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A nanohybrid of CdTe@CdS nanocrystals and titania nanosheets with p–n nanojunctions for improved visible light-driven hydrogen production

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ABSTRACT

A nanohybrid photocatalyst composed of CdTe@CdS nanocrystals and single-layered exfoliated titania nanosheets was synthesized through a well-defined restacking approach. The nanohybrid possessed an expanded layered structure, with ultrathin titania nanosheets randomly restacked upon each other and CdTe@CdS nanocrystals sandwiched between the nanosheets. The introduction of CdTe@CdS nanocrystals not only extended the light absorption of the photocatalyst to the visible range, but also formed p–n nanojunctions in the nanohybrid. The resultant materials containing same amount of CdTe@CdS nanocrystals exhibited over 43 times higher activity than pure CdTe@CdS nanocrystals for hydrogen production under visible light irradiation ($\lambda > 420$ nm) while titania nanosheets alone were not capable of producing any hydrogen under the same conditions. The superior photocatalytic efficiency of the nanohybrid can be attributed to the effective charge separation, which is achieved by the synergetic effect of proper energy bands alignment and p–n nanojunctions.

1. Introduction

Photocatalytic hydrogen production provides a potential solution for the future energy shortage, and thus draws great attention worldwide [1]. In photocatalytic reactions (artificial photosynthesis), a semiconductor photocatalyst is used to absorb incident light, generate excited charge carriers, and subsequently drive the redox reactions. Despite the large amount of work dedicated to developing different photocatalysts, titanium oxide (TiO_2) remains to be the most intensively researched material [2]. As a typical n-type semiconductor, TiO_2 has good stability and relatively good photocatalytic performance upon band gap excitation. However, due to its relative large band gap of 3.2 eV, TiO_2 is only able to utilize the high-energy UV irradiation, which merely accounts for less than 5% of the overall sunlight spectrum. In order to extend its light absorption, researchers have tried to dope TiO_2 with metal and non-metal elements, which can effectively introduce visible light absorbance to TiO_2 [3]. However, doping with guest elements often introduces recombination centers for electrons and holes, and although visible light activity can be obtained, the photocatalytic performance under the whole solar spectrum is deteriorated [4]. Another method to extend the light absorption is to couple TiO_2 with other narrow-band-gap semiconductors to form a heterogeneous structure [5]. Unlike doped TiO_2, heterogeneous photocatalysts have improved charge separation because the energy band alignment in the composite structure can allow photoinduced charge carriers to flow between the narrow-band-gap semiconductor and TiO_2.

In heterogeneous structures, the physicochemical interaction between different components near the interfacial region is critically important. In this regard, nanostructured materials are the ideal building blocks for heterogeneous structures due to their unique surface properties and enlarged specific surface area [6]. The successful preparation of various inorganic 2D semiconductor nanosheets (NSs) with surface charges using exfoliation process [7,8], makes it possible to deliberately synthesize some unique heterogeneous structures. Based on 2D semiconductor NSs, a series of hybrid materials with highly porous structure and well-controlled electronic properties were prepared by coupling NSs with guest species including metal oxide nanoparticles and different types of NSs [9–12]. In particular, the assembly of 2D NSs and 0D nanoparticles will form a layered structure with 0D nanoparticles pillared between 2D NSs, as a result of the house-of-cards-type stacking of the sheet-like titania crystallites. We also reported a nanohybrid of titania NSs and anatase nanoparticles, which greatly improved the

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performance of dye-sensitized solar cell (DSSC) and quantum dot sensitized solar cells (QDSSCs) due to suppressed charge recombination and unique properties related to its special porous structure such as excellent light scattering and increased dye adsorption [13,14].

To fabricate the aforementioned heterogeneous structures, various guest nanoparticles need to be incorporated into the restacked NSs. Among the wide variety of nanoparticles, we are particularly interested in metal chalcogenides nanocrystals (NCs) such as CdTe, CdSe, CdS, etc. because they generally possess small band gaps (visible light absorption) and high conduction bands (driving force for hydrogen production) [15–18]. Moreover, as these NCs are capped with stabilizing organic molecules, their surface charges can be easily tailored by ligand exchange or altering stabilizing molecules [18,19]. Compared to CdSe and CdS, CdTe has higher conduct band edge [20,21], which makes it an excellent candidate not only for photocatalytic and photoelectrochemical hydrogen production, but also for quantum dot sensitized solar cells (QDSSCs) [16,20,22,23]. Besides single phase NCs, type-II core-shell structure NCs such as CdTe@CdS, CdTe@CdSe and CdSe@CdS have also been constructed, which are found to have some advantages including prolonged charge lifetime, enhanced charge transfer, extended absorption edge and improved photo-stability [20,23,24]. A good example of typical type-II core-shell structure is CdTe@CdS, in which electrons are allowed to be transferred to the shell and the holes to the core. In addition, as CdTe is a p-type semiconductor while CdS is n-type, a p–n nanojunction will form at the interface, which can further promote charge separation with its induced electric field [20]. The concept of forming p–n junction in photocatalysts has been found to be very effective for promoting photocatalytic performance [25–27]. For example, Meng and co-workers directly grew p-type MoS_2 nanoplatelets onto n-type nitrogen-doped reduced graphene oxide (rGO) [28]. The nanoscale p–n junctions in the composites significantly improved the photocatalytic hydrogen production performance. Therefore, the special properties of CdTe@CdS make it a potentially better photocatalyst compared to pure CdTe.

