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Original Article

Economically viable route for synthesis of lead oxide (α-PbO) nanoparticles with an aim to reduce the manufacturing cost of lead acid batteries

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ABSTRACT

Almost uniform nanoparticles of lead oxide (PbO) having diameters of 70±20nm were successfully synthesized via a economical and fast process at low temperature of (~280°C) without using any additives. This organics free approach for the synthesis of lead oxide requires only lead metal and de-ionized water. The structure and morphology of the products were characterized by X scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX) and X-ray diffractometer (XRD). The possible formation mechanism of nanoparticles is proposed in brief. The advantage of producing nanoparticles with this method includes ease, flexibility, fast, cost effective and pollution free.

Keywords: Lead oxide; DI-water; economical synthesis; nanoparticles

INTRODUCTION

With quasi-monopolies on huge markets such as the automobile industry or the storage of renewable energies lead-acid batteries are still today the most sold of the secondary batteries. This is mainly due to their low cost compared to the other technologies. However, many people predict that in the long run the lead-acid battery is bound to disappear and will be completely replaced by rechargeable batteries with higher energy and power densities such as the Ni-MH or the Li-ion. To keep them competitive, it is therefore important to continue the research effort and to investigate new approaches to decrease their manufacturing cost even further [1].

Lead oxide is the basic material of the electrode active mass in lead acid batteries. It has wide industrial applications as the basic material of electrode active mass in lead acid batteries. The two predominant methods used to produce lead oxide are the 'ball mill' and the 'Barton-pot' method [2]. The lead oxide manufactured by the ball-mill process is almost 100% tetragonal (α-PbO) while that produced by the Barton (molten metal) system can contain varying and controlled ratios of α -PbO: β-PbO depending on the temperature during the process [3]. The crystal structure of PbO is of significant interest with respect to the plate making process [4]. There is a growing trend towards the use of pure lead monoxide for the production of positive plates. The advantage of using pure lead oxide is that it can eliminate the lead oxidation step and therefore, significantly reduce the curing time and processing cost. In recent years nanostructured materials have been of interest because they are distinguished from conventional polycrystalline materials by the size of materials that compose them. Results show that the nanocrystalline materials have remarkable electrochemical performance, high specific capacity and good cycle behavior [5].

Nevertheless, there are only few reports on the synthesis of lead oxide in nano-scale. Morlaes et al. showed that the spray pyrolysis method can be used for synthesis of lead oxide from lead salt solution; however, they did not focused on preparing nanostructures. They synthesized just a lead oxide thin film by spray pyrolysis of lead salt solution on a preheated surface [6]. Konstantinov et al. used the spray pyrolysis method for synthesis of nanostructured lead oxide [7]. They had a systematic study of the effect of various spray pyrolysis parameters such as temperature, solution concentration and solution flow rate on the morphology, crystallization process, crystal size and specific surface area. They synthesized globular shape lead oxide in the wide range of particle size of 20–127 nm [8]. There are many reports on the effect of ultrasonic waves on

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morphology and particle size in synthesized solutions. Zhang et al. have reported that the Sonochemical method is an effective way of stabilizing the nanometer-sized particles produced during synthesis processes [9]. The first and simplest effect of ultrasonic waves on synthesized solutions is preventing the particle growth and breaking agglomerated and colonial balls into small particles. Jia, et al. (2006) reported a new method for electrochemical synthesis of nanostructured PbO and used the obtained PbO as cathode of rechargeable batteries [10]. Karmi et al. (2008) synthesized uniform nanostructured lead oxide by sonochemical method [11]. Jiang et al. (2004) prepared the nanocrystalline lead oxide through two step chemical reactions and tested the obtained nanoparticles as the electrode active material for valve regulated lead acid battery [12]. They found that by using the nanocrystalline lead oxide, the pasted electrodes can be directly formulated without a curing process. Lee et al., (2002) showed that the spray pyrolysis method can be used for synthesis of lead oxide from lead salt solution, but they did not focus on preparing of nanostructures [13].

But most of the pathways suggested above for the synthesis of PbO involve environmentally malignant chemicals which are toxic and not easily degraded in the environment besides the cost of preparation is high. Water is particularly attractive because it is inexpensive, environmentally benign and bestowed with many virtues especially under supercritical conditions [14].

