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Full Length Research Paper

Synthesis and characterization of PbO nanostructure and NiO doped with PbO through combustion of citrate/nitrate gel

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Our goal in this research was to obtain lead oxide nanostructure and NiO doped with PbO through the combustion of a citrate/nitrate gel. In this method, lead oxide nanostructure and NiO doped with PbO was synthesized through the reaction of citric acid ($C_6H_7O_8.H_2O$) solution and lead acetate ($Pb(C_2H_3O_2)$) solution as stabilizer and precursor, respectively. At first, in the presence of metal nitrate and citric acid, transparent sol was obtained, and then the transparent sol was transformed into dry gel through two steps: evaporating in water bath to form wet gelatin and then drying in oven. In this synthesis, the molar ratio of citric acid to metal ions (MRCM) is equal to 1.5. The prepared lead oxide nanostructure and NiO doped with PbO ($Pb_{0.95}Ni_{0.05}O_{1.97}$) were characterized by FT-IR spectroscopy, X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX) and scanning electron microscopy (SEM). The prepared PbO consists of the crystallites about 59 nm.

Key words: PbO, combustion, nanostructure, NiO, $Pb_{0.95}Ni_{0.05}O_{1.97}$.

INTRODUCTION

In recent years, the synthesis of nanomaterials is an important research in the various scientific and industrial fields (Keating and Natan, 2003; Chen et al., 2005). Nano-materials have attracted the attention of researchers not only by their particular physical and chemical properties but also by their potential application in many domains such as gas sensors, fuel cells, paints, rechargeable batteries, pigments and so on (Salavati-Niasari et al., 2009; Ferg et al., 2010; Ghasemi et al., 2008). Lead element has a lot of oxide forms including PbO (α, β and amorphous), Pb_2O_3, Pb_3O_4, PbO_2 (α, β and amorphous). PbO itself has two forms: yellow β-PbO, which is stable at high temperature and red α-PbO, which is stable at low temperature. The α-PbO phase transformation to β-PbO takes place at about 490°C (Salavati-Niasari et al., 2009). Lead oxide (PbO), is an important industrial material due to its unique electronic, mechanical and optical properties mechanical and optical properties and its potential applications in nanodevices and functionalized materials (Xi et al., 2004) such as active materials of lead-acid batteries, valve-regulated lead acid (VRLA) batteries, and lithium secondary batteries (Karami et al., 2008; Lafronta et al., 2010; Martos et al., 2001). Because of the simplicity of design, low cost of manufacturing, reliability and relative safety when compared to other electrochemical systems of lead-acid batteries, there is a high interest to improve and develop lead oxide characteristics to obtain more discharge capacity and more cycle-life.

Therefore, research to improve discharge capacity of lead oxide and lead dioxide is still in demand. The Interactions between the lead oxide and Ni may change the electronic properties of PbO, which results in the further enhancement of discharge capacity (Soria et al., 2004; Yeh et al., 2001; Marco et al., 2006; Shiota et al., 2005; Wang et al., 2010). On the other hand, a variety of physicochemical methods, including thermal decomposition (Salavati-Niasari et al., 2009; Hashemi et al., 2011) spray pyrolysis (Konstantinov et al., 2006), selected-control synthesis (Cao et al., 2003; Shi et al., 2008), hydrothermal synthesis (Xi et al., 2004), sonochemical

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(Aboutorabi and Morsali, 2011; Aslani and Morsali, 2009; Sadeghzadeh et al., 2010; Sadeghzadeh et al., 2010; Sadeghzadeh and Morsali, 2010), microwave irradiation (Raju and Murthy, 2006; Li et al., 2005), synthesis by coordination polymers (Sadeghzadeh et al., 2010; Haddadian et al., 2009; Sadeghzadeh et al., 2010) and pulsed current electrochemical methods (Karami and Alipour, 2009) have been used to produce nanometer-sized lead oxides.

In the present study, the PbO nanostructure and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound were synthesized through the auto-combustion of the gel that comes from the citrate/nitrate sol–gel process. Sol-gel method shows considerable advantages relatively to the customary methods of its relatively low processing cost and the ability to control the grain size. Auto-combustion of sol–gel is a modification of sol–gel method, which can accelerate the synthesizing process and refine the grain or particles size of powders (Graca et al., 2010; Zheng and Li, 2010; Lian et al., 2004).

