Journal of Catalysis 352 (2017) 13–21

Contents lists available at ScienceDirect

Journal of Catalysis

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

Novel photocatalytic activity of vanadium-doped tantalum nitride sensitized/protected by polyaniline for efficient visible light water splitting

Thanh-Dong Pham [a], Byeong-Kyu Lee [a,*], Van Noi Nguyen [b], Van-Duong Dao [c]

[a] Department of Civil and Environmental Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan 680-749, Republic of Korea
[b] Faculty of Chemistry, Hanoi University of Science, Vietnam National University, Hanoi, Viet Nam
[c] Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 305-764, Republic of Korea

ARTICLE INFO

Article history:
Received 17 March 2017
Revised 22 April 2017
Accepted 22 April 2017
Available online 24 May 2017

Keywords:
Ta_3N_5
V dopant
PANI sensitizer
Water splitting
Solar fuels

ABSTRACT

Vanadium-doped tantalum nitride sensitized/protected by polyaniline (V–Ta_3N_5/PANI) was successfully synthesized for efficient photocatalytic water splitting under visible light. The vanadium was used as a dopant incorporated into the Ta_3N_5 lattice, where it acted as an intermediate band between the valence band and the conduction band of Ta_3N_5 to narrow the band gap energy of Ta_3N_5. This intermediate band of the V dopant also enhanced the electron–hole pair separation efficiency and prevented the recombination of the generated electrons and holes, thereby extending the lifetime of the electron–hole pairs. PANI, a conducting polymer with an extended π–π^* conjugated electron system, was used as a sensitizer/protector covering the V-doped Ta_3N_5 particles to enhance the charge transfer efficiency for migration of the photogenerated electrons and holes to the photocatalyst surface. The PANI cover also prevented Ta_3N_5 from oxidizing the generated holes (self photocorrosion). As a result, the synthesized V–Ta_3N_5/PANI material exhibited very high photocatalytic activity for water splitting, producing H_2 and O_2 even under visible light. The production rates of H_2 and O_2 generated from water splitting by V–Ta_3N_5/PANI were 745 and 370 (μmol g^{-1}cat h^{-1}), respectively.

1. Introduction

Since the pioneering work of Honda and Fujishima, photocatalytic water splitting into hydrogen has received much attention due to the economic and environmental promise of the resulting clean fuels [1]. Photocatalytic water splitting can be initiated by incident irradiation, which requires energy equal to, or greater than, the band gap energy of the photocatalyst. The irradiation promotes electrons to the conduction band (CB), leaving holes in the valence band (VB) of the photocatalyst. The generated electrons and holes reduce and oxidize the H^+ ions and H_2O, respectively, both adsorbed on the photocatalyst surface, to produce H_2 and O_2 [2,3]. Numerous photocatalytic systems have been reported to be active for water splitting. Most of them, however, require ultraviolet (UV) irradiation to initiate the process because of the wide band gap of the used photocatalysts, raising energy consumption and safety issues [4,5]. Among active visible light absorbers (narrow band gap energy), Ta_3N_5, which not only has a suitable band gap (2.1 eV) but also has suitable band positions for water decomposition, has become one of the main candidates for efficient solar light water splitting [6]. It has attracted intensive interest, because the possible theoretical maximum solar conversion efficiency of the photocatalyst is 15.9% [7]. However, the overall water splitting efficiency of the Ta_3N_5 photocatalyst remains low because of several drawbacks, including fast recombination of the generated electrons and holes, low charge transfer efficiency, and poor stability, because the generated holes can oxidize nitrides in Ta_3N_5 (self photocorrosion) in electrolyte solution [8,9]. Therefore, attempts are being made to modify Ta_3N_5 for highly efficient utilization of solar light [10]. Cong et al. modified the structure and size of Ta_3N_5 to enhance its photocatalytic activity [8]. The results indicated that the photocurrent of the nanostructured Ta_3N_5 was over three times higher than that of a regular Ta_3N_5 film. Several studies have aimed to couple Ta_3N_5 with other semiconductors, such as Bi_2O_3, Co_3O_4, and $AgPO_4$, to form composites to enhance the electron transfer efficiency and stability of the photocatalysts [7,11–15]. Recently, Ta_3N_5 has been doped with metals such as Na, K, Cs, and W increase the electron–hole separation efficiency and prevent the recombination of generated electrons and holes, thereby enhancing the photocatalytic activity of the Ta_3N_5 photocatalyst [16,17]. For example, Grigorescu et al. reported that W doping decreased the band gap energy of Ta_3N_5

