



Physicochemical properties of praseodymium hydroxide and oxide nanorods



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ABSTRACT

We synthesized hexagonal phase Pr(OH)₃ nanorods by a hydrothermal method and obtained cubic phase Pr₆O₁₁ by post-thermal annealing at above 550 °C. Pr(OH)₃ nanorod growth was found to occur in the [001] direction. Upon thermal annealing, the oxidation state of Pr(III) was changed to Pr(III, IV). The physicochemical properties were fully examined by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) crystallography, UV–Visible–NIR absorption, differential scanning calorimetry/thermogravimetric analysis (DSC/TGA), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction (TPR) and CO oxidation activity tests.

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1. Introduction

Praseodymium (Pr) oxides have been investigated for their potential usefulness as high-*k* gate dielectric material in Si electronics [1,2]. Pulsed laser deposition has been employed to deposit high-*k* Pr oxide films on Si substrate using Pr₆O₁₁ as a target [2]. Pan and Liao prepared a high-*k* Pr₂O₃ sensing membrane on Si deposited by the rf sputtering method and demonstrated that it had sensing properties such as pH sensitivity [3]. Pr₆O₁₁ is commonly obtained by thermal annealing of Pr(OH)₃ [4–14] or thermal decomposition of Pr complexes [15]. Under alkaline conditions, Pr³⁺ is known to react with OH[−] to form Pr(OH)₃ nanostructures [4–14]. However, various synthetic methods have been employed under different reaction conditions, including precipitation, hydrothermal, solvothermal, microwave-assisted, electrodeposition, and molten-salt methods [4–14]. Nanorods of Pr(OH)₃ have commonly been obtained in basic (e.g., NaOH, KOH and NH₄OH) water (or ethanol) solution by precipitation, hydrothermal, solvothermal and microwave-assisted methods [4–12]. Wang et al. reported that Pr₆O₁₁ single-crystal nanotubes were obtained by a molten salt method using NaCl or KCl [13]. An electrodeposition method was employed by Zhai et al. to synthesize porous Pr(OH)₃. Additionally, Pr oxides have shown potential applicability as catalysts or support materials [9,11,16–18]. For example, Huang et al. synthesized

Au-modified Pr₆O₁₁ nanorods and demonstrated complete CO oxidation at 140 °C [11], while no CO oxidation activity was observed for bare Pr₆O₁₁ nanorods. Luo et al. prepared Ce_xPr_{1−x}O_{2−δ} mixed oxides and tested their catalytic activities for CO, CH₃OH and CH₄ combustion [18]. Zhai et al. electrochemically synthesized porous Pr(OH)₃ nanobelt arrays, nanowire arrays, nanowire bundles and nanowires and found that the nanostructures efficiently removed dyes with −NH₂ groups such as Congo red [9].

In the present study, we synthesized Pr(OH)₃ and Pr oxide nanorods and fully characterized them by various experimental techniques. Although some studies have already reported the fundamental properties of Pr(OH)₃ and Pr oxide nanorods [4–14], in the present study, we provide deeper insight into UV–Visible–NIR absorption, XPS, TPR and CO oxidation activity, which help provide a deeper understanding of high-*k* dielectric materials.

2. Experimental section

The synthesis of Pr(OH)₃ nanorods is briefly described below. We first mixed 10 mL of 0.1 M Pr(III) nitrate pentahydrate (Sigma–Aldrich, 99.9%) and 15 mL of deionized water (18.2 MΩ cm resistivity) in a Teflon jar (120 mL), then added 0.5–2.0 mL of ammonia solution drop-wise to obtain white precipitates. The jar was subsequently tightly capped and placed in an oven (120 °C) for 12 h, after which the final precipitates were fully washed with Millipore water followed by ethanol and then dried in an oven (90 °C) for 24 h. Next, the surface morphology of the samples was observed by scanning electron microscopy (SEM). Additionally, high resolution transmission electron microscopy (HRTEM) was performed using a Tecnai G2 F20 S-TWIN TEM at an acceleration voltage of 200 kV. Diffuse reflectance spectra were recorded using a Cary 5000 UV–Visible–NIR absorption spectrophotometer. The X-ray diffraction (XRD) pattern samples were obtained using a