In this paper, we report a simple econimical route to fabricate novel uniform nanoparticles without any organics, templates, or surfactant at low temperature of ~280°C. The crystallinity, morphology, and structure of the samples were examined through various characterization techniques. The reported method besides being organics free is economical, fast, environmentally benign and free of pollution, which will make it suitable for large scale production. Systematic studies would be necessary to optimize the conditions for obtaining nanostructures of desired dimensions.

EXPERIMENTAL

Materials: Lead powder was used as a source of lead and was cleaned by ultra-sonication in acetone and water for 20 minutes in each solvent. The de-ionized water was produced in laboratory. For the synthesis of lead oxide nanoparticles, a closed cylindrical Teflon lined stainless steel chamber was used.

Synthesis: In a typical synthesis, 4mg of zinc metal foils was taken with 40 ml of de-ionized water in a Teflon-lined stainless steel chamber with 50 ml capacity. The prepared reaction mixture was kept at 280^{o}C in an oven for 24 hours. After the desired time, the system was allowed to cool down naturally and the resulting mixture was centrifuged. The zinc foils, collected from the reactions vessels, were washed with de-ionized water several times and finally dried in air.

Characterization of samples: The morphology of the products was carried out using Field Emission Scanning Electron Microscope (FEI SEM, NNL 200, Japan), coupled with energy dispersive X-ray spectrometer EDX (Gensis). Phase structure and the purity of the as prepared samples were characterized by powder X-ray diffraction (XRD) taken on a Philips (X'Pert PRO PW-3710) diffractometer with 2θ ranging from 10-70^{o}, using Cu Kα (λ =0.15141 nm) radiation operated at 40kV and 30mA. Photoluminescence spectra were recorded with Perkin- Elmer model LS55 luminescence spectrometer.

RESULTS AND DISCUSSION

Morphology examinations: The general morphologies of the as-grown structures, obtained after the reaction of zinc metal with water at 280^{o}C for 24h, was observed by SEM and demonstrated in figure 2 which confirms that the grown products are irregular particles in shape. Figure 2 (a,b) and (c,d) show the low-magnification SEM images of the particles and confirms that the particles are grown in a very high density over the whole foil substrate. The typical diameters of the as-grown nanoparticles are ~ 50 ±20nm.

To check the composition of the as-grown nanoparticles, EDX analysis was performed as shown in figure 2. It is confirmed from the EDX analysis that the grown nanoparticles are composed of lead and oxygen only. The molecular ratio of Pb/O of the nanoparticles, calculated from EDX and quantitative analysis data is close to that of bulk lead oxide. The measurement on the nanoparticles indicates that the product is composed of Pb and O.

The structure and purity of samples were determined by XRD patterns as shown in figure 3. The XRD patterns of the as prepared samples shows the samples consists of pure PbO. It can be clearly noticed that the peak with strongest intensity is (020) instead of that of (111), which is the strongest one according to the literature (JCPDS card no. 38-1477). With the reaction time prolonged, the relative intensity of (020) peak

increases, indicating the possibility of the orientation of PbO. The XRD pattern indicated the formation of well crystalline products.

In the figure 4, we show the photoluminescence spectra recorded at the excitation wavelength of 480 nm. We observe the maximum blue shift in case of the lowest wavelength emission band which is considered due to transition between valance and conduction bands. The photoluminescence (PL) methodology is generally adopted for investigating the radiative recombination emission processes due to the excitation, defect and impurity levels in semiconductors. It is well known that there are two kinds of emissions bands of UV and visible spectrum in PbO crystals. The emission in the UV region is attributed to the recombination between electrons in conduction band and holes in valence band. The visible emission is related to the defects related deep level emission such as oxygen vacancies and Pb interstitials. Therefore, a study of PL property of PbO can provide valuable information on the quality and purity of this material.

