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Research paper

Phase junction CdS: High efficient and stable photocatalyst for hydrogen generation

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ABSTRACT

CdS is a photocatalyst known for its desirable bandgap and availability but it is limited by photocorrosion and inefficiency issues in practical applications. According to band engineering theory, regulating the width of bonding region that exists between cubic phase and hexagonal phase, we design a suitable phase junction and achieve effective separation of electron-hole pairs. Thus, the problems caused by photocorrosion and phase exclusion can be resolved. The optimal photocatalytic activity of the prepared material is 4.9 mmol h^{-1} g^{-1} with 41.5% quantum efficiency at the wavelength of 420 nm, which is 60 times higher than that of the initial samples (cubic or hexagonal phase), and keeps high photocatalytic stability. This novel construction approach can be useful in designing ideal band structures and matching the phase bandgap of other binary sulfides.

1. Introduction

New and sustainable technologies for H_2 production are needed due to the shortage of traditional energy resources worldwide. Hydrogen can be used as a replacement to fossil fuel because it is environmentally friendly, reproducible and sustainable. Solar-driven water-splitting reaction is one of the best approaches to obtain hydrogen. In order to gain full and efficient utilisation of solar energy, much attention has been paid to semiconductor photocatalysts at home and abroad. Particularly, transition metal chalcogenides [1] are ideal candidates for semiconductor-based photocatalytic technology. CdS may be used as potential material for photocatalytic water splitting due to its suitable bandgap (Eg = 2.42 eV) and relatively negative conduction band [2–4], which can efficiently absorb visible light and reduce water to produce H_2. However, its application is limited by the rapid charge carrier recombination and poor stability under visible light [5,6].

Various strategies have been employed to resolve its drawbacks to inhibit the charge carrier recombination effectively and improve the stability of CdS. On the one hand, the integration of CdS with other materials has been adopted in many reports, which forms the heterononostructured photocatalysts or surface modification of CdS, such as CdS/rGO [7], MoS_2/CdS [8,9] and N-doped graphene/CdS [10]. Whilst the photocatalytic H_2 production activity of CdS is improved, the stability can be further enhanced. Further simplifying these methods is also possible. On the other hand, the high photocatalytic H_2 can be indeed achieved with the assistance of Rh, Au, Ru, and Pt noble metals, but a broader range of applications is limited because of their scarcity and costs [11,12]. Hence, new tactics to ameliorate photocatalytic performance of CdS-based photocatalysts need to be developed.

Intensive researches have focused on the morphology [13], crystallinity and particle size [14,15] of CdS. For example, using solvothermal synthesis, Chen et al. [16] and Gao et al. [17] reported multi-armed CdS nanorods in ethylenediamine, whereas Wang et al. [18] synthesised CdS multipods in dodecylamine. In terms of the methods above, the performance of CdS can be improved to some extent, and investigating the crystal structure of CdS is necessary for further improvement. Phase junction in some semiconductor compounds with multiple crystal phases has been proven to reliably lead to enhanced photocatalytic performance. One of the cross-sectional examples is P25 (Degussa TiO_2), a common photocatalyst that is made up of anatase and rutile TiO_2. As a matter of fact, P25 exhibits better photocatalytic activity than either rutile or anatase TiO_2 [19]. Researchers also have found similar phenomena in Ga_2O_3 [20] and $CaTa_2O_6$ [21] nanoparticles with phase junction. Nevertheless, application of CdS encounters difficulties upon the formation of the phase junction. Bao and Shen et al. found that hexagonal-cubic CdS nanocrystals showed worse photocatalytic activity than hexagonal or cubic phase CdS nanocrystals alone. This phenomenon was attributed to the crystalline defects occurring at the interface of the two phases [22]. By inserting Pt into the phase junction of core-shell hexagonal-cubic CdS nanoparticles,

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Hoffmann and co-workers successfully eliminated the surface states of hexagonal CdS core and improved photocatalytic H_2 production rate [23]. Through synthesising hexagonal-cubic core-shell nanorods, Li and Han improved the CdS photocatalytic activity [24]. Although the phase junction has been studied to some extent via above methods, the importance of phase junction has not been taken much concern really. Therefore, further studies on the phase junction are still needed.

Band engineering is important to acquire suitable band structures and facilitates the separation of electron-hole pairs. Using this concept, we designed an appropriate phase junction by regulating the bonding region width between cubic phase and hexagonal phase for the first time. The bonding region widths were studied to realise band structures with high H_2 conversion rate (4.9 mmol h^{-1} g^{-1} with 41.5% quantum efficiency). In addition, phase junctions with suitable bonding region widths have long-term stability of photocatalytic activity. This present strategy could be used as a basis to design binary sulfides and other related materials.

2. Experimental section

2.1. Materials

Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) and sodium sulfide ($Na_2S{\cdot}9H_2O$) were purchased from Aladdin. Ammonia solution ($NH_3{\cdot}H_2O$), absolute ethanol and lactic acid provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai) were of analytical reagent grade. All materials were used as received without further purification. Solutions were prepared freshly with deionised water.

