

FACILE SYNTHESIS AND OPTICAL PROPERTIES OF PbO NANOSTRUCTURES

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Abstract— PbO nanostructures were synthesized by the oxidation of lead sheets in a tube furnace under oxygen ambient using different temperatures, from 280 °C to 450 °C. X-ray diffraction patterns (XRD) indicated the formation of α -PbO nanostructures from the lead sheet with an increase in the temperature. Scanning electron microscope (SEM) results showed that flake-like shapes were starting to grow on the lead sheet that was placed in the 280 °C. In addition, the SEM studies showed nanoflake and nanoporous morphologies for the lead sheets that were placed at 330 °C and 450 °C, respectively. Raman measurements confirmed the XRD results and indicated two Raman active modes that belonged to the α -PbO phase for the nanoflakes and the nanoporous surface. The optical properties of the products were characterized using a photoluminescence (PL) technique. The PL results for the PbO nanoflakes and nanopores showed a peak in the visible region.

Keywords— PbO nanostructures; Oxidation method; Raman; Photoluminescence.

I. INTRODUCTION

Nanostructures have attracted much interest in the research and industrial fields because of their unique optical, electrical, magnetic, acoustic, and chemical properties. Among these, metal oxide nanostructures are important because of their application potential to different technologies such as opto-electronic devices, solar cells, batteries, etc.

Lead oxide is one of the metal oxides that have important applications in storage batteries, the glass industry, and pigments (Chen *et al.*, 2010). So far, various forms of PbO and their nanostructural compositions have been reported, including nanoplates and nanostars (Chen *et al.*, 2010), nanorods (Ghasemi *et al.*, 2008), nanopowders (Kashani-Motlagh and Karami Mahmoudabad, 2011), and nanosheets and nanotubes (Shi *et al.*, 2008). PbO is also a semiconductor with a direct band gap energy (~1.9 eV). Recently, several new routes have been used to synthesize PbO nanostructures, such as calcination (Li *et al.*, 2011), a sonochemical method (Soltanian Fard *et al.*, 2013), gel combustion (Karami Mahmoudabad and Kashani-Motlagh, 2011), anodic oxidation (Singh and Srivastava, 2011), a hydrothermal method (Jia and Gao, 2006), and thermal decomposition (Behnoudnia and Dehghani, 2012). Most of

these techniques are complex, expensive, and time consuming. In addition, the final products of these methods have not shown a good crystalline quality.

Among the various sintering methods, the direct thermal oxidation of a high purity metal sheet is a cost effective and simple method. In addition, it has great potential to be adopted for the large-scale production of metal oxide nanostructures. Recently, good experiment results were reported when this method was used to grow ZnO nanowires (Jamali-Sheini *et al.*, 2012). In addition, this method was recently used to grow CuO nanowires (Farbod *et al.*, 2012). Therefore, we used this method to grow lead oxide nanostructures in the current study. In this work, a simple oxidation of the lead sheets in a horizontal tube furnace under an oxygen ambient condition was carried out to synthesize PbO nanostructures. In addition, optical characterizations indicated that good-quality products were obtained from this method.

II. EXPERIMENTS

The PbO nanostructures were grown using a CVD setup in a tube furnace. First, four high purity Pb sheets (99.99%) were used as the substrates and source materials. These sheets were 1 × 1 cm in size and 0.5 mm thick. The sheets were ultrasonically cleaned in acetone and methanol for 10 min in each solvent. The furnace was heated to 450 °C, and the lead sheet temperatures were varied between 280 °C and 450 °C (280 °C, 330 °C, 390 °C, and 450 °C). A mixture of high purity N₂/O₂ gas (10:1) was fed into one end of the furnace at approximately 100 sccm, while the other end was connected to a rotary pump. The growth process was allowed to proceed for 2 h. A vacuum of 6 Torr was maintained inside the tube furnace during the oxidation of the Pb sheet.

The morphology and crystal structure of the products were investigated using a field emission scanning electron microscope (SEM, Hitachi S4160) and an X-ray diffractometer (XRD, Phillips PW3040/60). Room temperature photoluminescence (Perkin Elmer LS55) and Raman (Almega Thermo Nicolet Dispersive Raman Spectrometer) spectrometers were employed to study the optical properties and crystallinity of the PbO nanostructures, respectively. A Xenon arc lamp was used as the light source for the PL, and an Nd:YLF laser with a wavelength of 532 nm was used for the Raman measurements.

