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Mesocrystalline Ta_2O_5 nanosheets supported Pd–Pt nanoparticles for efficient photocatalytic hydrogen production

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ABSTRACT

We successfully synthesized mesocrystalline Ta_2O_5 nanosheets supported bimetallic Pd–Pt nanoparticles by the photo-reduction method. The as-prepared mesocrystalline Ta_2O_5 nanosheets in this work showed amazing visible-light absorption, mainly because of the formation of oxygen vacancy defects. And the as-prepared bimetallic Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets also showed highly enhanced UV–Vis light absorption and highly improved photocatalytic activity for hydrogen production in comparison to that of commercial Ta_2O_5, mesocrystalline Ta_2O_5 nanosheets, Pd/mesocrystalline Ta_2O_5 nanosheets and Pt/mesocrystalline Ta_2O_5 nanosheets. The highest photocatalytic hydrogen production rate of Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets was 21529.52 g^{-1} h^{-1}, which was about 21.2 times of commercial Ta_2O_5, and the apparent quantum efficiency of Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets for hydrogen production was about 16.5% at 254 nm. The highly enhanced photocatalytic activity was mainly because of the significant roles of Pd–Pt nanoparticles for accelerating the charge separation and transport upon illumination. The as-prepared Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets in this work could serve as an efficient photocatalyst for green energy production.

Introduction

Photocatalytic hydrogen production is often considered to be one of most promising strategies for efficient green energy development in the fields of solar energy utilization [1–3]. Photocatalytic hydrogen production have been attracting great attentions since Fujishima and Honda found the photocatalytic water splitting on TiO_2 electrode in 1972 [4–6]. Although a great number of semiconductor photocatalysts

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for photocatalytic hydrogen production have been successfully prepared nowadays, such as conjugated polymers [7], Tantalum-based semiconductors [8], Titanium dioxide-based nanomaterials [2] and plasmonic photocatalysts [9], the efficient and stabilized photocatalysts are still urgent [10,11]. And therefore, the synthesis of the efficient and wide spectral response photocatalysts is still the focus and challenge.

Tantalic oxide (Ta_2O_5) is a typical wide bandgap semiconductor with excellent photoelec-tric property [12–15]. Recently, Ta_2O_5 photocatalyst receives increasing concerns because the photocatalytic performances of Ta_2O_5 is more efficient in the UV region than P25 TiO_2 [8,14,16–18], though it does not response to visible light. Until now, many kinds of Ta_2O_5 photocatalysts with different morphologies have been successfully synthesized, such as F–Ta_2O_5 spheres [19], N-doping Ta_2O_5 nanoflower [20], Ta_2O_5 quantum dots [21], Ta_2O_5 nanotubes [22], Ta_2O_5 nanowires [23] and sulfur-doped Ta_2O_5 [24]. However, the fabrication of the novel and efficient Ta_2O_5 photocatalysts is still urgent for photocatalytic hydrogen production. As a class of highly ordered single-crystal like superstructure materials [16,25], the mesocrystal photocatalysts often show excellent photocatalytic performances, especially for TiO_2 mesocrystal photocatalysts [26,27]. Tetsuro Majima and his co-workers reported many works on preparation of TiO_2-based mesocrystals and its composites for efficient photocatalysis, such as Au–TiO_2 mesocrystals [28], $SrTiO_3$ mesocrystal [25], g-C_3N_4/TiO_2 mesocrystals [29], nitrogen and fluorine codoped TiO_2 mesocrystals [30] and controllable nanothorns TiO_2 mesocrystals [31]. Until now, there are no reports on the preparation of mesocrystalline Ta_2O_5 photocatalyst for photocatalytic hydrogen production reactions.

Nobel metal co-catalysts are of great significance for photocatalysts to effectively capture photo-generated electrons [32,33]. And the photocatalytic performance of the semiconductors are greatly influenced by the behaviors of photo-induced carriers [2,34]. And therefore, many photocatalysts coupled with nobel metal co-catalysts show highly enhanced photocatalytic performances, such as single-atom Pt/g-C_3N_4 [35], Pt/g-C_3N_4 [36] and Au/TiO_2 [37]. Besides, there were many researches on bimetallic co-catalysts for efficient photocatalysis, such as Au–Pt/TiO_2 [38], Au/Pt/g-C_3N_4 [39], AuPd–$BiVO_4$ [40] and Ni–Pd/TiO_2 [41], which showed great advantages in comparison to that of monometallic co-catalysts decorated semiconductor photocatalysts. And thus, it is interesting to synthesize bimetallic co-catalysts modified mesocrystalline Ta_2O_5 nanosheets nowadays.

