Photochemical synthesis of Ni-Ni(OH)$_2$ synergistic cocatalysts hybridized with CdS nanorods for efficient photocatalytic hydrogen evolution

Huizhen Zhang$^a$, Yuming Dong$^a,x$, Dandan Li$^a$, Guangli Wang$^a$, Yan Leng$^a$, Pingbo Zhang$^a$, Hongyan Miao$^a$, Xiuming Wu$^a$, Pingping Jiang$^a$, Yongfa Zhu$^a,b$

$^a$ International Joint Research Center for Photo-responsive Molecules and Materials, School of Chemical and Material Engineering, Jiangnan University, Wuxi, 214122, China
$^b$ Department of Chemistry, Tsinghua University, Beijing, 100084, China

1. Introduction

As the growing crisis in energy and environment resulting from fossil fuels, the construction of environmentally friendly renewable energy systems has become the focal point of worldwide attention.[1–3] Photocatalytic hydrogen evolution has been believed to be a sustainable and pollution-free technology to produce renewable energy.[4–6] The photocatalytic process is composed of three steps: light absorption, electron and hole transport and surface redox reaction, and the last of them is the speed control step.[7–9] Loading cocatalysts on the light absorbing semiconductors can accelerate the surface reaction and increase the photocatalytic efficiency.[10–12]

In recent years, some studies have demonstrated that metallic nickel (Ni$^0$) is an excellent cocatalyst in photocatalytic HER.[13,14] As reported by Kong et al, the HER rate of Ni/C$_3$N$_4$ is much faster than that of native C$_3$N$_4$.[15] Cao et al also found that nickel nanoparticles (Ni NPs) can greatly enhanced the HER performance of CdS.[16] Furthermore, nickel hydroxide also is a robust reduction cocatalyst in photocatalytic water splitting. For example, the HER activities of TiO$_2$ and CdS/g-C$_3$N$_4$ achieved 6-fold and 26-fold enhancement after the modification of Ni (OH)$_2$.[17,18] Recently, Wu’s group revealed that [Ni$^0$/Ni(OH)$_2$], including Ni(OH)$_2$ and Ni$^0$, can serve as the active center to boost water molecule dissociation and proton reduction.[19] Therefore, the combination of metallic nickel and nickel hydroxide is expected to build a remarkable cocatalyst for HER.

Herein, ternary Ni-Ni(OH)$_2$/CdS nanohybrids was synthesized by a simple and facile photodeposition strategy. Under visible light, the optimal HER rate of the Ni-Ni(OH)$_2$/CdS reached 428 mmol g$^{-1}$h$^{-1}$ and remained basically unchanged after 24 h using Na$_2$S/Na$_2$SO$_3$ aqueous solution. In particular, the Ni-Ni(OH)$_2$/CdS also displayed excellent photocatalytic hydrogen evolution reaction (HER) activity (13.3 mmol g$^{-1}$h$^{-1}$) in 40 vol% glycerol. A set of spectroscopy and electrochemical characterizations were performed to explore the photoinduced interfacial charge dynamics. Ni and Ni(OH)$_2$ were synergistic cocatalysts for improving charge utilization and photocatalytic performance.

2. Experimental section

2.1. Synthesis of CdS nanorods (NRs)

The CdS NRs were synthesized by a solvothermal method using cadmium chloride (CdCl$_2$·2.5H$_2$O, 10.13 mmol), thiourea (NH$_2$CSNH$_2$, 30.38 mmol) and ethylenediamine (30 mL) as cadmium source, sulfur source and solvent, respectively.[22] A mixture of three raw materials was added to autoclave and reacted 48 h at 160 °C. The yellow

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* Corresponding author.
E-mail address: dongym@jiangnan.edu.cn (Y. Dong).
precipitate was washed repeatedly to remove impurities and dried at 60 °C under vacuum.

2.2. Synthesis of Ni-Ni(OH)₂/CdS NRs

The Ni-Ni(OH)₂/CdS NRs was synthesized by means of photodeposition. Specifically, 50 mg CdS was ultrasonically dispersed into the mixed solution of 12.5 mg nickel acetate (Ni(CH₃COO)₂), 4 mL isopropanol, 2 mL triethanolamine and 4 mL water. Then the suspension changed from yellow to dark-green after degassing and 30 min of irradiation. Finally, the product was obtained by repeated washing and drying under nitrogen.

