



Carbon nanotubes as an auxiliary catalyst in heterojunction photocatalysis for solar hydrogen

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ABSTRACT

This study demonstrates that multi-walled carbon nanotubes (CNTs) effectively catalyzes photocatalytic hydrogen production in heterojunction suspensions under solar visible light (AM 1.5G; $\lambda > 420$ nm). Due to the high catalytic activity of CNTs, use of Pt can be significantly reduced. For this, quaternary composites (CdS/TiO₂/Pt/CNTs) are prepared by the creation of CdS on platinumized TiO₂ (TiO₂/Pt) subsequently to which chemically oxidized CNTs are loaded. A binary (CdS/TiO₂) and two ternaries (CdS/TiO₂/Pt and CdS/TiO₂/CNTs) are also prepared for comparison. A TEM analysis for the quaternary sample shows that TiO₂ is a central component that holds Pt nanoparticles, CNTs, and CdS clusters, while the last is spatially away from the catalysts. Photoluminescence (PL) emission bands of the binary excited at 325 nm and 410 nm are reduced by loading either Pt or CNTs, and further by co-loading of both catalysts. This suggests that the recombination of photogenerated charges under UV or visible light is inhibited due to cascaded charge transfer between TiO₂ and CdS, which is further decreased by Pt and/or CNTs. Photolysis confirms that either Pt or CNTs catalyzes effectively photocatalytic H₂ production in aqueous CdS/TiO₂ suspensions with sulfide/sulfite electron donor under visible light. Such activity is significantly enhanced by over 50% by co-loading of Pt and CNTs. It is found that the Pt amount can be reduced to approximately five- or one-tenth by additional loading of CNTs under an optimal condition. The maximized performance of the quaternary is also found in the significantly enhanced photocurrent generation compared to the two ternaries. The detailed mechanism and implications are discussed.

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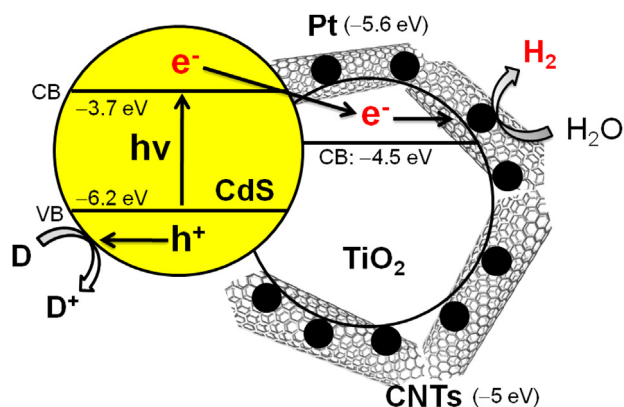
1. Introduction

Semiconductor photocatalysis-based solar hydrogen has received growing attention as an alternative to carbon-footprinted chemical fuels [1,2]. Its renewability and storability have great application potential to meet future global energy demands [2] as well as enable distributed power generation systems [3,4]. For high efficiency and low cost solar hydrogen, photocatalysts should absorb solar light abundantly, separate photogenerated charges efficiently, and catalyze hydrogen evolution effectively with reduced use of expensive materials [5]. Currently, a number of semiconductors are available as photocatalysts capable of producing hydrogen from water under normal sunlight or visible light. Among them, CdS may be the most ideal because of its narrow bandgap of max. 2.5 eV (corresponding to $\lambda < \text{ca. } 600$ nm) and the

suitable levels of the conduction band (CB: -0.75 V vs. NHE) and valence band (VB: 1.75 V vs. NHE). Although its photocorrosion still limits its widespread applicability, CdS is very useful as a model semiconductor for solar hydrogen.

