

Facile Solvent-Less Preparation, Characterization and Investigation of Photocatalytic Properties of Pr₆O₁₁ Nanostructures

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Pr₆O₁₁ nanostructures were synthesized through a facile solvent-less method. Nanostructures were prepared by heat treatment in air, using [Pr L(NO₃)₂]NO₃ (L = bis-(salicylaldehyde)-1,4-butadiimine Schiff base ligand), as new precursor, which was obtained by a solvent-free solid–solid reaction from praseodymium nitrate and Schiff base ligand. The as-obtained nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet–visible (UV–vis) spectroscopy. The obtained results demonstrated that utilizing of this precursor is suitable choice for preparation of Pr₆O₁₁ nanostructures with very uniform sphere-like morphology. The photocatalyst activity of as-obtained Pr₆O₁₁ was also examined by degradation of 2-naphthol as organic contaminant under ultraviolet light irradiation.

Keywords: Pr₆O₁₁, Nanostructures, Photocatalytic properties, Optical properties.

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1. INTRODUCTION

The preparation and characterization of nanomaterials have attracted world-wide attention due to the interesting properties and potential applications [1–4]. Among these nanomaterials, Pr₆O₁₁ as a momentous rare earth metal oxide extensively investigated for its utilizations in catalysts, ceramic pigments, materials with higher electrical conductivity and other applications [5,6]. So far, electrospinning, electrochemical, hydrothermal, thermal treatment and precipitation methods [7–11] have been employed to synthesize Pr₆O₁₁ nanostructures. The thermal treatment route is well known as convenient and practical technique for synthesis of various nanomaterials. In this research, we report preparation of Pr₆O₁₁ nanostructures by a facile thermal treatment route by employing of [Pr L(NO₃)₂]NO₃ (L = bis-(salicylaldehyde)-1,4-butadiimine Schiff base ligand), as new precursor, which was obtained by a solvent-free solid–solid reaction from praseodymium nitrate and Schiff base ligand. The as-prepared nanostructures were characterized by (SEM), (UV–vis) spectroscopy, (FT-IR) and (XRD) techniques. The photocatalyst activity of as-obtained Pr₆O₁₁ was also examined by degradation of 2-naphthol as organic contaminant under ultraviolet light irradiation.

2. MATERIALS AND METHOD

All the chemical reagents employed in our investigation were of analytical grade and were utilized without further purification. Fourier transform infrared spectra were recorded employing KBr pellets on an FT-IR spectrometer (Magna-IR, 550 Nicolet) in the 400–4000 cm⁻¹ range. A Hitachi s4160 Japan scanning electron microscope (SEM) was employed to visualize microscopic morphology of Pr₆O₁₁. X-ray diffraction (XRD) patterns were obtained with a Philips diffractometer using X'PertPro and the monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The electronic spectra of the Pr₆O₁₁

were obtained on a Scinco UV–vis scanning spectrometer (Model S-4100). To synthesize Pr₆O₁₁ nanostructures, certain amount of metal complex [PrL(NO₃)₂]NO₃ (L = bis-(salicylaldehyde)-1,4-butadiimine Schiff base ligand) as new precursor, which was obtained by a solvent-free solid–solid reaction from praseodymium nitrate and Schiff base ligand, subjected to heat treatment at in air at 600 °C for 5 h in the air.

The photocatalytic activity of obtained Pr₆O₁₁ nanostructures was examined by monitoring the degradation of 2-naphthol solution as organic contaminant in an aqueous solution. A quartz photocatalytic reactor was employed to carry out the degradation reaction. The photocatalytic degradation was performed by utilizing 0.0012 g of 2-naphthol solution including 0.05 g of Pr₆O₁₁ nanostructures at room temperature. To reach adsorption equilibrium, this mixture was aerated for 30 min. Later, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV source of 400 W mercury lamps. To hinder UV leakage, the light source and quartz vessel were placed inside a black box that equipped with a fan. Aliquots of the mixture were taken at definite interval of times during the irradiation, and after centrifugation they were analyzed by a UV–vis spectrometer. The 2-naphthol degradation percentage was calculated as follow:

$$D.P.(t) = ((A_0 - A_t)/A_0) \times 100 \quad (1)$$

where A_0 and A_t are the absorbance value of solution at 0 and t min, respectively.

