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Integration of an aminopyridine derived cobalt based homogenous cocatalyst with a composite photocatalyst to promote H₂ evolution from water[†]

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Inexpensive cocatalysts are promising materials to improve the performance of photocatalytic systems. However, a cocatalyst can be anchored onto a photosensitizer in certain amount and further loading can hinder the visible light by blocking the active sites of the photosensitizer. Herein, we introduce the utilization of a cobalt based homogenous cocatalyst with composite photocatalyst CdS/Ni₃C. The homogenous cocatalyst did not occupy the physical space on the photosensitizer and the performance of CdS/Ni₃C was significantly enhanced from 263 μ mol h⁻¹ to 750 μ mol h⁻¹. The present study showed that homogenous cocatalysts paved a way to further capture the electrons from photoexcited composite photocatalysts and have great potential to enhance the photocatalytic performance for low cost H₂ evolution under visible light.

Water splitting using solar energy has been considered as one of the best strategies to overcome the global energy and environmental crises since 1972.^{1,2} H₂ can replace the non-renewable fossil fuels owing to its several advantages such as straightforward synthesis pathway, benign burning products and superior chemical energy.^{3–5} Semiconductor photosensitizers have become prominent candidates for photocatalytic systems due to their high catalytic activity and excellent durability under catalytic conditions.^{6,7} Among them, TiO₂ and CdS have been studied broadly because of their excellent catalytic abilities for H₂ production.^{8–11} Contrary to TiO₂, the advantage of visible light activity of CdS made it the apple of researcher's eye. Unfortunately, CdS suffers from photocorrosion with the passage of time and the H₂ production yield decreases gradually under irradiation.^{12,13}

Several strategies have been adopted to overcome these rudimentary issues of CdS, such as doping, ligand attachment, anchoring a cocatalyst and integration of another suitable semiconductor.^{14,15} In the past few years, it has been well demonstrated that cocatalysts can efficiently suppress the charge recombination and photocorrosion of CdS by accepting photogenerated electrons.^{16,17} However, state of the art photocatalytic systems are based on noble metal cocatalysts, which suppress their industrial applications.^{20,21} Recently, numerous inexpensive and earth-abundant cocatalysts have been thoroughly studied such as metal sulfides, selenides, nitrides, oxides and carbides. However, a single cocatalyst on a photosensitizer cannot hamper the charge recombination sufficiently. Particularly, an anchored cocatalyst can boost H₂ production up to a certain loading amount. Further loading of the cocatalyst may result in decreased H₂ evolution due to the shielding of visible light and blocking the active sites of the photosensitizer.^{18,19} Therefore, it is highly demanding to utilize some additional strategies to further capture the photogenerated electrons from photosensitizers to sufficiently suppress charge recombination.20,21

Homogeneous cocatalysts proved themselves as highly efficient electron capturing species in homogenous photocatalytic reactions.^{22,23} The utilization of molecular cocatalysts in composite photocatalytic systems can be a promising strategy to further capture photogenerated electrons from photosensitizers. In the past decades, several homogenous cocatalysts based on particular ligands such as salen, porphyrin and phthalocyanine have been reported to exhibit excellent photocatalytic activities. However, less

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Paper

Herein, we report a highly efficient photocatalytic system consisting of an aminopyridine derived Co-complex as a homogenous cocatalyst integrated with a composite photocatalyst to boost its H_2 evolution activity from water under visible light. CdS/Ni₃C NR composites were chosen for this study as Ni₃C has been reported to be a promising alternative to noble-metal cocatalysts.^{24,25} The photocatalytic performance of CdS was enhanced to 263 µmol h⁻¹ on the usage of Ni₃C as a cocatalyst and further boosted remarkably on integration with a Co-molecular cocatalyst. The highest rate of 750 µmol h⁻¹ was achieved under optimal conditions and the system demonstrated robust stability of 80 hours. The maximum apparent quantum yield of 53.2% was obtained using monochromatic 420 nm light.

