



# Rare earth doped TiO<sub>2</sub>-CdS and TiO<sub>2</sub>-CdS composites with improvement of photocatalytic hydrogen evolution under visible light irradiation

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## ABSTRACT

In this paper, we report the obtention of a series of rare earth doped composite Pt/RE/TiO<sub>2</sub>-CdS (RE=La<sup>3+</sup>, Eu<sup>3+</sup>, Er<sup>3+</sup>, Gd<sup>3+</sup>) and TiO<sub>2</sub>-CdS photocatalysts prepared by a simple mechanical mixed method. The photocatalysts properties were studied by means of ultraviolet-visible spectroscopy, photoluminescence spectra, X-ray diffraction, transmission electron microscopy, specific surface areas and the electrochemistry method. Photocatalytic hydrogen evolution using Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as electron donor was investigated under visible-light ( $\lambda \geq 420$  nm) irradiation. The rare earth doping enhances the activities of Pt/RE/TiO<sub>2</sub>-CdS samples (with 1.0 wt% deposited Pt). Under optimum conditions, the activities of La<sup>3+</sup>, Eu<sup>3+</sup>, Er<sup>3+</sup>, Gd<sup>3+</sup> doped composite Pt/RE/TiO<sub>2</sub>-CdS increase by 62.0%, 40.4%, 34.7% and 30.0% respectively, when compared to that of Pt/TiO<sub>2</sub>-CdS, due to the prevention of electron-hole recombination and the flat-band potential of the conduction of TiO<sub>2</sub> shifting negatively by the doping.

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## 1. Introduction

Photocatalytic water splitting using solar light has been considered as one of the most promising routes for renewable hydrogen production [1–3]. There have been many semiconductors used for photocatalytic producing hydrogen, such as narrow-gap CdS [4–6] and InP [7], and wide-gap TiO<sub>2</sub> [8,9] and ZnO [10]. Among those, TiO<sub>2</sub> was applied widely for its excellent properties including non-toxicity, stability, and low cost. However, TiO<sub>2</sub> can only be excited by light of short wavelengths ( $\lambda \leq 387$  nm), leading to low efficiency for utilizing solar energy. The photoexcited carriers recombine easily, so its photocatalytic activity is low. To extend its absorbance extent to visible light and promote its photocatalytic efficiency, many methods have been employed [11–14]. An approach

for achieving this objective is to couple TiO<sub>2</sub> with a higher conduction band potential than that of TiO<sub>2</sub> by using a narrow-gap semiconductor. CdS coupled TiO<sub>2</sub> has been extensively studied in water splitting systems [15–17]. CdS/TiO<sub>2</sub> composite semiconductor extends TiO<sub>2</sub> response to visible light and depresses recombination of the photoexcited electrons and holes, but CdS/TiO<sub>2</sub> composite semiconductor is not ideal due to its low activity and quantum efficiency.

Recently, the photocatalysts activities of anatase TiO<sub>2</sub> matrix doped with rare earth have attracted much attention [18–20]. Researches indicated that rare earth doping could control TiO<sub>2</sub> particle growth, restrain its crystal transformation, and cause negative shift of the conduction band, and thus increase its photocatalytic activity.

Therefore, in the present paper, rare earth elements (La<sup>3+</sup>, Eu<sup>3+</sup>, Er<sup>3+</sup>, Gd<sup>3+</sup>) doped TiO<sub>2</sub> coupled with CdS composite photocatalysts (RE/TiO<sub>2</sub>-CdS) were prepared. Although there are many reports about pure TiO<sub>2</sub> matrix coupled with CdS, rare earth doped TiO<sub>2</sub> coupled with CdS

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has never been reported. Rare earth doping improves the photocatalytic hydrogen evolution under visible light irradiation. The effects of rare earth doping on the photocatalytic activity of RE/TiO<sub>2</sub>-CdS were investigated and the possible mechanism was discussed.

## 2. Experimental Procedure

### 2.1. Preparation of Photocatalysts

All reagents (Shanghai Reagents Company, China) were of analytic grade and used without further treatment. The rare earth oxides (RE<sub>2</sub>O<sub>3</sub>, RE=La, Eu, Er and Gd, Shanghai Reagents Company, China, purity 99.99%) were converted to soluble 0.10 mol L<sup>-1</sup> RE(NO<sub>3</sub>)<sub>3</sub> solution by reaction with 1:1 HNO<sub>3</sub> solution.

#### 2.1.1. Preparation of Rare Earth Doped TiO<sub>2</sub> Photocatalysts

A series of rare earth doped TiO<sub>2</sub> photocatalysts were prepared by using an impregnation method. The required amount of TiO<sub>2</sub> (anatase, Shanghai Caiyu Co Ltd, China, purity 99.99%) was added into a given volume of 0.10 mol L<sup>-1</sup> RE(NO<sub>3</sub>)<sub>3</sub> solution. The mixture was dispersed in an ultra-sonic bath for 15 min. After impregnation for 12 h, it was dried at 393 K. The samples were further treated at 673 K in air for 2 h. The prepared samples were denoted as RE/TiO<sub>2</sub>, where RE=La<sup>3+</sup>, Eu<sup>3+</sup>, Er<sup>3+</sup> and Gd<sup>3+</sup>.