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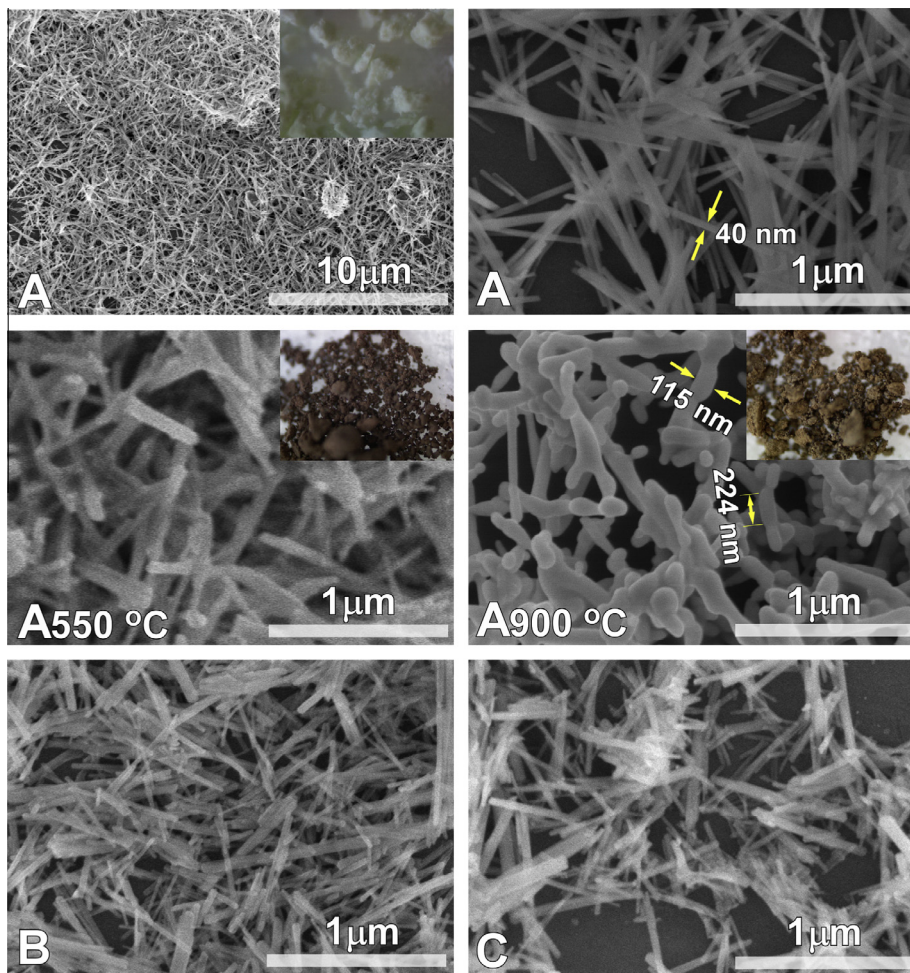


Fig. 1. SEM images of as-prepared (top two), 550 °C (middle left) and 900 °C (middle right)-annealed A samples prepared with 1.0 mL of ammonia. SEM images of B and C samples prepared with 0.5 and 2.0 mL of ammonia, respectively. Insets present optical microscopy images showing colors of the corresponding samples.

PANalytical X'Pert Pro MPD powder diffractometer with Cu K α radiation. We performed XPS experiments before and after Ar⁺ ion sputtering using a Thermo-VG Scientific MultiLab 2000 equipped with a monochromatic Al K α X-ray source and a hemispherical energy analyzer. Differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) was carried out using a TA Instruments thermal analyzer at a temperature ramp rate of 10 °C/min under N₂. Temperature programmed reduction (TPR) experiments were conducted using a Quantachrome ChemBET TPR/TPD apparatus under 5% H₂/He gas at a temperature heating rate of 10 °C/min. CO oxidation experiments were performed under the flow of mixed CO (1%) and O₂ (2.5%) in N₂ at a catalyst (10 mg a quartz U-tube) heating rate of 20 °C/min. The reaction products were examined using a SRS RGA200 quadrupole mass spectrometer.

3. Results and discussion

Fig. 1 displays the SEM images of as-prepared and thermal (550 °C and 900 °C) annealed samples. The as-prepared (A–C) samples prepared with different amounts (0.5–2.0 mL) of ammonia solution showed similar rod morphology with widths of ~50 nm and lengths of ~1 μm. The amounts used generated pH values of 10.7–11.0 and did not critically change the morphology. Upon thermal annealing to 550 °C, the rods became somewhat thicker and the color changed from white/green to dark brown (in the inset photos). Upon further annealing to 900 °C, the rods became much thicker, with a width of >100 nm. Additionally, the brown color became lighter, indicating a change in crystallinity. Huang et al. also found that the rod morphology of Pr(OH)₃ was significantly altered to a particle-like morphology upon thermal annealing at 800 °C [11].

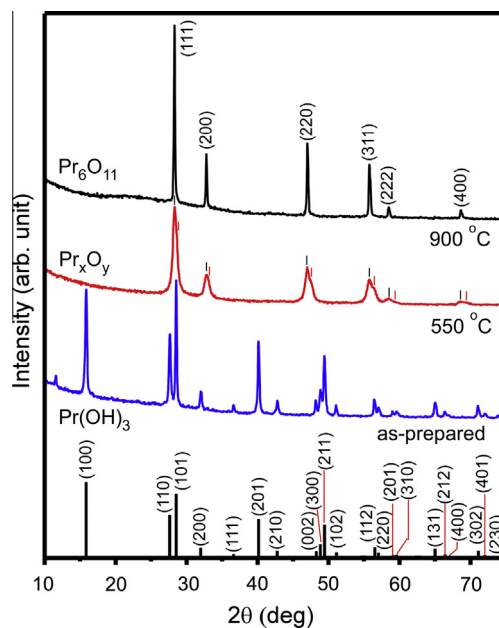


Fig. 2. Powder X-ray diffraction patterns of as-prepared, 550 °C and 900 °C-annealed samples (sample A in Fig. 1). The XRD patterns (JCPDS 01-083-2304) of Pr(OH)₃ are shown for reference.

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