Materials Research Bulletin 70 (2015) 13–19

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Enhanced visible light photocatalytic property of red phosphorus via surface roughening

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ARTICLE INFO

Article history:
Received 18 June 2014
Received in revised form 4 April 2015
Accepted 6 April 2015
Available online 8 April 2015

Keywords:
Red phosphorus
Surface roughening
Photocatalysis
Visible light
Rhodamine B

ABSTRACT

Red phosphorus with rough surface (SRP) was prepared by catalyst-assisted hydrothermal synthesis using Co^{2+} catalyst. The photocatalytic Rhodamine B (RhB) degradation of red phosphorus (RP) and SRP was studied for the first time in this work. Rough surface can enhance the dye adsorption ability of RP. About 75% RhB was absorbed by SRP after 30-min adsorption in 100 ml RhB solution with concentration of 10 mg l^{-1} in dark. After only 10 min of illumination by visible light, more than 95% RhB was degraded, indicating that SRP has a great application potential in the area of photocatalysis. The photocatalytic RhB degradation properties of RP are much weaker than those of SRP. The increase of the number of the active sites for the photocatalytic reactions, the electron mobility and the lifetime of the photogenerated electrons cause the significant improvement of the photocatalytic performance of SRP based on the experimental results obtained.

1. Introduction

With the depletion of energy sources and aggravation of environmental pollution, the development and utilization of renewable energy sources have become the key strategy of the present era. Within different renewable energy sources, solar energy is considered a ubiquitous clean energy. In recent years, several studies have focused on the efficient conversion of solar energy to electrical energy, chemical energy, and heat energy. To this end, photocatalytic degradation of organic pollutants, [1–3] hydrogen production by photocatalytic splitting of water [4–8], and solar cell [9–11] are considered to be enabling technologies for efficiently conversing and utilization utilizing solar energy. The photocatalytic degradation of organic dye is based on the separation of the photogenerated electrons and holes that undergo redox reactions with organic pollutants. So far, this technology has gone through nearly 40 years of development and has made considerable progress. However, some issues are still existed and they are limiting the extensive application of this technology, such as narrow absorption range of the photocatalysts, low photo quantum yield, high cost of photocatalysts, and the challenges associated with the complete separation of photocatalysts from the solution, etc.

Originally, TiO_2 [12], and ZnO [13–15] were investigated as the photocatalysts for the degradation of organic dyes, due to their advantages, such as high photo quantum yield and economic viability. However, TiO_2 and ZnO are wide band gap semiconductors, and hence their photocatalytic activity is restricted to the ultraviolent region. Simultaneously, photocatalysts that response to visible light were also developed. Among them, WO3 [16], $BiVO_4$ [17], $ZnFe_2O_4$ [18], BiOX (X = Br, I), [19] and g-C_3N_4 [20,21] are considered to be the potential semiconductors. However, their photo quantum yields are relatively low. Recently, it was reported that Ag@AgX (X = Cl, Br, I) [22], which has surface plasmon resonance effect, exhibits novel photocatalytic properties. It possesses light absorption capacity in almost the entire visible light region, and at the same time, exhibits relatively high photo quantum yield. This novel photocatalyst possesses very strong visible light photocatalytic degradation capability of organic pollutants. However, these photocatalysts are very expensive, which limits their further application potential. Meanwhile, after the successful degradation of organic effluents, the photocatalyst needs to be separated and recovered from the solution, the failure

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http://dx.doi.org/10.1016/j.materresbull.2015.04.009
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of which might cause secondary contamination of the solution. Lately, studies have demonstrated that the development of magnetically separable photocatalyst [23], or loading photocatalysts onto some porous ceramic or fiber clothes [24,25] can circumvent this problem.

Single-element silicon sparked a revolution of human information age, and it is also the first generation solar cell material. In recent years, single-element carbon has also emerged with exciting application potentials. In particular, “Football carbon,” carbon nanotubes, and graphene have demonstrated excellent functionalities for application in the areas of electronics, optics, and solar energy utilization [26–29]. Although silicon exhibits photocatalytic properties [30], its application is hindered by its own photocorrosion, as well as its high price. On the other hand, carbon does not possess photocatalytic properties although it is a highly multi-functional material. Therefore, it is of urgent need to develop visible light responsive, cheap, stable, and green single-element photocatalysts.

Red phosphorus (RP) is one of most abundant elements in reserves on the Earth. Recent studies have indicated that RP is non-toxic, cheap, highly stable, and the light absorption region of RP extends to the vicinity of 700 nm [31]. Due to these properties, RP is considered as an ideal candidate in the field of photocatalytic degradation of organic pollutants. In 2012, Wang et al. [31] demonstrated that RP exhibits excellent photocatalytic performance towards hydrogen production by splitting water. Through density functional theory (DFT) calculations, they found that the potentials of the valence and conduction bands met the complete decomposition of water into hydrogen and oxygen. They prepared P/YPO_4 composite using hydrothermal method, and found that it can further enhance the performance of photocatalytic hydrogen production from water splitting [32]. Following that, Yuan et al. [33] prepared $RP/g\text{-}C_3N_4$ heterojunction composite material and demonstrated the significant improvement of the performance of the photocatalytic hydrogen production by splitting water. However, to the best of our knowledge, the application of RP as a photocatalyst for the degradation of organic pollutants has not yet been reported. Although it has application potential in the area of photocatalysis, RP still has some disadvantages, such as big particle sizes, less surface catalytic reaction active sites and low quantum yield, etc., which lead to the existence of a certain gap in the photocatalytic performance of RP and other traditional photocatalysts [31,32,34,35]. Therefore, some modification methods need to be carried out to enhance the photocatalytic performance of RP.

