

Morphological and Electrochemical Properties of Crystalline Praseodymium Oxide Nanorods

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Received: 24 August 2009 / Accepted: 17 January 2010 / Published online: 5 February 2010
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Abstract Highly crystalline Pr_6O_{11} nanorods were prepared by a simple precipitation method of triethylamine complex at 500°C . Synthesized Pr_6O_{11} nanorods were uniformly grown with the diameter of 12–15 nm and the length of 100–150 nm without any impurities of unstable PrO_2 phase. The Pr_6O_{11} nanorod electrodes attained a high electrical conductivity of 0.954 Scm^{-1} with low activation energy of 0.594 eV at 850°C . The electrochemical impedance study showed that the resistance of electrode was significantly decreased at high temperature, which resulted from its high conductivity and low activation energy. The reduced impedance and high electrical conductivity of Pr_6O_{11} nanorod electrodes are attributed to the reduction of grain boundaries and high space charge width.

Keywords Praseodymium oxide · Nanorods · Impedance spectroscopy · Electrochemical property

Introduction

The crystalline praseodymium oxide (PrOx) is a promising material for many potential applications in nanodevices and microelectronics devices due to its high-K dielectric with an effective dielectric constant of around 30 and very low leakage currents [1]. Praseodymium oxides have been used as high electrical conductive materials [2], a semiconducting oxide for dielectric materials [3], sensing materials for

detection of ethanol vapor [4], organic light-emitting diode [5], oxygen-storage components of three-way automotive catalysts [6] and non-volatile ferroelectric random access memory (Nv-FRAM) devices [7]. Among PrOx such as PrO_2 , Pr_2O_3 and Pr_6O_{11} , Pr_6O_{11} shows exceptionally high electrical conductivity due to electron hopping between the mixed metal ion valence states of the lattice [8].

It was reported that Pr_6O_{11} nanotubes and nanorods were synthesized by a molten salt method [9] and a hydrothermal method [10], respectively. The morphological properties of Pr_6O_{11} nanomaterials were reported in literature [2, 11]. However, there are few reports on electrochemical properties such as conductivity and impedance of the praseodymium oxide nanomaterials, even though these materials are having advanced morphological and crystalline properties. In this paper, we report the electrochemical properties as well as morphological properties of the synthesized polycrystalline Pr_6O_{11} nanorods by a simple precipitation method.

Experimental

Synthesis of Pr_6O_{11} Nanorods

In a typical synthesis, 2 g of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ powder (purity 99.5%, Sigma–Aldrich chemicals) was dissolved in a mixture of isopropanol and cyclohexane with the ratio of 1:4 and stirred until the solution become transparent. Triethylamine was added in the reaction mixture as complexing agent. The white precipitate was formed after a few minutes. The obtained precipitate was filtered and washed with distilled and deionized water and dried at 80°C in air. The crude synthesized powder was calcined at 500°C for 2 h in an ambient condition to produce Pr_6O_{11} nanorods.

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Characterizations

Electrochemical impedance spectroscopy (EIS) was taken with the thin film electrode of Pr_6O_{11} coated on fluorine-doped tin oxide glass (FTO, Hartford Glass Co., $8 \Omega/\text{sq}$, 80% transmittance). For the preparation of Pr_6O_{11} nanorods films, Pr_6O_{11} nanorods slurry was prepared using aqueous polyethylene glycol (Fluka, MW 20,000) solution under vigorous grinding. Thus, prepared uniform slurry was coated on FTO glass with a thickness of about $10 \mu\text{m}$ and active area of $\sim 0.5 \times 0.5 \text{ cm}^2$ by a doctor blade technique. The film was calcined at 400°C for 1 h. To fabricate an electrochemical cell, a Pt counter electrode glass was placed over the Pr_6O_{11} electrode and the edges of the cell were sealed with 60- μm -thick sealing sheet (SX 1170-60, Solaronix) by pressing the two electrodes together on a double hot-plate at 70°C . Finally, an electrolyte of LiI (0.5 M) and I_2 (0.05 M) in acetonitrile was introduced into the cell through one of two small holes drilled in the counter electrode. EIS measurement of fabricated Pr_6O_{11} electrochemical cells was performed using an AC impedance analyzer (VersaSTAT 4) in the frequency range from 10 to 1 MHz with signal amplitude of 10 mV. Electrical conductivity of Pr_6O_{11} nanorods material was measured in air by four-probe DC method in the temperature range of

$20\text{--}850^\circ\text{C}$. Pr_6O_{11} nanorod powder was pressed into cylindrical pallet and then calcined at $1,000^\circ\text{C}$ for 5 h.

