



# Visible light driven hydrogen evolution by photocatalytic reforming of lignin and lactic acid using one-dimensional NiS/CdS nanostructures

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## ABSTRACT

Uniform one-dimensional (1D) NiS/CdS nanocomposites have been fabricated using CdS nanowires (NWs) and NiS nanoparticles as building blocks through two-pot solvothermal synthesis. The synergistic interaction between CdS and NiS, stemming from their intimate contact, efficiently enhanced charge carrier separation, with the NiS, as a non-noble metal cocatalyst, enriching the active sites for H<sub>2</sub> production from water. Consequently, compared with pristine CdS NWs, the 1D NiS/CdS nanocomposite exhibited improved visible light reactivity in the generation of H<sub>2</sub>. The activity of NiS/CdS with 20 mol% of NiS loading, under the coexistence of lactic acid and lignin as hole scavengers, is 5041 times that of pristine CdS, with an apparent quantum efficiency (AQE) of 44.9% for H<sub>2</sub> generation. To gain deeper insight into the mechanism behind the enhanced performance, ultrafast dynamics studies based on femtosecond transient absorption (TA) techniques have been applied to probe the charge carrier dynamics. The results reveal that presence of 0.2 molar ratio of NiS improved the average charge carrier lifetime of CdS NWs by 97 times, potentially leading to more efficient charge separation and transfer. However, further increasing the NiS loading resulted in shorter lifetime or faster electron-hole recombination, attributed to aggregation of NiS nanoparticles. The dynamics results agree well with the photocatalytic results in that the longer charge carrier lifetime correlates with improved performance in hydrogen evolution. This work demonstrates a simple approach to controlled synthesis of well-shaped 1D nanocomposite photocatalysts for visible-light driven energy conversion, particularly involving the use of biomass.

## 1. Introduction

Hydrogen energy is an ideal alternative to fossil fuels and is predicted to play an indispensable role in renewable energy technologies in the future [1,2]. Enlightened by natural photosynthesis, varieties of semiconductors, for instance nitrides [3], metal-organic frameworks (MOFs) [4,5], TiO<sub>2</sub> or ZnO based photocatalysts [6,7], and (oxy) sulfides [8–11], have been widely researched as photon absorbers and photocatalysts in artificial light driven water splitting for hydrogen evolution reaction (HER). Among them, CdS is attractive on account of its wanted bandgap (2.4 eV) and matching band-edge stations [12]. Nevertheless, CdS has two limitations. First, its photocatalytic efficiency is seriously confined by rapid recombination of photogenerated charge carriers [13]. Second, CdS is subjected to photocorrosion under light irradiation, with S<sup>2-</sup> in CdS self-oxidized by photoinduced holes instead of the oxidation of others [14]. Therefore, attempt have been made to either reduce recombination rate of charge carriers or prevent self-photocorrosion of CdS, such as doping or modifying with other

semiconductors [15,16]. Among kinds of strategies, co-catalyst decoration is one of the most effective ways [17–21]. In particular, noble metals have been proved to be efficient co-catalysts for HER. However, the high price of noble metals limits their applications in practice. Therefore, it is urgent to exploit inexpensive, non-noble metal-based, and valid co-catalysts for HER.

Nickel sulfide (NiS), a *p*-type semiconductor, has caused increasing concern because of its low-cost, good electrical properties, and other unique property such as highly electrocatalytic effect toward the polysulfide reaction [22,23]. For example, Zhang et al. prepared NiS modified TiO<sub>2</sub> using solvothermal method for the photocatalytic H<sub>2</sub> production with an evolution rate of 0.7 mmol h<sup>-1</sup> g<sup>-1</sup> [24]. Chen et al. synthesized g-C<sub>3</sub>N<sub>4</sub>/NiS hybrid photocatalysts through in situ template-free ion-exchange process with H<sub>2</sub> production rate of 0.45 mmol h<sup>-1</sup> g<sup>-1</sup> [25]. Furthermore, Xu et al. found that NiS can be employed to cocatalyst of CdS for photocatalytic water splitting from lactic sacrificial solution via a simple hydrothermal method, and the H<sub>2</sub> evolution rate reached 2.8 mmol h<sup>-1</sup> [26]. Yu et al. developed NiS