The formation of lead oxide nanoparticles by the reaction of lead with water can be explained as follows. Lead gives hydrogen on reaction with water according to the reaction

$$2Pb + 2H_2O\,(l) \rightarrow 2PbO\,(s) + 2H_2\,(g)$$

Here (s), (l) and (g) represent solid, liquid and gas respectively. The Pb metal on reaction with water slowly gives out hydrogen (g) and the liberated oxygen reacts with metal to give oxides as shown in the above reaction. The Pb reacts with oxygen and forms nuclei, which further serve as seed for PbO nanoparticles growth. The growth of nanoparticles could be occurring at the small oxide nuclei that may be present on the metal surfaces. As the concentration of Pb and OH^- ions exceeds a critical value, the precipitation of PbO nuclei starts, the $Pb(OH)_2$ can be transformed PbO crystals. The precipitates of $Pb(OH)_2$ are more soluble as compared to PbO precipitates, therefore, $Pb(OH)_2$ precipitates formed tend to continuously produce Pb and OH^- ions, which form the PbO nuclei. The lead oxide nuclei formed are the building blocks for the formation of final products. Moreover, water at higher temperatures plays an essential role in the precursor material transformation because the vapour pressure is much higher and the state of water at elevated temperatures is different from that at room temperature. The solubility and the reactivity of the reactants also change at high pressures and high temperatures and high pressure is favourable for crystallizations.

Economics stimulated investigations of faster, and more productive methods to produce lead oxides for battery use as shown schematically in figure 5. In 1898, G.B. Barton patented a process where molten lead was stirred mechanically in the presence of air and steam, and the resulting oxide continuously transported away for collection via an air stream drawn through the process chamber. This process became commonly known as the Barton Pot. Another oxide production method involved the adaptation of a ball mill commonly used for wet or dry grinding of ores, pigments, and other materials by the action with iron balls into a large rotating chamber or by using lead balls tumbling against one another. In a 1926 patent, G. Shimadzu described this process where friction created sufficient heat to oxidize the outside surface of these lead balls as the horizontal cylindrical mill turned; the oxide dust was carried away by a stream of as for collection. Both the above methods produced a partially-oxidized product which contained a wide ranging percentage of free metallic particles. Barton material was initially used as feed for litharge furnaces since it was discovered that conversion of the remaining free lead to PbO was rapidly accomplished. The production time of lead monoxide was reduced from 30 h per batch in the above-mentioned furnace process, to about 3–4 h with the Barton and furnace processes combined. It was soon found, however, that these so called ‘leady’ oxides could be used directly in paste formulations and, by about 1925, they were rapidly replacing litharge and red lead. Since then new techniques have emerged continuously but the cost of the product remained a challenge. The present work is a humble attempt to address the cost issue, simplicity of production and a process which is benign to environment.

CONCLUSIONS

In this method, we developed a technique which is economical and easy method for preparing homogeneous lead oxide nanoparticles. The prospects of the method are bright and promising. This facile, reproducible and low cost approach should promise us a future large scale synthesis of PbO nanostructures for many applications in nanotechnology.