#### 2.1.2. Preparation of Pt/TiO<sub>2</sub> or Pt/RE/TiO<sub>2</sub> Photocatalysts

Photocatalyst TiO<sub>2</sub> or RE/TiO<sub>2</sub> with deposited Pt was prepared by photodeposition [9]: 0.4000 g TiO<sub>2</sub> or RE/TiO<sub>2</sub>, 10.80 mL 1.93 × 10<sup>-3</sup> mol L<sup>-1</sup> H<sub>2</sub>PtCl<sub>6</sub>, 2 mL ethanol and 87.20 mL distilled water were mixed, and then the suspension kept by stirring was irradiated with a 400 W high pressure Hg lamp under a nitrogen atmosphere for 1 h to deposit Pt on TiO<sub>2</sub> or RE/TiO<sub>2</sub>. After filtrated and washed with distilled water three times, dried at 393 K for 10 h and milled, 1.0 wt% Pt/TiO<sub>2</sub> or 1.0 wt% Pt/RE/TiO<sub>2</sub> was obtained.

#### 2.1.3. Preparation of CdS

CdS was prepared by a precipitation method. A solution of 0.40 mol L<sup>-1</sup> Na<sub>2</sub>S was added dropwise to a 0.40 mol L<sup>-1</sup> CdSO<sub>4</sub> solution with a molar ratio of 1:1, and then stirred for 1 h at room temperature. The resulting precipitate was filtered and washed with deionized water several times and then dried in a vacuum at 333 K for 6 h.

#### 2.1.4. Preparation of Pt/TiO<sub>2</sub>-CdS or Pt/RE/TiO<sub>2</sub>-CdS photocatalysts

Composite photocatalyst with variation of molar ratio was prepared by a simple mechanical mixed method. CdS was mixed with Pt/TiO<sub>2</sub> or Pt/RE/TiO<sub>2</sub> by grinding to ensure intimate physical contact between CdS and Pt/TiO<sub>2</sub> or Pt/RE/TiO<sub>2</sub> powders. The prepared samples were denoted as Pt/TiO<sub>2</sub>-CdS or Pt/RE/TiO<sub>2</sub>-CdS.

### 2.2. Characterizations

Ultraviolet-visible (Uv-vis) spectra were obtained on a HITACHI U-3310 spectrophotometer equipped with an

integrating sphere accessory. X-ray diffractometer (XRD) patterns were measured on a Britain Bede D1 System, employing Cu K<sub>α</sub> radiation λ=0.15406 nm. The Rietveld analysis of crystalline structures was performed with XRD data using the Topas-Academic software package. The crystal cell parameters were calculated at the same time. Transmission electron microscope (TEM) images were observed with a JEM-2010 transmission electron microscope equipped with an energy-dispersive spectrometer (EDS). Photoluminescence spectra (PL) were measured on a Hitachi F-4600 fluorescence spectrophotometer. The specific surface areas (BET) of the samples were determined on a ST-08 analyzer by the volumetric BET method using nitrogen as absorbent. Electrochemistry test was operated on the LK98BII microcomputer-based electrochemical analyzer.

### 2.3. Electrode Preparation and Electrochemical Test

ITO conducting glass (1.5 cm × 4.5 cm) was washed with ethanol and distilled water. 0.0500 g photocatalyst was dispersed in 10 mL ethanol in an ultrasonic bath for 30 min. Then, 10 drops of the resultant solution was spread on the glass, and dried under infrared lamp irradiation. Finally, the film electrode was calcined at 673 K for 30 min. A copper wire was fixed at the bare end of the glass with epoxy. In the photoelectrochemical experiment, the prepared electrode, platinum electrode and saturation calomel electrode were used as a working electrode (WE), counter electrode and reference electrode, respectively. The electrolyte was KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub> aqueous solution (pH=4.0). Before measurement, WE was activated in the electrolyte for 6 h. A 400 W high-pressure mercury lamp was used as the light source. All the experiments were conducted at room temperature.

### 2.4. Photocatalytic Activity

Photocatalytic reactions were conducted in a 190 mL Pyrex cell with a flat side window for illumination. A 400 W high-pressure mercury lamp was used as the light source with a cutoff filter (λ ≤ 420 nm) to remove radiation below 420 nm. Typically, a 0.10 g catalyst was suspended in a 100 mL aqueous solution containing 0.10 mol L<sup>-1</sup> Na<sub>2</sub>S and 0.020 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub>. Before irradiation, the suspension of catalyst was dispersed in an ultrasonic bath for 5 min and N<sub>2</sub> was bubbled through the reaction mixture for 30 min to remove oxygen. The top of the cell was sealed with a silicone rubber septum. Sampling was made intermittently through the septum during experiments. The photocatalytic activity was determined by measuring the amount of hydrogen production for 2 h irradiation on a gas chromatography (TCD, 13X molecular sieve column, N<sub>2</sub> as gas carrier).

The apparent quantum yield of photocatalyst was estimated by the following equation:

$$\phi_{\text{H}_2} = 2 \times \frac{\text{mole of hydrogen evolved}}{\text{mole of incident photon}} \quad (1)$$

The average photon flux of the incident light determined on a FGH-1 Ray virtual radiation actinometer (light spectrum: 400–700 nm) was 920 μmol m<sup>-2</sup> s<sup>-1</sup> (20 mW cm<sup>-2</sup>).

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