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nanoparticle decorated CdS nanorods photocatalysts using a convenient two-step hydrothermal approach, with an  $H_2$  evolution rate of  $1.13 \text{ mmol h}^{-1} \text{ g}^{-1}$  [27]. As far as we know, 1D NiS/CdS nanowire composite has yet to be applied to HER.

In the meantime, the water-splitting process is inherently unfavorable thermodynamically, and rapid reaction between  $O_2$  and  $H_2$  produced limited hydrogen production [28]. For the sake of address these topics, one approach is to put in sacrificial agents to expend the oxygen-derived groups generated, preventing subsequent  $O_2$  production and its reverse reaction with  $H_2$ . Besides, the sacrificial agents serve as hole scavengers, increasing the separation efficiency of electrons and holes. One ideal scenario to address these issues is by photoreforming of alcohols in the photocatalytic HER. The photoreforming of alcohols, for example methanol [2,29], ethanol [30] or glycerol [31], has been completely investigated over the past decade. These alcohols are classified the first generation of biofuels, as they are derived from biomass, for example starches, sugars, or vegetable oils. Yet the consumption of these substances as a hydrogen precursor threatens with their application as food. Therefore, the utilization of lignocellulosic biomass has been paid high attention to the second generation of biofuels, for they can be planted in combination with crop or on barren soil. Lignocellulose contains three main biopolymers, that is lignin (15–20%), hemicellulose (25–35%) and cellulose (40–50%) [32]. Lignin is the most stubborn of the three components of lignocellulosic biomass. Bled by paper industries and pulp as discards from wood and crude materials, lignin results in the pulp and paper wastewater tough to deal with conventional wastewater treatment technology. Therefore, if lignin could also serve as sacrificial agents (hole scavengers) to reduce the rate of charge carrier recombination, the photocatalytic method for degradation of lignin can be used in conjunction with the production of hydrogen from water splitting. Nevertheless, this approach has not been extensively investigated previously.

In this work, we fabricated 1D NiS/CdS nanocomposites using a two-step solvothermal method. The nanocomposite shows obviously enhanced HER activity compared with pure CdS nanowires (NWs). The  $H_2$  evolution rate obtained using the optimized photocatalyst is up to  $147.7 \mu\text{mol h}^{-1} \text{ g}^{-1}$  ( $\lambda \geq 400 \text{ nm}$ ) and the apparent quantum efficiency (AQE) was 44.9% from aqueous solution of lignin and lactic acid. The stronger light absorption and more efficient electron transfer of the nanocomposites are confirmed by UV–vis spectroscopy and the photoelectrochemical properties, which could lead to the enhanced photocatalytic water splitting ability in comparison with that of pristine CdS. Furthermore, the effect of the NiS loading on charge carrier dynamics has been researched using femtosecond transient absorption (TA) spectroscopy, which offers information about charge separation and transfer from CdS to NiS. These results prove that the appropriate amount of loading of NiS can substantially enhance charge carrier separation and transfer, correlating with significant enhancement in the photocurrent density. This work demonstrates the potential of NiS/CdS nanocomposite as an effective photocatalyst for hydrogen evolution utilizing lignocellulosic biomass.

## 2. Experimental section

### 2.1. Materials

All the chemical reagents used in the experiment were provided by Sinopharm Chemical Reagent Co., Ltd, Shanghai without further purification. Deionized water was employed in all the experiments throughout.

