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Two-dimensional g-C_3N_4/$Ca_2Nb_2TaO_{10}$ nanosheet composites for efficient visible light photocatalytic hydrogen evolution

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ABSTRACT

Scalable g-C_3N_4 nanosheet powder catalyst was prepared by pyrolysis of dicyandiamide and ammonium chloride followed by ultra-sonication and freeze-drying. Nanosheet composite that combines the g-C_3N_4 nanosheets and $Ca_2Nb_2TaO_{10}$ nanosheets with various ratios were developed and applied as photocatalysts for solar hydrogen generation. Systematic studies reveal that the g-C_3N_4/$Ca_2Nb_2TaO_{10}$ nanosheet composite with a mass ratio of 80:20 shows the best performance in photocatalytic H_2 evolution under visible light-irradiation, which is more than 2.8 times out-performing bare g-C_3N_4 bulk. The resulting nanosheets possess a high surface area of 96 m^2/g, which provides abundance active sites for the photocatalytic activity. More importantly, the g-C_3N_4/$Ca_2Nb_2TaO_{10}$ nanosheet composite shows efficient charge transfer kinetics at its interface, as evident by the photoluminescence measurement. The intimate interfacial connections and the synergistic effect between g-C_3N_4 nanosheets and $Ca_2Nb_2TaO_{10}$ nanosheets with cascading electrons are efficient in suppressing charge recombination and improving photocatalytic H_2 evolution performance.

1. Introduction

Over the past two decades, sustainable energy has become a great interest to address the global energy crisis and environmental pollution. The development of technologies that enable to use renewable energy source such as solar energy has been driven by semiconductor in photocatalytic water splitting, which involves the conversion of solar energy and water into chemical energy stored by hydrogen. To design photocatalytic water splitting system the semiconductor photocatalyst mainly requires high efficiency, stability, capability to harvest light in the visible spectrum, environmentally benign, and inexpensive [1,2]. However, there are many issues needed to be solved in order to meet the demanding photocatalytic performance, such as limited visible-light response and high recombination rate of photogenerated electron-hole pairs [3].

Hybridization between different photocatalyst materials attracts a great interest to overcome the limitation of a conventional single-photocatalyst design [4,5]. The synergistic coupling is effective in optimizing their performance and even creating unexpected functionality for practical applications [6,7]. Since the chemical interactions between each kind of chemical species are important to realize the benefit of hybridization, hence an expanded surface area nanostructures becomes anticipated for fabricating functional hybrid materials [8,9]. Graphitic carbon nitride (g-C_3N_4), a typical layered structure, has been studied in various areas such as CO_2 reduction [10], degradation of organic pollutant [3,11], photocatalytic water splitting [4,12]. g-C_3N_4 is attractive because of its suitable band gap for visible light absorption, band edge positions straddle water splitting redox potential, and good chemical and thermal stability. Nevertheless, the efficiency is unsatisfactory and hampers its practical application due to high recombination rate of photogenerated electron-hole pairs. Therefore, several strategies have been developed, including the construction of a porous structure [13], doping with nonmetal elements [14], modification with carbon material [15], and coupling with other semiconductors to form hybridized composites [16].

Niobium phase layered perovskite Dion-Jacobson compounds have a general chemical formula $A_x[B_{n-1}Nb_nO_{3n+1}]$, where A represents an alkaline ion K^+, Rb^+, Cs^+; B represents an alkaline earth ion Ca^{2+}, Sr^{2+}, lead, bismuth, lanthanides, and n represents NbO_6 octahedral perovskite-like slab stacking along the (001)

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direction to form a three-dimensional crystal. Recently, Dion-Jacobson phase $Ca_2Nb_2TaO_{10}$ was reported to exhibit the good photocatalytic activity of restacked nanosheet for H_2 evolution from an aqueous methanol solution under ultraviolet irradiation [17]. However, to date there is no report focusing on the composite photocatalyst design by rationally combining two types of g-C_3N_4 and $Ca_2Nb_2TaO_{10}$ nanosheets. In this study, we report the hybridization of these two types of two-dimensional nanostructured materials for an efficient hybrid photocatalyst via a facile solution exfoliation-reassembly process. The resultant materials exhibited remarkably improved H_2 evolution perforamance under visible light. The crystal structure and morphology of the nanocomposites were investigated systematically and the photocatalytic activity of the nanocomposites for H_2 evolution was discussed in details.

2. Experimental section

2.1. Catalyst preparation

The g-C_3N_4 bulk was prepared by thermal condensation of dicyandiamide according to a reported method [4]. In a typical synthesis, dicyandiamide precursor was placed in an alumina crucible and thermally heated in a muffle furnace at 550 °C for 4 h. The obtained yellow agglomerate product was collected and ground into a powder for further use.

As for the synthesis of g-C_3N_4 nanosheet, it was prepared according to a reported method [18] with some modification. 1 g of dicyandiamide was firstly mixed with 10 g of ammonium chloride and ground in a mortar for 30 min. The obtained mixture was transferred into an alumina crucible and thermally treated in a muffle furnace at 550 °C for 4 h, resulting in a pale yellow sponge-like product. Subsequently, 0.3 g of the product was ground and immersed in 100 ml, Milli-Q water then treated under ultrasonication for 1 h. After the ultrasonication was completed, the nanosheet product was centrifuge at 3000 rpm for 5 min. The supernatant was separated from unexfoliated g-C_3N_4, and g-C_3N_4 nanosheets with a concentration of ca. 0.7 g/L were obtained.

