Multicarbazole-Based D−π−A Dyes Sensitized Hydrogen Evolution under Visible Light Irradiation

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ABSTRACT: Donor−π bridge−acceptor (D−π−A) organic dyes, well studied in dye-sensitized solar cells (DSSCs), are found to possess great potential in light-inducing hydrogen evolution due to their distinguished light-harvesting ability and suitable electron energy level. In this work, multicarbazole-based organic dyes (2C, 3C, 4C) were used as photosensitizers of Pt/TiO₂ for photocatalytic hydrogen evolution (PHE) from water under visible light irradiation. 3C-Pt/TiO₂ shows the best photocatalytic activity among the three dye-sensitized photocatalysts, with a hydrogen evolution rate of 24.7 μmol h⁻¹ and a turnover number of 247 h⁻¹. The activity of 3C-Pt/TiO₂ declines significantly after 3 h irradiation. The deactivation was caused by the partial degradation of the electron acceptor, cyanoacrylate moiety, during the photocatalytic process, which was evidenced by UV−vis, Fourier transform infrared spectra (FT-IR), NMR, and mass spectra. This work is expected to contribute toward the understanding of stability issues of organic dyes and the development of more efficient and steady dyes for hydrogen evolution from water splitting.

1. INTRODUCTION

Hydrogen, with water as the only reaction product, when it combusts, is an ideal candidate for the replacement of fossil fuels in the future. Photocatalytic hydrogen evolution (PHE) through water splitting using visible light is a promising method and is attracting much attention recently.¹−³ A great number of photocatalysts including TiO₂ are used to reduce water into hydrogen gas, while many of them suffer from low photocatalytic activity because of low quantum yield, fast recombination of photoinduced charge carriers, or poor absorption of visible light.⁴−⁵

As a strategy for expanding absorption spectrum, photosensitization of TiO₂ photoelectrode with dyes, which was originated from the dye-sensitized solar cells (DSSCs) found by Graetzel,¹ were reported to be efficient in promoting PHE.⁹−¹⁵ The dye molecules work as antennas to collect optical energy and then inject electrons from the photoexcited dye into the conduction band (CB) of semiconductor to achieve the enhanced photocatalytic activity.

Most frequently used dyes for PHE are limited to noble and rare metal (e.g., Ru and Ir) complexes,⁶,¹⁰−¹⁷ or halogenated xanthene,¹⁸−²⁰ such as tetrabromofluorescein (eosin Y) showing high PHE rate but rapid dehalogenation.¹⁹ Metal-free donor−π bridge−acceptor (D−π−A) organic dyes, which are studied extensively in DSSCs,²¹−²⁵ have a profoundly higher extent of light-harvesting capability than the metal complexes because of their special D−π−A dipolar architectures.²⁴,²⁵ Under visible light irradiation, intramolecular charge transfer from the donor core to acceptor end-group occurs, and subsequently photogenerated electrons are injected into the CB of TiO₂. Several D−π−A organic dyes including phenothiazine,²⁶−³⁰ triphenylamine,³¹−³³ carbazole,²⁵,³⁴,³⁵ indole,³⁶ perylene,³⁷ and coumarin²⁸,³⁹ units have been reported for PHE. However, their hydrogen evolution rates are not high enough. Moreover, a key problem is the instability and degradation of the dyes taking place quite often during the photocatalytic processes.²⁶,²⁹,³⁰,³³ For example, the excited states of phenothiazine-based dyes are decomposed through some chemical reactions.²⁶,³³ Obviously, degradation of dye sensitizers results in a decreased activity and even cessation of hydrogen evolution with irradiation time. Until now, very few studies have paid attention to the degradation of dyes.²⁶,³³ We do not know what happens to dye sensitizers during the photocatalytic reaction.