Results and discussion

The as-synthesized photocatalysts were utilized for the investigation of photocatalytic H₂ evolution performances under visible light ($\lambda > 420$ nm). The real amount of nickel in each sample was investigated by ICP-AES and is given in Table S1 (ESI[†]). Fig. 1a shows the comparison of photocatalytic outcomes of pristine CdS and samples NC1-NC5. The reaction mixtures were prepared using 1 mg photocatalyst, 1.05 M Na₂SO₃ and 0.75 M Na2S in 20 mL Millipore water. The results demonstrate a relatively poor H₂ production rate of 27 μ mol h⁻¹ mg⁻¹ for pure CdS NRs. This deficient performance of CdS NRs may be due to the fast recombination of photogenerated electron-hole pairs. Loading of Ni₃C on CdS NRs enhances the H₂ production rate to 63μ mol h⁻¹ and it further improves with the increasing content of Ni₃C. The highest H₂ evolution rate of 182 μ mol h⁻¹ was detected for NC3 suggesting the optimum amount of Ni₃C on CdS NRs. After this, a decrease in H₂ production rate was observed for samples NC4 and NC5. This phenomenon proves that loading of an optimum amount of cocatalyst to semiconductor photocatalysts is critical for enhanced photocatalytic activity.26,27

Initially, Ni₃C offers catalytic active sites to CdS NRs for the transfer of photogenerated electrons, which suppress the rapid recombination of photogenerated charges. The photo-induced electron transfer enhances with the increased content of Ni₃C on CdS NRs, and therefore enhances the H₂ production rate. Further loading of Ni₃C than the optimal amount hinders the active sites of CdS NRs and inhibits the visible light absorption. Ultimately, a decrease in the photogenerated electrons is observed, which leads to a decreased rate of H₂ evolution.^{18,28} Moreover, pure Ni₃C did not show H₂ evolution rate than CdS/Ni₃C NR samples exhibited higher H₂ evolution rate than CdS NRs proving that Ni₃C alone cannot produce H₂ but it plays a crucial role to enhance the photocatalytic activity of CdS NRs as cocatalyst.

The concentration of the sacrificial reagent critically affects the rate of H_2 evolution in a photocatalytic system.^{29,30} Fig. 1b shows the effect of concentration of Na₂S and Na₂SO₃ on the



Fig. 1 (a) Photocatalytic H₂ activities of CdS/Ni₃C NR samples and pure CdS NRs. Photocatalytic samples contained 1.0 mg photocatalyst, 0.75 M Na₂S and 1.05 M Na₂SO₃ in 20 mL Millipore water. (b) Effect of concentration of electron donors: (A) 0.5 M Na₂S, 0.7 M Na₂SO₃; (B) 0.75 M Na₂S, 1.05 M Na₂SO₃; (C) 1.0 M Na₂S, 1.40 M Na₂SO₃; (D) 1.25 M Na₂S, 1.75 M Na₂SO₃; (E) 1.5 M Na₂S, 2.1 M Na₂SO₃. (c) H₂ evolution profiles of 0.01 mM cocatalysts **PX1**, **PX2**, Co₂₊ and ligand of **PX1** on 1 mg NC3 using 1.0 M Na₂S and 1.40 M Na₂SO₃ as sacrificial reagents in 20 mL Millipore water. (d) Molecular structures of cobalt-based homogenous cocatalysts.

photocatalytic H₂ production rate of NC3. The concentration ratio of Na₂S and Na₂SO₃ was kept constant at 5:7. At the low concentration of 0.5 M Na₂S and 0.7 M Na₂SO₃, the H₂ evolution rate was 145 µmol h⁻¹. An enhancement was observed with the increased concentration of sacrificial reagents. The optimum concentration was 1.0 M:1.4 M (Na₂S:Na₂SO₃) at which the highest H₂ evolution rate of 263 µmol h⁻¹ was observed. Further increase in concentration showed a decrease in the rate of H₂ evolution. Initially, the increased amount of sacrificial reagents enhances the H₂ evolution by reducing the increased number of photogenerated holes. As the concentration of sacrificial reagents further increases, the solution becomes over saturated and solid particles can shield the visible light, which leads to a decrease in the H₂ production rate.³⁰

Furthermore, the effect of molecular cocatalysts on the H₂ evolution rate of the current photocatalytic system was thoroughly studied (Fig. 1c). Molecular cocatalysts PX1 and PX2 (Fig. 1d) show increased H₂ evolution rate than the composite photocatalyst. The highest H₂ production rate of 554 μ mol h⁻¹ was obtained for PX1 probably due to its higher solubility in water as compared to PX2. The enhanced solubility of a molecular cocatalyst enables it to interact more with a photosensitizer, which results in a high electron capturing ability. On the other hand, poor solubility of a molecular cocatalyst results in the formation of aggregates, which leads to low electron transfer processes. Ultimately, the H₂ evolution rate of the photocatalytic system decreases.³⁰ Besides, Co ions were employed as the cocatalyst, which resulted in lower H2 production than PX1, inferring the significant role of the homogenous cocatalyst. On the other hand, the ligand of PX1 did not show enhancement, which means that a ligand without central metal ions is not effective. Moreover, the concentration of the