EXPERIMENTAL

Material

All chemicals and reagents in this work were used as received without further purification. These were: lead(II) nitrate (Merck, 99%), nickel(II) nitrate (Merck 99%), citric acid (Merck, 99.5%) and ammonia solution. In all experiments, distilled water was used.

Characterization

XRD pattern was recorded by powder X-ray diffractometer (Philips, PW 3710, operated at 40 kV, 30 mA) employing Cu Kα radiation (λ = 1.5406 Å). The average crystallite size of the product was calculated from the Scherrer equation (Eshaghi et al., 2010), using the major diffraction peak of the corresponding PbO (111):

$$t = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where t is the average crystallite size, K is a constant (0.9), λ is the wavelength of X-ray (Cu Ka), β is the full width at half maxima, and θ is the diffraction angle in degree.

Particle morphology and compositional analyses of the prepared PbO nanostructure and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound were carried out using a scanning electron microscopy and an energy dispersive X-ray analysis (EDAX) set up attached to an SEM (Philips XL-30). The samples were coated with gold in order to increase their conductivity before scanning. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-8400S spectrophotometer in KBr pellets in the wave number range of 400–4000 cm^{-1}.

Synthesis of PbO nanostructure

The appropriate proportion of lead nitrate and deionized water were dissolved in a 100 ml beaker to obtain 25 ml aqueous solution with 1 M metal ion in it. The MRCL was taken as 1.5. The aqueous solution was then stirred for 0.5 h in order to mix the solution uniformly. The ammonia solution (25% aqueous solution) was being dropped gradually into the aqueous solution during stirring until transparent colloidal suspension was obtained. The transparent sol was transformed into dry gel through two steps: evaporating for 20 h at 80°C water bath to form wet gelatin and then drying at 130°C in oven for 8 h. The dry gel was then heated to ignite auto-combustion. Finally, the combustion ash was calcined at 500°C for 2 h to form PbO nanostructure.

Synthesis of $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound

The appropriate proportion of lead nitrate, nickel nitrate and deionized water were dissolved in a 100 ml beaker to obtain 25 ml aqueous solution with 1 M metal ion in it. The MRCL was taken as 1.5. The aqueous solution was then stirred for 0.5 h in order to mix the solution uniformly. The ammonia solution (25% aqueous solution) was being dropped gradually into the aqueous solution during stirring until transparent colloidal suspension was obtained. The transparent sol was transformed into dry gel through two steps: evaporating for 20 h at 80°C water bath to form wet gelatin and then drying at 130°C in oven for 8 h. The dry gel was then heated to ignite auto-combustion. Finally, the combustion ash was calcined at 500°C for 2 h to form PbO nanostructure. The flow chart for the synthesis of PbO and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound powders is shown in Figure 1.

RESULTS AND DISCUSSION

Gel formation

Conditions of formation of gels strongly depended on the nature of the organic acid employed. With citric acid added, white precipitate immediately appeared that it is lead acetate. Formation of the gel takes place by solvent evaporation during heating. Building of a 3-D interconnected molecular edifice may occur when lead-chelated molecules are close enough to make hydrogen bonds after reducing the solution volume. The hydrogen bonds very often take place in aqueous media, and more especially with organic acids (Dupont et al., 2003). Such hydrogen bond bridging molecules can therefore explain the high viscosity.

FT-IR studies

Figure 2 shows the FT-IR spectra of PbO nanostructure after calcination at 500°C for 2 h with MRCL=1.5. In the FT-IR spectrum of the PbO nanostructure, a peak appears at ca. 600 cm^{-1}, which is assigned to the Pb-O bond. As can be seen, there are not any residual organic matters in the sample. This indicated that the calcination temperature was suitable to form PbO nanostructure.