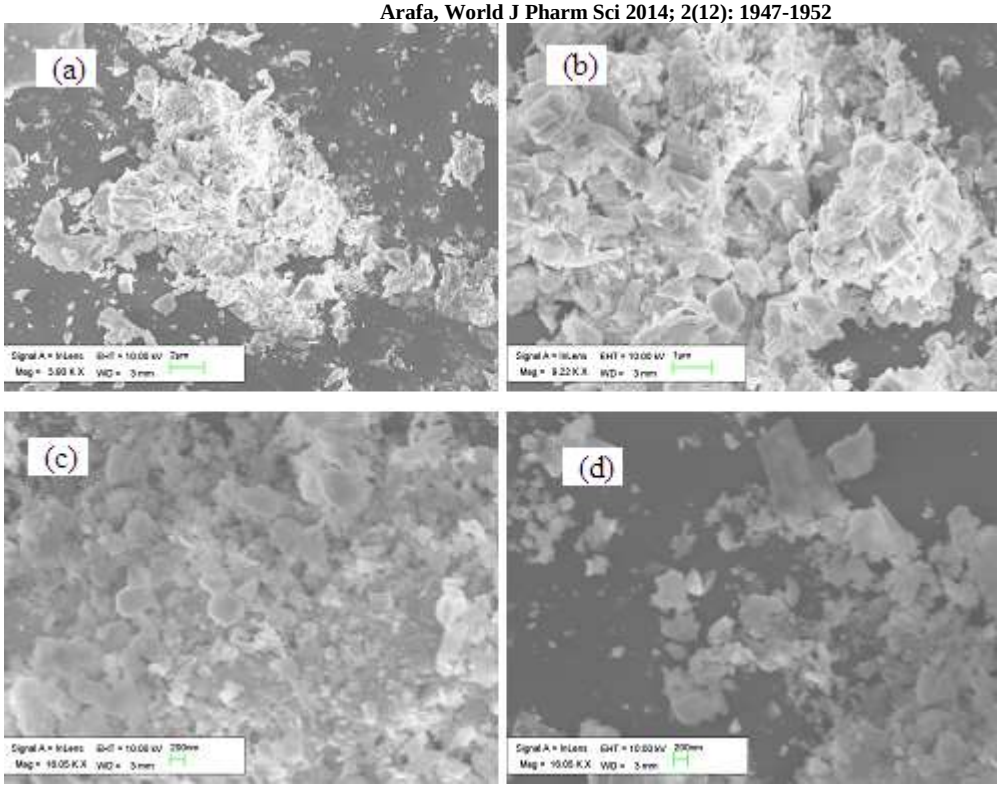

Figure 1 (a,b) and (c,d) shows the low and high magnification images of FESEM images of nanoparticles of PbO prepared by lead metal with water at 280ºC for 24h.