2.3. Photocatalytic hydrogen production

The photocatalyst was dispersed in aqueous solution of sacrificial agent by ultrasound, and then the air in the reaction system was removed by bubbling N₂. The light source was visible light or sunlight provided by Xe lamp (300 W) with corresponding filter. After irradiation, the gas phase products were passed into gas chromatography (GC-9790) for qualitative and quantitative analysis.

2.4. Photoelectrochemical measurements

Three-electrode system composed of working electrode, reference electrode (Ag/AgCl) and counter electrode (Pt net), was connected to electrochemical analyzer (CHI600E) to measure the photocurrent and impedance of the catalysts. Preparation of the working electrodes was as follows: 5 mg sample was mixed with 225 μL ethanol and 25 μL perfluorinated resin (Nafion®) and dispersed by ultrasound. The working electrodes were obtained by dripping 30 μL suspension onto the FTO plate (1 × 1 cm²). The electrolyte was 0.5 M Na₂SO₄ solution and the light source was visible light.

2.5. Characterisation

D8 X-ray diffractometer was utilized to study crystal phase structure by analyzing XRD patterns. The surface morphology was inspected by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100). TEM-EDX and EDX-mapping (FEI, USA) were used to investigate the element composition and distribution. Surface chemical state of the catalysts was determined by X-ray photoelectron spectroscopy (ESCALAB 250 XI). The content of nickel in the sample was tested by inductively coupled plasma emission spectrometer (ICP-OES, Agilent S1101). The light absorption performance of the material was evaluated by UV–visible diffuse reflection spectroscopy (DRS, UV-3600). The steady-state, transient fluorescence spectra (FLS980) and surface photovoltage (SPV) spectra (self-made equipment) were used to observe the charge separation and transfer behavior of the catalysts under light excitation.

3. Results and discussion

3.1. Preparation of Ni-Ni(OH)₂ synergistic cocatalyst

The CdS nanorods served as photosensitizer and support. Ni(CH₃COO)₂, isopropanol and triethanolamine were used as nickel source, sacrificial agent and complexing agent respectively. After 30 min of irradiation under simulated sunlight, the Ni-Ni(OH)₂ was successfully prepared and deposited on CdS nanorods. The Ni 2p XPS spectra were used to detect the surface states and local electronic structures of the Ni species. When the methanol or ethanol was used as sacrificial agent, the peak at 856.3 eV in Fig. S1a and b corresponded to the reported values of Ni(OH)₂ [23]. In the case of isopropanol as the donor (Fig. S1c, d), there was an additional peak at 852.7 eV, confirming the formation of metallic Ni₀ [23]. Furthermore, in isopropanol aqueous solution, the obtained Ni deposits showed better dispersion on the CdS (Fig. S2–S4). However, when the concentration of isopropanol increased from 20 vol% to 40 vol %, nickel deposits became larger in size and had some aggregation (Fig. S5). Based on 40 vol% isopropanol as the sacrificial agent, the
addition of triethanolamine can realize the good dispersion of Ni deposits (Fig. S6) and keep its species unchanged (Fig. 1b). Therefore, we can conclude that the appropriate sacrificial agent and complexing agent are critical to the formation of the Ni and Ni(OH)₂ composite.

3.2. Structure and composition of Ni-Ni(OH)₂/CdS

We characterized the Ni-Ni(OH)₂/CdS catalyst prepared on the condition that isopropanol (40 vol%) and triethanolamine (20 vol%) were used as sacrificial agent and complexing agent, respectively. This catalyst didn’t show any obvious shift compared with the peaks of pristine CdS (Fig. S7), perhaps because of the low content (4.30 wt%, Table S1) and good dispersion of the Ni deposits. Besides, we used XPS spectra to determine the chemical states of the catalysts. The XPS survey spectrum showed the Ni-Ni(OH)₂/CdS was composed of four elements: Cd, S, O and Ni (Fig. 1a). In the Ni 2p spectrum (Fig. 1b), the peak at 852.7 eV was ascribed to metallic nickel, and the two peaks at 856.2 and 862.1 eV corresponded to Ni(OH)₂.[23] Therefore, the nickel deposits contain both metallic nickel and nickel hydroxide. Fig. 1c and Fig. 1d showed the Cd 3d XPS spectrum and S 2p XPS spectrum, respectively. The results indicated the successful synthesis of CdS.[24] Compared to pure CdS, the peaks of Cd 3d and S 2p shifted towards higher binding

Fig. 2. (a) TEM, (b) HRTEM images and (c) TEM/EDX result of Ni-Ni(OH)₂/CdS. EDX-Mapping images (d) for Cd, S and Ni in Ni-Ni(OH)₂/CdS.