2.2. Synthesis of preliminary CdS nanoparticles

CdS nanoparticles were prepared by a one-step hydrothermal method. Keeping the molar proportion of Cd/S equal to 1:1, 0.925 g Cd $(NO_3)_2{\cdot}4H_2O$ and 0.721 g $Na_2S{\cdot}9H_2O$ were dissolved in 20 mL ammonium chloride (ammonia) solution, with concentration of 1%, 3%, 5%, 7% and 9%. Subsequently, the solutions were agitated using a magnetic stirrer for 15 min and placed in a 25 mL Teflon-lined autoclave and maintained for 24 h at temperatures of 150 °C, 180 °C, 200 °C and 220 °C. The products with optimal concentration of 5% ammonia solution were used for hydrothermal treatment at reaction times of 3, 6, 9, 12, 15, 18, 21 and 27 h to further study the influence of the bonding region width. After cooling to room temperature, the precipitate was filtered, washed with ethanol and water several times and dried at 80 °C for 24 h in a vacuum drying chamber.

2.3. Characterisations

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8-Advance X-ray powder diffractometer with a Cu-Kα radiation (λ = 0.15418 nm). Scanning electron microscopy (SEM) images were collected using a Hitachi S-4800 microscope equipped with an energy-dispersive X-ray analyser (EDS, Horiba EMAX Energy EX-350). TEM and HRTEM images were obtained with a Philips Tecnai 20U-Twin microscope at an acceleration voltage of 200 kV. UV–vis diffuse reflectance spectroscopy (DRS) was conducted using a Shimadzu UV2550 recording spectrophotometer equipped with an integrating sphere with wavelength of 200 nm to 900 nm. $BaSO_4$ was used as a reference. The room-temperature Raman spectra of samples were recorded on a LabRam HR system from Horiba Jobin Yvon at room temperature using the 532 nm solid laser as the exciting source. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was performed using monochromated Al-Kα radiation (1486.8 eV). The fluorescent lifetime was obtained by Opolette 355 II Instrument (USA).

2.4. Photocatalytic activity test

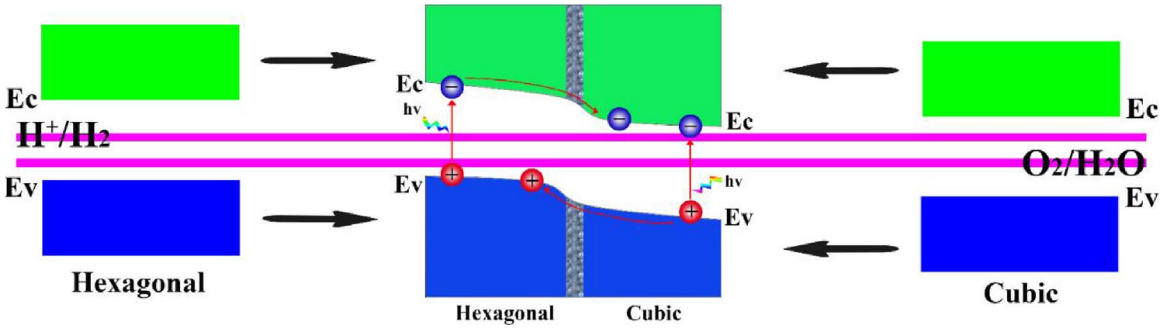
Photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Fifty milligrams of catalysts were dispersed in 100 mL of aqueous solution containing 20 mL of lactic acid as sacrificial agents. The suspension was then thoroughly degassed and irradiated by a Xe lamp (300 W) equipped with an optical cutoff filter (λ = 420 nm) to eliminate ultraviolet light. The temperature of the reactant solution was maintained at 5 °C during the reaction. The amount of H_2 produced from water-splitting was analysed using online gas chromatography (Gc7900 Tianmei Shanghai China). The photocatalytic activity of the CdS nanoparticles was assessed by the average rate of H_2 evolution in 5 h.

2.5. Photoelectrochemical activity measurements

The PEC measurement system in this study was a CHI660D workstation (Shanghai Chenhua, China) with a three-electrode configuration using the as-obtained samples as the working electrodes, a Pt plate as the counter electrode, Ag/AgCl as the reference electrode and a 300 W Xe lamp equipped with an optical cutoff filter (λ = 420 nm) as the light source. Na_2SO_4 aqueous solution (0.5 M) with 20% lactic acid was used as the electrolyte. The working electrodes were prepared as follows: 10 mg of as-prepared nanoparticles were dispersed in absolute ethanol and the suspension was directly deposited onto an FTO conductive glass plate and then dried at 80 °C in a vacuum oven.

3. Band engineering design theory

CdS possesses two typical structures: hexagonal phase and cubic phase. Given the disparity of bandgaps between cubic phase and hexagonal phase, band bending exists when the two phases contact each other. Further integrating band engineering theory with phase junction, the concept of band structure with high hydrogen production is shown in Scheme 1. In these two phases, the electron-hole pairs recombine quickly due to the limitation of their own band structure. As the hexagonal phase possesses higher conduction band level than the cubic phase, the photo-generated electrons transfer from the conduction band



Scheme 1. Schematic theories illustrating the regulation of band structure through phase junction with bonding region.