Fig. 2 (a) Comparison of H₂ evolution rates of different samples. (b) Comparison of inexpensive cocatalysts with 1 wt% Pt on CdS and NC3 (CdS/Ni₃C), respectively. Photocatalytic samples contained 1.0 mg photocatalyst, 1.0 M Na₂S and 1.40 M Na₂SO₃ in 20 mL Millipore water.

molecular cocatalyst has a significant effect on the H₂ evolution rate of the photocatalytic system. Fig. S4 (ESI[†]) shows that with the increase in the concentration of **PX1**, the H₂ evolution rate increases. This result illustrates that a greater number of **PX1** molecules can capture more electrons from NC3 photosensitizer, suppressing the charge recombination effectively. The highest H₂ evolution rate of 750 µmol h⁻¹ was observed for 0.02 mM of **PX1** depicting it as the optimal concentration of the molecular cocatalyst for the current photocatalytic system. Further increase in the concentration of the molecular cocatalyst can shield the visible light, resulting in a decreased H₂ evolution rate.³¹

Fig. 2a shows the comparison of different photocatalytic samples. Ni₃C/PX1 produced no H₂ in the absence of a photosensitizer, suggesting that neither Ni₃C nor **PX1** is visible light active and their role in the current photocatalytic system is merely as cocatalysts. Moreover, CdS integrated with molecular cocatalyst PX1 showed an enhanced H₂ evolution rate of 321μ mol h⁻¹, indicating the efficient charge separation ability of molecular cocatalysts. When CdS was simply mixed with Ni₃C, poor H₂ evolution rate (105 μ mol h⁻¹) than that of CdS/ Ni₃C composite was observed indicating the crucial role of the interfacial contact of CdS and Ni₃C in NC3. Employment of molecular cocatalyst PX1 with NC3 results in the highest H₂ evolution rate of 750 μ mol h⁻¹, which might be due to the synergistic electron capturing effect of Ni₃C and PX1, resulting in the effective suppression of charge recombination. To confirm the efficiencies of current cocatalysts, their performances were compared with that of well-known noble metal cocatalyst, 1 wt% loaded Pt. Fig. 2b depicts the higher H₂ evolution rates of CdS/ Ni₃C and CdS/Ni₃C/PX1 NRs than that of CdS/Pt and CdS/Ni₃C/Pt NRs, respectively. These results prove that Ni₃C and PX1 are highly efficient cocatalysts for CdS under present conditions.

The apparent quantum yields (AQYs) of the photocatalytic reaction system were estimated in 1.0 M Na₂S and 1.4 M Na₂SO₃ aqueous solution under monochromatic visible light (λ = 420 nm). Fig. 3a shows that an average AQY of 47% was obtained during 6 hours of irradiation. The maximum AQY value reached to 53.2%, indicating the efficient catalytic performance of NC3/**PX1** NR photocatalyst for H₂ evolution from water. Furthermore, the stability of the photocatalytic system was evaluated over long-term irradiation (Fig. 2b). The current photocatalytic system showed good stability over 80 hours of visible light irradiation



Fig. 3 (a) Apparent quantum yield of sample NC3/**PX1**. The photocatalytic system contained 1.0 mg photocatalyst, 0.02 mM molecular cocatalyst (**PX1**), 1.0 M Na₂S and 1.4 M Na₂SO₃ in 20 mL Millipore water. (b) Long-term H₂ production using 2.5 mg NC3 as photocatalyst, 0.02 mM molecular cocatalyst (**PX1**), 1.0 M Na₂S and 1.4 M Na₂SO₃ as sacrificial reagents in 50 mL Millipore water under visible light ($\lambda > 420$ nm). (c) The cyclic runs of photocatalytic H₂ evolution. (d) Comparison of photocatalytic H₂ evolution under air and inert atmosphere. Photocatalytic samples contained 1.0 mg NC3 as photocatalyst, 0.02 mM molecular cocatalyst (**PX1**), 1.0 M Na₂S and 1.4 M Na₂SO₃ in 20 mL Millipore water.

