



Red phosphorus: An elemental photocatalyst for hydrogen formation from water

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ABSTRACT

A novel property of red phosphorus for visible light driven photocatalytic H₂ formation from water by photogenerated electrons has been discovered. The detection of hydroxyl radicals and results from photoconductivity measurements confirmed the photogeneration of electrons and holes. Theoretical calculations also indicated that the reduction of water by photogenerated electrons would be energetically possible. A P-type semiconductor behavior of red phosphorus was observed. Our findings may provide insights for developing phosphorus-based photocatalysts.

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1. Introduction

The finding of new properties of materials, especially for elemental materials, has ignited revolutions in science and technology. Over the past decade, new applications have been discovered for silicon and carbon materials in optical, electronical, optoelectronical and photocatalytic research fields [1–4]. Photocatalytic hydrogen production from water is a clean and renewable source of energy [5–9]. In this system, a photocatalyst with a suitable conduction band energy for transferring the photogenerated electrons to water is needed [10]. Moreover, the band gap of a desirable photocatalyst should be around 2.0 eV to utilize solar energy effectively. Because of these stringent requirements, it is difficult to develop new visible-light-driven photocatalysts, especially simple elemental ones. For example, silicon quantum dots have been employed as a photocatalyst for the degradation of methyl red and the oxidation of benzene [11]. However, this element cannot be used alone in water splitting due to its unsuitable bandgap structure [12]. Recently, a complicated system of poly(ethylene glycol) diamine functionalized carbon nanoparticles with gold or platinum coating was found to be somewhat active for hydrogen evolution from water [13]. Much simpler materials must be used for photocatalytic systems to be economically viable. This communication reports for the first time the novel photocatalytic property of elemental red phosphorus.

Red phosphorus is one of the most versatile elements. It is used in organic chemistry and chemical warfare, including igniters, incendiaries, screening smoke ammunition and smoke signal [14–16]. Recently, phosphorus was incorporated into titanium dioxide to improve the solar spectrum response of TiO₂ [17,18]. This band gap narrowing is probably due to the mixing of the P 3p and O 2p states [19]. Pure red phosphorus by itself as a solar-responsive photocatalyst, however, has never been reported. Photocatalytic systems based on elemental substances are obviously a more elegant approach than those involving highly complex materials.

2. Experimental

2.1. Preparation of crystalline red phosphorus

Commercial red phosphorus was dispersed in water and put into a Teflon-lined stainless autoclave. The autoclave was heated to 200 °C and maintained for 12 h to remove surface oxidation. The treated red phosphorus was crystallized in a vacuum tube furnace at 450 °C for 12 h. The crystallized product was washed with water and methanol, and then dried at 60 °C. Different amounts of Pt loaded red phosphorus were prepared by photochemical reduction of H₂PtCl₆ in presence of red phosphorus aqueous suspension.

2.2. Preparation of red phosphorus films

Red phosphorus films were prepared by a vacuum deposition method. 100 mg of red phosphorus powder were put into a quartz glass tube (0.7 cm × 5.0 cm) with a quartz sheet (0.5 cm × 2.0 cm)

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inside. The system was sealed under vacuum. The glass tube was heated to 650 °C at 1 °C min⁻¹ and kept at that temperature for 12 h. The resulting sheets were cut into the size of 0.5 cm × 0.5 cm for photoconductivity measurements and electrical tests. The film thickness was ca. 10 μm as measured by a Techcor Alpha-Step 500 Surface Profiler system.

2.3. Characterizations

Scanning electron microscopy (SEM) imaging was recorded on a FEI Quanta 400 microscope. Standard transmission electron microscopy (TEM) images were recorded using a CM-120 microscope (Philips, 120 kV) coupled with an energy-dispersive X-ray (EDX) spectrometer (Oxford Instrument). The electron microscopy samples were prepared by dispersing the powder in ethanol with ultrasonication for 20 s. XRD patterns were recorded with a Rigaku SmartLab X-ray diffractometer using Cu Kα irradiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and applied current were 40 kV and 40 mA. The BET surface areas were measured by a Micromeritics ASAP 2010 instrument. UV–vis diffuse reflectance spectra were achieved using a UV–vis spectrophotometer (Cary 100 scan spectrophotometers, Varian). The concentration of phosphate ions leaching from the possible dissolution of red phosphorus were measured by Metrohm 792 Basic Ion Chromatography with a column of Grace Allsep Anion 7u (150 mm × 4.6 mm). The eluent was 2.0 mM NaHCO₃ and 0.8 mM Na₂CO₃.