Herein we report a new nanohybrid photocatalyst for efficient visible light hydrogen production, which is prepared by hybridization of single-layered exfoliated titania NSs and CdTe@CdS NCs. Even though titania NSs were inactive in the visible region ($\lambda > 420$ nm) while pure CdTe@CdS NCs had extremely low activity, the as-prepared nanohybrid showed dramatically enhanced photocatalytic activity under the same conditions. By coupling CdTe@CdS hetero-NCs and ultrathin exfoliated titania NSs, numerous p–n nanojunctions were formed in the composite, which forms good energy band structure alignment and can enhance the electron transfer from CdTe to titania through CdS, suppress the charge recombination, and subsequently improve the photocatalytic hydrogen production under visible light irradiation.

2. Experimental

2.1. Synthesis of titania nanosheets

Titania NSs were synthesized according to our previous report [13]. The layered titanate precursor $Cs_{0.68}Ti_{1.83}O_4$ was prepared by thorough grinding of Cs_2CO_3 (7.694 g) and TiO_2 (10 g) and subsequent calcination at 760 °C for 12 h. The as-prepared $Cs_{0.68}Ti_{1.83}O_4$ was treated with excess amount of HCl (1 M) for 3 days, and the HCl was refreshed every day. After proton-exchange, the sample was washed with copious deionized water and dried. The obtained $H_{0.68}Ti_{1.83}O_4{\cdot}H_2O$ was then dispersed in tetrabutylammonium hydroxide (TBAOH) solution so that the amount of TBA^+ ions equals to that of intercalated protons in the titanate. The suspension was placed in a shaker for 2 weeks and centrifuged under 8000 rpm for 10 min to remove unexfoliated titanates. The obtained titania NSs with a nominal composition of $Ti_{0.91}O_2$ has a concentration of ca. 1.79 g/L.

2.2. Synthesis of CdTe@CdS nanocrystals

The CdTe@CdS NCs were prepared via a simple one-pot hydrothermal reaction [29]. Typically, $CdCl_2$ (51.52 mg), tri-sodium citrate dehydrate (560 mg) and mercaptosuccinic acid (MSA) (141.4 mg) were dissolved in 66 mL of deionized water in 3-neck flask. The solution was bubbled with N_2 gas for some time. Then 2 mL of Na_2TeO_3 solution (0.014 M) was added to the flask rapidly under vigorous stirring and N_2 gas bubbling. After 5 min, 2 mL freshly prepared $NaBH_4$ solution (0.93 M) was quickly added to the flask. When color of the solution became golden, it was transferred to a Teflon-lined autoclave and heated in oven at 180 °C for 50 min. In the synthesis process, the amount of Cd^{2+} is excessive so the concentration of the CdTe core is determined to be 0.096 g/L based on the concentration of Te source.

2.3. Synthesis of the nanohybrid

CdTe@CdS NCs suspension was first washed in order to remove excessive organic chemicals and other ions. CdTe@CdS NCs suspension was mixed with equal volume of ethanol, and centrifuged at 4500 rpm for 10 min. After centrifugation, the supernatant solution was removed and the deposits were re-dispersed in deionized water to keep the same concentration. Under vigorous stirring, 10 mL of CdTe@CdS NCs suspension was added to 25 mL of titania NSs suspension. CdTe@CdS NCs and titania NSs were allowed to fully mix for 30 min, and 5 ml of poly(ethyleneimine) (PEI) solution (0.125 wt%) was then added. After stirring for another 1 h, the suspension was centrifuged at 4700 rpm and washed several times. The nanohybrid was finally dried at 40 °C in a vacuum oven, and ca. 45 mg of final product was obtained. In this nanohybrid, the ratio of CdTe is calculated to be 2.1 wt% based on the concentrations of $Ti_{0.91}O_2$ NSs and CdTe core.

2.4. Characterizations

The as-prepared NCs, NSs and nanohybrid were comprehensively characterized by powder X-ray diffraction (XRD, Rigaku Miniflex) with Co Kα ($\lambda = 1.78897$ Å) radiation, UV–Vis spectrometer (Shimadzu 2200), X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, a monochromatic Al KR x-ray source), Fluorescence spectrometer (FLS 920, Edinburgh Instruments), zetasizer (Zetasizer Nano ZS, Malvern Instruments) and transmission electron microscopy (TEM, JEOL JEM2100).

2.5. Photocatalytic hydrogen reaction

The photocatalytic hydrogen production reactions were carried out in a quartz reactor connected to a closed-gas circulation and evacuation system. In a typical test, certain amount of catalyst was suspended in 300 mL aqueous solution containing Na_2S/Na_2SO_3 (0.01 mol). 1 wt% of Pt was added as co-catalyst. The reactor was thoroughly evacuated before the photocatalytic reaction, and then irradiated by a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV) equipped with an optical cut-off filter ($\lambda > 420$ nm) to remove UV light. A water filter was applied to eliminate infrared light. A cooling water cycle system was used to keep the temperature at 293 ± 5 K. The produced H_2 gas was detected by gas chromatography (GC) with Ar as the carrier gas.