XRD, EDAX and SEM studies

Figure 3 shows the XRD pattern of the obtained PbO

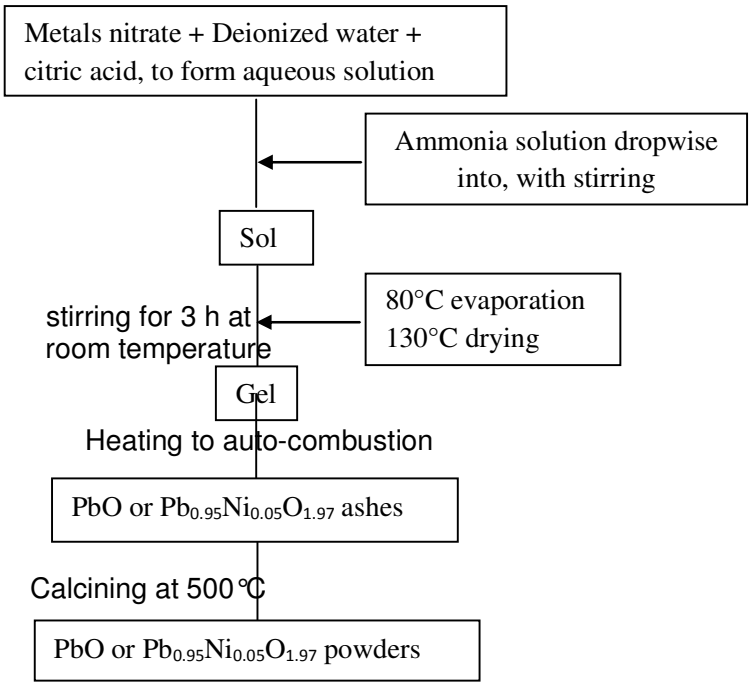

Figure 1. Flow chart for preparation of PbO or $Pb_{0.95}Ni_{0.05}O_{1.97}$ powders.

