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Novel visible light-driven Nb-doped Ta_3N_5 sensitized/protected by PPy for efficient overall water splitting

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ABSTRACT

We successfully synthesized niobium-doped tantalum nitride sensitized/protected by polypyrrole (Nb–Ta_3N_5/PPy) for efficient overall photocatalytic water splitting to produce hydrogen and oxygen under visible light. Niobium as a dopant was incorporated into the Ta_3N_5 lattice to act as an intermediate band between the valence band (VB) and the conduction band (CB) of Ta_3N_5 to enhance the electron-hole pair separation efficiency, thereby enhancing its photocatalytic activity. PPy, a conducting polymer with an extended π-π* conjugated electron system, was used as a sensitizer to enhance the charge transfer efficiency for migration of the photogenerated electrons and holes to its surface to prevent the recombination of the pairs and thus increase their lifetime. The migration of the photogenerated holes to the PPy surface also prevented the self photocorrosion of Ta_3N_5 (via reaction between the generated holes and nitrides in Ta_3N_5) in the electrolyte solution and thus enhanced its stability. Therefore, the synthesized Nb–Ta_3N_5/PPy photocatalyst exhibited very high photocatalytic activity and stability for overall water splitting to produce H_2 and O_2 even under visible light at production rates of 65.1 and 32.8 μmol g^{-1}cat. h^{-1}, respectively.

Introduction

Developing new renewable energy technologies has become an important task in recent years because human is facing a severe energy crisis due to the depletion of fossil fuels, which are the dominant source of global primary energy supply [1]. Hydrogen is currently considered an ideal future clean energy source because its excellent and clean energy carrier (high combustion enthalpy and CO_2 zero-emission property) [2,3]. Photocatalytic water splitting is a very promising method for hydrogen production [4,5]. Numerous photocatalysts such as TiO_2, $NaTaO_3$, Ge_3N_4, $K_2La_2Ti_3O_{10}$, CdS, $NaNbO_3$, GaN, $SrTiO_3$, g-C_3N_4 and ZnO_2 have been explored for photocatalytic water

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splitting [1,4,6–10]. However, the major challenges of the photocatalysts are their wide band gap energies (Eg > 3.0) and fast recombination of photogenerated electrons and holes, resulting in low efficiency of the photocatalysis and limited utilization of solar energy. In addition, most of reported photocatalytic system could only half-split water to single generate H_2 or O_2. For an efficient practical solar water splitting system, the band gap energy of a certain photocatalyst, which is the minimum energy needed to excite one electron from the valence band (VB) to the conduction band (CB), should be around 2.0 eV [8]. Recently, tantalum nitride (Ta_3N_5) has attracted attention as an ideal visible-light-driven photocatalyst for water splitting due to its band gap energy of approximately 2.1 eV, corresponding to visible light absorption up to 600 nm. The theoretic solar energy conversion efficiency of Ta_3N_5 is approximately 15.9%, suggesting a huge potential application of the photocatalyst in future industry [8]. In theory, the Ta_3N_5 system could also overall split water to simultaneously generate both H_2 and O_2. In addition, Ta_3N_5 is more stable and less toxic than other narrow band gap energy materials such as CdS and CdSe [11]. However, the water splitting system using Ta_3N_5 as a single photocatalyst has faced several obstacles including the fast recombination of the generated electrons and holes, low charge transfer efficiency and self photocorrosion (poor stability) because the generated holes can oxidize nitrides in Ta_3N_5 in electrolyte solution [12,13]. Various strategies have been conducted to overcome these barriers [8,14–18]. Doping the Ta_3N_5 lattice with metals or non-metals can improve the internal quantum transfer and trapping of electrons, thereby reducing the recombination of the photogenerated electrons and holes and thus increasing the photocatalytic activity of the photocatalyst [8,14–16,18]. Ma et al. reported that alkaline metal-doped Ta_3N_5 had better crystallinity, smaller particles and, most importantly, 6-fold enhanced photocatalytic activity for O_2 evolution compared to the conventional Ta_3N_5 [15] . Nb has been recognized as a very promising dopant for enhancing the photocatalytic activity of the TiO_2 photocatalyst [19–22] as it can substitute Ti^{4+} in the TiO_2 lattice, and thus induce the formation of Ti^{3+} and oxygen vacancies in the lattice, increase the internal quantum capacity, electron-hole separation efficiency and charge transfer efficiency of the TiO_2, and greatly enhance its photocatalytic activity. However, no study using Nb as a dopant to dope Ta_3N_5 lattice has yet been published. Therefore, the first aim of the study is to use Nb as dopant into the Ta_3N_5 lattice to enhance its photocatalytic activity for efficient solar light water splitting.