CdS is often coupled to TiO₂ (hereafter CdS/TiO₂) to improve photocatalytic performance under ultraviolet + visible light or visible light only [6–11]. It was reported that the amount of H₂ produced in CdS/TiO₂ suspension is almost double of that in CdS under visible light ($\lambda > 420$ nm) [6]. A comparison of the photocurrent showed a similar degree of enhancement in the former. To further increase H₂ production, many catalysts are often deposited on CdS/TiO₂, among which platinum is by far the best. When Pt is located on the CdS surface (Pt/CdS/TiO₂), however, the Pt effect is very limited. For a maximal catalytic effect, Pt should be located on the TiO₂ surface (CdS/TiO₂/Pt) because most photogenerated electrons are effectively transferred to TiO₂ (Scheme 1) [6,12]. In comparison to Pt/CdS/TiO₂, H₂ production with ca. 40 times greater in CdS/TiO₂/Pt suspension shows the importance of the Pt location and particle-to-particle contact.

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Scheme 1. Illustration of photogenerated charge transfers occurring in visible-light irradiated CdS/TiO₂/Pt/CNTs suspensions. CB, VB, and D refer to conduction band, valence band, and electron donor, respectively. Numbers are approximate work functions relative to vacuum levels. Under visible light ($\lambda > 420$ nm), photogenerated electrons are transferred from CdS to TiO₂ due to the wider work function (or lower CB position) of the latter. They continue to move forward interfacial CNTs and/or Pt because both are highly conductive. In this Scheme, Pt is illustrated as a final electron reservoir due to its wider work function (-5.6 eV) than CNTs (-5 eV). H₂ can be produced from CNTs as well, yet the amount may be smaller than that from Pt.

Recently, carbon materials have been employed for photocatalysis. When coupled to semiconductors (e.g., TiO₂ [13–15], CdS [16,17], CdSe [18,19]), the carbon materials enhance the photocatalytic activity primarily due to their unique physicochemical properties such as a large work function (4–5 eV), low electrical resistivity, high thermal conductivity, and large surface area [20,21]. For example, coupling of multi-walled carbon nanotubes (CNTs) to CdS (CdS/CNTs) enhances H₂ production by a factor of 17 under visible light [16]. Such an enhancement was attributed to the high electrical conductivity and catalytic surfaces of the CNTs. Although the surface area and the graphitic property (e.g., I_p/I_C) of the CNTs also influence H₂ production, a key factor may be the electrical conductivity [18]. Hence highly conductive graphites ($\sim 10^6$ S/m) are superior to CNTs with lower conductivity ($\sim 10^5$ S/m) in terms of H₂ production in visible light-irradiated CdSe suspensions [18].

In this study we examined the effects of CNTs on the photocatalytic H₂ production in CdS/TiO₂ composite suspensions under a simulated solar visible light ($\lambda > 420$ nm, AM 1.5G, 100 mW/cm²). The primary aim is to address the following questions: (1) Can CNTs enhance the photocatalytic activity of the composites? (2) If so, can CNTs replace Pt as a hydrogen production catalyst? (3) If not, can CNTs be used as an auxiliary catalyst of Pt? For this, CNTs were chemically oxidized to increase the aqueous dispersibility, surface area, and electrical conductivity [18]. Then, the optimal amounts of CNTs and Pt on CdS/TiO₂ were determined in terms of H₂ production. Various surface analyses and photoelectrochemical studies were also performed to understand the effect and role of CNTs.

2. Experimental

2.1. Single materials

Multi-walled carbon nanotubes (CM-100, Hanwha Nanotech) were used as-received or after acid treatment. For the acid treatment, CNTs (1 g/L) were refluxed in aqueous nitric acid (1 M) for 1 h, filtered with 0.45- μ m PTFE filters (Millipore), washed with a copious amount of distilled water, and subsequently dried overnight at 80 °C. When necessary, CNTs were annealed at 500 °C for 10 min. TiO₂ (Degussa P25) was employed as a supporting material. It is a mixture of anatase and rutile (8:2) with a primary particle size of ca.