### 2.2. Material synthesis

The 1D NiS/CdS nanocomposites were assembled by a template-free and mild two-step solvothermal method. The first step was the fabricate CdS NWs. In a typical process, cadmium

diethyldithiocarbamate ( $\text{Cd}(\text{S}_2\text{CNET}_2)_2$ ), prepared by sediment from a stoichiometric precursor mixture of cadmium chloride (0.01 mol) and sodium diethyldithiocarbamate trihydrate (0.01 mol) in 50 mL of deionized water, was transferred to a Teflon-lined stainless steel autoclave with. Then, the autoclave was filled with 40 mL of ethylenediamine. The autoclave was heated at  $180^\circ\text{C}$  for 24 h and then cooled down to room temperature. The pale yellow sediment was collected and washed several times with absolute ethanol and deionized water. The final products were dried in a vacuum oven at  $60^\circ\text{C}$  for 12 h.

The second step was to fabricate 1D NiS/CdS nanocomposites. The above prepared CdS NWs were ultrasonically dispersed in 70 mL of ethylene glycol solution containing nickel nitrate (0.58 g) and thiourea (0.3 g). Then the solution was transferred into a 100 mL stainless steel autoclave and heated at  $180^\circ\text{C}$  for 12 h after stirring for 0.5 h. The obtained precipitates were collected by centrifugation, washed with deionized water before being dried in a vacuum oven at  $60^\circ\text{C}$ . The molar ratio of NiS and CdS was varied (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) by adjusting the CdS amount.

### 2.3. Characterization

The morphologies of the samples were determined with scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL TEM-2010) and high-resolution transmission electron microscopy (HRTEM, JEM-2010 FEM). Elemental analysis of the photocatalysts was conducted by an energy dispersive X-ray spectrometer (EDS) attached to TEM. The crystal phases of the samples were characterized with a Bruker D8-advance X-ray diffraction (XRD), performed on with  $\text{Cu K}\alpha$  radiation. The results were obtained at a scanning speed of  $4^\circ$  steps over the  $2\theta$  ranged from  $20^\circ$  to  $80^\circ$ , and the accelerating voltage and operating current were 40 kV and 40 mA, respectively. The specific surface areas were measured by BET method utilizing nitrogen adsorption-desorption apparatus (JW-BK122W, China). The pore volume and distribution were determined by the Barrett, Joyner, and Halenda (BJH) method. The X-ray photoelectron spectroscopy (XPS) was conducted with Thermo 163 Fisher ESCALAB 250Xi. UV–vis diffuse reflectance spectra (DRS) were collected with a Shimadzu UV-2550 spectrometer with  $\text{BaSO}_4$ -coated integration sphere. Fourier-transform infrared (FT-IR) spectra were determined by using a Thermo Fisher Nicolet iS10 Fourier-transform infrared spectrometer. Inductively coupled plasma mass spectrometry (ICP-MS) was recorded on a PerkinElmer 350 D instrument.

### 2.4. The evaluation of photocatalytic hydrogen production

Photocatalytic hydrogen production test was evaluated in an airtight glass reactor with high transparent quartz on top of the glass cover. Before all experiments, 0.100 g sample was added into 100 mL solution (including different sacrificial agent). The sample was treated with ultrasonication for 10 min and then the whole equipment was evacuated with vacuum pump for 0.5 h to exhaust the air as well as establish adsorption-desorption equilibrium in the reactor. The reaction mixture was stirred gently, and the reaction temperature was kept at room temperature by cooling water circulation system. A 300 W Xe lamp with a cutoff filter ( $\geq 400 \text{ nm}$ ) was irradiated from the top of glass reactor. The gaseous  $H_2$  was periodically extracted from the hydrogen production device and measured by gas chromatograph (CEL-GC7900), assembled with a thermal conductivity detector (TCD), ultrapure nitrogen as carrier gas. The gases generated in the reaction were quantified with standard curve of  $H_2$  gas. The AQE of  $H_2$  production was performed under the same photocatalytic conditions. The AQE was estimated by the following equation.

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