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Pd-Gardenia-TiO_2 as a photocatalyst for H_2 evolution from pure water

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ABSTRACT

The photocatalytic activity for H_2 evolution from pure water over Pd loaded TiO_2 prepared by gardenia extract (Pd-Gardenia-TiO_2) is systematically investigated. The as-prepared photocatalysts are characterized by X-ray diffraction, high resolution transmission electron microscopy, Fourier transform infrared spectra, and X-ray photoelectron spectroscopy. Gardenia extract functions as reducing and stabilizing agents simultaneously. The mean size of the as-prepared Pd nanoparticles is in the range of 2.3 ± 0.5 nm based on TEM images. The Pd-Gardenia-TiO_2 catalyst exhibits good photocatalytic activity for H_2 evolution (93 $\mu mol \cdot h^{-1} \cdot g^{-1}$), which is much higher than that of Pd photodeposited on TiO_2. Possible factors for its photocatalytic activity from pure water are also investigated.

1. Introduction

Nano-sized TiO_2 photocatalytic water splitting offers a promising way for clean, low-cost and environmentally friendly hydrogen production [1]. However, the high recombination rate of photogenerated electron-hole pairs is a major factor limiting the photocatalytic efficiency of TiO_2 for water splitting [2]. Hence, the development of high performance photocatalyst is an important subject for research.

Several approaches have been adopted to promote the photocatalytic activity of TiO_2, including the preparation of nano-sized TiO_2 [3], doping and coating with metals [4,5] or modifying with other semiconductors [6]. Many efforts to assist electron and hole separation in TiO_2 by immobilizing metal particles (e.g., Pd [5,7], Pt [8], Ag [9], Cu [10], Au [11]) on TiO_2 have been made by various deposition methods, such as sputtering [4], photodeposition [8], sol-gel [12], photoelectrical deposition [13] and photocomposition method [14]. Recently, special attentions have been paid to the utilization of polymer to improve the photocatalytic performance [15,16]. The introduction of organic compound to immobilize noble metal on TiO_2 makes it a promising method for developing highly efficient hydrogen generation system. However, in these procedures support modification requires complicated steps and some modifiers poison the catalyst [17]. Therefore, even though many synthetic methods for loading noble metal on TiO_2 have been proposed, cost-effective and "greener" approaches for photocatalytic application are still needed. More recently, there are few reports focusing on the deposition of metal particles with biological method [18].

In this article, the aim is to propose a new preparation method that uses gardenia extract to load Pd particles on TiO_2.

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The as-prepared Pd-Gardenia-TiO_2 catalysts are characterized by X-ray diffraction, high resolution transmission electron microscopy, Fourier transform infrared spectra, and X-ray photoelectron spectroscopy. Then, the photocatalytic activity for H_2 evolution from pure water over Pd-Gardenia-TiO_2 catalyst is systematically investigated.

2. Experimental

2.1. Sample preparation

The appropriate amount of TiO_2 (Degussa P25) was added to 72 mL gardenia extract (0.06 g · L^{-1}) prepared by our previous study method [19], and then the suspension was constantly stirred at 80 °C water bath for 16 h. The intermediate product was defined as Gardenia-TiO_2. Aqueous $PdCl_2$ solution (0.025 M, 3 mL) was added into Gardenia-TiO_2 suspension. The mixture was constantly stirred at 80 °C water bath for 6 h. Finally, the product was filtered and fully washed with deionized water to remove the excess gardenia extract. The collected catalyst was dried at 80 °C for 24 h. The as-prepared dark brown product would be referred to as Pd-Gardenia-TiO_2 catalyst. Gardenia-TiO_2 catalyst was collected after filtration, fully washing with deionized water and drying in an oven at 80 °C for 24 h.