III. RESULTS and DISCUSSION

Figure 1 shows the XRD patterns of the sheets that were placed at 280 °C, 330 °C, and 450 °C. It can be seen that the XRD pattern of the sheet that was placed at 280 °C shows a single phase from the Pb sheet, while the XRD pattern of the sheet that was placed at 330 °C indicates two phases, one Pb phase and another α -PbO phase with a tetragonal structure (JCDPDS Card No.50561). The XRD pattern of the sample that was placed at 390 °C (which is not shown here), indicated the same pattern as the sample that was placed at 330°C. In addition, Fig. 1 shows the XRD pattern of the sheet that was placed at 450 °C. It can be observed that the phase of the sheet at this temperature was completely the α -PbO phase, because the Pb phase disappeared. However, a small amount of β -PbO also appears in this sample.

Figure 2 shows SEM images of the sheets that were placed at different temperatures. It can be seen that some nanoflakes started to grow on the sheet that was placed at 280 °C (Figs. 2a and 2b). The formation of these nanoflakes improved when the growth temperature increased to 330 °C (Figs. 2c and 2d). The average diameter of the nanoflakes was approximately 538 nm, with an average thickness of approximately 23 nm. Figures 2e and 2f show a porous morphology with nanosize holes in the sample that was placed at 430 °C. The average diameter of the holes was approximately 50 nm.

Raman spectroscopy is an effective technique for estimating the crystallinity of materials. According to the group theory, single crystalline α -PbO belongs to the D_{7h}^{17} space group having two formula units per primitive cell. A factor-group analysis, as well as a site symmetry analysis, gives the representation Γ_{opt} for the optical vibration modes of α -PbO,

$$\Gamma_{opt} = A_{1g} + B_{1g} + 2E_g + A_{2u} + E_u, \quad (1)$$

where A_{1g} , B_{1g} , and E_g are the Raman active modes, and A_{2u} and E_u are the infrared active modes (Wiechert *et al.*, 2005; Baleva and Tuncheva, 1994). Figure 3 shows the Raman spectra of the nanoflakes and nanopores. The Raman spectrum of the nanoflakes exactly matches the

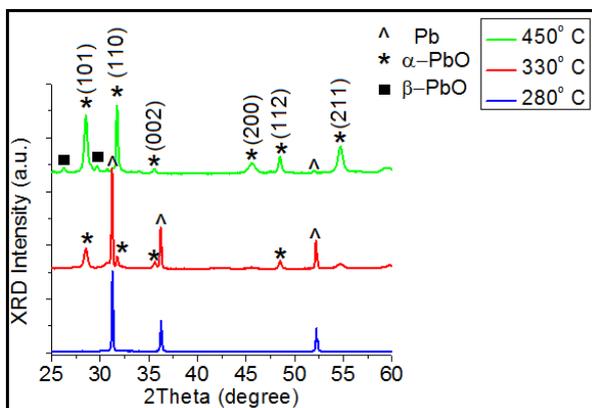


Figure 1. XRD patterns of the lead sheets that were placed at different temperatures. The patterns show that α -PbO phase forms at 330 °C and completes at 450 °C. However, a small amount of β -PbO phase also observes at 450 °C.

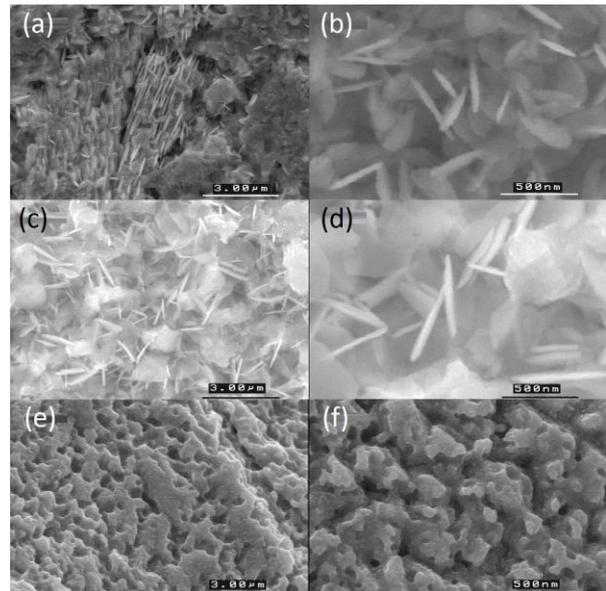


Figure 2 .SEM images of the nanostructures that form at different temperatures of the lead sheets with different magnifications (a-b) 280 °C, (c-d) 330 °C, and (e-f) 450 °C.