---

* Corresponding author. Fax: +82 52 259 2629.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

http://dx.doi.org/10.1016/j.jcat.2017.04.024
0021-9517/© 2017 Elsevier Inc. All rights reserved.

from 2.1 eV (bare Ta_3N_5) to 1.75 eV (W-doped Ta_3N_5), which increased the electron–hole separation efficiency of the doped material [17]. To the best of our knowledge, no study has yet used V as a dopant for Ta_3N_5. In our previous study, we used V as a dopant for the TiO_2 lattice [18]. The V dopant migrated to the TiO_2 lattice, leading to formation of Ti^{3+} and V^{4+}, which increased the electron–hole pair separation efficiency and generation capacity and also prevented the recombination of generated electrons and holes of the TiO_2, which in turn enhanced the photocatalytic activity of the photocatalyst. In the present study, we therefore used V as a dopant in the Ta_3N_5 lattice because of its ability to migrate to the Ta_3N_5 lattice (similar to the role played by the V dopant in the TiO_2 lattice) to enhance its photocatalytic activity for efficient solar light water splitting.

Recently, conducting polymers with extended π-conjugated electron systems, such as polyaniline (PANI), polythiophene, polypyrrole, and their derivatives, have been reported as promising sensitizers to increase the visible light response of photocatalysts such as TiO_2, ZnO, and CdSe, because of their high visible light absorption coefficients, high charge transfer efficiency, and excellent stability [19–22]. Thus, the second aim of the study is to use PANI to sensitize the V-doped Ta_3N_5 photocatalyst in order to increase the charge transfer efficiency, prevent the recombination of the generated electrons and holes of the V-doped Ta_3N_5 system, and thereby enhance the photocatalytic activity of the synthesized materials for efficient solar light water splitting. The increase in charge transfer efficiency is also expected to prevent the self photocorrosion of Ta_3N_5 in electrolyte solution (or enhance the stability of Ta_3N_5) because the generated holes of the V-doped Ta_3N_5 system can be quickly transferred to the PANI surface, and therefore cannot oxidize nitrides in Ta_3N_5.

2. Experimental

2.1. Materials synthesis

Ta_3N_5 was synthesized by heating Ta_2O_5 powder (Sigma-Aldrich, 99.9%) in a quartz tube reactor under a flow of ammonia gas at 1000 °C for 10 h. To synthesize V-doped Ta_3N_5 (V-Ta_3N_5), Ta_2O_5 powder was added into a 0.05 M NH_4VO_3 solution. The weight of Ta_2O_5 and the volume of NH_4VO_3 solution were calculated to ensure that the V/Ta atomic percentage was 5%. Then the mixture was ultrasonicated for 1 h and stirred for 24 h to obtain a uniform suspension. The suspension was dried in an oven at 200 °C for 24 h. The obtained powder was also calcined for 10 h in a quartz tube reactor under a flow of ammonia gas at 1000 °C to obtain V–Ta_3N_5 material. To synthesize Ta_3N_5 sensitized/protected by PANI (Ta_3N_5/PANI) and V-Ta_3N_5 sensitized/protected by PANI (V-Ta_3N_5/ PANI), the synthesized Ta_3N_5 and V-Ta_3N_5 were respectively dispersed in deionized water with stirring for 30 min. Then, designed amount of aniline was added to the above mixture with ultrasonication for another 30 min, after which 0.5 M ammonium peroxydisulfate solution was added dropwise into the mixture as an oxidant for polymerization of the aniline. Then, the obtained suspension was filtered. Finally, the precipitates were washed with water, acetone and ethanol and then dried at 80 °C for 10 h to obtain Ta_3N_5/PANI and V-Ta_3N_5/PANI. The weight percentages of PANI/Ta_3N_5 in both Ta_3N_5/PANI and V-Ta_3N_5/PANI were 5%. PANI was also synthesized under the same conditions except for the presence of Ta_3N_5 or V-Ta_3N_5 for comparison.

