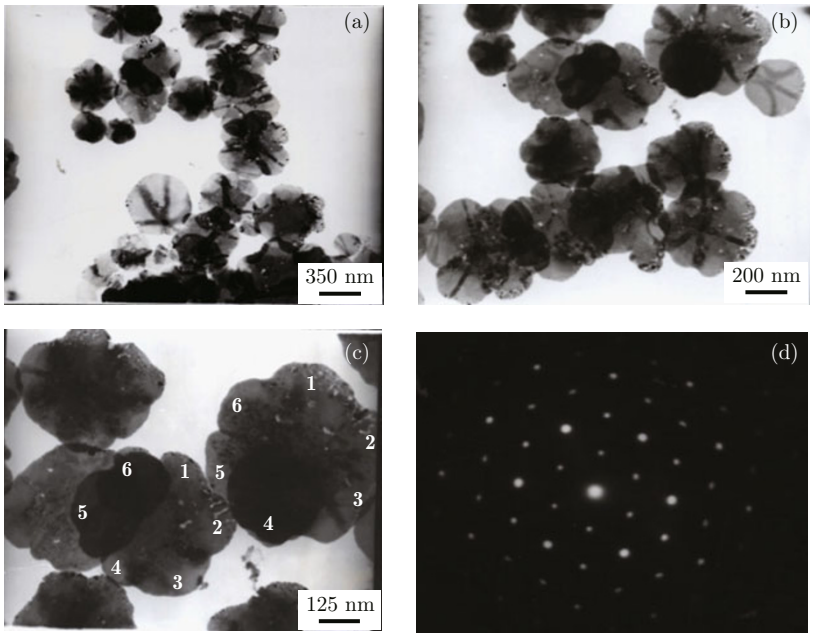

Fig. 3 (a) TEM micrographs of flower-like structures of lead oxide synthesized at 6 V. (b) Magnified TEM micrographs of the flower-like structures. (c) TEM micrographs revealing that these structures are six petals flower like. (d) The SAED pattern from the single flower-like structure.

clearly six petals obtained at higher applied potentials. The diameter of the flower-like structures is 200-500 nm and each petal has the size 100-200 nm. Figure 3(d) is the SAED pattern from a single flower-like structure.

The white product obtained after several electrolysis runs was collected and further characterized by XRD for structural analysis. Figure 4 is the XRD pattern from the materials obtained after several electrolysis run at 6 V for 1 h. The diffraction peaks from these flower-like structures were indexed to the orthorhombic system of α-PbO_2 with lattice parameter a=4.971 Å, b=5.956 Å, c=5.438Å, confirming that the synthesized materials were α-PbO_2. In addition to the delaminated nanostructures in the electrolyte, investigations of the lead anode, which were subjected to electrolysis runs, revealed the presence of large numbers of PbO_2 micron-

sized crystals.

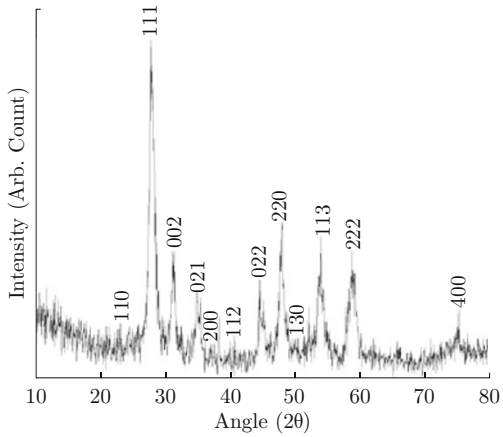

Fig. 4 XRD pattern from the materials obtained after electrolysis at 6 V for 1 h. The diffraction peaks could be indexed to orthorhombic system of α-PbO_2 with lattice parameter (a=4.971 Å, b=5.956 Å, c=5.438 Å).