α -PbO structure that was previously reported (Wiechert *et al.*, 2005; Baleva and Tuncheva, 1994). As shown in Fig. 3, the Raman spectra of the PbO nanostructures show a sharp, strong, and dominant peak at 140 cm^{-1} , corresponding to the A_{1g} mode of the Raman active mode, which is a characteristic peak for the motion of the lead atoms parallel to the c-axis. On the other hand, the peak that appeared at 341 cm^{-1} , corresponding to the B_{1g} mode of the Raman active, is a characteristic peak for the motion of the lighter oxygen atoms parallel to the c-axis. In fact, these peaks indicate a high crystal quality for the obtained products. However, the Raman spectrum of the nanopores shows an additional weak peak at 233 cm^{-1} , which belongs to the β -PbO structure. In fact, the Raman results are in good agreement with the XRD results.

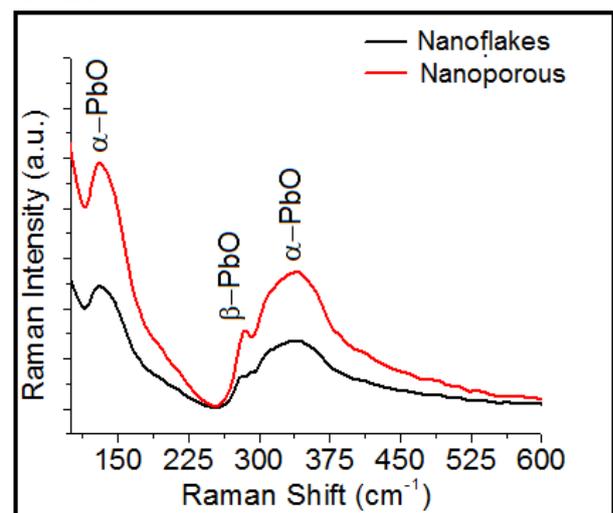


Figure 3. Raman spectra of the α -PbO nanostructures. The spectra show the Raman active modes of the α -PbO structure for the both samples. However, the Raman spectrum of the nanopores indicates a weak peak at 230 cm^{-1} that belongs to β -PbO structure.

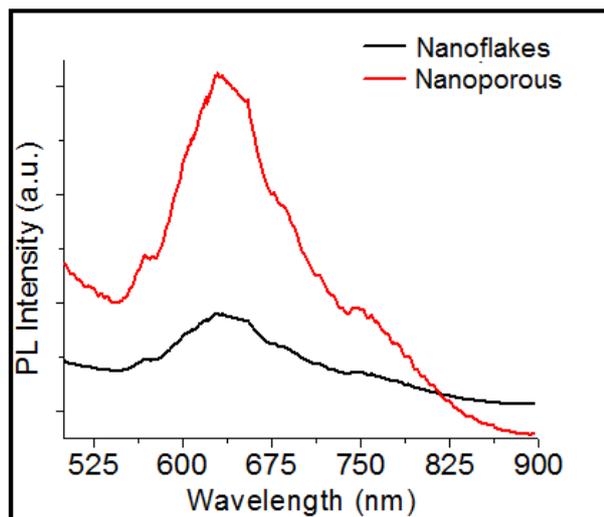
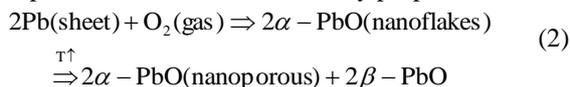


Figure 4. PL spectra of the α -PbO nanostructures. The spectra indicate a band gap for the α -PbO nanostructures in the visible region.

According to obtained results, the formation of a different phase of PbO can be tentatively proposed.



PL emission and excitation spectroscopy has a direct connection to the optical transitions contributing to the light emission process; therefore, it is one of the most sensitive methods for investigating electronic levels. Figure 4 shows the PL spectra of the PbO nanostructures.

The PL spectra show a broad peak in the visible region at 651 nm (1.9 eV) for the PbO nanoflakes and nanopores. The value 1.9 eV is in good agreement with the reported band gap values of α -PbO (Veluchamy and Minoura, 1995). The PL peak at a wavelength of approximately ~651 nm is associated with the transition of electrons from the conduction band edge to holes, trapped at interstitial Pb^{2+} sites. However, the PL spectrum of the nanopores shows a stronger and sharper peak in comparison to the PL spectrum of the nanoflakes. In addition, the full width at half maximum (FWHM) of the PL peak of the PbO nanopores is smaller than that for the PbO nanoflakes, which indicates better the optical quality of the PbO nanopores. This could be the result of the higher crystalline quality of the PbO nanopores, according to the XRD results. In fact, the Pb phase shown in the XRD pattern as a metal had an effect on the PL spectrum of the PbO nanoflakes because of the low work function of the metal (Fang *et al.*, 2011). It is expected that, because of the presence of a band gap in the visible region, it might be possible to use the obtained products as a photovoltaic unit.