In this work, bimetallic Pd–Pt nanoparticles modified mesocrystalline Ta_2O_5 nanosheets were successfully prepared by the facile photo-reduction method. We investigated the important roles of bimetallic Pd–Pt co-catalyst nanoparticles on mesocrystalline Ta_2O_5 nanosheets for hydrogen production in comparison to the mesocrystalline Ta_2O_5 nanosheets and monometallic co-catalyst modified mesocrystalline Ta_2O_5 nanosheets. And the photocatalytic mechanism of Pd–Pt nanoparticles modified mesocrystalline Ta_2O_5 nanosheets was also proposed.

Experimental

Preparation of Pd–Pt/mesocrystalline Ta_2O_5 nanosheets

The mesocrystalline Ta_2O_5 nanosheets were fabricated by annealing $(NH_4)_2Ta_2O_3F_6$ nanorods at 800 °C [14,21]. Firstly, 0.30 g $Ta(C_2H_5O)_5$ was added into 6 mL NH_4F-ethylene glycol mixture in an container (1.6 M) with continuous stirring. And then the container was put into the Teflon line with 8 mL distilled water. After sealing the autoclave, the hydrolysis reactions were carried out at 160 °C for 24 h. The as-prepared $(NH_4)_2Ta_2O_3F_6$ nanorods was separated, washed and dried in an oven at 60 °C for 24 h. Then, the $(NH_4)_2Ta_2O_3F_6$ nanorods were annealed at 800 °C with a heating rate of 5 °C/min in a muffle furnace for 3 h, and mesocrystalline Ta_2O_5 nanosheets were obtained.

Bimetallic Pd–Pt nanoparticles decorated mesocrystalline Ta_2O_5 nanosheets were prepared by facile in-situ photo-reduction method. In generally, 0.05 g mesocrystalline Ta_2O_5 nanosheets with 1.0 wt% Pd and 2 wt% Pt co-catalyst were dispersed in methanol aqueous solution with ultrasonication for 30 min to form a mixture. And the in-situ photo-reduction reaction was carried out in a sealed gas circulation and evacuation system (LabSolar-ⅢAG, Beijing PerfectLight Co., Ltd., China). At first, the system was pumped and the pressure achieved to about −0.1 MPa, the photo-reduction reaction was carried out by a 300 W Xe lamp (PLS SXE300C, Beijing PerfectLight Co., Ltd., China) for 60 min under magnetic stirring. The product was collected by centrifugation and drying at 60 °C. Besides, the Pt/Ta_2O_5 mesocrystals (2.0 wt %) and Pd/Ta_2O_5 mesocrystals (1.0 wt %) were also prepared by the same method for comparison in this experiment.

Characterization

The morphologies of the as-prepared $(NH_4)_2Ta_2O_3F_6$ nanorods, mesocrystalline Ta_2O_5 nanosheets and Pd–Pt/mesocrystalline Ta_2O_5 nanosheets were investigated by a cold field emission scanning electron microscopy (SEM) (Hitachi, SU8010) and Transmission electron microscope (TEM) (Tecnai, G2F30) and HRTEM. The phase structures of $(NH_4)_2Ta_2O_3F_6$ nanorods, mesocrystalline Ta_2O_5 nanosheets and Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets were determined by an X-ray diffractometer (PANalytical, X'Pert PRO) using Cu Kα radiation ($\lambda = 0.15406$ nm). The element chemical states of Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets were analysized on an X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, ESCALAB 250Xi). The fluorescence emission spectrum of mesocrystalline Ta_2O_5 nanosheets and Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets were recorded on a photoluminescence instrument (Hitachi, F-4600). The UV–vis diffuse reflection absorption spectra of commercial Ta_2O_5, mesocrystalline Ta_2O_5 nanosheets and Pd–Pt/mesocrystalline Ta_2O_5 nanaosheets were obtained using double-beam ultraviolet–visible spectrophotometer (Beijing's general instrument co., LTD, TU-1900) with $BaSO_4$ as reference standard. Nitrogen adsorption/desorption tests of commercial Ta_2O_5 and Pd–Pt/