Here, we report three multicarbazole-based organic dyes (2C, 3C, 4C, Figure 1) sensitized Pt/TiO₂ for photocatalytic hydrogen evolution under visible light irradiation. These dyes,
formerly achieving relatively high light-to-electricity conversion rates up to 6.8%, exhibit good PHE performances. Nevertheless, a decrease in PHE activity was observed with light illumination. A possible photocatalytic mechanism was inferred and the process of degradation of dyes was also discussed. This work is expected to contribute toward the understanding of stability issues of organic dyes and the development of more efficient and steady dyes for hydrogen evolution from water splitting.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Organic Dyes. The three multi-carbazole-based organic dyes (2C, 3C, 4C) were synthesized mainly through the Suzuki coupling and Knoevenagel reaction with carbazole as the main starting material. The experimental details were depicted in our previous work.

2.2. Preparation of Pt/TiO2. A photoreduction method reported in our previous work was utilized to prepare platinized TiO2 nanoparticles (Pt/TiO2). In brief, TiO2 Degussa P25 (1.00 g) was suspended in a solution of deionized water (100 mL) and anhydrous ethanol (5 mL), and then H2PtCl6 aqueous solution (1.93 × 10−3 mol L−1, 13.5 mL) was added into it. After stirring for 0.5 h, the suspension was illuminated with a 150 W high-pressure Hg lamp for 2 h. Then, the Pyrex cell containing the suspension was placed under an illumination of a 250 W high-pressure Hg lamp with a cutoff filter at 420 nm. Sampling was conducted at 5°C for 30 min. After another filtration, the filtrates were acidified to pH = 4 with HCl aqueous solution and extracted with CHCl3. The obtained solution was dried and distilled under reduced pressure to give red solids.

2.6. Characterization. FT-IR spectra were recorded on an IR Prestige-21 instrument (Shimadzu, Japan) by the transmission method using the KBr pellet technique. UV−vis absorption spectra were collected with a UV-2550 spectrophotometer (Shimadzu, Japan). UV−vis diffuse reflectance spectra (DRS) of the dye@Pt/TiO2 composites were obtained on a spectrophotometer of U-3310 (Hitachi, Japan) equipped with an integrating sphere accessory (BaSO4 was used as a reference). The liquid state 1H and 13C NMR spectra were measured on an AV 500 MHz spectrometer (Bruker, Germany) using a gas chromatograph (TCD, 13X molecular sieve column, N2 gas carrier).

2.3. Preparation of Dyes@Pt/TiO2. For testing the interaction between dyes and Pt/TiO2 by Ultraviolet−visible (UV−vis) absorption spectra and Fourier transform infrared spectra (FT-IR), dye-sensitized Pt/TiO2 composites (dye@Pt/TiO2) were prepared. Typically, to a 20 mL dimethylformamide (DMF) containing a certain amount of dye, Pt/TiO2 powder (0.3 g) was added and continuously stirred overnight at room temperature. Then, DMF was removed by filtration, and the obtained solids were dried in an oven at 60°C for 5 h. The final composites were labeled as 2C@Pt/TiO2, 3C@Pt/TiO2, and 4C@Pt/TiO2, respectively.

2.4. H2 Evolution Measurement. The three multi-carbazole-based organic dyes (2C, 3C, 4C) were used as sensitzers for Pt/TiO2 to split water and produce H2 under visible light. Typically, in a Pyrex cell (190 mL) with a flat window, Pt/TiO2 (0.1 g) was dispersed in dye−DMF solutions (10 mL, 1.0−10.0 × 10−6 mol L−1) and kept stirring for 30 min. Aqueous solution containing 10 vol % triethanolamine (TEOA, 70 mL) previously neutralized with HCl aqueous solution was added. The suspension was stirred in an ultrasonic bath for 5 min and purged with N2 for 30 min to remove O2. Then, the Pyrex cell containing the suspension was placed under an illumination of a 250 W high-pressure Hg lamp with a cutoff filter at 420 nm. Sampling was conducted at each hour through a septum on top of the Pyrex cell during experiments. The amount of evolved hydrogen was quantified using a gas chromatograph (TCD, 13X molecular sieve column, N2 gas carrier).

2.5. Measurement of Dyes Degradation. The degradation of dyes in the H2 evolution measurement was investigated by means of UV−vis spectra, FT-IR spectra, 1H and 13C nuclear magnetic resonance (NMR), and mass spectra of the desorbed dyes after PHE for 8 h. For retrieving the desorbed dyes, the suspension was filtered to gain colorless filtrates and red particles. The latter was immersed in a mixture of 0.1 M aqueous NaOH solution (10 mL) and tetrahydrofuran (THF) (10 mL) for 30 min. After another filtration, the filtrates were acidified to pH = 4 with HCl aqueous solution and extracted with CHCl3. The obtained solution was dried and distilled under reduced pressure to give red solids.