In order to further enhance charge transfer efficiency and prevent the self photocorrosion of Ta_3N_5, several studies have coupled Ta_3N_5 with other semiconductors, such as Bi_2O_3, Co_3O_4 and $AgPO_4$, to form composites. The coupled semiconductor can act as a charge acceptor for migration of the photogenerated electrons and holes of Ta_3N_5 to its surface, thereby enhancing the photocatalytic activity of the composite and preventing the oxidation of the generated holes with the nitride of Ta_3N_5 [23–25]. Recently, conducting polymers with π-conjugated electron systems, such as polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTs), have been coupled with photocatalysts, such as carbon composite, TiO_2, CdS and Fe_2O_3, to enhance their photocatalytic activity and stability [26–30]. This was because the polymers have excellent optical absorption properties, highly mobile charge carriers and good environmental stability [27,28]. A proper conducting polymer can form an outer layer on the photocatalyst surface to sensitize its photocatalytic activity. When the photocatalyst/polymer system is excited by a certain incident light, this outer polymer layer can support electron transfer for the transfer of electrons from the VB to the CB of the photocatalyst [27,31]. The polymer can also act as a charge acceptor to prevent recombination of the photogenerated electrons and holes of the photocatalyst. As compared to PANI and PTs, PPy has a higher conductivity and stability and is easier to synthesize [27]. Therefore, the second aim of the study is to use PPy to sensitize the Nb-doped Ta_3N_5 photocatalyst in order to increase the charge transfer efficiency, prevent the recombination of the generated electrons and holes of the Nb-doped Ta_3N_5 system, and thereby enhance its photocatalytic activity for efficient solar light water splitting. The outer PPy layer is also expected to prevent the self photocorrosion of Nb–Ta_3N_5 in electrolyte solution.

Experimental

Material synthesis

To synthesize Ta_3N_5, Ta_2O_5 powder (Sigma-Aldrich, 99.9%) was calcinated in a quartz tube reactor under a flow of ammonia gas (50 mL/min) at 1000 °C for 10 h [32]. To synthesize Nb-doped Ta_3N_5 (Nb–Ta_3N_5), niobium ethoxide was diluted in 1 M acetic acid solution, to which Ta_2O_5 powder was added. The weight of Ta_2O_5 and the volume of niobium ethoxide were calculated to ensure a Nb/Ta ratio of 5 % wt. Then, the mixture was ultrasonicated for 2 h and stirred for 22 h to obtain a uniform suspension, which was then dried at 200 °C in an oven for 24 h. The obtained powder was also calcinated in a quartz tube reactor under a flow of ammonia gas at 1000 °C for 10 h to obtain Nb–Ta_3N_5. To synthesize Ta_3N_5 sensitized/protected by PPy (Ta_3N_5/PPy) and Nb–Ta_3N_5 sensitized/protected by PPy (Nb–Ta_3N_5/PPy), the synthesized Ta_3N_5 and Nb–Ta_3N_5 were respectively dispersed in deionized water with stirring for 30 min. Then pyrrole monomer was added to the above mixture with ultrasonication for another 30 min, after which 0.5 M $(NH_4)_2S_2O_8$ solution was added dropwise into the mixture as an oxidant for polymerization of the pyrrole. The mixture was continuously stirred for 3 h and then filtered. The obtained precipitate was washed with water, acetone and ethanol several times and then dried at 80 °C in a vacuum oven for 10 h to obtain Ta_3N_5/PPy and Nb–Ta_3N_5/PPy. PPy was also synthesized under the same conditions except for the presence of Ta_3N_5 or Nb–Ta_3N_5 for comparison.

Photocatalyst characterization

The pristine Ta_2O_5 and the synthesized photocatalysts were analyzed by a Thermo Fisher K-Alpha X-ray Photoelectron Spectrometer (XPS) system. The XPS spectra were fitted by Gaussian multi-peak shapes to characterize the elemental states of the niobium, tantalum and nitrogen in the photocatalysts. X-ray diffraction (XRD) spectra of the pristine Ta_2O_5

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