



# Optical and photocatalytic properties of indium phosphide nanoneedles and nanotubes



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## ABSTRACT

Large scale indium phosphide (InP) nanoneedles and nanotubes were synthesized through a facile solvothormal reaction. The morphology and microstructure of the samples were analyzed by employing scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and Ultraviolet-visible (UV–vis) spectroscopy. The room temperature photoluminescence (PL) measurements showed that the InP nanoneedles and nanotubes possessed a pronounced blue shift in contrast to the bulk counterpart, which was ascribed to the crystalline defects effect. Moreover, the InP nanotubes exhibited an enhanced photocatalytic performance as compared to the InP nanoneedles and nanoparticles.

## 1. Introduction

Low dimensional nanostructures attract much attention in the past decades thanks to their novel electrical and optical properties induced by size and/or morphology effect. Therefore, nanostructured materials show a wide range of potential applications in the fields of ion storage, energy conversion, and environment protection [1,2]. Particularly, photocatalysts based on semiconductor nanomaterials show powerful ability in air and water purification with excellent efficiency and durability [3–5]. Different kinds of semiconductor materials, typically including metal oxides, sulfides, (oxy)nitrides, metal-free semiconductors, and their composites have been successfully developed for the photocatalytic degradation of organic pollutants in air or solution [3]. The degradating performance is highly dependent on the intrinsic properties and geometric dimension of the photocatalyst, for example, phase structures, composition, specific surface area, exposed facets, morphology, and so on [3–5]. Although much progress has been made in the degradation of pollutants based on photocatalytic mechanism, there is still an urgent need to develop other novel photocatalysts.

As an important class of compound semiconductors, metal phosphides (MPs) nanostructures have recently been studied as catalysts for hydrodesulfurization and hydrogen evolution reactions [6–8]. Among different MP semiconductors, indium phosphide (InP) materials have been explored in modern electronic devices and high-speed communications due to the advantageous of metalloid characteristics and good electrical conductivity [9]. Nevertheless, the potential photocatalytic applications of InP nanomaterials have not been studied yet, and the

effect of morphology on the optical and photocatalytic properties of InP nanomaterials is still unclear.

Currently, there are several methods have been used to prepare InP nanostructures, i.e., vapor deposition [10] or laser ablation [11] route, and solution phase method. In the former methods, metal organic compounds are used as indium and phosphide sources to grow InP nanostructures. However, these metal organic compounds are toxic and sensitive to ambient environment. In addition, the rigid reaction parameters control and expensive equipment restrict the large scale synthesis and wide applications of InP nanomaterials. In comparison, solution phase reaction represents a facile and green route to prepare InP nanostructures with well controlled geometric parameters and chemical compositions. In previous studies, we have successfully developed a facile solvothormal method to synthesize one-dimensional (1D) InP single crystals. Importantly, the morphology of the products can be controlled as nanoneedles or nanotubes by selecting suitable phosphorus source [12].

In this work, we study the optical and photocatalytic properties of InP nanoneedles and nanotubes in detail. The morphology and microstructure of the samples are studied by microscopy and spectroscopy. The room temperature photoluminescence (PL) results show that InP nanoneedles and nanotubes possess a pronounced blue shift in contrast to the bulk InP due to the intrinsic crystal defects. In addition, the InP nanotubes show an enhanced photocatalytic performance as compared with the InP nanoneedles and nanoparticles.

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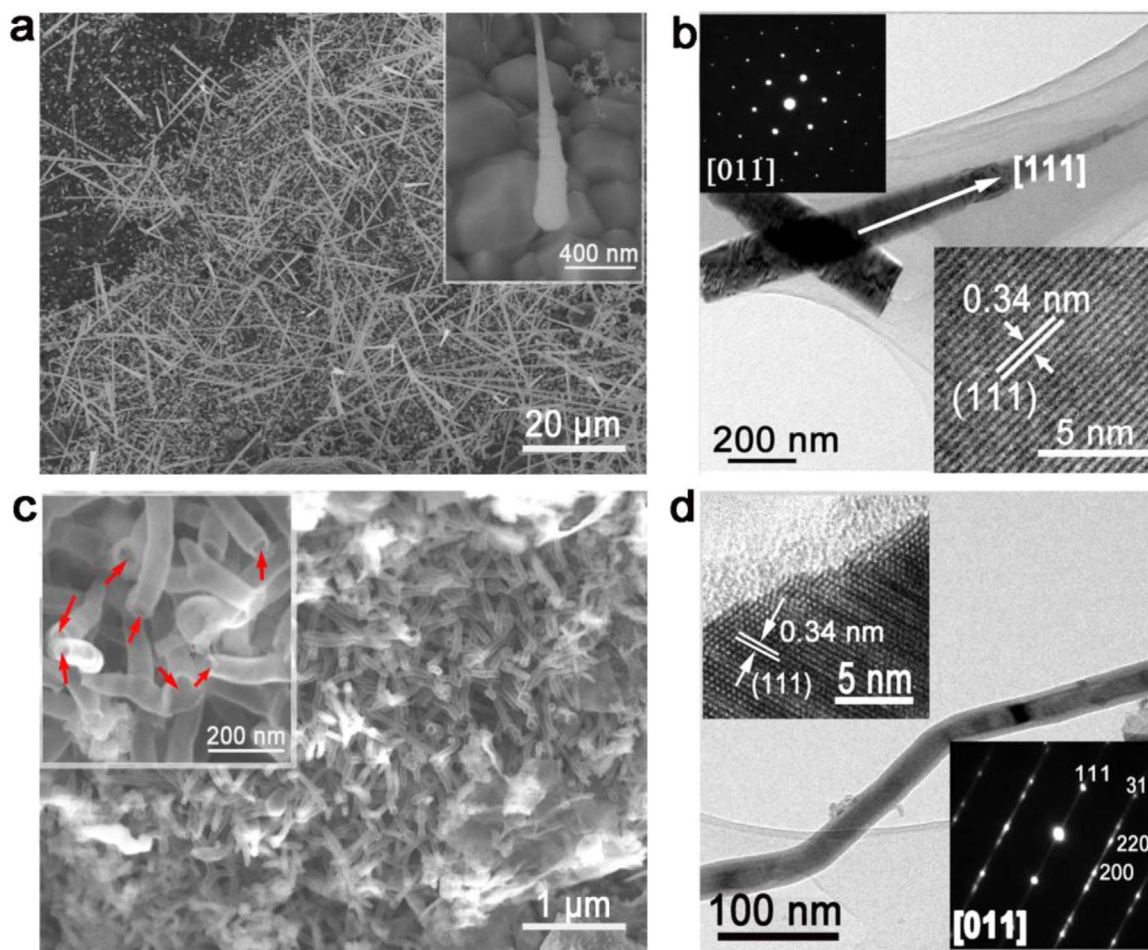