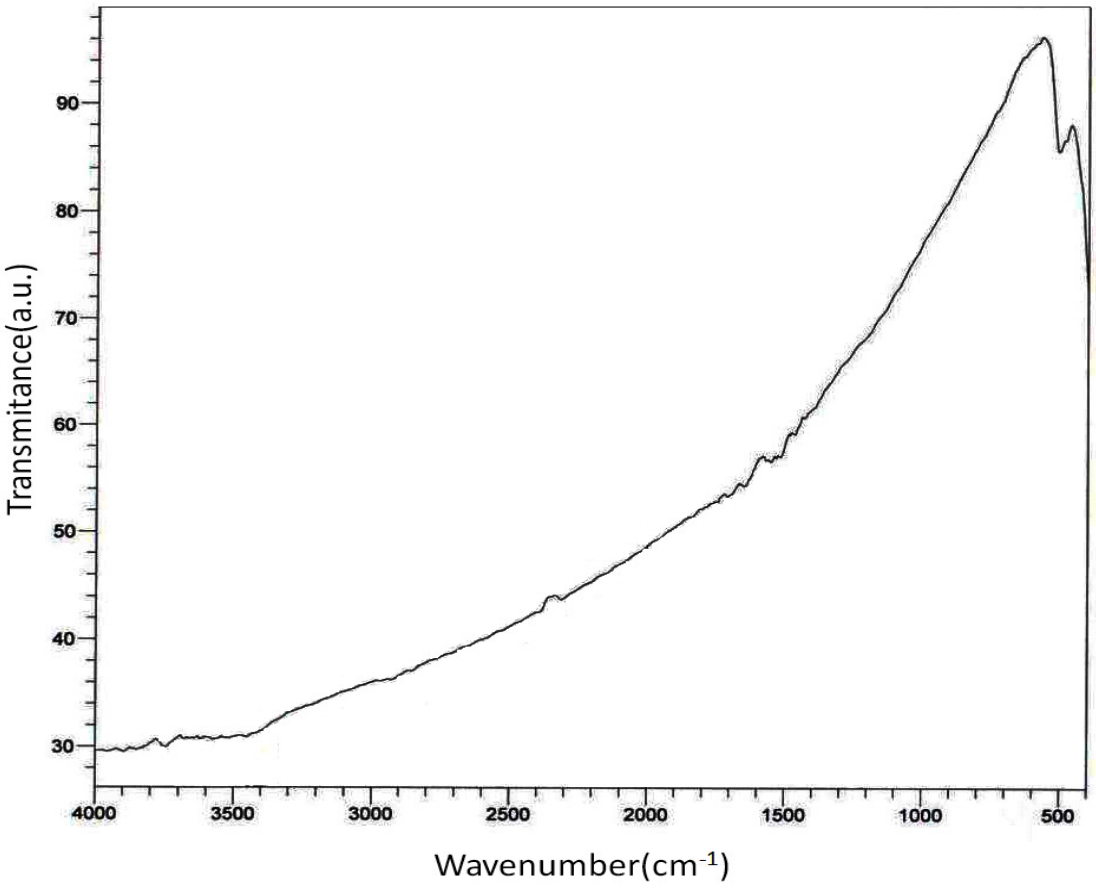

Figure 2. FT-IR spectra of PbO nanostructure after calcination at 500℃ for 2 h with MRCL=1.5.

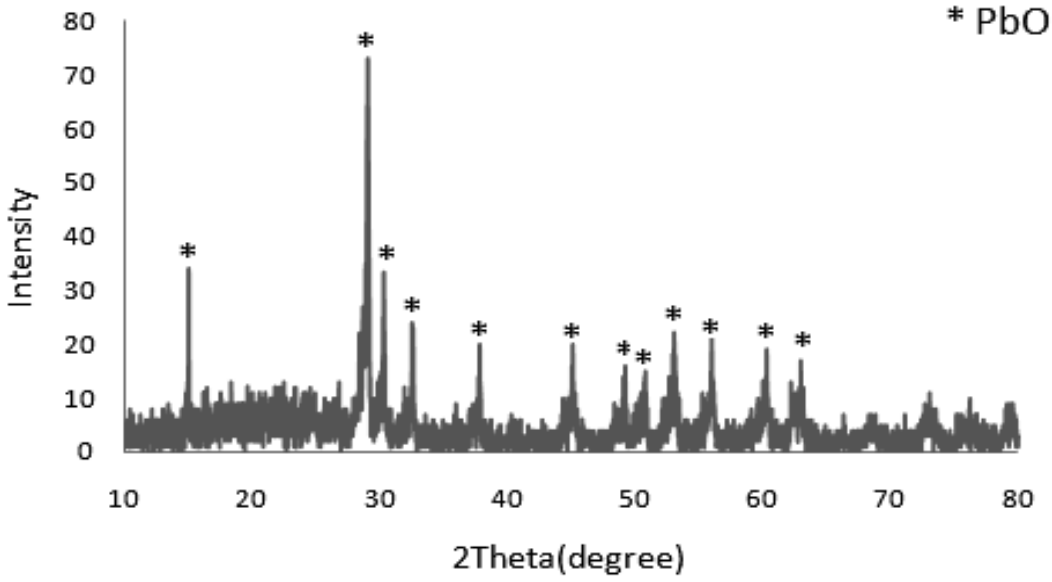

Figure 3. XRD pattern of PbO nanostructure after calcination at 500°C for 2 h with MRCL=1.5.

nanostructure when MRCL is 1.5.

Diffraction peaks can be perfectly indexed to PbO according to the peak position (JCPDS 38-1477), and no impurity peak was observed. This indicated that the obtained product was pure PbO. Organic acid employed for the gelification process has no effect on the obtained lead oxide structure. Very sharp and strong peaks indicate a very good crystallization of the product. Crystallite size was calculated by the Sherrer's method for sample heat treated at 500°C (t = 59 nm). Figure 4 shows the XRD patterns of the obtained PbO nanostructure and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound. No characteristic peaks of impurities, such as nickel oxide or other lead oxides were observed, indicating the high purity of the products. The absence of any peak from nickel oxide confirms that Ni acts as a substitutional dopant. With comparing patterns, it can be seen that the 2θ values of the $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound shift slightly towards higher angles. It is because that the ionic radius of Pb^{2+} is larger than that of Ni^{2+}, the substitution of Pb^{2+} with Ni^{2+} caused the decrease of the lattice constant, which testifies that nickel is well into the crystal lattice of lead oxide (Guan et al., 2008). It is interesting to note that the crystallite size decreases strongly from 59 to 41 nm, when the nickel ions are inserted into the PbO structure, due to the different sizes of the ionic radii and valences among the Ni and Pb ions.