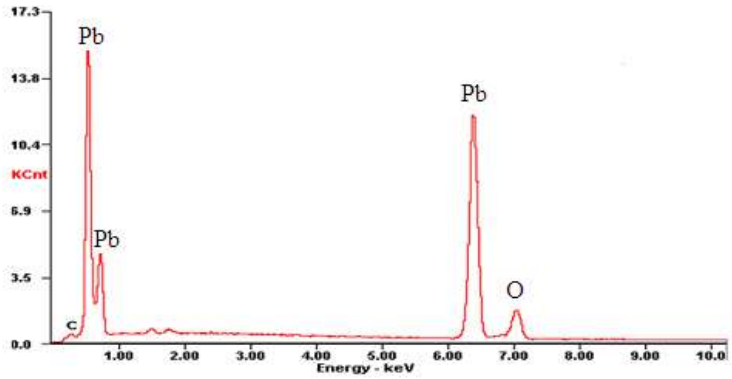

Figure 2. The EDX pattern of the samples

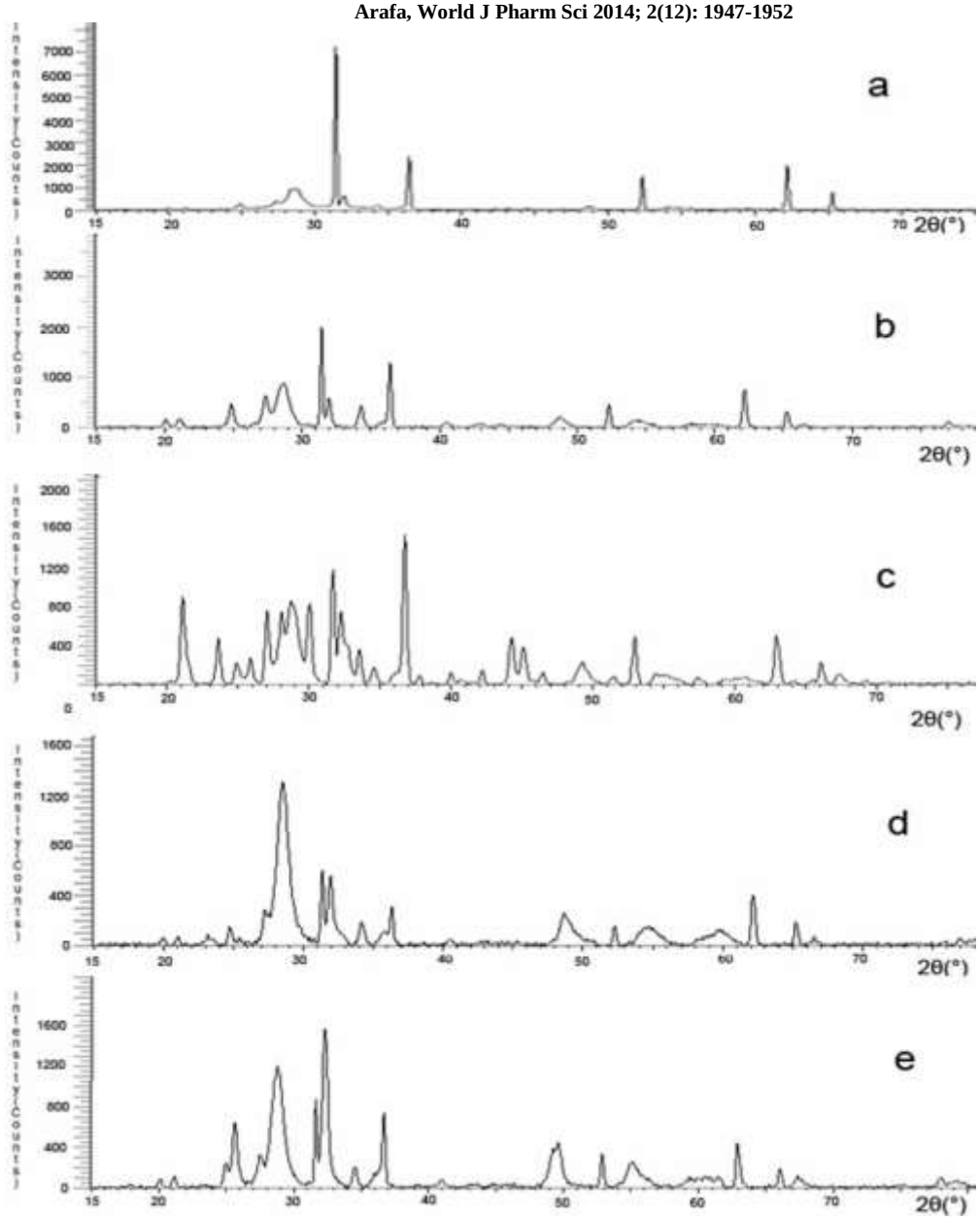

Figure 3. XRD patterns for the samples which synthesized at different temperature of 0ºC (a), 20ºC (b), 45 ºC (c), 70ºC (d) and 100ºC (e)

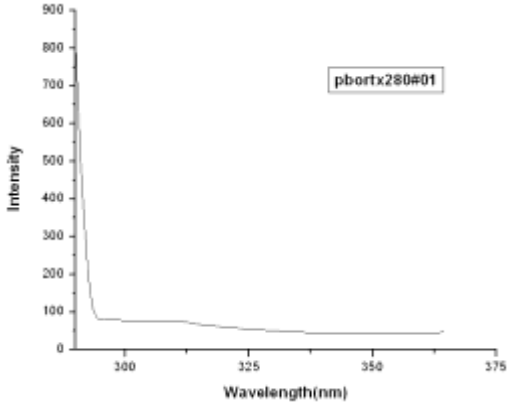

Figure 4. Room temperature photoluminescence spectra of PbO nanoparticles prepared at 280^{o}C for 24h.

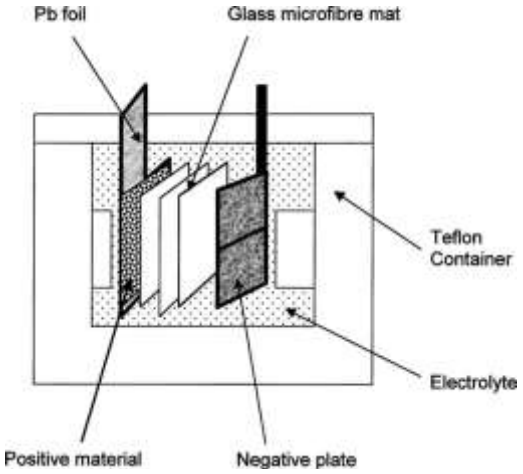

Figure 5 shows the schematic representation of cell used in electrochemical experiments

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