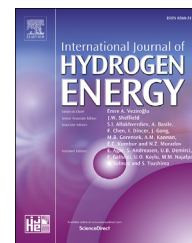




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Precisely locate Pd-Polypyrrole on TiO₂ for enhanced hydrogen production

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ABSTRACT

Noble metal (Pd) and conducting polymer (PPy) are considered as two promising candidates to modify photocatalyst. In this work, TiO₂-Pd-PPy was prepared via one-step simultaneous photoreduction of palladium chloride and photooxidation of pyrrole monomers on TiO₂ (P25). The TiO₂-0.5Pd-0.6PPy exhibits higher H₂ production rate of 601 μmol h⁻¹ under UV–visible light irradiation, which is about 3.1 and 11.7 times than that of TiO₂-0.5Pd and TiO₂, respectively. One-step simultaneous photo-deposited method allows for precisely locating Pd and PPy on TiO₂, in other words, the places where Pd and PPy nanoparticles deposited are just the active sites that the photo-induced electrons and holes participate in the photocatalytic reaction, which is beneficial for separation of photo-induced carriers. As a result, TiO₂-0.5Pd-0.6PPy synthesized by one-step simultaneous photo-deposited method displays much higher H₂ production activity than TiO₂-0.5Pd-0.6PPy synthesized by other methods.

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Introduction

Molecular hydrogen (H₂), a carbon free fuel, is regarded as an ideal energy source to take the place of fossil fuels for reducing carbon output [1–4]. Since photocatalytic splitting of water into oxygen and hydrogen on TiO₂ electrodes was firstly reported by Fujishima and Honda in 1972 [5], semiconductor photocatalysis provides a hopeful strategy that can directly convert solar energy into hydrogen (H₂) to achieve goal of clean energy in the near future. Up to now, thousands of materials have been developed as photocatalysts for generation of hydrogen via water splitting using solar energy. The prime photocatalyst titanium dioxide (TiO₂), has been

regarded as the most promising photocatalyst for its photo-stability, availability and eco-friendliness [6–9]. Unfortunately, the large band gap (~3.2 eV) and low quantum yield of TiO₂ limit its practical application to a large extent. Recently, various methods have been employed to improve the photocatalytic efficiency of TiO₂, such as doping with metal or nonmetal ion [10], depositing noble metal [11,12], sensitizing by organic dye [13] and coupling with narrow band gap semiconductors [14]. Among them, depositing noble metal (Pd, Pt and so on) has been proven to be one of the most promising strategies. Served as isolated “nanoislands” to create heterointerfaces, Pd nanoparticles resting on the surfaces of TiO₂ can capture the photo-induced electrons and

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inhibit the recombination of photo-induced electron-hole pairs [15].

As another promising approach to extend the light absorption of TiO_2 , dye sensitization is also well explored. However, the frequently-used organic dyes, such as Ru-bipyridyl complexes (Rubpy), alizarin dye, erythrosin B, safranin-O (Saf-O/SO), etc [16] are easily dissolved and degraded during photocatalytic processes, which are extremely unfavorable for the photocatalytic activity. In recent years, conducting polymers with extended π -conjugated electron systems are used as stable photosensitizers to modify TiO_2 nanoparticles because of their high absorption coefficient in visible light region, high mobility of charge carriers, excellent stability and biocompatibility. Among them, Polypyrrole (PPy), as a traditional conducting polymer, is widely used in batteries, super capacitors, electrochemical or biological sensors, conductive textiles and fabrics, actuating mechanism, electromagnetic screen, anti-static paint and drug delivery systems [17–19]. Besides superior conductivity, electrochemical reversibility and high polarizability, PPy displays good chemical and thermal stability to avoid be dissolved in acidic and neutral solution, and undergoes only slight photocatalytic degradation in ambient atmosphere due to overoxidation [20]. Therefore, PPy is expected to be a good candidate to enhance the photoactivity of inorganic semiconductors, and it has been successfully used to improve the performances of TiO_2 [21–36], C_3N_4 [37,38], $\text{Bi}_2\text{O}_2\text{CO}_3$ [39], Bi_2WO_6 [40,41], $\gamma\text{-Fe}_2\text{O}_3$ [42], $\alpha\text{-Fe}_2\text{O}_3$ [43], CdS [44] and so on. The outstanding functions of Pd and PPy nanoparticles lead us to conceive the novel TiO_2 -Pd-PPy visible light photocatalyst.