Fig. 3. Photocatalytic hydrogen evolution under visible light (a) and sunlight irradiation (b) in 0.75 M Na₂S and 1.05 M Na₂SO₃ solution. Time course of H₂ production on Ni-Ni(OH)₂/CdS photocatalyst under simulate sunlight (c) and solar irradiation (d) in 50 mL of glycerol (40 vol%) aqueous solution.
energy after the Ni-Ni(OH)\textsubscript{2} deposition (Fig. 1c,d). The results may be due to the interfacial interactions between CdS and Ni deposits result in lower electron density. According to the XPS analysis, we can draw the conclusion that the as-prepared catalyst is composed of Ni, Ni(OH)\textsubscript{2} and CdS.

The surface morphology of the catalysts were illustrated in SEM and TEM images. CdS showed an obvious one-dimensional nanorod structure (Fig. S8a). After the deposition of Ni species, there were about 10 nm of tiny nanoparticles on the CdS NRs (Fig. 2a, S6 and S8b). Besides, HRTEM was used to analyse the structure of the catalysts in more detail. The lattice spacing of 0.31 nm was ascribed to the (101) plane of hexagonal CdS,\textsuperscript{[24]} and those of 0.21 nm and 0.27 nm corresponded to the (0001) plane of Ni(OH)\textsubscript{2} (Fig. 2b) \textsuperscript{[25]}. TEM/EDX and EDX-Mapping images further confirmed the homogeneous distribution of Cd, S, Ni and O elements (Fig. 2c,d). All these results further demonstrated that Ni and Ni(OH)\textsubscript{2} were successfully deposited on the CdS NRs by photochemical method.

### 3.3. Photocatalytic performance

First of all, we investigated the effects of sacrificial agents (alcohols) on hydrogen production activity of the photocatalysts obtained under the same volume fraction of the donors (20 vol\%) and duration of the illumination (30 min). The available data (Fig. S9a) of the photocatalysts (in the order of increasing H\textsubscript{2} evolution rate) showed as follows: 20 vol\% methanol (182 mmol g\textsuperscript{-1} h\textsuperscript{-1}) < 20 vol\% ethanol (257 mmol g\textsuperscript{-1} h\textsuperscript{-1}) < 20 vol\% isopropanol (318 mmol g\textsuperscript{-1} h\textsuperscript{-1}). Beyond this, the H\textsubscript{2} evolution rate increased with the increasing isopropanol concentration and reached the peak value (367 mmol g\textsuperscript{-1} h\textsuperscript{-1}) at 40 vol\% (Fig. S9b). When the isopropanol concentration was over 40 vol\%, the H\textsubscript{2} evolution activity showed a downward trend. Finally, on the premise of using 40 vol\% isopropanol as a sacrificial agent, we also studied the effect of complexing agents (triethanolamine) on the hydrogen evolution performance of the catalysts. When the concentration of triethanolamine was 20 vol\%, the performance of the catalyst (Ni-Ni(OH)\textsubscript{2}/CdS) achieved optimization (428 mmol g\textsuperscript{-1} h\textsuperscript{-1}) (Fig. S9c), which was 18 times that obtained on the native CdS sample (Fig. S10). Besides, a large number of studies have shown platinum is a highly efficient hydrogen production cocatalyst. Therefore, we prepared 4.4 wt\% Pt/CdS NRs by photochemical deposition method and contrasted its activity (154 mmol g\textsuperscript{-1} h\textsuperscript{-1}) with Ni-Ni(OH)\textsubscript{2}/CdS NRs (4.3 wt\% Ni loading) (Fig. S11), further illustrating that Ni and Ni(OH)\textsubscript{2} are excellent cocatalysts for HER.

Both remarkable catalytic activity and excellent stability are also indispensable to robust photocatalytic system. As a result, we evaluated the stability of the Ni-Ni(OH)\textsubscript{2}/CdS by a long time hydrogen production experiment. After 24 h, the H\textsubscript{2} evolution rate showed no significant decrease under visible light in 0.75 M Na\textsubscript{2}SO\textsubscript{4}/1.05 M Na\textsubscript{2}SO\textsubscript{4} (Fig. 3a). Furthermore, Ni-Ni(OH)\textsubscript{2}/CdS photocatalyst produced more than 800 mmol H\textsubscript{2} after 6 h of solar radiation (Fig. S12 and 3b). On the other hand, we investigated the photocatalytic HER performance of the Ni-Ni(OH)\textsubscript{2}/CdS in 40 vol\% glycerol aqueous solution. As illustrated in Fig. 3c, the Ni-Ni(OH)\textsubscript{2}/CdS exhibited steady H\textsubscript{2} production rate (13 mmol g\textsuperscript{-1} h\textsuperscript{-1}) during 12 h under simulated sunlight (Fig. S13). The H\textsubscript{2} evolution reached 53 mmol g\textsuperscript{-1} from glycerol and water by the Ni-Ni(OH)\textsubscript{2}/CdS after sunlight irradiation for 6 h (Fig. 3d). Therefore, such ternary heterostructure has an encouraging prospect for efficient and stable HER under sunlight.