3. RESULTS AND DISCUSSION

3.1. FT-IR analysis. To elucidate the interaction between dyes and Pt/TiO2, the FT-IR spectra of dyes and dye@Pt/TiO2 were characterized as shown in Figure 2.

![Figure 2. FT-IR spectra of (A) dyes, (B) dye@Pt/TiO2, and Pt/TiO2 samples.](https://dx.doi.org/10.1021/acsomega.9b04135)

The 2C, 3C, and 4C have similar spectra with absorption bands at around 3046, 2958, 2930, 2871, 2213, 1585, 1482, 1363, 1139, 1077, and 800 cm−1. The characteristic absorption bands of the dye appear in dye@Pt/TiO2 but with reduced intensities, demonstrating the presence of the dye in the dye@Pt/TiO2. Moreover, some characteristic absorption bands of the dye in the dye@Pt/TiO2 shift remarkably, for example, the band at 1363 cm−1 (related to vibration of −COO−) in 3C
shifts to 1380 cm⁻¹ in 3C@Pt/TiO₂ and the band at 1139 cm⁻¹ (related to vibration of S–C in thiophene) in 3C shifts to 1156 cm⁻¹ in 3C@Pt/TiO₂ (Figure S1 in the Supporting Information); this apparent blue shift implies that the 3C molecule could be adsorbed onto Pt/TiO₂ through the carboxyl group (carboxylate coordination or/and ester-like bonding) and S atoms (coordination interaction with Ti≡ on the surface of TiO₂), and the large wavenumber shift demonstrates that intensive chemical interaction occurs between them. These interactions can be beneficial to electron transfer from the excited dye to Pt/TiO₂, thereby enhancing photocatalytic hydrogen evolution.

3.2. DRS Analysis. The DRS spectra of 3C@Pt/TiO₂, 3C, Pt/TiO₂, and TiO₂ are shown in Figure 3. The pure TiO₂ can only absorb UV light, while 3C and Pt/TiO₂ have absorption both during UV and visible light ranges. In Pt/TiO₂, a visible light absorption band is due to surface plasmon resonance (SPR) effects of the Pt nanoparticle on the TiO₂ surface. After being sensitized with the dye, the 3C@Pt/TiO₂ composite displays a broad absorption over a wide spectral range from 400 to 650 nm, which is attributed to the improved light-harvesting nature of the photocatalyst composites. The 2C and 4C have very similar results (Figure S2 in the Supporting Information), and the DRS spectra suggest that three dyes can effectively sensitize Pt/TiO₂ in a broad visible light region.

3.3. Photocatalytic Hydrogen Evolution. The reaction conditions were as follows: 0.10 g Pt/TiO₂; 2.0 × 10⁻⁶ mol L⁻¹ dye; pH 7.0; triethanolamine as electron donor, visible light (λ > 420 nm) irradiation. The three multicarbazole-based organic dyes (2C, 3C, 4C) were evaluated as sensitizers for Pt/TiO₂ to produce H₂ under visible light using triethanolamine as a sacrificial electron donor. Notably, DMF was used as a solvent for each dye without being removed by filtration to prevent particle agglomeration. For making a difference with dye@Pt/TiO₂ prepared for FT-IR and DRS measurements, the photocatalytic systems based on 2C, 3C, and 4C were named as 2C-Pt/TiO₂, 3C-Pt/TiO₂, and 4C-Pt/TiO₂, respectively.

