Artificial Photosynthesis

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Hydrogen Production on a Hybrid Photocatalytic System Composed of Ultrathin CdS Nanosheets and a Molecular Nickel Complex

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Abstract: The production of clean and renewable hydrogen through water splitting by using solar energy has received much attention due to the increasing global energy demand. We report an economic and artificial photosynthetic system free of noble metals, consisting of ultrathin CdS nanosheets as a photosensitizer and nickelbased complex as a molecular catalyst. Emission quenching and flash photolysis studies reveal that this hybrid system allows for effective electron transfer from the excited CdS nanosheets to the nickel-based complex to generate reduced intermediate species for efficient hydrogen evolution. Notably, the unique morphological and structural features of the ultrathin CdS nanosheets contribute to the highly efficient photocatalytic performance. As a consequence, the resulting system shows exceptional activity and stability for photocatalytic hydrogen evolution in aqueous solution with a turnover number (TON) of about 28000 versus catalyst and a lifetime of over 90 h under visible light irradiation.

Solar-driven production of hydrogen (H₂) from water by using earth-abundant materials is considered as one of the promising means to provide clean fuels in a postfossil age.^[1,2] Inspired by natural photocatalysis, many attempts have been made in mimicking the basic principles of nature's masterpiece and designing artificial photosynthetic systems for H₂ generation.^[3–5] In this context, recent studies on various homogeneous artificial photosynthetic systems have shown high activity.^[6] However, most of these homogeneous systems typically suffer from short lifetimes, mainly because of decomposition of photosensitizer molecules.^[7] Thus, the search for robust H₂-evolving

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photocatalytic systems with both high activity and long-term stability still remains a significant challenge.

In comparison with traditional organic or organometallic photosensitizers, colloidal semiconductor nanocrystals are more promising light-harvesting materials because of their broad spectral absorption and good photostability.^[4,8] Among them, two-dimensional (2D) semiconductor nanosheets (NSs) with ultrathin thickness have sparked intense interest because of their novel electronic structures, distinctive physicochemical properties, and high specific surface areas, as compared with conventional nanocrystallites and bulk materials.^[9-11] These semiconductor materials possess tunable absorption spectra and high molar absorptivity, and thus they can continuously absorb multiple photons even after electrons or holes are accumulated on the semiconductors. These attractive characteristics render them excellent candidates to fulfil multiple functionalities required in artificial photosynthetic systems as photosensitizers, charge accumulation sites, and electron donors when coupled with redox catalysts for H₂ generation. Despite fundamental progress made in the development of heterogenization of molecular catalysts on the surfaces of semiconductors with various morphologies,^[8,12-26] such as nanoparticles (NPs),^[12] nanorods,^[13-15] nanowires,^[16] and quantum dots $(QDs)_{r}^{[8,17-22]}$ the solar-driven production of H₂ from artificial photocatalytic systems, composed of ultrathin semiconductor NSs and molecular catalysts, is still in its infancy.

Herein, we employed ultrathin 2D CdS NSs with a thickness of about 4 nm, stabilized by L-cysteine (L-Cys-CdS NSs), as a photosensitizer, Ni-based complex (Ni complex 1) as a molecular catalyst, and triethylamine (TEA) as the sacrificial electron donor, and developed a robust and efficient photocatalytic system for H₂ evolution from aqueous solution at room temperature. Under optimal conditions, this hybrid photocatalytic system generates a turnover number (TON) of over 28000 for H₂ (with respect to the catalyst) with a lifetime of over 90 h under visible light irradiation ($\lambda > 420$ nm). Notably, the unique morphological and structural features of the L-Cys-CdS NSs with ultrathin thickness contribute to the high photocatalytic activity and long-term stability.