3. RESULTS AND DISCUSSION

In the IR spectrum of as-obtained sample, the band at 430 cm⁻¹ is related to the Pr–O vibration which confirms the formation of Pr₆O₁₁. A weak peak at 1635 cm⁻¹ and the relatively strong absorption band at 3442 cm⁻¹ are attributable to the $\nu(\text{OH})$ bending and stretching vibrations, respectively, which demonstrate the presence of physisorbed water molecules linked to Pr₆O₁₁ sample.

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To determine the composition, crystal structure and average crystallite size of the as-synthesized sample, powder X-ray diffraction method was employed. All the diffraction peaks in XRD pattern of the as-prepared Fm $\bar{3}$ m space group (JCPDS 42-1121). No impurities are product (Fig.1) can be readily indexed to pure cubic Pr $_6$ O $_{11}$ with detected from this XRD pattern. Utilizing Sherrer formula [12], the average crystallite size of the as-obtained Pr $_6$ O $_{11}$ from the XRD results was estimated to be about 23 nm.

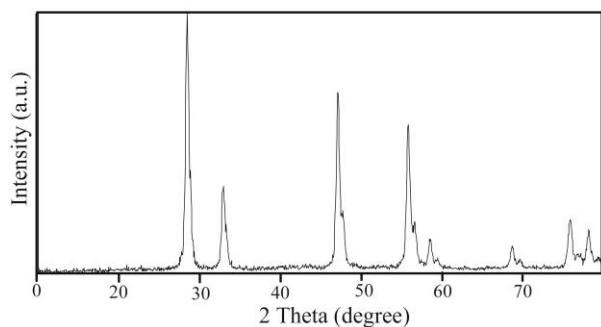


Fig. 1 – XRD pattern of as-obtained Pr $_6$ O $_{11}$ nanostructures.

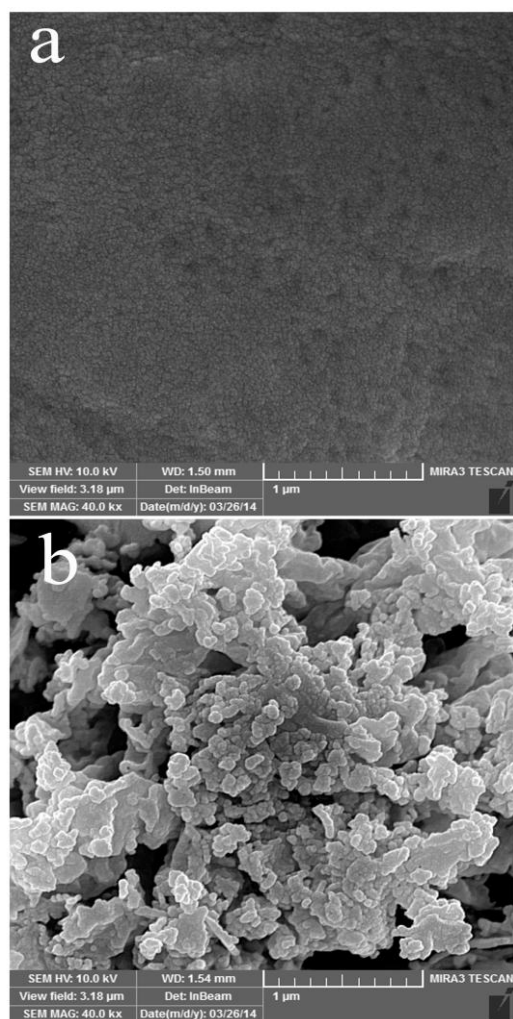


Fig. 2 – SEM images of samples prepared from Pr(III) complex in molar ratios of (a) 1:1 and (b) 1:4, by thermal treatment of precursor.

SEM images of as-prepared Pr $_6$ O $_{11}$ nanostructures are shown in Fig.2a and b. As seen, by increasing the molar ratio from 1:1 to 1:4, agglomerated uniform spherical nanoparticles as well as separated nanoparticles with less uniform spherical morphology were prepared, respectively (Fig. 2a and b). It seems that when (L) content increases, the aggregation between Pr $_6$ O $_{11}$ nanoparticles decreases because of steric hindrance effect of (L).

