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# Composition dependent activity of $Fe_{1-x}Pt_x$ decorated ZnCdS nanocrystals for photocatalytic hydrogen evolution

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ABSTRACT

In this work, ZnCdS nanoparticles (NPs) were decorated with FePt alloy, forming nanocomposites via ethylene glycol reduction method. The photocatalytic $H_2$ production of the $Fe_{1-x}Pt_x$–ZnCdS NPs was studied by changing the composition and weight percentage of $Fe_{1-x}Pt_x$ alloy in the nanocomposites under visible light ($\lambda \geq 420$ nm) irradiation. The results showed that the hydrogen production rate of $Fe_{1-x}Pt_x$–ZnCdS NPs had a significant enhancement over the pure ZnCdS (740 μmol $g^{-1}$ $h^{-1}$). The activity of the nanocomposites was dependent on the composition of $Fe_{1-x}Pt_x$ alloy and the highest hydrogen production rate of 2265 μmol $g^{-1}$ $h^{-1}$ was achieved by the 0.5 wt% $Fe_{0.3}Pt_{0.7}$–ZnCdS nanocomposites, which was even better than that of 0.5 wt% Pt–ZnCdS (1626 μmol $g^{-1}$ $h^{-1}$) under the same condition. This study highlights the significance of Pt base alloys as new cocatalysts for the development of novel composite photocatalysts.



## Introduction

Due to global energy crisis and environmental issues, developing clean and renewable energy resources has become an urgent demand for the sustainable development of human society. Among many renewable energy resources, hydrogen has been regarded as one of the most important energy resources for its high fuel value, storable and environmental friendly nature [1,2]. Since Honda and Fujishima discovered the photocatalytic water splitting on $TiO_2$ electrode, numerous semiconductor photocatalysts have been developed for hydrogen production by water splitting [3–6]. One of the representative materials is CdS [7]. It has a band gap of approximately 2.4 eV with flat band potential at −0.66 V,

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which is available for light harvest and proton reduction in aqueous solution. It's well known that CdS is unstable for photocatalytic $H_2$ production due to the oxidation of $S^{2-}$ in CdS by photo-induced holes in the valence band of CdS. Many efforts have been made to improve the activity and stability of CdS, such as metal ions doping [8,9], noble metal deposition [10–12] and composite heterojunction [13]. Among these techniques, combing CdS with other wide band gap semiconductors to form solid solutions is an effective way to control the photocatalytic properties. In this regard, $Cd_xZn_{1-x}S$ solid solution has shown superior photoactivity than binary CdS due to the shift of both valance band and conduction band positions [14–16]. So far, a great quantity of work on $Zn_xCd_{1-x}S$ photocatalysts has been reported [9,17,18]. Both wurtzite and zinc-blende structured $Zn_xCd_{1-x}S$ materials were fabricated and the solid solution with specified composition yielded the highest photocatalytic $H_2$ production [19]. For example, Guo et al. reported a one-step hydrothermal method for $Zn_xCd_{1-x}S$/ZnO heterostructures and demonstrated the balancing the band-gap and band offset of the heterostructure is important for $H_2$ production [20]. Weng et al. studied the effect of annealing on the structure, optical properties as well as photocatalytic activity of $Zn_xCd_{1-x}S$ arrays [21]. Du et al. reported that metallic $Li_xMoS_2$ as a new cocatalyst for $Cd_{0.5}Zn_{0.5}S$ NPs to enhance their photocatalytic $H_2$ production [22]. The photocatalytic activity of the $Zn_xCd_{1-x}S$ needs to be further optimized to meet the fundamental requirement of practical application.

On the other hand, Pt is considered to be the most effective cocatalyst for photocatalytic $H_2$ production from water due to its empty d electron orbital and high work functions. In the water splitting process, Pt serves as photo-excited electrons receiver of semiconductors and reveals low over-potential of $H_2$ formation [23–25]. Also, alloying transition metals with Pt has shown superior cocatalytic properties [26,27]. For example, $CoPt_x$ modified CdS and $TiO_2$ nanoparticles showed better activity than pure Pt modified ones under visible light [28]. By preparing bimetallic PtAu nanoparticles-loaded mesoporous-assembled $TiO_2$–$SiO_2$ photocatalysts, the photocatalytic activity reached an acceptably high level as observed in the case of the 1.25 wt% Pt loading [29].