The L-Cys-CdS NSs were prepared according to the previously reported procedures^[27] and used directly (see Experimental Section and Figure S1 in the Supporting Information). The L-Cys-CdS NSs were selected as the photosensitizer, owing to their broad visible absorption ability, aqueous dispersion, simple preparation, suitable conduction band (CB) potential for proton reduction, and economical advantage over noble-

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Scheme 1. Schematic illustration of the photocatalytic process for H_2 evolution in the artificial photocatalytic system comprising L-Cys-CdS ultrathin NSs as the photosensitizer and Ni complexes as the molecular catalyst.

metal-based photosensitizers. The Ni complexes 1–4 were synthesized by the reaction of NiCl₂- $6H_2O$ with various ligands (Scheme 1 and Experimental Section in the Supporting Information). The solid-state molecular structure of Ni complexes 1, 2, and 3 was determined by single-crystal X-ray crystallography (Figure S2 and Table S1–S3 in the Supporting Information). Ni complex 4 was identified through the MALDI-TOF mass spectrometry (Figure S3 in the Supporting Information). We first selected Ni complex 1 as the model molecular catalyst to couple with L-Cys-CdS NSs for the photocatalytic H₂ production. Of particular interest is that the as-obtained Ni complex 1 has a good solubility in alkaline aqueous solution, making it possible for the construction of artificial photocatalytic system that can operate in aqueous solution.

The photocatalytic H₂ evolution experiments were carried out in an aqueous ethanol solution (EtOH/H₂O of 1:1, v/v)) in the presence of Ni complex **1** (3.25×10^{-5} M), L-Cys-CdS NSs (0.045 mg mL⁻¹), and TEA (4.7%, v/v) under visible light irradiation ($\lambda > 420$ nm) at room temperature. The generated H₂ was characterized by means of online gas chromatography (GC, Agilent 7890A) with methane as the internal standard. Control experiments indicated that L-Cys-CdS NSs, Ni complex **1**, and TEA are all essential for efficient H₂ production. The absence of any of the three components results in no significant H₂ generation (Figure S4 in the Supporting Information).

The activity of light-driven H₂ production was found to depend on the pH value of the solution, the concentration of the photosensitizer (L-Cys-CdS NSs), and the sacrificial electron donor (TEA). As shown in Figure 1 a, a maximal rate for H₂ generation was achieved at pH 12.5, while lower amounts of H₂ were observed at both lower and higher pH values. The decrease in H₂-evolving activity at higher pH value is probably a result of the lower proton concentration in solution.^[28,29] Simultaneously, H₂ generation would become thermodynamically unfavorable with increasing pH values.^[28] In contrast, lowering the pH value also leads to a slower H₂ evolution rate, which may be due to the fact that the protonation of TEA weakens its ability to function as an electron donor, and the decomposition of TEA⁺ becomes less facile under such conditions.^[5, 28] Moreover, the solubility of Ni complex 1 in aqueous solution is poor at lower pH values, which is unfavorable for the contact between the photosensitizer and the molecular catalyst. The concentration of L-Cys-CdS NSs also affects the activity of H₂ production. At a fixed concentration of Ni complex 1 and TEA at pH 12.5, the optimal concentration of photosensitizer was found to be 0.045 mg mL⁻¹. As shown in Figure 1 b, the H₂-evolving rate was improved by increasing the concentration of L-Cys-CdS NSs from 0.011 to 0.045 mg mL⁻¹. When the concentration of L-Cys-CdS NSs was increased to 0.056 mg mL⁻¹, no clear increase in H₂ production can be observed. However, increasing the concentration of L-Cys-CdS NSs to 0.18 mg mL⁻¹ re-

sulted in a lower rate of H₂ evolution. Aggregation of CdS photosensitizer can be clearly observed after only 5 h of irradiation (results not shown here). The results may be attributed to the light-filter effect at a high concentration of photosensitizer, as reported in other hybrid photocatalytic systems.^[18] Moreover, the concentration of TEA also has an influence on the rate of H₂ production, with an optimal concentration of 4.7% (v/v; Figure S5 in the Supporting Information). In the presence of L-Cys-CdS NSs, Ni complex 1, and TEA, photocatalytic H₂ production can also be implemented in pure water under the same irradiation conditions. However, the rate of H₂ evolution is much lower than in EtOH/H₂O (1:1, v/v), which is probably due to the poor solubility of TEA in pure water (Figure S6 and S7 in the Supporting Information).