The 0.8 wt% Pd photodeposited on TiO_2 was prepared by mixing TiO_2 powder (1.0 g) with an aqueous solution of $PdCl_2$ (0.025 M, 3 mL) and 100 mL H_2O completely. Then, the suspension was illuminated by Hg lamp (125 W) for 5 h. Finally, the precipitate was filtrated, washed by deionized water and dried at 80 °C for 24 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was recorded with an X'Pert Pro x-ray diffractometer (PANalytical BV, The Netherlands) at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. The morphology characterization of the supported metallic particles was carried out by using high resolution transmission electron microscopy (TEM), performed on a Philip Analytical FEI Tecnai 30 electron microscope at an accelerating voltage of 300 kV. The size distribution of the particles was estimated on the basis of TEM images with the assistance of SigmaScan Pro software (SPSS Inc., version 4.01.003). Fourier transform infrared spectra (FTIR) were analyzed by FTIR Nicolet Avatar 360 (Nicolet, USA). The spectra were recorded in the region of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}, using coaddition of 32 scans. X-ray photoelectron spectroscopy (XPS) analyses were performed on a PHI Quantum 2000 Scanning ESCA microprobe with a monochromatized microfocused Al X-ray source. The binding energy was calibrated by C 1s as reference energy (C 1s 284.8 eV).

2.3. Photocatalytic H_2 production

The photocatalytic reaction for H_2 evolution from pure water was carried out in a self-made quartz inner irradiation type annular reaction vessel. The catalyst (0.1 g) was suspended in deionized water (H_2O, 160 mL) by a magnetic stirrer. Prior to irradiation, the solution was continuously bubbled with N_2 at a rate of 60 mL · min^{-1} for 30 min, and then the gas content was checked by GC to confirm that no oxygen was present. Irradiation was conducted by a 125W Hg lamp with the maximum energy at 365 nm and continuum radiation from 200 to 600 nm. The reaction temperature was kept at 50 °C. The gases evolved were gathered and analyzed by GC (TCD, molecular sieve 5 A ° column and Ar carrier).

3. Results and discussion

3.1. Characterizaion of photocatalyst

XRD patterns of 2 and 0.9 wt% Pd-Gardenia-TiO_2 catalysts and Degussa P25 are shown in Fig. 1. The structure of the Pd-Gardenia-TiO_2 catalyst is analogous to that of Degussa P25 which can be indexed to TiO_2 in anatase and rutile phases. No obvious peaks belonging to Pd nanoparticles are observed when metal loading is less than 1 wt%. Maybe it is caused by high dispersion and low metal loading. When the Pd loading is 2 wt%, the hypothesis is verified by the emergence of the peak near 40.0°. The peak is attributed to the (111) crystallographic plane of Pd nanoparticles. The pattern matches well with the standard crystallographic tables JCPDS card 01-087-0643. This result confirms that Pd^{2+} is reduced to Pd^0 in Pd-Gardenia-TiO_2 catalyst. Moreover, further evidence for the existence of Pd nanoparticles is offered by TEM images.

Fig. 2 shows the TEM images and particle size distribution of the Pd-Gardenia-TiO_2 catalysts. Some dark spots on TiO_2 surface which are assigned to Pd nanoparticles can be observed. The Pd nanoparticles are small, round and well distributed. The mean particles sizes estimated on the basis of TEM images from 0.7 to 0.9 wt% are found to be 2.8 ± 0.1 nm, 2.1 ± 0.1 nm, and 1.8 ± 0.1 nm, respectively. The well distribution would be attributed to the stabilizing function of gardenia extract [19]. The mean particles size is decreasing with the increase in the Pd loadings. The phenomenon would be caused by the difference in the Pd nucleation rate and the

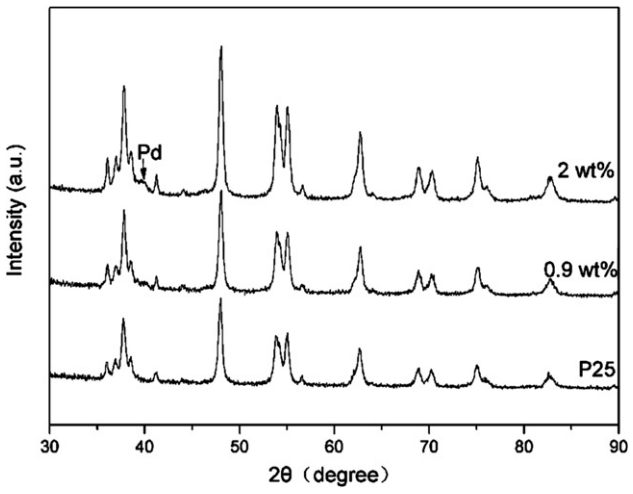

Fig. 1 – X-ray diffraction patterns of 2 and 0.9 wt% Pd-Gardenia-TiO_2 catalysts and Degussa P25.