The optical characteristics of the Pr $_6$ O $_{11}$ nanostructures were examined by UV–vis diffuse reflectance analysis. Fig. 3a shows the UV–vis diffuse reflectance spectrum of the Pr $_6$ O $_{11}$ nanostructures with sphere-like morphology. The nanostructures show the absorption spectrum with an absorption band at 352 nm. Utilizing Tauc's formula, the band gap can be obtained from the absorption data. The energy gap (E_g) of the as-obtained Pr $_6$ O $_{11}$ has been calculated by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis (Fig. 3b). The E_g value of the as-obtained Pr $_6$ O $_{11}$ estimated to be 3.3 eV.

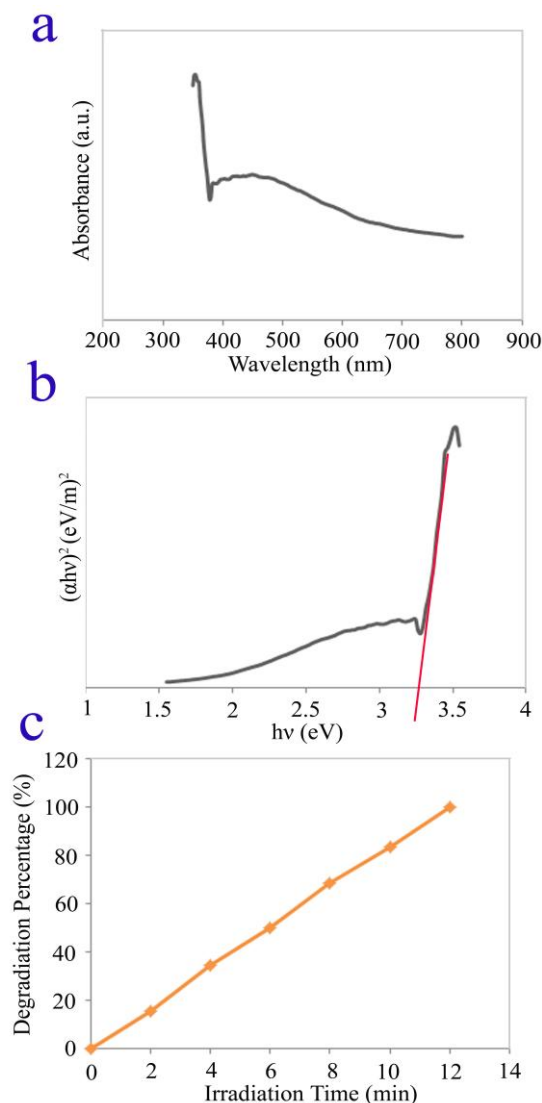


Fig. 3 – UV–vis diffuse reflectance spectrum (a), plot to determine the band gap (b) and Photocatalytic 2-naphthol degradation of under UV light of the Pr $_6$ O $_{11}$ obtained by thermal treatment of Pr(III) complex in molar ratio of 1:1.

The photocatalytic activity of the Pr₆O₁₁ nanostructures with sphere-like morphology was studied by monitoring the by photooxidation of 2-naphthol in an aqueous solution, under irradiation under UV light irradiation (Fig. 3c). No 2-naphthol was practically broken down after 12 min without using UV light irradiation or Pr₆O₁₁ nanostructures. This observation indicated that the contribution of self-degradation was insignificant. According to photocatalytic calculations by Eq. (1), the 2-naphthol photooxidation was about 100% after 12 min irradiation of UV light, and as-obtained nanostructures shown high photocatalytic activity and can be employed as an interesting candidate for photocatalytic applications under UV light.

4. CONCLUSIONS

Shortly, Pr₆O₁₁ nanostructures with very uniform sphere-like morphology were successfully prepared by a

facile and practical thermal treatment process with employing of praseodymium complex [PrL(NO₃)₂]NO₃ (L = bis-(salicylaldehyde)-1,4-butadiimine Schiff base ligand) as new precursor. This study indicated that employing of this new precursor is an effective choice for preparation of Pr₆O₁₁ nanostructures with very uniform sphere-like morphology. High purity of the as-obtained Pr₆O₁₁ nanostructures was confirmed by XRD and FT-IR analyses. The obtained Pr₆O₁₁ nanostructures can be employed as an interesting candidate for photocatalytic applications under UV light such as removal of 2-naphthol, since the degradation percentage of the 2-naphthol was found to be 100 within 12 min.

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