 $(\lambda > 420 \text{ nm})$. A total of 50.1 mmol H₂ was produced with the highest rate of 758 µmol h⁻¹ indicating good stability of the current photocatalytic system. The reusability of the photocatalyst was also confirmed by time course analysis of H₂ evolution (Fig. 3c). Four consecutive runs were performed in 1.0 M Na₂S and 1.4 M Na₂SO₃ aqueous solution. The produced H₂ was removed from the flask after each run of 3 hours. No significant decrease was observed during four consecutive runs suggesting the good stability and reusability of the photocatalyst. Fig. 3d shows the photocatalytic activity of NC3/**PX1** NRs in 1.0 M Na₂S and 1.4 M Na₂SO₃ aqueous solution under air and inert atmosphere. The results describe a higher H₂ production rate under inert atmosphere than air. The lower H₂ evolution rate under air can be assigned to the presence of O₂, which may lead the reaction backward and produce H₂O on the catalytic surface.³²

The successful synthesis of photocatalysts and particular role of cocatalysts was thoroughly analyzed using several analytical techniques. Fig. 4a shows the XRD patterns of Ni₃C. It is obvious from the diffraction peaks that the currently synthesized Ni₃C is a hexagonal Ni₃C (JCPDS No. 06-0697). The peaks located at 39.27°, 41.76°, 44.52°, 58.63°, 71.21° and 78.10° can be assigned to (110), (006), (113), (116), (300) and (119) crystal planes, respectively.³³ Pure CdS NRs presented its typical hexagonal structure (JCPDS No. 77-2306).^{31,34} Furthermore, similar structure of CdS NRs was detected in samples NC1–NC5 (Fig. 4b). No distinguished peak of Ni₃C was found in samples NC1-NC3, which may be due to the less content of Ni₃C on CdS NRs or due to the less crystalline nature of Ni3C as compared to CdS. However, a new peak can be seen in sample NC4 at 44.85° corresponding to the (113) face of Ni₃C. Moreover, three additional peaks were observed in sample



Fig. 4 (a) Powder XRD patterns of pristine Ni_3C . (b) Powder XRD patterns of CdS, CdS/Ni_3C samples and Ni_3C (* shows the peak positions of Ni_3C in CdS/Ni_3C samples).

NS5 at 39.49° , 41.85° and 44.85° , which can be attributed to (100), (002) and (101) planes, respectively.

The morphologies of the photocatalysts were studied using SEM and TEM images. Fig. 5a displays the SEM image of pure CdS NRs proving the nanorod morphology with diameters of 40-95 nm and lengths of 0.4-2 µm. On the other hand, the SEM image of NC3 shows a solid mass, which is in well contact with CdS NRs suggesting the presence of Ni₃C (Fig. 5b). Moreover, the TEM image also shows the existence of black mass over CdS NRs further confirming the presence of Ni₃C (Fig. 5c). Fig. S5 (ESI[†]) displays the HRTEM image having lattice fringes of 0.33 nm and 0.20 nm, which can be attributed to 002 and 113 crystal faces of CdS and Ni₃C, respectively.^{19,25} EDX data was collected to confirm the presence of expected elements in the sample. In Fig. 5d, the EDX spectrum of NC3 shows the existence of Ni, C, Cd, S, Au and Cu. Au appeared as it was sprayed on the sample for better conductivity and the signal of Cu was detected due to the Cu grid.

X-ray photoelectron spectroscopy (XPS) was performed to explore the presence and valence state of elemental composition of sample NC3/**PX1**. In Fig. 6a, the XPS survey spectrum showed the presence of Cd, S, Ni, C and Co. The high resolution spectrum of Cd showed two binding energies at 404.5 eV and 411.1 eV corresponding to Cd $3d_{3/2}$ and Cd $3d_{1/2}$ (Fig. 6b).³⁵ In Fig. 6c, two peaks appeared that can be attributed to S $2p_{3/2}$ (160.9 eV) and S $2p_{1/2}$ (162.1 eV). The Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks were observed at 853.2 eV and 870.4 eV, respectively (Fig. 6d).^{36,37} The peak at 284.7 eV can be attributed to C 1s, which is consistent with the previous reports (Fig. 6e).^{38,39} Moreover, no peak of metallic Ni was observed. These outcomes prove the successful formation of pure CdS/Ni₃C NR photocatalysts. Fig. 6f shows the high resolution spectrum of Co 2p having peaks at 780.64 eV and 796.46 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively.³¹