Motivated by the concept of less platinum and higher efficiency in the development of photocatalysts, we report a new composite photocatalysts by loading $Fe_{1-x}Pt_x$ alloy on ZnCdS ($Zn_{0.5}Cd_{0.5}S$) nanocrystals via an ethylene glycol reduction metal method. By rational tuning the composition of FePt cocatalyst, the activity of the $Fe_{1-x}Pt_x$–ZnCdS increased significantly and the optimized photocatalytic $H_2$ production was achieved for $Fe_{0.3}Pt_{0.7}$–ZnCdS nanocomposites, which was higher than that of Pt–ZnCdS with the same weight percentage loading. The mechanisms for the composite photocatalysts toward water splitting were investigated.

## Experimental section

### *Synthesis of $Fe_{1-x}Pt_x$–ZnCdS NPs*

$Fe_{1-x}Pt_x$–ZnCdS nanocomposites were fabricated by loading $Fe_{1-x}Pt_x$ nanoparticles on ZnCdS nanoparticles (NPs) via an ethylene glycol reduction method. The synthesis includes two processes. Firstly, 2 mmol of $ZnCl_2$ and 2 mmol of $CdCl_2{\cdot}2H_2O$ were mixed with 20 ml of ethylene glycol in a 100 ml round-bottom flask. Under the flow of nitrogen, the compound was heated to 160 °C with stirring, then the cut-and-dried ethylene glycol containing 4 mmol of $Na_2S{\cdot}9H_2O$ was transferred to the flask. The mix solution became yellow immediately and the temperature was dropped to 120 °C. After the temperature was maintained at 120 °C for 5 min, 0.1 mmol 1, 2-hexadecanediol (20 mg), a certain amount of $H_2PtCl_6$ and $FeCl_2$ were added to the mixed solution. The solution was heated up to the reflux temperature (180 °C) for 1 h at a rate of 10 °C/min. In the synthesis of FePt alloy, the weight percentage and the composition of FePt alloy were tuned by changing the amount of Fe and Pt precursors. After the reaction solution slowly cooled down to room temperature, 30 ml of ethanol was added, the supernatant was discarded and the dull yellow products were precipitated by centrifugation. The samples were washed by ethanol and deionized water respectively. Finally, the purified $Fe_{1-x}Pt_x$–ZnCdS NPs were obtained by drying (70 °C) in the vacuum oven for 12 h.

### *Fabrication of thin film electrodes*

In three-electrode electrochemical system, a platinum sheet was used as a counter electrode, and an Ag/AgCl electrode worked as the reference electrode to provide a stable electrode potential. The fabrication of working electrode is as follows: 50 mg of photocatalysts and 20 mg of polyethylene glycol (M = 20,000 g/mol) were dispersed in 1 ml aqueous ethanol solution to form uniform slurry by sonication. The slurry was blade-coated onto the FTO conductive glass to form a thin film electrode with electrode area ca. 1 $cm^2$, and then the electrodes were sintered at 450 °C for 30 min [30,31].

### *Material characterization*

The microstructure of $Fe_{1-x}Pt_x$–ZnCdS NPs with Different concentrations were examined by X-ray diffraction (XRD, Bruker advanced D8) with Cu Kα radiation, scanning electron microscopy (SEM, JSM-7100F) and transmission electron microscopy (TEM, FEI Tecnai 20). The band gap energies of the photocatalysts were determined by the UV-3600 spectrophotometer (Shimadzu). Electrochemical characterization was conducted by electrochemical analyzer (CHI760E). The bonding states of Zn, Cd, Pt and Fe elements in samples were examined by X-ray photoemission spectroscopy (XPS) using Al Kα radiation (hυ = 1486.6 eV).

The photocatalytic activity of all samples was investigated under visible light irradiation (CEL-HXF300, a 300 W xenon lamp with a 420 nm light filter) with $Na_2S/Na_2SO_3$ as the electron donor. In detail, 100 mg of photocatalyst, 0.35 M $Na_2SO_3$ and 0.25 M $Na_2S$ were dispersed in 100 mL deionized water, and the solution was deoxygenated by bubbling nitrogen for 10 min. The focused light intensity on flask was about 200 mW/$cm^2$ measured by full spectrum light optical power meter (CEL-NP2000, Ceaulight, Beijing). In the illumination process, magnetic stirring was employed to achieve uniform suspension. The rate of photocatalytic $H_2$ production was analyzed by a gas chromatograph named GC-2018 (GC-2018,

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