Although the exact mechanism for the formation of lead oxide nanostructures is not quite understood, a plausible explanation for the formation of lead oxide nanostructures by electrolysis can be provided. The reactions for the formation of α-PbO_2 structures from Pb electrodes during electrolysis can be described by the mechanism suggested by Lee et al. [31]. In our case the electrochemical situation is [Pt/water(mildly acidic)/Pb], with applied voltage greater than ~1.23 V, which corresponds to electrolysis with moderate to vigorous oxygen and hydrogen evolution. As we apply the potential greater than 2 V, the water gets electrolyzed. Under this condition the hydrogen is liberated at the platinum electrode whereas a continuous layer of surface adsorbed oxygen molecules is expected at the lead electrode. Simultaneously the lead electrode was oxidized into lead ions, which after reaction with the surface-adsorbed oxygen molecules, resulted in the lead oxide nanostructures. The formation of PbO_2 nanostructures, as is evident from Fig. (1, 2 and 3), is dependent dominantly on the applied potential. At mild applied potential of 2 to 4 V, oxygen evolution is expected to be mild and the migration of fresh Pb^{2+} ions from the interior will be slow [32]. The formation of lead ions and surface-adsorbed oxygen and hence the reaction kinetics depends on the applied potential, which governs the formation of different lead oxide nanostructures. The reactions for the formation of α-PbO_2 structures from Pb electrodes after electrolysis can be described by the following equations [31,33].

$$H_2O \longrightarrow OH_{ads} + H^+ + e^-$$
$$Pb \longrightarrow Pb^{2+} + 2e^-$$
$$Pb^{2+} + 2\ OH_{ads} \longrightarrow Pb(OH)^{2+}$$
$$Pb(OH)^{2+} + H_2O \longrightarrow PbO_2 + 3H^+ + e^-$$

Figure 5 presents a schematic on the formation of different structures of PbO_2 at various applied potential of 2 V, 4 V and 6 V. Left-side images are schematic presentation of the structures and the right-side images are corresponding to the nanomaterials as obtained at various applied potentials. It is a very simple and cost-effective method for the synthesis of the desired micron-sized hexagon-like structures or nano-sized six-petal flower-like structure.

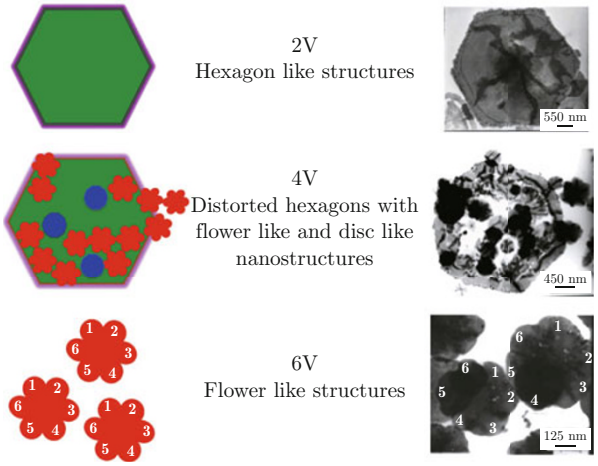

Fig. 5 Schematic presentation of the different nanostructures at various applied potentials. Left-side images are schematic and right-side images are as obtained after anodization at the corresponding applied potentials.

There are several effective parameters that can affect the structure, morphology and yield of the product, such as the distance between the electrodes, temperature, time of oxidation, and applied potential. Among all of these parameters, the applied potential between the electrodes was the most influential for the synthesized nanostructures. That is why the effect of the applied potential has been studied in detail, keeping in mind that the rest of the parameters could also influence on the yield of the products. As we increase the time of oxidation at a particular applied potential, we obtain a higher yield of the corresponding nanomaterials.

Conclusions

Submicron sized hexagons and six-petal flower-like structures of α-PbO_2 have been synthesized by a very simple route of anodic oxidation of lead sheet. Anodic oxidation at 2 V results in the formation of hexagon-like structures, with a size ranging from 1 to 2 μm in the electrolyte. Applied potential of 6 V results in six-petal flower-like structures of PbO_2.

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