We found the morphology of CdS-based photosensitizer was also an important factor that governs the activity of photocatalytic H₂ evolution. Figure 2a shows the photocatalytic activities on various CdS-based photosensitizers. The morphologies of CdS-DETA hybrid NSs, CdS-NS-based aggregates, L-Cys-CdS QDs, as well as CdS NPs were shown in Figure S8 (see the Supporting Information). It was found that L-Cys-CdS NSs exhibited the highest activity compared with other CdS-based photosensitizers (Figure 2a), indicating that shape effects on the H₂ evolution activities exist in this hybrid photocatalytic system. We hypothesize that the catalytic system functions through light absorption by the CdS photosensitizer, subse-

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and TEA (4.7%, v/v).



L-Cys-CdS NSs concentration / mg mL⁻¹ Figure 1. a) Photocatalytic H₂ production in EtOH/H₂O (1:1, v/v) solution at different pH values containing Ni complex 1 (3.25×10^{-5} M), L-Cys-CdS NSs (0.045 mg mL⁻¹), and TEA (4.7%, v/v). b) Photocatalytic H₂ production at initial pH 12.5 in EtOH/H₂O (1:1, v/v) solution as a function of concentration of

the L-Cys-CdS NSs photosensitizer containing Ni complex 1 (3.25×10^{-5} M)

quent electron transfer from CdS to the molecular catalyst, and proton reduction by the molecular catalyst. The exceptional enhancement in the system comprising L-Cys-CdS NSs may be attributed to their unique morphological and structural features. Firstly, L-Cys-CdS NSs could offer a high specific surface area and large fraction of uncoordinated surface atoms for harvesting more photons and absorbing the catalyst molecules. $^{[27, 30, 31]}$ Secondly, the band gap of these L-Cys-CdS NSs is larger than that of other CdS-based photosensitizers because of the quantum size effect (Figure S9 and S10, and Table S4 in the Supporting Information), which may lead to a larger shift of the CB and the increase in reducing power for proton reduction. Additionally, the ultrathin thickness shortens the transfer distance and facilitates fast transfer of the photogenerated charge carriers on the surface of the photosensitizer.^[30,31]

Considering all above experimental trials, we carried out the photocatalytic reaction under the optimized condition, that is, EtOH/H2O solution (1:1, v/v, 42 mL) containing Ni complex **1** $(3.25 \times 10^{-5} \text{ m})$, L-Cys-CdS NSs $(0.045 \text{ mg mL}^{-1})$, and TEA (4.7%, v/v) at pH 12.5. The system continuously produces H₂ at a relatively constant rate for over 90 h, as shown in Figure 2b. A TON (based on Ni complex 1) of about 28000 is achieved and the initial TOF is determined to be about 311 h⁻¹. Both the photocatalytic activity and stability are remarkably superior to those of the homogeneous catalytic system containing fluorescein as the photosensitizer (Figure S11 in the Supporting InforCHEMISTRY

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Figure 2. a) Photocatalytic H₂ production at pH 12.5 in the presence of various photosensitizers (A-E) in mixed EtOH-H₂O (1:1, v/v) solution containing Ni complex 1 $(3.25 \times 10^{-5} \text{ m})$, photosensitizer (0.045 mg mL⁻¹), and TEA (4.7%, v/v): A: CdS NPs; B: L-Cys CdS QDs; C: CdS-DETA hybrid NSs; D: CdS NS-based aggregates; E: L-Cys-CdS NSs. b) Photocatalytic H₂ evolution under the optimized conditions containing Ni complex 1 (3.25×10^{-5} M), L-Cys-CdS NSs (0.045 mg mL⁻¹) and TEA (4.7%, v/v) in EtOH/H₂O (1:1, v/v) at pH 12.5. The inset is the comparison of the H₂ evolution activities in the presence of the same concentration of Ni complex 1 and Ni²⁺.