Results and Discussion

Figure 1 shows the low and high magnification field emission scanning electron microscopy (FESEM, Hitachi 4700) images of synthesized Pr_6O_{11} nanorods. The Pr_6O_{11} nanorods were uniform and well grown with 12–15 nm diameter and 100–150 nm length. The energy-dispersive X-ray spectroscopy (EDX) analysis was performed to investigate the compositional analysis of synthesized Pr_6O_{11} nanorods as shown in Fig. 2a. It is observed that the atomic percentage of each element is same as the stoichiometric ratio of Pr_6O_{11} materials (Pr:O = 0.545:1). The variation in stoichiometric ratio is within the 2% accuracy limit of error. Therefore, the synthesized Pr_6O_{11} nanorods contain only Pr and O elements without other impurity elements as confirmed by XRD result (Fig. 2b). All of the peaks of XRD pattern are perfectly indexed as pure face-centered cubic phase (space group: Fm3 m-225) with calculated lattice constant $a = 5.4678 \text{ \AA}$, which is consistent with the standard diffraction pattern of Pr_6O_{11} (JCPDS 42-1121). The well-defined XRD peak indicates that

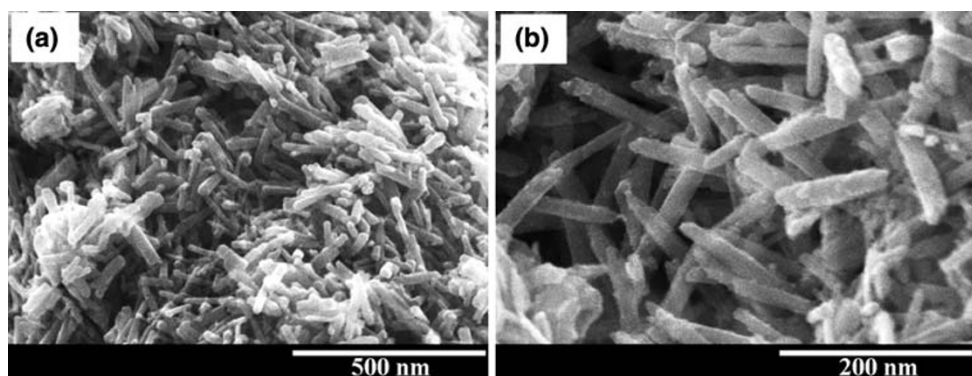
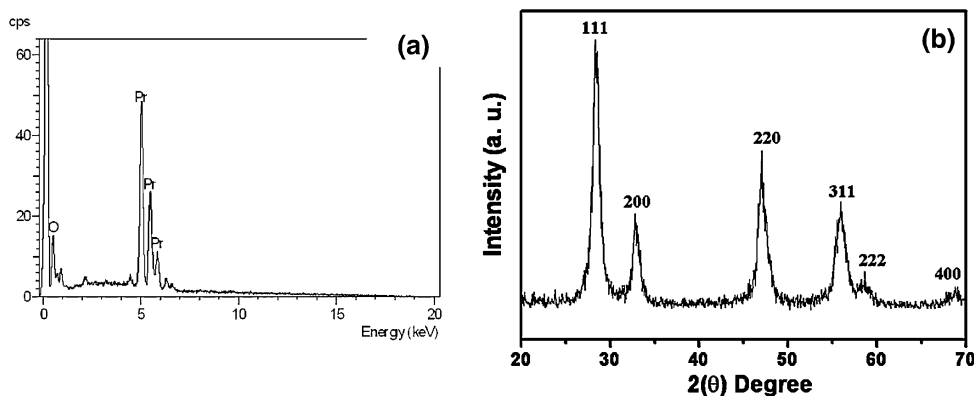


Fig. 1 **a** low and **b** high magnification FESEM images for Pr_6O_{11} nanorods synthesized at 500°C

Fig. 2 **a** EDX spectrum and **b** XRD pattern of Pr_6O_{11} nanorods synthesized at 500°C



Pr_6O_{11} nanorods have good crystalline properties without any impurities.