30 nm and has a BET surface area of ca. 50 m²/g. CdS was prepared with a simple hydrolysis method [6,7,16]. A solution of sodium sulfide (Na₂S) was added dropwise to cadmium acetate solution (Cd(CH₃COO)₂·2H₂O) with a molar ratio of 1:1, which was stirred for 1 h, filtered with 0.45-mm PTFE filters, washed with distilled water, and dried overnight at 80 °C.

2.2. Heterojunction materials

TiO₂/Pt was prepared by following a typical photodeposition method [22]. In brief, TiO₂ suspensions at 0.5 g/L with methanol (1 M) and various Pt(IV) (H₂PtCl₆·6H₂O, Aldrich) concentrations (0.01 mM, 0.05 mM, and 0.1 mM) were irradiated with a 1.4-W UV lamp (Moolim, F8T5BLB) for 2 h, washed with distilled water, and collected as a dried powder. TiO₂/CNTs (or TiO₂/Pt/CNTs) composites were prepared with a hydration/dehydration method [13]. First, approximately 10 mg CNTs (virgin or acid-treated) were dispersed in water in a 200-mL beaker and sonicated for 20 min. Three different amounts of TiO₂ powder (or TiO₂/Pt) were added to the CNTs suspensions to make the relative amounts of CNTs be 1, 5, and 10 wt% during sonication. Then, the mixed suspensions were heated to 80 °C on a stir plate with air-flowing across the surface of the suspension to accelerate the evaporation of water. After evaporation, the composite was dried overnight in an oven at 104 °C to avoid any physicochemical change of the CNTs that occurs at higher temperatures in the presence of oxygen. CdS/TiO₂, CdS/TiO₂/Pt, CdS/TiO₂/CNTs, and CdS/TiO₂/Pt/CNTs were prepared by following the above CdS preparation method in aqueous suspensions of TiO₂, TiO₂/Pt, TiO₂/CNTs, and TiO₂/Pt/CNTs, respectively, at a weight ratio of 7:1 (CdS:TiO₂). For comparison, (CdS/TiO₂)/CNTs was also prepared by loading CNTs on as-prepared CdS/TiO₂ composites.

2.3. Photocatalytic and photoelectrochemical tests

Aqueous suspensions containing samples (0.5 g/L) and electron donors (0.1 M Na₂S and 0.1 M Na₂SO₃) were stirred in a Pyrex-glass reactor equipped with a quartz disc for light penetration. Prior to irradiation, nitrogen gas was purged through the suspension for 30 min, and the reactor was sealed from ambient air during the irradiation. A solar simulator equipped with AM 1.5G filter (LS-150 Xe, Abet Technologies) was used as a light source (100 mW/cm²) with a cutoff filter ($\lambda > 420$ nm). To avoid thermal effects, the reactor was cooled to room temperature with an air cooler fan. During irradiation, the headspace gas of the reactor was intermittently sampled and analyzed for H₂ using a gas chromatograph (Young Lin, ACME 6100) equipped with a thermal conductivity detector and a carboxen 1000 packed column.

Photocurrents were collected on an inert working electrode (Pt wire) immersed in aqueous suspensions of photocatalysts (0.5 g/L, 0.95 M NaOH) using methyl viologen (MV²⁺, 0.5 mM) as an electron shuttle described elsewhere [23]. A saturated calomel electrode (SCE) and a graphite rod were used as a reference and counter electrode, respectively. For the measurement of the MV²⁺-mediated photocurrent, the working electrode was held at -0.4 V vs. SCE with a potentiostat/galvanostat (Versastat 3–400). Before and during irradiation, nitrogen gas was continuously purged through the suspensions, and a solar simulator with a cutoff filter ($\lambda > 420$ nm) was used as a light source (see Fig. 7 inset).

2.4. Surface analysis

UV–vis diffuse reflectance absorption spectra (DRS) were obtained by using a UV–vis spectrometer (UV-2450, Shimadzu). BaSO₄ was used as a reflectance standard. Transmission electron microscopy (TEM, Hitachi LTD, H-7600) was employed for examining the morphology of the samples. Photoluminescence spectra

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