IV. CONCLUSIONS

The oxidation of lead sheets in a CVD setup at different temperatures was used to grow PbO nanostructures. The XRD patterns showed that the α -PbO phase started to form at 330 °C and was completed at 450 °C. However, a small amount of the β -PbO phase was also formed at

450°C. SEM studies revealed nanoflake and nanoporous morphologies for the lead sheets that were placed at 330°C and 450°C, respectively. Raman measurements indicated two Raman active modes that belonged to the α -PbO phase for the nanoflakes and the nanopores. The PL results showed that the band gap of the α -PbO nanostructures was 1.9 eV.

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REFERENCES

- Baleva, M. and V. Tuncheva, "Optical characterization of lead monoxide films grown by laser-assisted deposition," *J. Solid State Chem.*, **110**, 36-42 (1994).
- Behnoudnia, F. and H. Dehghani, "Synthesis and characterization of novel three-dimensional-cauliflower-like nanostructure of lead (II) oxalate and its thermal decomposition for preparation of PbO," *Inorg. Chem. Commun.*, **24**, 32-39 (2012).
- Chen, K.C., C.W. Wang, Y.I. Lee and H.G. Liu, "Nanoflakes and nanostars of β -PbO formed at the air/water interface," *Colloids Surf. A*, **373**, 124-129 (2010).
- Farbod, M., N. Meamar Ghaffari and I. Kazeminezhad, "Effect of growth parameters on photocatalytic properties of CuO nanowires fabricated by direct oxidation," *Mater. Lett.*, **81**, 258-260 (2012).
- Fang, Y.J., J. Sha, Z.L. Wang, Y.T. Wan, W.W. Xia and Y.W. Wang, "Behind the change of the photoluminescence property of metal-coated ZnO nanowire arrays," *Appl. Phys. Lett.*, **98**, 033103 (2011).
- Ghasemi, S., M.F. Mousavi, M. Shamsipur and H. Karami, "Sonochemical-assisted synthesis of nanostructured lead dioxide," *Ultrason. Sonochem.* **15**, 448-455 (2008).
- Jamali-Sheini F, R. Yousefi and K.R. Patil, "Surface characterization of Au-ZnO nanowire films," *Ceram. Int.*, **38**, 6665-6670 (2012).
- Jia, B. and L. Gao, "Synthesis and characterization of single crystalline PbO nanorods via a facile hydrothermal method," *Mater. Chem. Phys.*, **100**, 351-354 (2006).
- Karami Mahmoudabad, M. and M.M. Kashani-Motlagh, "Synthesis and characterization of PbO nanostructure and NiO doped with PbO through combustion of citrate/nitrate gel," *Int. J. Phys. Sci.*, **6**, 5720-5725 (2011).
- Kashani-Motlagh, M.M. and M. Karami Mahmoudabad, "Synthesis and characterization of lead oxide nanopowders by sol-gel method," *J. Sol-Gel Sci. Technol.*, **59**, 106-110 (2011).

- Li, L., X. Zhu, D. Yang, L. Gao, J. Liu, R. Vasant Kumar and J. Yang, "Preparation and characterization of nano-structured lead oxide from spent lead acid battery paste," *J. Hazard. Mater.*, **203-204**, 274-282 (2012).
- Shi, L., Y. Xu and Q. Li, "Controlled Growth of Lead Oxide Nanosheets, Scrolled Nanotubes, and Nanorods," *Cryst. Growth Des.*, **8**, 3521-3525 (2008).
- Singh, D.P. and O.N. Srivastava, "Synthesis of micron-sized hexagonal and flowerlike nanostructures of lead oxide (PbO₂) by anodic oxidation of lead," *Nano and Micro Letters*, **3**, 223-227 (2011).
- Soltanian Fard, M.J., F. Rastaghi and N. Ghanbari, "Sonochemical synthesis of new nano-two-dimensional lead (II) coordination polymer: As precursor for preparation of PbO nano-structure," *J. Mol. Struct.*, **1032**, 133-137 (2013).
- Veluchamy, P. and H. Minoura, "Selective formation of β -PbO and α -PbO films on Pb electrodes by potentiostatic anodization in alkaline solutions," *J. Electroanal. Chem.*, **396**, 211-217 (1995).
- Wiechert, D.U., S.P. Grabowski and M. Simon, "Raman spectroscopic investigation of evaporated PbO layers," *Thin Solid Films*, **484**, 73-82 (2005).

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