The morphology of synthesized Pr_6O_{11} nanorods is further examined by transmission electron microscope (TEM, JEOL JEM-2010) and high-resolution TEM (HRTEM) as shown in Fig. 3a and c. The TEM images again affirm that the synthesized Pr_6O_{11} are nanorods morphology with the average diameter of 12–15 nm and length of 100–150 nm. The size of synthesized Pr_6O_{11} nanorods is smaller than that of the reported work [11]. The small size of nanorods may attribute to slow dehydration of $\text{Pr}(\text{OH})_3$ during the preparation. Figure 3b exhibits the selected area diffraction (SAED) patterns of a single Pr_6O_{11} nanorod. The SAED pattern of Pr_6O_{11} indexed as a cubic Pr_6O_{11} single crystal, recorded from the [111] zone axis [11]. Figure 3c shows the corresponding HRTEM image with the interplanar distance $d_{111} = 0.313$ nm and is grown along (111) direction. The orientation of the planes and their calculated interplanar distances are consistent with the Fast Fourier Transform (FFT, Fig. 3d) of HRTEM and XRD analysis.

Two major X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Inc.) peaks of Pr (Pr 3d) and oxygen (O 1s) are measured to explain the surface binding between Pr and O atoms as shown in Fig. 4. Pr 3d exhibits the two peaks at 933.2 eV and 953.6 eV (Fig. 4a), which correspond

to Pr 3d_{3/2} and Pr 3d_{5/2} of Pr_6O_{11} nanorods, respectively. It is demonstrated that the peaks at 930 eV and 945 eV in the Pr 3d XPS of Pr_6O_{11} might ascribe to the existence of Pr^{3+} ions in the products [12]. However, Yan et al. reported that the peaks at 933 eV and 954 eV in Pr 3d attributed to Pr 3d_{3/2} and Pr 3d_{5/2} due to the existence of Pr^{3+} ions in Pr_6O_{11} [11]. Fig. 4b shows the resolved O 1s spectra at 528.1, 530.7 and 532 eV for Pr_6O_{11} nanorods. The lower binding energy (528.1 eV) originated from the oxygen atoms in the lattice [13], and the higher binding energy (531 and 532 eV) can be ascribed to hydroxyl groups on or near the surface of the samples [14]. The relative intensity of lower binding energy (528.1 eV) in O 1s is weaker than those of higher binding energies (531 and 532 eV), indicating the presence of oxygen few deficiency on the surface of Pr_6O_{11} nanorods due to interstitial oxygen chemisorbed on the surface during the synthesis of Pr_6O_{11} nanorods [15]. Atomic ratio of O per Pr on the surface of the praseodymium oxide nanorods is calculated by ~ 1.86 , which is almost consistent with the theoretical value of Pr_6O_{11} (1.83). It is again confirmed that the synthesized praseodymium oxide Pr_6O_{11} is stable when compared to unstable PrO_2 phase, which is in good agreement with XRD results.

Figure 5 shows the conductivity of as grown Pr_6O_{11} nanorods as a function of temperature and the Arrhenius