In this paper, TiO_2 -Pd-PPy was synthesized by one-step simultaneous photo-deposition method, which allows for precisely locating Pd and PPy on TiO_2 . Once a photon is absorbed by TiO_2 , an electron-hole pair is generated. The photo-induced electron will reduce Pd^{2+} to Pd, meanwhile, the photo-induced hole will oxidize pyrrole monomers to polypyrrole. Different from other reported synthetic methods, this method can precisely locate Pd and PPy on TiO_2 , the places where Pd and PPy nanoparticles deposited on the surface of TiO_2 are just the active sites that the photo-induced electrons and holes participate in the photocatalytic reaction. Besides, the method in our paper is simple, mild condition, time-saving, without template molecule and surfactant-free. The fabricated TiO_2 -Pd-PPy exhibits a higher photocatalytic H_2 production activity and photocurrent intensity than TiO_2 -Pd and single TiO_2 , which can be attributed to the synergistic effect of Pd and PPy for a better separation of the charge carriers and photoresponse in TiO_2 -Pd-PPy system. Moreover, TiO_2 -0.5Pd-0.6PPy synthesized by the method in our paper displays much higher photocatalytic H_2 production activity than TiO_2 -0.5Pd-0.6PPy synthesized by other methods.

Experimental section

Preparation of catalysts

TiO_2 -Pd-PPy nanoparticles were prepared via simultaneous photoreduction of palladium chloride and photooxidation of pyrrole monomers on the surface of TiO_2 (P25). In a typical

experiment, 300 mg TiO_2 powder was dispersed in 100 mL deionized water via 5 min sonication. Then, 250 μL of 0.0564 M palladium chloride (PdCl_2) and 1.2–3.0 mg of pyrrole (Py) monomers were added slowly to the above dispersion solution with constant stirring. After purging with high-purity N_2 for 30 min to remove dissolved oxygen, the resulting solution was irradiated in UV light using a 300 W high-pressure Xe lamp for 30 min. The nanoparticles were centrifuged, washed with DI water and ethanol several times and dried at 60 °C for 12 h in air. Loading concentration of Pd was 0.5 wt%, and PPy's loading concentration was changed from 0.4 wt% to 1.0 wt%, the corresponding photocatalysts were denoted as TiO_2 -0.5Pd-0.4PPy, TiO_2 -0.5Pd-0.6PPy, TiO_2 -0.5Pd-0.8PPy and TiO_2 -0.5Pd-1.0PPy.

TiO_2 -0.5Pd nanoparticles were also prepared for comparison. Without pyrrole monomers, 250 μL of 0.0564 M palladium chloride and 10 mL methanol were putted into 100 mL TiO_2 (3 mg mL^{-1}) aqueous suspension. The slurry pH was adjusted to ~ 3.0 using 1 M NaOH. Then, the suspension purged with N_2 and irradiated in UV light for 30 min, respectively. Finally, the TiO_2 -0.5Pd powder can be gained after centrifuged, washed and dried at 60 °C in air.

In addition, the TiO_2 -0.5Pd-0.6PPy nanoparticles were also prepared by other three methods, as follows: (1) one-step simultaneous deposited method without illumination at room temperature: 250 μL of 0.0564 M PdCl_2 and 1.8–3.0 mg of pyrrole monomers were added to 100 mL TiO_2 (3 mg mL^{-1}) aqueous solution with constant stirring for 12 h at room temperature, the corresponding photocatalyst was denoted as TiO_2 -0.5Pd-0.6PPy-RT; (2) two-step deposited method (firstly loaded Pd and then PPy): 300 mg TiO_2 -0.5Pd prepared as the above experimental procedure was re-dispersed in a solution containing 1.8–3.0 mg pyrrole monomers and 0.44 mg FeCl_3 via 5 min sonication, the reaction mixture was then stirred in ice-water bath for 12 h to ensure complete reaction, the photocatalyst we gained was denoted as TiO_2 -0.5Pd-0.6PPy-T1; (3) two-step deposited method (firstly loaded PPy and then Pd): 300 mg TiO_2 , 1.8–3.0 mg pyrrole monomers and 0.44 mg FeCl_3 were stirred in ice-water bath for 12 h to obtain TiO_2 -0.6PPy nanoparticles, then, 250 μL of 0.0564 M palladium chloride and 10 mL methanol were putted into TiO_2 -0.6PPy aqueous suspension. The suspension purged with N_2 and irradiated in UV light for 30 min, respectively, after adjusting the pH slurry to ~ 3.0 . The final product was denoted as TiO_2 -0.5Pd-0.6PPy-T2.

Characterization of catalysts

The powder X-ray diffraction (XRD) patterns were characterized by a Bruker AXS D8 Advance powder diffractometer with a $\text{Cu K}\alpha$ X-ray tube ($\lambda = 0.154056$ nm) at room temperature. The morphologies of as-prepared samples were obtained by scanning electron microscopy (SEM) (Hitachi S-4800). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were used to further analyze the morphology and crystallinity of the products on a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV 2500 recording spectrophotometer equipped with

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