Fig. 1. Typical SEM images of InP (a) nanoneedles and (c) nanotubes. The red arrows in (c) show the open end of the nanotubes. TEM images of (b) nanoneedles and (d) nanotubes. The insets in (b) and (d) are corresponding HRTEM images and SAED patterns, respectively.

## 2. Experimental

InP nanostructures were synthesized by a facile benzene-based solvothermal method as we reported previously [12]. InP nanoneedles and nanotubes were obtained by using white and red phosphorus as the sources, respectively. The samples were then characterized by employing a scanning electron microscope (SEM, JEM-6301F, 5 kV), and a transmission electron microscope (TEM, JEM-2011, 200 kV). The Raman measurements were performed in a back scattering geometry with an excitation wavelength of 514 nm (Renishaw inVia confocal micro-Raman spectrometer). PL spectra were required by using FLS920PL spectrograph with a slit of 5 nm. The Brunauer–Emmett–Teller (BET) surface area was measured by using nitrogen adsorption–desorption isotherms at 77 K (Micromeritics ASAP 2010).

Rhodamine B (RhB) aqueous solution in a Pyrex beaker (250 mL) was used as a probe and a photoreactor vessel to study photocatalytic activity of the samples. Typically, the reaction suspension was prepared by mixing samples (20 mg) and RhB solution (100 mL). The mixture was magnetically stirred in the dark until reaching a complete adsorption–desorption equilibrium. The suspension was then exposed to UV irradiation (Xenon-Lamp-Beijing Trusttech PLS-SXE300, 300 W, 13 cm away from the suspension) under continuous stirring at room temperature. After initiation of the photocatalytic reaction by UV irradiation, a sample of the suspension (5 mL) was taken out at regular intervals and centrifuged to completely remove the catalyst. UV–vis spectra of the centrifuged solution was recorded by using a UV-2550 UV–vis spectrophotometer (Shimadzu, Japan).

## 3. Results and discussion

Typical SEM images show that large scale InP nanoneedles (Fig. 1a and the inset) and nanotubes (Fig. 1c and the inset) were successfully synthesized through a solvothermal method by using white phosphorus and red phosphorus as precursors, respectively. The average size for the tip and root parts of the InP nanoneedles are of ~50 and 150–180 nm, and the mean diameter of the InP nanotubes is ~80 nm. The needle- and tube-like morphologies of the products are also confirmed by the TEM observations (Fig. 1b and d). Moreover, there are several alternating bright/dark contrast fringes in nanoneedles, indicating the existence of planar defect structures as proved in previous works [13–16]. The selected area electron diffraction (SAED) patterns show that the InP nanoneedle is single crystal with a growth direction along [111], while the InP nanotube possesses a twinning structure nature. The clear lattice fringes with spacing of ~0.34 Å shown in HRETEM images correspond to the (111) planes of sphalerite InP phase.

Room temperature Raman spectra of the InP nanoneedles and nanotubes (Fig. 2a) exhibit the characterized bands of InP crystal. Specifically, the Raman bands located at ~300  $\text{cm}^{-1}$  and ~335  $\text{cm}^{-1}$  are ascribed to the transverse optical (TO) and longitudinal optical (LO) modes of InP, respectively. Compared to InP nanoneedles, the Raman bands for InP nanotubes shift to lower frequency direction (red shift). In addition, the bands for both the nanosized samples show red shift when comparing with the bulk counterpart (304  $\text{cm}^{-1}$  and 345  $\text{cm}^{-1}$  [17,18]). It has been demonstrated that quantum and phonon confinement effects [19] and the possible nanocrystal nature [20] can induce red shift in Raman bands. Once the characteristic length of

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