The photocatalytic activity of hydrogen evolution of dye-Pt/TiO₂ upon visible light irradiation is presented in Figure 4. Hydrogen evolution was not observed in the Pt/TiO₂ or TiO₂ system. All of the three dye-Pt/TiO₂ composites display remarkable photocatalytic activity in the order of 3C-Pt/TiO₂ > 4C-Pt/TiO₂ > 2C-Pt/TiO₂. 3C-Pt/TiO₂ has the highest rate of hydrogen evolution of 24.7 μmol h⁻¹. The turnover number, which is defined as twice the ratio of the amount of evolved hydrogen to the amount of dye in unit time, is 247 h⁻¹. The rate of hydrogen evolution of the dye-Pt/TiO₂ in our study is
not high compared with other reports on the dye-related H₂ production with xenon lamp as a light source, because the visible light source in this study is a 250 W high-pressure mercury lamp, whose radiation intensity is low.

Why does 3C shows the best photocatalytic activity as in our previous study on DSSC? The probable reason is that more twisted structures and alkyl side chains can inhibit dye aggregation and charge recombination, and thus, the 3C shows better photocatalytic activity than 2C. However, a further increase of carbazole units (dye 4C) does not increase its photocatalytic property, which may be caused by loose packing by its larger twisted structure and more n-butyl chains compared with 3C. The loose packing leads to some voids through which TEOA⁺ (the oxidized TEOA) could penetrate the dye layer and recombine with an electron on Pt/TiO₂.

The lowest unoccupied molecular orbital (LUMO) levels of 2C, 3C, and 4C are −1.42, −1.48, and −1.47 V (vs NHE), respectively. The LUMO levels are much more negative than that of the CB of TiO₂ (~ −0.5 V). Such a result indicates that electron injection from the excited dyes into the CB of TiO₂ was permitted thermodynamically. The highest occupied molecular orbital (HOMO) levels of 2C, 3C, and 4C are 0.99, 0.94, and 0.94 V (vs NHE), respectively, which are more positive than TEOA/TEOA⁺ reduction potential value (0.82 V), implying that TEOA in the reaction system could thermodynamically reduce the oxidized dyes which are produced after electron injects into the CB of TiO₂. A reaction mechanism of 3C-sensitized hydrogen evolution is illustrated in Figure 5. When 3C-Pt/TiO₂ composites are irradiated by visible light, 3C can be excited by photons, and electrons in the HOMO (located in multicarbazole and thiophene units) are promoted to the LUMO (located in the cyanoacrylate moiety). The photoinduced electrons in the LUMO can be easily injected into the CB of TiO₂, and the injected electrons are immediately trapped by the Pt on the surface of TiO₂ and react with adsorbed H⁺ from H₂O to produce H₂.

The effect of concentration of the dye on the photocatalytic hydrogen evolution was investigated. As shown in Figure 6, the activity of Pt/TiO₂ without the dye upon visible light was not observed, while the hydrogen evolution activity is enhanced distinctly when a low level of 3C is involved, indicating that hydrogen evolution is induced by dye photosensitization. The photocatalytic activities increase with increasing concentration of dyes to show a maximum at a dye concentration of 2.0 × 10⁻⁶ mol L⁻¹ and thereafter a decrease. When 3C increases from 0 to 2.0 × 10⁻⁶ mol L⁻¹, the antenna effect of light harvesting is enhanced, more excited dye is formed, and hydrogen evolution is improved. However, when the dye concentration further increases (>2.0 × 10⁻⁶ mol L⁻¹), all of the sites on the surface of TiO₂ have been adhered to by dye molecules and no active sites are available to be accommodated further; thus, the rate of hydrogen evolution do not gain an enhancement and the activity is inversely reduced due to deactivation of excited dye molecules from the agglomeration effect. Although the TON was found to increase progressively when decreasing the concentration of the dye, with a maximum value of 380 h⁻¹ at a dye concentration of 1.0 × 10⁻⁶ mol L⁻¹. This means that the dye is more effective at a low concentration in hydrogen evolution; a similar phenomenon was reported by other scholars.

3.4. Discussion of Stability Issue. The stability of 3C-Pt/TiO₂ photocatalyst during the photocatalytic reaction was investigated. As in Figure 7, the time course of hydrogen evolution reveals that the activity of 3C-Pt/TiO₂ photocatalyst during the photocatalytic reaction was relatively high within 3 h of irradiation and then displays some declining trend. The reaction conditions as in Figure 4.