mation). As shown in the inset of Figure 2b, when the same concentration of Ni²⁺ ions were added into the reaction solution to replace the Ni complex 1, the photocatalytic activity of Ni²⁺ ions was fairly lower than the Ni complex 1 catalyst. The results further indicated that the high photocatalytic H₂-evolution activity of Ni complex 1 can be only attributed to the efficient electron transfer form L-Cys-CdS NSs to Ni complex 1, in which the proton is reduced to H₂. The quantum efficiency (QE) of this photocatalytic system for H_2 production is 11.5%, which was obtained under optimized conditions at 420 nm. The re-addition of Ni complex 1 restarted H₂ production, while the re-adding of CdS or TEA could not regenerate H₂ under irradiation (Figure S12 in the Supporting Information). These results indicate that the deactivation of the system is mainly due to the decomposition of the Ni complex 1 and that the CdS photosensitizer is still active. After over 100 h of irradiation, the CdS photosensitizer was separated from the solution by centrifugation and washed several times. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis results suggested that the sheet-like morphology can be retained and no Ni signals can be detected in the EDX spectrum (Figure S13 in the Supporting Information). The unusual longevity may be attributed to the use of semiconductor as the photosensitizer, as reported in some other hybrid photosynthetic systems.^[8] When other Ni complexes with similar structures to 1 are employed as molecular catalysts, such as Ni complex 2, 3, and 4, high photocatalytic activity for H₂ evolution can be also obtained (Scheme 1 and Figure S14 and S15

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in the Supporting Information), demonstrating the general applicability of this hybrid photocatalytic system for H_2 production.

The photophysical properties of this artificial photocatalytic system were further investigated to understand the reaction mechanism. Steady-state photoluminescence (PL) spectra were measured to explore the charge transfer pathways in this hybrid photocatalytic system. As shown in Figure 3 a, the emission spectrum of L-Cys-CdS NSs shows a strong excitonic emission peak centered at around 430 nm in the EtOH/H₂O (1:1, v/v) solution. With the addition of Ni complex 1 into the L-Cys-CdS NSs solution, the intensity of this excitonic emission band immediately showed a significant decrease. In view of the small spectroscopic overlap of absorption of Ni complex 1 and the emission of L-Cys-CdS NSs (Figure 3a), the energy transfer between excited L-Cys-CdS NSs to Ni complex 1 would be negligible if it occurs, so the emission quenching may be attributed to the photoinduced electron transfer from L-Cys-CdS NSs to Ni complex 1. When the same concentration of Ni complex 1 was added into EtOH/H₂O (1:1, v/v) solution of other CdSbased photosensitizers, the emission was also quenched. However, the quenching efficiency for other CdS-based photosensitizers is lower than that for L-Cys-CdS NSs (Figure S16 in the Supporting Information). The direction of charge transfer between L-Cys-CdS NSs and Ni complex 1 can be further predicted according to the energy band structure of CdS and the redox potential of Ni complex 1. We measured the energy of the CB of our L-Cys-CdS NSs by photoreduction of the redox-



Figure 3. a) UV-vis absorption spectrum of Ni complex 1 (left) in EtOH/ H₂O (1:1, v/v) and emission spectra of the L-Cys-CdS NSs at pH 12.5 in the absence (curve 1) and presence of Ni complex 1 (curve 2) or Ni complex 1 + TEA (curve 3), excited at 380 nm. b) Transient absorption spectrum of Ni complex 1 and L-Cys-CdS NSs in EtOH/H₂O (1:1, v/v) at pH 12.5 upon laserpulsing (wavelength 355 nm). The inset of b) is the kinetic decay monitored at 370 nm.