2.2. Photocatalyst characterization

The pristine Ta_2O_5, PANI, and the synthesized tantalum-based materials were analyzed by a Thermo Fisher K-Alpha X-ray photoelectron spectrometer (XPS) system. The XPS spectra were fitted by Gaussian multipeak shapes to characterize the elemental states of the vanadium, tantalum, and nitrogen in the materials. X-ray diffraction (XRD) spectra of the photocatalysts were obtained using a Bruker AXN model equipped with a Cu-Kα radiation source (λ = 1.5418 Å) and operated at a scan rate of 0.02° s^{-1} over the 2θ range 15–55°. A JEOL TEM-2010F system was used to obtain transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images of the synthesized V–Ta_3N_5/PANI. The optical absorption ability of the synthesized photocatalysts was characterized by an Evolution 300 spectrophotometer (UV-1700 Shimadzu). Photoelectrochemical measurements were performed in a conventional three-electrode cell using Pt and Ag/AgCl (saturated KCl) as counter and reference electrodes, respectively. The synthesized material was dispersed in a dimethyl formamide (DMF) solution (1 mg sample/0.1 mL DMF). Then the mixture was sonicated to obtain a slurry, which was spread onto FTO conductive glass to prepare the working electrode. To improve adhesion, the working electrode was further dried at 373 K for 2 h. Current response was measured with a 0.5 M Na_2SO_4 solution as the electrolyte (pH 6.8).

2.3. Experimental system

A continuous gas system was designed for photocatalytic water splitting experiments. First, 0.2 g of synthesized photocatalyst was added into a 350 mL top and bottom quartz reactor containing 200 mL deionized water. An external cooling system was set up in the reactor sidewall to maintain the temperature of the reactor. The reactor was put into a reaction chamber, which was a cask with a dark cover. White light bulbs (EFTR 20EX-D, Kumho Co., Ltd) were placed at the top and bottom of the reaction chamber to generate visible light in the range 400–700 nm. Before irradiation, the reactor was thoroughly degassed with N_2 and Ar in order to drive off the air inside. The light bulbs were turned on to generate visible light with a power density of 0.1 W/cm^2 for photocatalytic water splitting when the residual air content in the reactor was confirmed to be negligible. The produced gases were collected by an online sampling loop (1 mL) at intervals of 30 min and analyzed by a gas chromatography (GC) system (a thermal conductive detector equipped with a 3.5 m long molecular sieve 5A packed column with Ar as carrier gas).

3. Results and discussion

3.1. Materials characteristics

3.1.1. Crystalline structure and morphology

Fig. 1 shows XRD patterns of pristine Ta_2O_5, synthesized Ta_3N_5, V–Ta_3N_5, Ta_3N_5/PANI, and V–Ta_3N_5/PANI. The main diffraction peaks observed at 2θ values of 22.9°, 28.3°, 28.8°, 36.7°, and 46.9° indicate that the pristine Ta_2O_5 existed in the form of orthorhombic Ta_2O_5 (JCPDS 25-0922) [23]. The XRD pattern of the synthesized Ta_3N_5 corresponds to the typical XRD pattern of Ta_3N_5 [24]. No impurity peak was observed in the XRD pattern, indicating that Ta_2O_5 was completely nitrided to Ta_3N_5. As compared with the XRD pattern of the synthesized Ta_3N_5, the XRD pattern of the synthesized V–Ta_3N_5 shows a shift in the peak position toward smaller diffraction angles, accompanied by a peak broadening. This was due to the migration of the V dopant to the Ta_3N_5 lattice, where it was incorporated [25]. The diffraction lines in the XRD patterns of Ta_3N_5/PANI and V–Ta_3N_5/PANI were similar to those of Ta_3N_5 and V–Ta_3N_5, respectively. This indicates that PANI did not affect the crystalline structure of the Ta_3N_5 and V–Ta_3N_5 particles. The TEM and HRTEM results of V–Ta_3N_5/PANI show that PANI existed as a nanolayer covering the V–Ta_3N_5 particles (Fig. 2).