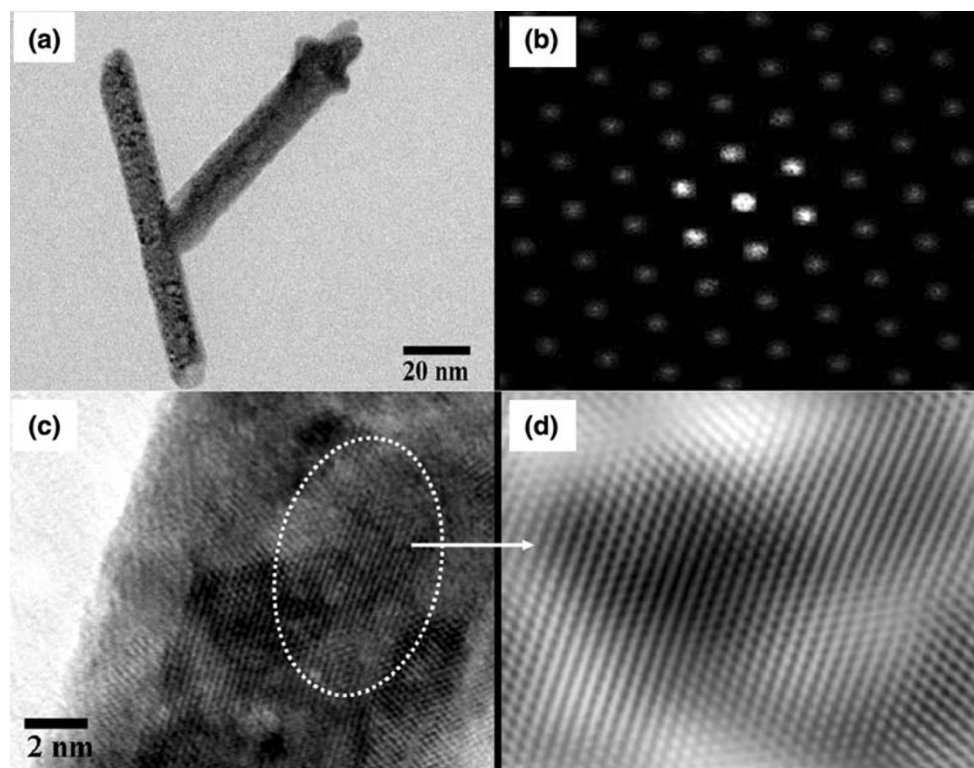


Fig. 3 **a** TEM image of the Pr_6O_{11} nanorods **b** SAED pattern, **c** HRTEM image of individual Pr_6O_{11} nanorods and **d** Fast Fourier transform (FFT) of HRTEM

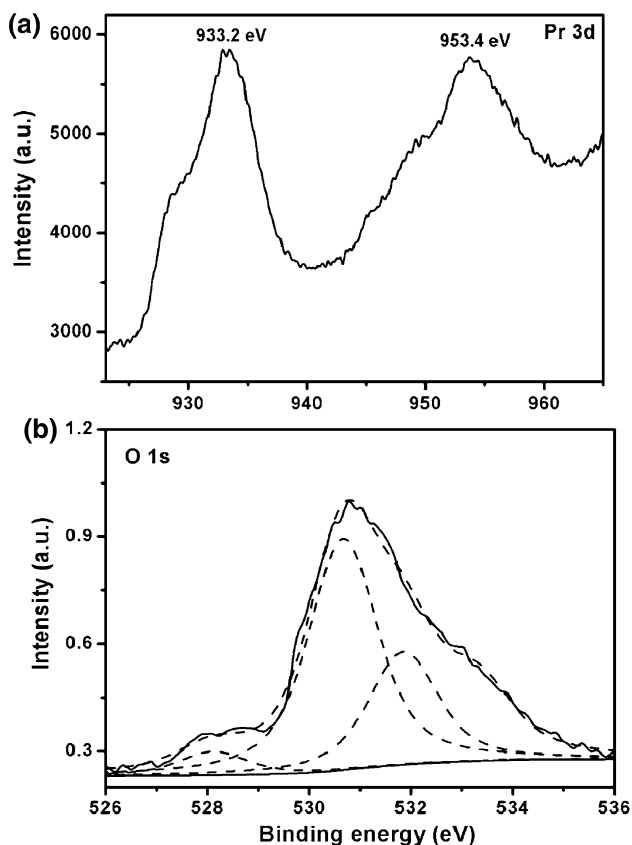


Fig. 4 XPS spectra of **a** Pr 3d and **b** O 1s of synthesized Pr_6O_{11}

plot of $\ln\sigma T$ vs. $1/T$ is depicted in inset of Fig. 5, where σ is conductivity (Scm^{-1}) and T is absolute temperature. The electrical conductivity linearly increases as increasing temperatures from 200° to 850°C. The temperature