For the preparation of $Ca_2Nb_2TaO_{10}$ nanosheet, firstly layered $KCa_2Nb_2TaO_{10}$ was synthesized by the polymerized complex method then followed by proton exchange and exfoliation according to the method reported by in literature [17,19,20]. In a typical synthesis, 4.15 g of $NbCl_5$ and 2.75 g of $TaCl_5$ and 36.02 g of anhydrous citric acid powder was dissolved in 117 ml of methanol with vigorous stirring. After complete dissolution was achieved, 18.01 g of $CaCO_3$, 0.63 g of KCl and 58 g of ethylene glycol were added to the solution. The solution mixture was heated on a hot plate with stirring in a fume cupboard to 100 °C to promote dissolution. Then, the as-obtained transparent solution was heated to 130 °C with continuous stirring for methanol evaporation. After 30 min of continuous stirring, the temperature is increased to 200 °C and kept stirring for several hours to promote polymerization and to remove excess ethylene glycol until the solution became highly vicious and its color turn from clear transparent to brown transparent. The resin was pyrolyzed in air at 375 °C for 4 h resulted in a black power. Then, the black powder was ground and placed on an alumina plate then heated at 650 °C for 4 h in static air. The as-obtained powder was further calcined at 1000 °C for 2 h in an alumina crucible at a ramping rate 10 °C/min. The resulting powder 5 g was stirred in 200 ml of aqueous nitric acid (1 M) at room temperature (the fresh aqueous nitric acid was replaced every 24 h) for 1 week. The proton-exchanged product was isolated by centrifugation, washed with copious water to remove acid residue and finally air-dried overnight. Finally, the proton-exchanged powder was mixed with aqueous tetra(*n*-butyl)ammonium hydroxide (Aldrich chemical Co., 40 wt.% in H_2O) and shaken at room temperature for 1 week. The nanosheet product was centrifuged at 3000 rpm for 5 min. The supernatant was separated from unexfoliated $Ca_2Nb_2TaO_{10}$, to obtain the exfoliated $Ca_2Nb_2TaO_{10}$ nanosheets (concentration: 2.39 g/).

The typical preparation of g-C_3N_4/$Ca_2Nb_2TaO_{10}$ nanosheet composite photocatalysts was as follows [21]: The pH of $Ca_2Nb_2TaO_{10}$ nanosheets suspension was adjusted to be 9–11 by diluted tetrabutylammonium hydroxide solution. The polyethylenimine (PEI, Mw = 7.5×10^5 g) solution with a concentration of 50 g/L and pH 9–11 (5 ml) was slowly added into $Ca_2Nb_2TaO_{10}$ solution. The mixture $Ca_2Nb_2TaO_{10}$ nanosheet suspension was stirred 2 h then g-C_3N_4 was added to the mixture and stirred overnight. The g-C_3N_4/$Ca_2Nb_2TaO_{10}$ nanosheet composite was centrifuge at 20,000 rpm, the precipitated was freeze-dried. The dried composite powder was added into a crucible and then heated in a muffle furnace at 400 °C, for 1 h with a heating rate of 1 °C/min. The final g-C_3N_4/$Ca_2Nb_2TaO_{10}$ nanosheet photocatalysts were obtained. For the preparation of g-C_3N_4/$Ca_2Nb_2TaO_{10}$ bulk, the g-C_3N_4 bulk and $Ca_2Nb_2TaO_{10}$ bulk was mixed in a mortar for 15 min. the as-obtained mixture was calcined in a muffle furnace at 400 °C, for 1 h with a heating rate of 1 °C/min. The final g-C_3N_4/$Ca_2Nb_2TaO_{10}$ bulk composite photocatalysts were obtained.

2.2. Sample characterization

The synthesized samples crystallinity was characterized by X-ray diffractometer (Bruker Advanced, 40 kV and 30 mA) with Cu Kα radiation. The diffuse reflectance spectra were conducted using UV–vis spectrometer (V-650, Jasco) equipped with an integrating sphere in the range of 300–800 nm. The chemical characterization was obtained by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, a monochromatic Axis ULTRA X-ray). The surface morphology was analyzed by field-emission scanning electron microscopy (FESEM; JSM7100, JEOL, Tokyo, Japan), transmission electron microscopy (TEM; JEOL 1010, Tokyo, Japan) and a high resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Tokyo, Japan). The amount of H_2 evolved from the photocatalyst samples inside the photocatalytic reactor was measured by a gas chromatography (Shimadzu, GC-2014). The surface charge was measured by Zetasizer (Nano-ZS) from Malvern Instruments. The surface area measurement of the solid material was analyzed by Micromeritics TriStar 3000.

2.3. Photocatalytic hydrogen evolution test

The photocatalytic H_2 evolution reactions were carried out in a quartz top irradiation reactor connected with gas chromatography (Shimadzu, GC-2014) equipped with a thermal conductive detector (TCD) and a 5A° molecular sieve column, with Argon as the carrier gas. The temperature of the reactor was maintained at 0 °C by a jacket with the flow of cooling water during the photocatalytic reaction. A 300 W Xenon arc lamp with an output power of 19 A was used as light source. In a typical reaction, 50 mg photocatalyst was suspended in 200 ml aqueous solution containing triethanolamine 10 vol%, and H_2PtCl_6 solution equivalent to 1 wt% Pt was added into a glass reactor. Prior to the photocatalytic reaction experiment, the reactor system was vacuumed several times to remove gasses. The reactor was illuminated for 30 min by in situ photodeposition for loading Pt co-catalyst on photocatalyst surface by with a 300 W Xe lamp equipped with a 400 nm cut-off filter.