To investigate the stable behavior of the NC3 photocatalyst and molecular role of PX1 during the photocatalytic reaction, XRD patterns, SEM image, EDX and XPS spectra were obtained. The photocatalyst was collected after 6 hours of irradiation and thoroughly washed with water. The diffraction peaks of the samples before and after irradiation are well aligned with each other suggesting the stable crystal structure of NC3 (Fig. S6a, ESI[†]). SEM images were obtained to examine the variation in the morphology of the photocatalyst. Fig. S6b (ESI⁺) shows the intact nanorod morphology of the photocatalyst during irradiation. Furthermore, EDX data was attained to confirm the elemental composition of the photocatalyst after irradiation. Fig. S7 (ESI⁺) displays the presence of all building elements of NC3, Cd, S, Ni and C, which demonstrates the excellent stability of CdS/Ni₃C NRs. Furthermore, no Co peak was detected, suggesting the absence of elemental Co after irradiation. Besides, XPS spectra were collected to investigate the changes in the photocatalyst after irradiation. Fig. S8 (ESI⁺) illustrates that no change in the shape and position of peaks occurred in the high resolution spectra of Cd and Ni, further confirming the robust stability of the present photocatalytic system. However, the characteristic peak of Co 2p was absent after irradiation, which confirms that PX1 did not decompose to elemental cobalt and plays a crucial role in current enhancement as a molecular cocatalyst.

The optical properties of the photosensitizer and cocatalysts were studied using UV-vis diffuse reflectance absorption spectrosopy. Fig. S8a (ESI[†]) shows that CdS NRs depicted its



Fig. 5 (a) SEM image of CdS NRs. (b) SEM image of NC3. (c) TEM image of NC3. (d) EDX spectrum of NC3.



Fig. 6 (a) XPS survey spectrum of NC3. (b) High resolution spectrum of Cd 3d. (c) High resolution spectrum of S 2p. (d) High resolution spectrum of Ni 2p. (e) High resolution spectrum of C 1s. (f) High resolution spectrum of Co 2p.

characteristic absorption at 520 nm corresponding to a band gap of 2.39 eV and molecular cocatalyst PX1 showed a broad absorption peak (Fig. S9a, ESI⁺).²⁸ Moreover, Ni₃C does not show significant absorption edge in the visible region describing the metallic character of Ni₃C. CdS/Ni₃C NRs (NC3) sample proves that it cannot change the band gap of photocatalyst (Fig. S9b, ESI⁺).³⁰ Furthermore, no change in the absorption edge of sample NC3 was observed upon loading of PX1, which confirms that PX1 does not affect the band gap of the photocatalyst and the enhanced H₂ evolution rate might be due to the efficient electron transfer process. To further investigate the role of cocatalysts, steady state photoluminescence (PL) spectroscopy was used. Fig. 7a shows the obtained PL spectra of CdS NRs, CdS/Ni₃C NRs and CdS/Ni₃C/PX1 NRs. Two distinct PL peaks were observed for pristine CdS NRs at ~ 504 nm and ~ 700 nm using an excitation wavelength of 405 nm.⁴⁰ The intense peak at 504 nm probably corresponds to the near-band-edge emission and a broad peak at 700 nm may appear due to surface defects.^{32,41} The intensity of these PL emission bands reduces notably upon loading of Ni₃C on CdS NRs (NC3) and further decrease was observed in the case of NC3/PX1, indicating the fast electron transfer processes at their interfaces. Besides, a low PL intensity at 700 nm was also observed, which confirms the passivation of surface defects. These phenomena increase the opportunity of the photoinduced electron to produce more photocatalytic H₂.42,43

The photoelectrochemical measurements were achieved to examine the electron transfer process between the photosensitizer and cocatalysts under visible light irradiation. The fluorine-doped tin oxide (FTO) electrode coated with CdS NRs, CdS/Ni₃C NRs and



Fig. 7 (a) Photoluminescence spectra of CdS, CdS/Ni3C (NC3) and CdS/Ni3C/**PX1** excited at a wavelength of 405 nm. (b) Transient photocurrent responses of CdS, CdS/Ni₃C and CdS/Ni₃C/**PX1** samples. (c) Cyclic voltammogram (CV) of 0.5 mM **PX1** prepared in dry acetonitrile. The solution contained 0.1 M TBAPF₆ as the electrolyte and 0.2 M ferrocene as the internal standard. (d) CVs of 0.5 mM **PX1** in the presence of different concentrations of acetic acid. The scan rate of CV was kept at 50 mV s⁻¹ using a glassy carbon working electrode.