2.4. Gas evolution tests

The photocatalytic H₂ evolution experiments were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. 50 mg of the sample were dispersed in 100 mL of aqueous solution containing 5 vol% methanol as a hole sacrificial agent. The suspension was purged with argon to remove dissolved air before irradiation. The solution was irradiated by a 300 W xenon lamp with an appropriate cut-off filter and a water filter (a 400 nm cut-off filter was used in all tests except the experiment related to Fig. 7b). The amount of hydrogen generated from photocatalytic water splitting was measured by Techcomp GC7900 gas chromatography with TCD detector and a capillary column (molecular sieve 5 Å). High purity nitrogen gas was used as a carrier gas. A control experiment was carried out without the addition of methanol. Amounts of O₂ were measured under the same condition with that of H₂ except high purity helium gas was used as a carrier gas.

2.5. Detection of photogenerated OH radicals

A stock terephthalic acid solution with final concentrations of $4 \times 10^{-4} \text{ M}$ terephthalic acid and $2 \times 10^{-3} \text{ M}$ NaOH was prepared. 30 mg of crystalline P were added to 40 mL of the stock solution. The suspension was irradiated by a 300 W halogen lamp (with a 400 nm filter). At every 30 min, 2 mL of the suspensions were collected and centrifugated. The resulted supernatants were diluted four times for PL measurements. Fluorescence spectra of generated 2-hydroxyterephthalic acid were measured on a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 320 nm.

2.6. Computational details

VASP computational package was used for all the calculations in this article [20–23]. We applied projector-augmented-wave method with Perdew–Burke–Ernzerhof GGA functional [24–26]. Electronic convergence limit was set to be $1 \times 10^{-5} \text{ eV}$. Optimization of atomic coordinates was considered to be converged if

Hellmann–Feynman force was smaller than $1 \times 10^{-2} \text{ eV \AA}^{-1}$. The slab consists of 4-layers of polyphosphide tubes exposing (001) and (00 $\bar{1}$) surface. The 2 polyphosphide tubes layers in the middle were held fixed during optimization. The vacuum region is about 12 Å in height. We applied Monkhorst–Pack scheme $3 \times 3 \times 1$ for *k*-point selection and resulted in 5 irreducible *k*-points.

2.7. Photoconductivity measurements and electrical tests

Two Ag wires were connected to the opposite edges of the film by using Ag conductive epoxy. Photoconductivity measurements were carried out on an electrochemical workstation (CHI 660C, Shanghai Chen Hua Instrument Company, China). Photocurrent–voltage and the photocurrent response to on–off cycles were recorded under the illumination of a fiber optics equipped with a tungsten lamp (Cole-Parmer illuminator, 41720 series). The light intensity was about 200 mW/cm².

Electrical properties of the red phosphorus films were measured by the Van der Pauw 4-probe method (Bio-Rad Hall System) [27]. The mobility was calculated from the sheet resistance and Hall coefficient.

3. Experimental results and discussion

3.1. Sample characterizations

The crystalline red phosphorus was synthesized by heating an amorphous red phosphorus under vacuum at 450 °C (see Section 2) [28]. Fig. 1a and b shows the morphology of crystalline red phosphorus, indicating the product is microparticles with a layer of nanorods on their surface. The selected-area electron diffraction (SAED) pattern reveals the single-crystal nature of nanorods (Fig. 1d). Fig. 1c shows a typical XRD pattern of the product. All the diffraction peaks are readily indexed to the standard monoclinic phase of phosphorus (JCPDS card no. 44-0906). The absorption edge of red phosphorus shifts from 700 nm to 680 nm after crystallization, as shown in Fig. 2. The blue-shift is due to decreased imperfections and disordering of structure [29]. The bandgap of crystalline red phosphorus is estimated to be 1.7 eV.

3.2. Photocatalytic H₂ formation over red phosphorus

Rates for H₂ evolution were measured by irradiating a 100 mL of solution containing 50 mg of products and 5 mL of methanol (as a hole sacrificial agent). H₂ is produced at a rate of 0.08 μmol h⁻¹ for crystalline red phosphorus. An amorphous red phosphorus sample is also tested and found to be only half as effective for hydrogen evolution (Fig. 2). As the BET surface area of the crystalline red phosphorus (ca. 39 m²/g) is larger than that of amorphous one (ca. 18 m²/g), the enhanced photocatalytic activity after crystallization can be explained by the increased surface area and a decrease in the number of electron–hole trapping centers [30,31]. The gas evolution stopped when the light was turned off, suggesting the reaction was initiated by the absorption of visible light. It is noted that a small amount of oxygen was detected on crystalline red phosphorus samples (data not shown), indicating the presence of a trace amount of P₂O₅. P₂O₅ is a white powder and control experiments show no photocatalytic activity over it. Our results clearly indicate that red phosphorus exhibits a photocatalytic property for H₂ formation from water under irradiation.

Different amounts of platinum was loaded onto red phosphorus by photo-reduction of a H₂PtCl₆ solution to investigate their photocatalytic performance. The mean diameter of the loaded Pt NPs is ca. 12 nm and the range is from 5 nm to 20 nm (Fig. S1). The rate constants were calculated from Fig. S2, and are summarized in

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