Herein, for the first time, the authors studied the photocatalytic degradation performance of RP using a model organic dye, Rhodamine B (RhB). SRP was prepared by Co^{2+}-assisted hydrothermal synthesis. Furthermore, the influence of surface roughness on the photocatalytic performance of RP under visible light was further analyzed. Results indicate that surface roughness can increase the active reaction sites, and enhance organic dye degradation performance of RP under visible light.

2. Experimental

2.1. Preparation of red phosphorus (RP) and surface roughening red phosphorus (SRP)

The preparation of RP was performed by hydrothermal method, using commercial RP (Aladdin reagent corporation, AR, Purity >98.5%, China, Shanghai) as raw material. To obtained RP, the commercially purchased RP was pretreatment as follows. In a typical process, 3 g of commercially purchased RP was mixed with 60 ml of deionized water. This mixture was then transferred to a hydrothermal autoclave with a polytetrafluoroethylene linear tube with volume of 100 ml. The autoclave was subsequently sealed and hydrothermally reacted at 200 °C for 12 h. After the reaction, the resulting precipitate was filtered and washed repeatedly with deionized water and anhydrous ethanol. Finally, RP was obtained after drying the resulting precipitate at 80 °C for 4 h. Similarly, SRP was prepared by adding trace Co^{2+} catalyst in the hydrothermal reaction. In a typical process, 0.3 g of the prepared RP was added into a hydrothermal reactor, into which a pre-determined amount of $Co(NO_3)_2{\cdot}6H_2O$ and 60 ml of deionized water were added. The Co^{2+} catalyst reaction mixture was well stirred, and then transferred to the hydrothermal autoclave and reacted at 150 °C for 5 h. The resulting precipitate was separated from the solution and washed repeatedly with deionized water and anhydrous ethanol. Finally, SRP was obtained by drying the precipitate at 80 °C for 4 h. The amount of $Co(NO_3)_2{\cdot}6H_2O$ added in the reaction was controlled at 3% atomic ratio of Co to P. All reagents used in this study were analytical ones purchased from Aladdin reagent corporation, China.

2.2. Photoelectrode preparation

A fluorine-doped tin oxide (FTO) glass (13 × 10 mm) was first ultrasonically cleaned with acetone of analytical grade for 5 min, rinsed with deionized water, and then dried with a clean, dry airflow. One longitudinal edge of the conductive side was then carefully covered with insulating tape, with the exposed effective area of the FTO glass measuring 1 cm^2. In total, 10 mg of prepared RP or SRP powder was mixed with 0.1 ml of deionized water in an agate mortar, and the mixture was carefully ground for 10 min to form a homogeneous suspension. Then, 0.025 ml of the as-prepared suspension was evenly distributed onto the exposed area of the conductive side of the FTO glass. The insulating tape on the edge of the FTO glass was removed after the suspension had dried in the air. Finally, the FTO glass deposited with the as-prepared suspension was heated to 120 °C for 2 h under vacuum condition. A copper wire was connected to the conductive side of the FTO glass using conductive silver tape. Uncoated parts of the conductive side of the FTO glass were isolated with parafilm after the conductive silver tape had dried.

2.3. Characterizations of the prepared RP and SRP

The morphologies and the microstructure of the synthetic products were analyzed using a field emission scanning electron microscope (FESEM) (NoVa^{TM} Nano SEM 430, FEI Company, USA) and a transmission electron microscope (TEM, FEI Tecnai G20, FEI Company, USA). The elemental compositions, the crystalline structures and bonding information of the synthetic products were analyzed using an energy dispersive spectrometer (EDS, FEI Tecnai G20, FEI Company, USA), an X-ray diffraction (XRD, D/MAX-2500/PC; Rigaku Co., Tokyo, Japan), and an X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical Ltd., England). The optical absorption properties were investigated using a UV/vis diffuse reflectance spectrophotometer (U-41000; HITACHI, Tokyo, Japan). The luminous intensities of the photoelectrodes prepared by RP and SRP were studied using photoluminescence spectroscopy (PLS) (PL, Fluoro Max-4, HORIBA Jobin Yvon, France). The BET values were tested by surface area analyzer (BET, AutoChem II 2920, USA).

2.4. Photoelectrochemical measurements

Photoelectrochemical measurements were performed in a three-electrode experimental system using CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The prepared series photoelectrodes, saturated