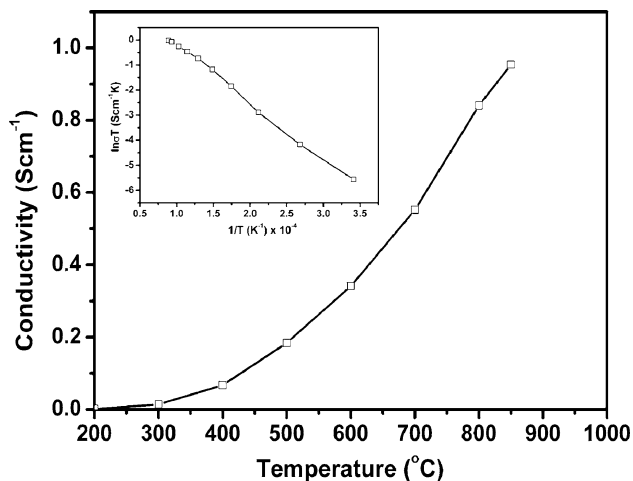


Fig. 5 The conductivity of synthesized Pr_6O_{11} nanorod as a function of temperature. Inset shows the Arrhenius plot of DC conductivity ($\ln\sigma T$) vs $1/T$ for as prepared Pr_6O_{11} nanorods. The accuracy of obtained conductivities with the larger temperature variation (200–850°C) is to be accurate about $\pm 1\%$ error by measurement system

dependence of the electrical conductivity of Pr_6O_{11} nanorods indicates a typical semiconductor material behavior. The electrical conductivity (σ) of material seems to be governed by small polaron hopping mechanism as following equation:

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

Where σ_0 = pre-exponential factor, E_a = activation energy for hopping conduction, k = Boltzmann's constant, T = absolute temperature. The maximum conductivity of as synthesized Pr_6O_{11} nanorods is 0.954 Scm^{-1} at 850°C, which is much higher than those of reported bulk materials $\text{Pr}_{0.97}\text{Sr}_{0.07}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$ (0.1 Scm^{-1} at 850°C) [16]. The activation energy (E_a) of electrical conductivity of Pr_6O_{11} nanorods is calculated to be 0.504 eV from the Arrhenius plot as shown in the inset of Fig. 5. Interestingly, Pr_6O_{11} nanorod electrode shows the lower E_a (0.504 eV) when compared to the $\text{Pr}_{0.97}\text{Sr}_{0.07}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$ bulk materials ($E_a = 0.88 \text{ eV}$) [16]. It is suggested that synthesized Pr_6O_{11} nanorods constituted the high electronic carriers on the surface of grains upon the removal of chemisorbed oxygen with the increase of temperature, resulting in the high electrical conductivity with low enthalpy [17]. Moreover, the low activation energy of metal oxide supplied the favorable route for charge carrier conduction at high temperature, which leads to the high electronic conductivity [18]. This enhanced electrical conductivity with low activation energy delivers the improved electrochemical properties and high space charge carriers.

To elucidate the charge transport and space charge carrier mobility properties of Pr_6O_{11} nanorod materials, EIS measurements were carried out by applying a 10 mV alternative current (AC) signal over the frequency range of 10–1 MHz. Fig. 6 shows the AC impedance curve of fabricated electrochemical cells by Pr_6O_{11} nanorods in the temperature range of 25–80°C. By the EIS study, it can be demonstrated the charge-transfer across the electrode–electrolyte interface, the order of space charge width in the solid oxide matrix and impedance growth at the surface [19]. As shown in inset of Fig. 6, equivalent circuit can be proposed by consisting of the resistance of electrolyte solution (R_s), the charge transfer resistance at the interface of electrolyte and Pr_6O_{11} nanorods (R_{ct}), the charge transfer resistance at the interface of Pr_6O_{11} nanorods and FTO ($R_{P/TCO}$), the capacitance of electron accumulation layer in Pr_6O_{11} (C_{acc}) and space charge capacitance (C_{SC}) [20]. The value of real impedance (Z_{re}) at high and low frequencies represents the $R_{P/TCO}$ and R_{ct} . The value of R_{ct} at 25°C is estimated approximately $\sim 7285.5 \Omega$ in Pr_6O_{11} nanorods electrodes, which is lower than that of reported value in the order of $10^4 \Omega$ [2]. While the value of R_{ct} at 80°C decreases to $\sim 4816.2 \Omega$. The impedance results indicate that Pr_6O_{11} nanorods exhibit the superior electrical