EDAX spectra of $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound are shown in Figure 5. It is found from the figure that content of Pb and Ni is about 95 and 5%, respectively, which is shown that Ni doped into PbO and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound is formed. Figures 6a and b shows the morphology of pure PbO nanostructure and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound respectively. The figures reveal that the pure PbO

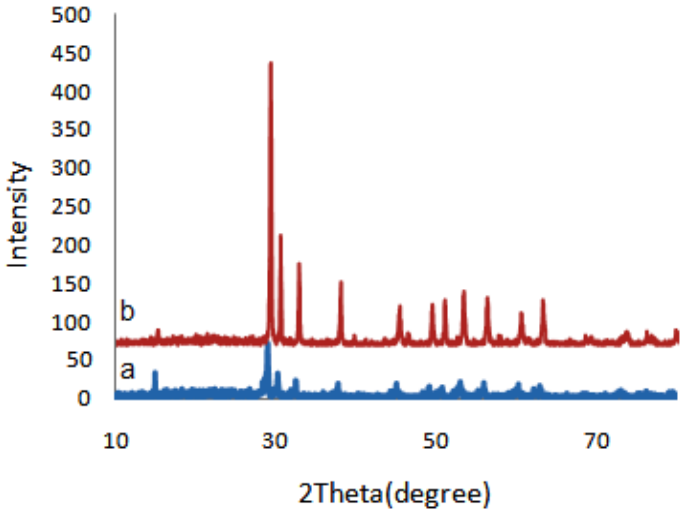

Figure 4. XRD patterns of (a) PbO nanostructure (b) Pb0.95Ni0.05O1.97 compound after calcination at 500°C for 2 h with MRCL=1.5.

consists of large aggregates which are transformed to more fine aggregates with doping the Ni ions into the PbO nanostructure. SEM investigations of samples reveal the crystallites nature of nanoparticles.

Conclusion

In summary, we have demonstrated the synthesis of PbO nanostructure or $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound via combustion of citrate/nitrate gel. This method is simple, inexpensive and economical. The prepared PbO consists