CdS/Ni₃C/PX1 NRs was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. 0.5 M solution of Na2SO4 was used as the electrolyte. A considerable photocurrent response was observed for both samples under visible light irradiation. Fig. 7b displays the higher photocurrent of CdS/Ni₃C NRs sample as compared to pure CdS NRs. Besides, significant enhancement in photocurrent was observed for CdS/ Ni₃C/PX1 NRs inferring that it possesses the highest charge transport ability, which enhances the photocatalytic activity. Furthermore, electrochemical impedance spectra were obtained to elucidate the charge transfer resistance of present photocatalysts. Fig. S10 (ESI⁺) clearly shows that the arc radius of NC3/PX1 is the smallest as compared to pure CdS and NC3 (CdS/Ni₃C). It shows that PX1 effectively separated the photogenerated charge carriers and significantly supressed the charge recombination.⁴⁴ These results are consistent with PL analysis and photocatalytic H₂ production experiments, further proving that Ni₃C and PX1 can synergistically enhance the performance of CdS NRs as cocatalysts under optimized conditions.

To know more about the mechanistic role of **PX1** in the present photocatalytic system, cyclic voltammetric (CV) measurements were performed. Experiments were carried out using 0.5 mM **PX1** in dry acetonitrile containing 0.1 M TBAPF₆ as electrolyte and 0.2 M ferrocene as internal standard. Fig. 7c shows the reductive scan having an obvious wave at -8.45 (V vs Fc⁺/Fc), which can be assigned to Co(π)/Co(i). Upon addition of acetic acid, the Co(π)/Co(i) peak remains nearly constant but an increase in current was observed, which continuously increased with the increasing concentration of acetic acid. This observation can be attributed to the production of H₂ involving the formation of Co(i) species as an essential step (Fig. 7d).

Comprehensively, visible light excites CdS NRs and produces electron–hole pairs. From the conduction band of CdS, photogenerated electrons move towards the nearby Ni₃C. The more number of Ni₃C entities can guarantee the rescue of more number of electrons from recombination to holes. Consequently, this can result in an increased photocatalytic H₂ evolution. However, further loading of Ni₃C than the optimal amount is not fruitful as it can block the visible light active sites of the photosensitizer. Besides, the Co-based molecular cocatalyst swiftly accepts the excess photogenerated electrons. After accepting the electrons, the



 $\label{eq:scheme1} Scheme 1 \quad Schematic depiction of CdS/Ni_3C/PX1 \ photocatalytic system.$

molecular cocatalyst reduces to the Co(1) oxidation state. Furthermore, Co(1) species interact with H^+ and Co(11)H are generated. Further protonation of cobalt hydride species could mediate the consequent production of H_2 (Scheme 1). On the other hand, photogenerated holes scavenge the sacrificial electron donors and a systematic cycle runs smoothly. Therefore, a dramatic increase in the photocatalytic H_2 production of the composite photocatalyst was observed.

Conclusions

In summary, a molecular cocatalyst was synthesized by a facile method and successfully employed with a composite photocatalyst CdS/Ni₃C NRs for highly improved photocatalytic H₂ evolution. The photocatalytic activity of the system was boosted to 750 μ mol h⁻¹ due to the efficient electron capturing ability of molecular cocatalyst PX1. The highest apparent quantum yield of 53.2% was attained using monochromatic 420 nm light. The present photocatalytic system demonstrated excellent durability and long-term stability reached to 80 hours under visible light irradiation. PL spectra and photocurrent responses inferred the swift electron transfer at the interface of cocatalysts and CdS NRs, which hindered the rapid recombination of charge carriers. Interestingly, Ni₃C and PX1 synergistically enhanced the H₂ production ability of CdS NRs, which also reinforced the stability by inhibiting the photocorrosion process. This study presents an excellent strategy to build highly productive and non-noble metal photocatalytic system for H₂ evolution having potential large-scale applications.

Conflicts of interest

There are no conflicts to declare.

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