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Direct Z-scheme composite of CdS and oxygen-defected $CdWO_4$: An efficient visible-light-driven photocatalyst for hydrogen evolution

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ABSTRACT

Direct Z-scheme photocatalyst, which enables efficient charge separation and retains high redox ability, is promising material for visible-light-driven hydrogen evolution. Here we developed a one-step solvothermal method to fabricate direct Z-scheme $CdS/CdWO_4$ composite via treating $W_{18}O_{49}$ with CH_3CSNH_2 and $Cd(CH_3COO)_2$. By controlling the dosage of $Cd(CH_3COO)_2$, CdS nanoparticles decorated $CdWO_4$ nanowires (CS-2) is synthesized. UV–vis DRS and XPS spectra demonstrate that the $CdWO_4$ possesses a large amount of oxygen vacancies, which help to form ohmic contact and broaden light absorption. Compared with CdS, CS-2 Exhibits 18 times higher visible-light H_2 evolution activity using lactic acid as sacrificial agent and shows 7.8-fold higher photocurrent density. Moreover, photoelectrochemical test manifests the efficient separation of the photo-induced charge carriers. Radical-trapping experiments along with in-situ Pt photodeposition further prove that the charge transfer and separation follows Z-scheme mechanism. This work highlights the critical role of defects in the formation of direct Z-scheme composite.

1. Introduction

Photocatalytic hydrogen evolution is one of the most promising and eco-friendly solutions for clean energy production [1–4]. However, the development of effective and stable visible-light photocatalyst remains a great challenge. In the past few decades, various strategies have been proposed to design and fabricate highly efficient photocatalysts [5–7]. Among them, the combination of different semiconductors into composites can take full advantage of each component and is in favour of photocatalytic hydrogen evolution. Type II heterojunction is the most common composite in which both conduction band and valence band of one semiconductor are either higher or lower than the other [8–10]. The staggered band alignment formed on the interface can drive photo-induced electrons to the semiconductor with lower conduction band potential and holes to the one with higher valence band potential, respectively. As a result, the spatial separation of charge carriers is achieved, and the recombination of charges that is the main factor limiting the photocatalytic performance is alleviated to some degree. However, this improvement on charge separation is at the cost of weakening the redox ability, because the photo-induced electrons and holes are concentrated on the band with lower redox potentials. This is not favourable for the photocatalytic process requiring high redox ability, especially for H_2 production.

Z-scheme photocatalytic system has been designed to solve the problem of Type II heterojunction [11,12]. Actually, it has the same band alignment with Type II heterojunction, but exhibits an opposite direction of charge transfer. The photo-induced electrons on the semiconductor with lower conduction band potential will combine with the holes on another semiconductor with higher valence band potential, and the electrons and holes with stronger redox ability remain on two semiconductors. In that way, the Z-scheme system can achieve efficient charge separation and strong redox ability simultaneously. Typical Z-scheme system is composed by two individual photocatalysts and using electron shuttles (IO_3^-/I^- or Fe^{3+}/Fe^{2+}) as redox mediators, but it is complicated and suffers from various backward reaction between redox mediators and photocatalysts. Recently, the redox-mediator-free Z-scheme system attracts increasingly interest. It is worth noting that the ohmic

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contact between two semiconductors is indispensable and the presence of metal conductors between two semiconductors such as Au and Pt could help the formation of ohmic contact [12–14]. Although the metal conductors generally show stronger ability for charge transfer due to the lower electrical resistance, the direct Z-scheme without conductors is more cost-effective. Therefore, optimizing the contact interface is of great significance.

Recently, oxygen-defected semiconductors are attracting intensive interest as visible-light-active photocatalyst [15–17]. The introduction of oxygen vacancies can create defect levels between the valence and conduction band, which induces new channels for light absorption and thus improves solar harvesting [16–19]. Furthermore, it is believed that abundant defects aggregating at the contact interface of composites is beneficial to the formation of ohmic contact, because the interfacial defects can act as the centers for charge recombination [12,20]. Thus, the introduction of oxygen vacancies may also contribute to the construction of direct Z-scheme.

CdS is regarded as one of the most promising material for solar-driven hydrogen evolution due to the optimal band gap and suitable conduction band level [21,22]. However, its activity and stability are far from satisfactory because of the rapid charge recombination and photo corrosion [22,23]. Combining CdS with other semiconductors is an effective way to solve this problem [24,25]. For example, CdS/$CdWO_4$ composite can form Type II heterojunction and inhibits the electron-hole recombination [26,27]. However, the $CdWO_4$ produced is defect-free and the bandgap is very large (~3.8 eV) that limits the light harvesting and hinders photocatalytic application [26–29]. In $CdWO_4$ crystal, W^{6+} and Cd^{2+} ions both have octahedral oxygen coordination and each octahedron shares two corners with its neighbors [28–30]. The existence of WO_6 octahedra indicates the feasibility of oxygen vacancy introduction, as broadly studied in tungsten oxides [31,32]. So the light absorption of the composite can be further improved via defect engineering and the defects on the contact interface may help to form ohmic contact, thus favors the construction of direct Z-scheme.