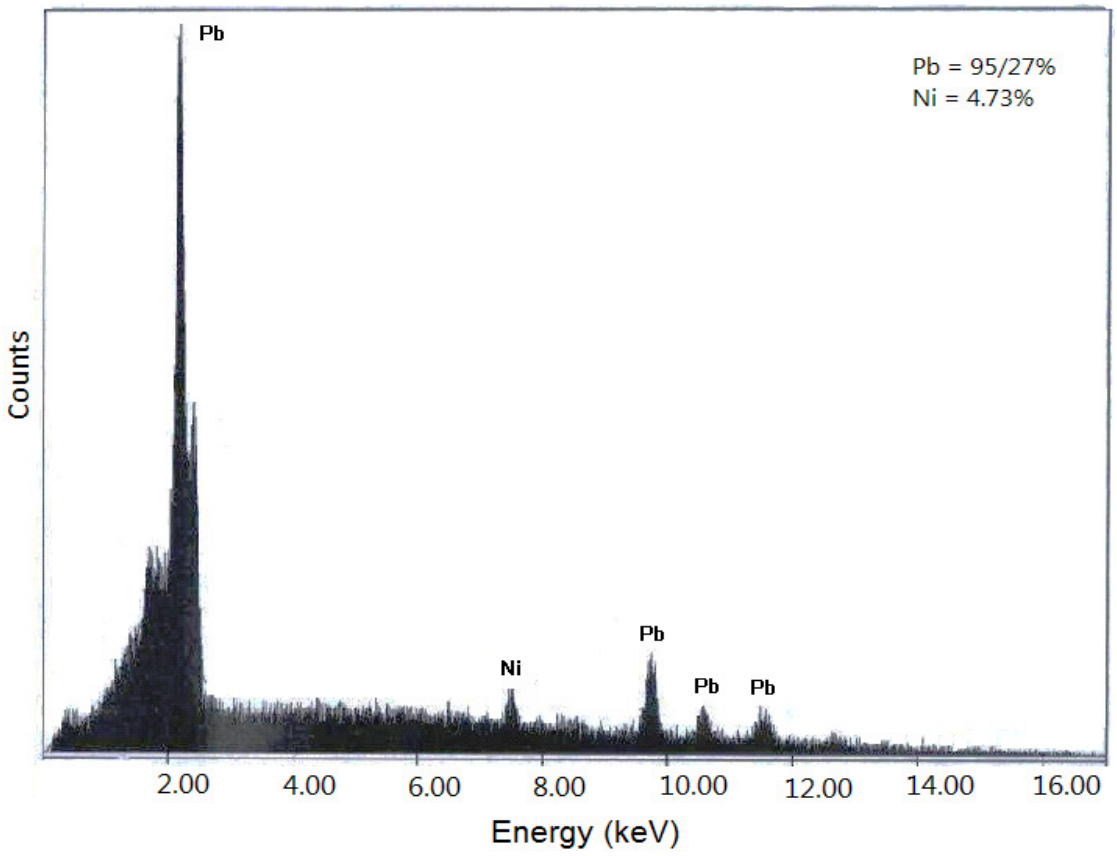

Figure 5. EDAX spectra of $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound.

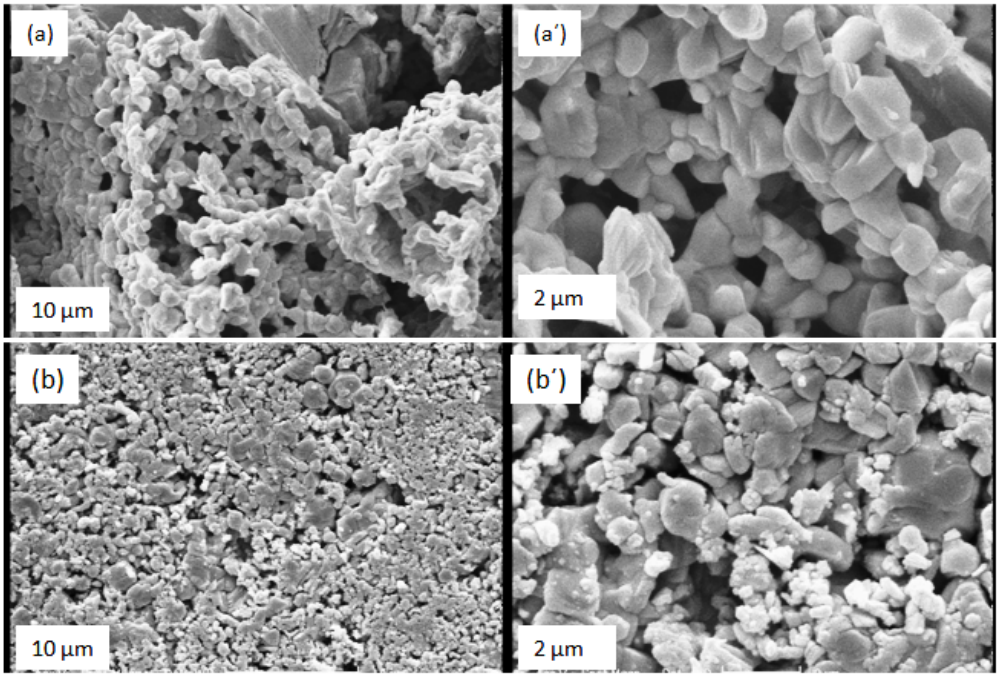

Figure 6. SEM images of (a) PbO nanostructure (a: 10 µm and a´: 2 µm scale bar) (b) $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound. (b: 10 µm and b´: 2 µm scale bar). With calcination temperature 500°C for 2 h and MRCL = 1.5.

of the crystallites about 59 nm. The experimental results (EDAX and XRD) showed that Ni^{2+} were doped into structure of PbO and $Pb_{0.95}Ni_{0.05}O_{1.97}$ compound successfully was synthesized. Crystallite size was decreased strongly from 59 to 41 nm, when the nickel ions are inserted into the PbO structure.

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