Figure 8. (A) UV-vis absorption, (B) ¹H NMR, (C) FT-IR spectra, and (D) mass spectra of the dye (a) before and (b) after photocatalytic reaction. The peaks marked with asterisk and triangle are attributed to DMSO and H₂O, respectively.
To clarify the above phenomenon, UV−Vis, FT-IR, $^1$H and $^{13}$C NMR, and MS of original 3C and the residual (3C-R) retrieved after the photocatalytic reaction were characterized. As shown in Figure 8A, the UV−vis spectrum of 3C exhibits an UV absorption band with center at ∼305 nm and a Vis absorption band with center at ∼445 nm. The former is ascribed to the $\pi-\pi^*$ transition of carbazole moieties and the latter is the intramolecular charge transfer (ICT) transition from the HOMO (multicarbazole and thiophene units) to the LUMO (cyanoacrylate moiety). For 3C-R, its UV absorption band has no significant change while the Vis absorption band almost disappears, indicating that carbazole units are unchanged but cyanoacrylate or/and thiophene unit may be destroyed. The initial concentration of the dye had little effect on UV−vis spectra of 3C-Rs (Figure S3 in the Supporting Material). In Figure 8B, $^1$H NMR spectra have little difference, especially at 7−9 ppm, revealing that the multicarbazole unit still remains after the photocatalytic reaction, and $^{13}$C NMR spectra also support this point (Figure S4 in the Supporting Information). FT-IR spectra of Figure 8C displays that the peaks of carboxyl group ($-\text{COOH, } \sim 1580 \text{ cm}^{-1}, \nu\text{asy}$) and cyano group ($-\text{CN, } \sim 2210 \text{ cm}^{-1}$) in the dye undergoing photocatalysis become weak dramatically, and the peak related to thiophene ($\sim 800 \text{ cm}^{-1}$) has no obvious change. The result suggests that the electron acceptor cyanoacrylate moiety in dye 3C has been removed to a large part, so a decreased hydrogen evolution was found in our study. To better understand the deactivation of 3C, mass spectra are presented in Figure 8D. 3C-R presented a main peak at $m/z = 856$, 44 lower than 3C ($m/z = 900$), corresponding to decarboxylation, which can be the cause of disappearance of the ICT absorption band in Figure 8A. The other two peaks at $m/z = 833$ and 709 indicate that further deterioration of cyano moiety and thiophene takes place. Therefore, we suppose that the degradation of 3C during irradiation probably proceeds in a route presented in Figure 9, which differs with that reported in ref 26.

The carbazole group exhibits high stability, which may be attributed to the positive charge separation by N atoms when the electrons of 3C are injected into the CB of TiO$_2$ and became an oxidation state. Cyanoacrylate is the most vulnerable moiety in molecular structure because of decarboxylation, a phenomenon may proceed like in the synthesis of cinnamic acid using malonic acid and benzoaldehyde.

The above discussions on dye stability prove that carbazole-based D−π−A organic dyes with cyanoacrylate moiety as electron acceptor is efficient for PHE, but not stable in aqueous solution during the photochemical reaction. This conclusion inspires us to develop new steady organic dyes with other electron acceptors (such as oxosilane and phosphate group). Further studies are in progress.

4. CONCLUSIONS

Multicarbazole-based organic dyes (2C, 3C, 4C) were developed as photosensitizers for photocatalytic hydrogen evolution from water under visible light irradiation. 3C shows the best photocatalytic properties with a rate of H$_2$ generation of 24.7 μmol h$^{-1}$ and the turnover number of 247 h$^{-1}$. The activity of 3C@Pt/TiO$_2$ declines significantly after 3 h irradiation, which is proved to be caused by the partial removal of electron acceptor cyanoacrylate moiety from the dye molecule during the photocatalytic process. This conclusion inspires us to develop new steady organic dyes with other electron acceptors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04135.