active dye methyl viologen (MV²⁺) and obtained an approximate value of -0.77 V (vs. NHE, pH 7; Figure S17 in the Supporting Information). The reductive potential of -0.53 V (vs. NHE) of the Ni complex 1 was taken from cyclic voltammograms (Figure S18 and Table S5 in the Supporting Information). The results implied that the electron transfer from excited L-Cys-CdS NSs to Ni complex 1 is thermodynamically favorable (Figure S19 in the Supporting Information). Moreover, when the electron donor TEA was added together with Ni complex 1, the PL intensity of L-Cys-CdS NSs further dropped, indicating that the presence of TEA can consume the photogenerated holes on excited L-Cys-CdS NSs. The electron transfer from L-Cys-CdS NSs to complex 2, 3, or 4 is also thermodynamically favourable. There is no significant change in the potentials for the Ni^{II}/Ni^I couple among Ni complexes 1–4 (Figure S18, S20 and Table S5 in the Supporting Information). Interestingly, however, these four complexes, 1-4, exhibit different activities for H₂ production. Ni complex 4 clearly shows lower PL quenching efficiency for L-Cys-CdS NNs and smaller H₂-generating rate than other three complexes, which may be attributed to its poor solubility in this photocatalytic system (Figure S15 and S21 in the Supporting Information).

A flash photolysis study was carried out to further verify the photoinduced electron-transfer process. On laser excitation of the L-Cys-CdS NSs with light of 355 nm wavelength, no characteristic absorption signal could be detected (Figure S22 in the Supporting Information). In contrast, when Ni complex **1** was introduced, a strong absorption at around 370 nm and a broad absorption at the range of 510~600 nm emerged immediately with a lifetime of ~62 ns at 370 nm (Figure 3b). Although it is difficult to determine its structure, it is reasonable to speculate that a Ni¹ intermediate species is generated through the reduction of Ni complex **1**, as many other Ni complexes reported in the literatures.^[32-34]

In light of the above experimental observation and spectroscopic analysis, we can propose a plausible mechanism for the efficient photocatalytic H₂ generation. As shown in Scheme 1, the photoexcited electron in the CB of L-Cys-CdS NSs transfers to the Ni complex 1, leading to the formation of a reactive reduced Ni¹ center, which would play a critical role in subsequent electron transfer to a proton to be involved in a catalytic cycle for H₂ production. Many other Ni¹ species have also been proposed as important intermediates in photocatalytic H₂ production by other Ni-based complexes.^[23, 32-34] The photogenerated hole remaining in the L-Cys-CdS NSs after light irradiation is subsequently coupled with electrons transferred from the sacrificial electron donor TEA, thus suppressing the recombination of photogenerated charge carries and allowing the forward reactions. Further studies are needed to describe the mechanism in full detail for the catalytic processes and to investigate the exceptional stability of this complex catalyst in such reaction conditions.

In summary, a robust, inexpensive, and highly efficient heterogeneous photocatalytic system, comprising \bot -Cys-CdS NSs with a thickness of ~4 nm as the photosensitizer and a Nibased complex (Ni complex 1) as the molecular catalyst, has been achieved for H₂ production in aqueous solution. Under

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optimal conditions, this noble-metal-free system can function for over 90 h and is capable of producing H₂ with a TON of ~28000 under visible light irradiation (λ > 420 nm) at room temperature. We demonstrated the shape of CdS photosensitizer had a great influence on the activity of H₂ evolution in this heterogeneous environment. The exceptional robustness of ultrathin L-Cys-CdS NSs demonstrated a promising candidate for photosensitizers in the design of heterogeneous artificial photosynthetic systems. Importantly, the understanding of shape effects of semiconductor photosensitizers on H₂ production activity in hybrid artificial photosynthetic systems may lead to better design and preparation of semiconductor materials, which could result in improved performance for enhanced solar energy conversion applications.[35,36]

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COMMUNICATION

Artificial Photosynthesis

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Hydrogen Production on a Hybrid Photocatalytic System Composed of Ultrathin CdS Nanosheets and a Molecular Nickel Complex



Hydrogen evolution: A robust, efficient, and stable heterogeneous photosynthetic system comprising 2D CdS nanosheets as photosensitizers and Ni complex 1 (see scheme; TON = turnovernumber, TEA = triethylamine) as a molecular catalyst has been successfully constructed for H₂ production form aqueous solution under visible light irradiation. The results pave a new route to design artificial photosynthetic systems for solar energy conversion applications.

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