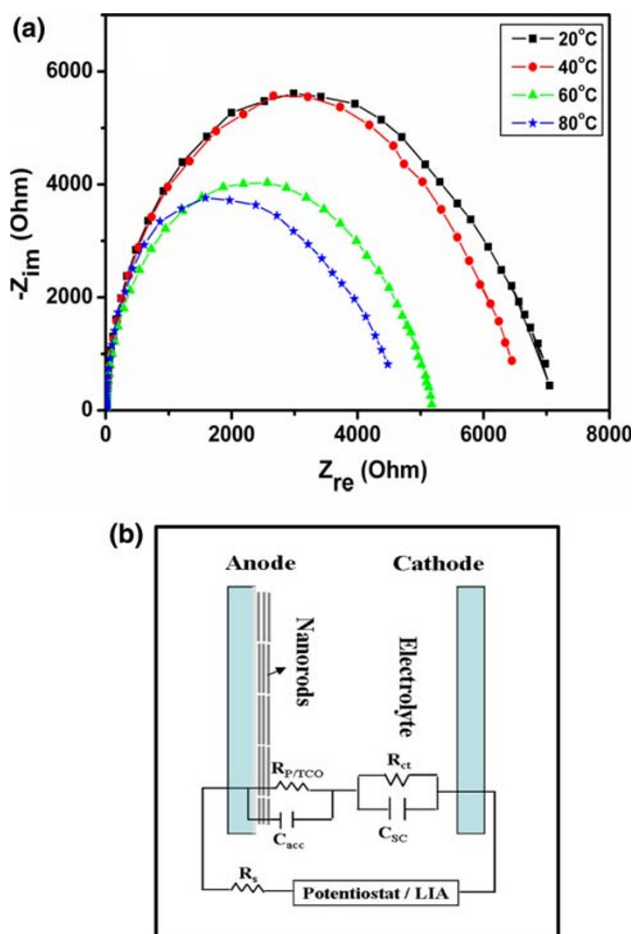


Fig. 6 **a** Impedance spectra (Z_{im} vs. Z_{re}) of synthesized Pr_6O_{11} nanorod as a function of temperature in frequency range of 10–1 MHz and **b** the equivalent circuit of fabricated cells. The accuracy of impedance measurement is probably with the error limit of $\pm 3\%$ by AC impedance analyzer (VersaSTAT 4)

conductivity and high magnitude of space charge width in the nanometric range. The superior electrical conductivity and enlargement of space charge width may attribute to the reduction of grain boundary of synthesized Pr_6O_{11} nanorods [2]. It is known that a small R_{ct} suggests the fast electron transfer in between the electrode to electrolyte interfaces, while a large R_{ct} indicates slow electron transfer in between the electrode to electrolyte interfaces [20]. The impedance (Z) values were dramatically decreased as increasing the temperature in the range of 25°–80°C (Fig. 6). In general, AC impedance of bulk material cells related to their grain size, grain boundaries and electrolyte–electrode interface, which are responsible for high ionic conduction. The decreased resistance at high temperature is due to the reduction of grain boundaries and enlargement of grain sizes, which improves the ionic interaction at electrolyte–electrode interface, resulting in the low R_{ct} . Therefore, the low R_{ct} value of synthesized Pr_6O_{11} nanorods is ascribed to the high charge transfer properties

within the electrode to electrolyte interface and the reduction in grain boundaries.

Conclusions

Highly crystalline Pr_6O_{11} nanorods were successfully synthesized by a simple precipitation method. The morphological and crystalline analysis showed that as synthesized Pr_6O_{11} nanorods possess a polycrystalline cubic phase grown in (111) direction with the diameter of 10–15 nm and the length of 100–150 nm. The synthesized Pr_6O_{11} nanorod electrode exhibited the high electrical conductivity with low activation energy and the reduced impedance at high temperature. It is attributed to the reduction of grain boundaries and enlargement of grain size, resulting in the enhanced ionic interaction at electrolyte–electrode interface and low R_{ct} . The synthesized Pr_6O_{11} nanorod electrodes would be promising materials for various electrical and sensing devices.

Acknowledgments This research is supported by the National Research Foundation (NRF) of Korea through the grant No. R01-2007-000-20810-0 and the Brain Korea 21(BK21) program of the “Center for Future Energy Materials and Devices” in Chonbuk National University. We also wish to thank Korea Basic Science Institute (KBSI) Jeonju branch, and Mr. Jong-Gyun Kang, Centre for University Research Facility (CURF) for performing SEM and TEM images, respectively.

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