### 3.4. Proposed photocatalytic mechanism

The UV–vis spectra were used to study the light-absorption properties of the catalysts (Fig. 4a). The CdS and Ni-Ni(OH)\textsubscript{2}/CdS had the same absorption edge, indicating that CdS still maintained its original structure after being loaded with nickel species. However, the absorption intensity (500–800 nm) of the composite photocatalyst was obviously enhanced relative to pure CdS. The HER activities of the Ni-Ni(OH)\textsubscript{2}/CdS under single wavelength light were consistent with absorption spectrum of CdS, not that of Ni-Ni(OH)\textsubscript{2}/CdS NRs (Fig. 4a).
Therefore, we can conclude that the enhanced visible absorption was not contributing positively to the increased activity, and the Ni and Ni(OH)\textsubscript{2} performed the role of cocatalyst in this photocatalytic system.

To explore the crucial roles of Ni and Ni(OH)\textsubscript{2} cocatalysts in determining the excellent performance of the hybrid photocatalyst, a range of characterizations were recorded to study the photoinduced interfacial charge dynamics. First, photoluminescence (PL) spectra were performed at 405 nm light excitation (Fig. 4b). After modification of Ni-Ni(OH)\textsubscript{2}, the PL emission intensity of CdS dropped significantly, indicating that the photogenerated carriers recombination was obviously inhibited by Ni and Ni(OH)\textsubscript{2} cocatalysts. Time-resolved fluorescence (TRPL) spectra were performed and the decay times were obtained by exponential fitting of the decay curves. The average radiative lifetime for Ni-Ni(OH)\textsubscript{2} was 0.67 ns, which was much shorter than that of pure CdS (7.17 ns) (Fig. 4c and Table S3). Besides, SPV spectra showed that Ni-Ni(OH)\textsubscript{2}/CdS presented markedly increased signal in the range of 300–520 nm compared to CdS (Fig. 4d). Finally, Fig. 5 shows that Ni-Ni(OH)\textsubscript{2} can improve the photocurrent and reduce the electrochemical impedance of CdS. These results illustrated Ni and Ni(OH)\textsubscript{2} were effective cocatalysts for the rapid charge transfer.

Based on the above results and discussion, the photocatalytic HER mechanism of Ni-Ni(OH)\textsubscript{2}/CdS was put forward (Fig. 6). Under illumination, CdS was excited to produce electron-hole pairs, and electrons transited to conduction band (CB) from valence band (VB). The CB position (-0.7 V) of CdS is lower than the reduction potential of Ni\textsuperscript{2+} (-0.23 V).[26,27] Therefore, Ni(OH)\textsubscript{2} was partially transformed to metallic Ni, and inherent and converted Ni\textsuperscript{2+} served as reduction cocatalyst to boost electrons transportation.[28,29] Although Ni(OH)\textsubscript{2} with poor conductivity has almost no ability to accept electrons,[30] it can boost the dissociation of H\textsubscript{2}O into H\textsuperscript{+}.[31,32] Consequently, Ni(OH)\textsubscript{2} and Ni jointly promote the photocatalytic HER activity of CdS.

### 4. Conclusions

The Ni-Ni(OH)\textsubscript{2}/CdS was prepared by photodeposition using isopropanol and triethanolamine as sacrificial agent and complexing agent, respectively. Under visible light and nature sunlight, the Ni-Ni(OH)\textsubscript{2}/CdS performed outstanding activity and stability for HER in Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{4} solution. Furthermore, the photocatalytic system can be used for efficient conversion of glycerol to H\textsubscript{2} in the sunlight. The synergistic effect of metallic nickel and nickel hydroxide was contributed to the extraordinary performance of the Ni-Ni(OH)\textsubscript{2}/CdS.

### CRediT Authorship Contribution Statement


### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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### References