FT-IR spectra of 3C and 3C@Pt/TiO$_2$; UV−vis diffuse reflectance spectra of some materials; UV−vis absorption spectra of the dye after the photocatalytic reaction; $^{13}$C NMR spectra of the dye before and after the photocatalytic reaction (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Kim, J. H.; Hansora, D.; Sharma, P.; Jang, J. W.; Lee, J. S. Toward practical solar hydrogen production—an artificial photosynthetic leaf-to-farm challenge. Chem. Soc. Rev. 2019, 48, 1908–1971.
(2) Afroz, K.; Moniruddin, M.; Bakranov, N.; Kudaiabergenovc, S.; Nuraje, N. A heterojunction strategy to improve the visible light sensitive water splitting performance of photocatalytic materials. J. Mater. Chem. A 2018, 6, 21696–21718.
(3) Wang, M.; Yang, Y.; Shen, J.; Jiang, J.; Sun, L. Visible-light-absorbing semiconductor/molecular catalyst hybrid photoelectrodes for H2 or O2 evolution: recent advances and challenges. Sustainable Energy Fuels 2017, 1, 1641–1663.
(4) Acar, C.; Dincer, I.; Natener, G. F. Review of photocatalytic water-splitting methods for sustainable hydrogen production. Int. J. Energy Res. 2016, 40, 1449–1473.
(5) Yuan, Y. J.; Yu, Z. T.; Chen, D. Q.; Zou, Z. G. Metal-complex chromophores for solar hydrogen generation. Chem. Soc. Rev. 2017, 46, 603–631.
(6) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. Chem. Soc. Rev. 2009, 38, 253–278.
(7) Babu, V. J.; Kumar, M. K.; Nair, A. S.; Kheng, T. L.; Allakherdevi, S. I.; Ramakrishna, S. Visible light photocatalytic water splitting for hydrogen production from N-TiO2 rice grain shaped electro spin nanostructures. Int. J. Hydrogen Energy 2012, 37, 8897–8904.
(8) O’Regan, B.; Graetzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature 1991, 353, 737–739.
(9) Willkomm, J.; Orchard, K. L.; Reynal, A.; Pastor, E.; Durrant, J. R.; Reisner, E. Dye-sensitised semiconductors modified with molecular catalysts for light-driven H2 production. Chem. Soc. Rev. 2016, 45, 8–23.
(10) Liu, X.; Li, Y. X.; Peng, S. Q.; Lu, G. X.; Li, S. B. Photocatalytic hydrogen evolution over Erythrosin B-sensitized graphitic carbon nitride with in situ grown molybdenum sulfide cocatalyst. Energy Fuels 2013, 27, 11709–11719.
(11) Liu, X.; Li, Y. X.; Peng, S. Q.; Lai, H. Progress in visible-light photocatalytic hydrogen production by dye sensitization. Acta Phys.-Chim. Sin. 2015, 31, 612–626.
(12) Cecconi, B.; Manfredi, N.; Montini, T.; Fornasiero, P.; Abbottto, A. Dye-sensitized solar hydrogen production: The emerging role of metal-free organic sensitizer. Eur. J. Org. Chem. 2016, 2016, 5194–5215.
(13) Li, Y. X.; Guo, M. M.; Peng, S. Q.; Lu, G. X.; Li, S. B. Photocatalytic hydrogen evolution over Erythrosin B-sensitized graphitic carbon nitride with in situ grown molybdenum sulfide cocatalyst. Int. J. Hydrogen Energy 2009, 34, 5629–5636.
(14) Li, Y. X.; Xie, C. F.; Peng, S. Q.; Lu, G. X.; Li, S. B. Eosin Y-sensitized nitrogen-doped TiO2 for efficient visible light photocatalytic hydrogen evolution. J. Mol. Catal. A: Chem. 2008, 282, 117–123.
(15) Qin, J. Y.; Huo, J. P.; Zhang, P. Y.; Zeng, J.; Wang, T. T.; Zeng, H. P. Improving photocatalytic hydrogen production of Ag/g-C3N4 nanocomposites by dye-sensitization under visible light irradiation. Nanoscale 2016, 8, 2249–2259.
(16) Maeda, K.; Sahara, G.; Eguchi, M.; Ishitani, O. Hybrids of a ruthenium(II) polypryridyl complex and a metal oxide nanosheet for dye-sensitized hydrogen evolution with visible light: effects of the energy structure on photocatalytic activity. ACS Catal. 2015, 5, 1700–1707.
(17) Castillo, C. E.; Gennari, M.; Stoll, T.; Fortage, J.; Deronzier, A.; Collomb, M. N.; et al. Visible light-driven electron transfer from a dye-sensitized p-type NiO photocathode to a molecular catalyst in solution: Toward NiO-based photoelectrochemical devices for solar hydrogen production. J. Phys. Chem. C 2015, 119, 5806–5818.
(18) Zhang, W. Y.; Li, Y. X.; Peng, S. Q. Template-free synthesis of hollow Ni/reduced graphene oxide composite for efficient H2 evolution. J. Mater. Chem. A 2017, 5, 13072–13078.
(19) Xu, J. Y.; Li, Y. X.; Peng, S. Q. Photocatalytic hydrogen evolution over Erythrosin B-sensitized graphitic carbon nitride with in situ grown molybdenum sulfide cocatalyst. Int. J. Hydrogen Energy 2015, 40, 353–362.
(20) Xu, J. Y.; Li, Y. X.; Peng, S.; Lu, G.; Li, S. Eosin Y-sensitized inorganic photocathode for solar hydrogen production. J. Phys. Chem. C 2013, 117, 7657–7665.
(21) Shin, S. S.; Suk, J. H.; Kang, B. J.; Yin, W.; Lee, S. J.; Noh, J. H.; Ahn, T. K.; Rotermund, F.; Cho, I. S.; Seok, S. I. Energy-level engineering of the electron transporting layer for improving open-circuit voltage in dye and perovskite-based solar cells. Energy Environ. Sci. 2019, 12, 958–964.
(22) Yang, J. B.; Ganesan, P.; Teuscher, J.; Moehl, T.; Kim, Y. J.; Yi, C. Y.; Comte, P.; Pei, K.; Holcombe, T. W.; Nazeeruddin, M. K.; Hua, J. L.; Zakeeruddin, S. M.; Tian, H.; Grätzel, M. Influence of the donor size in D−π−A organic dyes for dye-sensitized solar cells. J. Am. Chem. Soc. 2014, 136, 5722–5730.