In this work, we develop a novel method to synthesis CdS decorated oxygen-defected $CdWO_4$ nanowires using $W_{18}O_{49}$ as precursor. Benefited from the reductive environment of synthetic solution, the oxygen vacancies in $W_{18}O_{49}$ precursor are well retained and the as-synthesized composite possesses a well-built contact interface that facilitates the formation of ohmic contact. Meanwhile, the oxygen-defected $CdWO_4$ in composite greatly promotes the visible light harvesting ability. As a result, the composite exhibits remarkably enhanced visible-light-driven hydrogen evolution activity, and, contrary to the reported type II CdS/$CdWO_4$ junction, shows a Z-scheme pathway for charge transfer. This work highlights the role of defects in the direct Z-scheme composite and provides a facile way for the design of direct Z-scheme interface.

2. Experimental

2.1. Materials

WCl_6,$Cd(CH_3COO)_2{\cdot}2H_2O$ and Rhodamine B (RhB) were obtained from J&K Chemical Co. CH_3CSNH_2, *n*-Propanol, ethanol, lactic acid, ammonium oxalate, isopropyl alcohol, 1,4-benzoquinone, ammonium acetate and hydrogen peroxide (30 wt.% aqueous solution) were purchased from Tianjin Guangfu Fine Chemical Research Institute. All the chemicals were of reagent grade and used as received.

2.2. Synthesis of photocatalysts

Spindle-like $W_{18}O_{49}$ was prepared by alcoholysis of WCl_6 according to literature [33] and was used as precursor. Typically, 0.297 g WCl_6 was dissolved in 50 mL *n*-Propanol, transferred to a Teflon-lined autoclave (100 mL) and heated at 200 °C for 24 h. The produced $W_{18}O_{49}$ was collected via centrifugation, washed thoroughly with ethanol and dispersed in 40 mL ethanol with sonication. 1.77 mmol CH_3CSNH_2 was added in the above solution and stirred for 1 h, then a 40 mL ethanol solution of $Cd(CH_3COO)_2{\cdot}2H_2O$ was added dropwise and stirred for another 1 h. The mixture (with 80 mL total volume) was solvothermally treated in a 100 mL Teflon-lined autoclave at 150 °C for 12 h. Finally the product was centrifuged, washed with ethanol and dried at 40 °C overnight. With the increase of Cd dosage, the molar ratio of $Cd(CH_3COO)_2$ to CH_3CSNH_2 was fixed as 1, 1.5, 2 and obtained products were named as CS-1, CS-1.5, CS-2, respectively.

CdS was synthesized similar to CS-1 but without adding $W_{18}O_{49}$. CS-2H was synthesized similar to CS-2, except $W_{18}O_{49}$ were pretreated by 50 mL H_2O_2 (30 wt.%) to remove some oxygen vacancies. The preparation of $CdWO_4$ was similar to CS-2 by replacing CH_3CSNH_2 with CH_3COONH_4 and the as-synthesized $CdWO_4$ was treated with hydrogen at 500 °C for 2 h to obtain oxygen-defected $CdWO_4$.

2.3. Characterizations

Crystal structures were recorded using a Rigaku D/max-2500 X-ray diffractometer (XRD) equipped with a Cu Kα irradiation source. Morphology and microstructure were examined on a Tecnai G^2 F-20 transmission electron microscope (TEM). Energy dispersive spectrum (EDS) characterization was performed with an EDX system attached to TEM. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded with a Hitachi U-3010 spectrometer equipped with a 60 mm diameter integrating sphere using $BaSO_4$ as the standard reflectance. The surface composition and chemical states were analyzed using a PHI-1600 X-ray photoelectron spectroscope (XPS) equipped with Al Ka radiation, and the binding energy was calibrated using the C1s peak (284.6 eV) of the contaminated carbon.

2.4. Photocatalytic hydrogen evolution

The photocatalytic activity was evaluated with 20 mg photocatalyst suspended in 100 mL aqueous solution containing 10 vol.% of lactic acid as the sacrificial agent. The suspension was sealed in a quartz vessel, sonicated for 10 min and purged with argon gas for 30 min to remove all air in solution and headspace. After degassing, the vessel was vertically irradiated by a 300 W Xe lamp (PLS-SXE 300/300UV, Beijing Perfectlight Technology Co. Ltd.) coupled with a UV cutoff filter (>420 nm). The irradiation area was ca. 20 cm^2, the light density was 23 mW/cm^2 at 420 nm as measured with a radiometer (Photoelectric Instrument Factory, Beijing Normal University, Model UV-A). The temperature of reaction solution was maintained at 0 °C. Cocatalysts (0.5 wt.% Pt) were introduced by in-situ photodeposition using H_2PtCl_6 as precursor [34,35]. The amount of generated H_2 was analyzed by a gas chromatograph (Bruker 450-GC) with a thermal conductivity detector (TCD, molecular sieve 5A, argon carrier gas 99.999%).

2.5. Photoelectrochemical measurements

Photoelectrochemical measurements were performed on Ivium CompactStat.e20250 workstation using a three-electrode cell with a working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. Na_2SO_4 (0.2 M) was used as the electrolyte solution and lactic acid (10 vol.%) was served as the hole scavenger. The