(23) Cai, Z. X.; Lu, H. W.; Qi, P. L.; Wang, J. G.; Zhang, G. X.; Liu, Z. T.; Zhang, D. Q. Alternating conjugated electron donor–acceptor polymers entailing pechmann dye framework as the electron acceptor moieties for high performance organic semiconductors with tunable characteristics. Macromolecules 2014, 47, 2899–2906.

(24) Patir, I. H.; Azlan, E.; Yanalak, G.; Karaman, M.; Sarilmaz, A.; Can, M.; Can, M.; Ozel, F. Donor−π−acceptor dye-sensitized photoelectrochemical and photocatalytic hydrogen evolution by using Cu2W6S6 co-catalyst. Int. J. Hydrogen Energy 2019, 44, 1441–1450.

(25) Kumari, A.; Mondal, I.; Pal, U. A simple carbazole based sensitizer attached to a Nafion-coated-TiO2 photocatalyst: the impact of controlling parameters towards visible light driven H2 production. New J. Chem. 2015, 39, 713–720.

(26) Cecconi, B.; Manfredi, N.; Ruffo, R.; Montini, T.; Romero-Ocaña, I.; Fornasiero, P.; Abbotta, A. Tuning thiophene-based phenothiazines for stable photocatalytic hydrogen production. ChemSusChem 2015, 8, 4216–4228.

(27) Watanabe, M.; Hagiwara, H.; Inibe, A.; Ogata, Y.; Shiomi, K.; Staykov, A.; Ida, S.; Tanaka, K.; Ishihara, T. Spacer effects in metal-free organic dyes for visible-light-driven dye-sensitized photocatalytic hydrogen production. J. Mater. Chem. A 2014, 2, 12952–12961.

(28) Lee, J.; Kwak, J.; Ko, K. C.; Park, J. H.; Ko, J. H.; Park, N.; Kim, E.; Ryu, D. H.; Ahn, T. K.; Lee, J. Y.; Son, S. U. Phenothiazine-based organic dyes with two anchoring groups on TiO2 for highly efficient visible light-induced water splitting. Chem. Commun. 2012, 48, 11431–11433.

(29) Manfredi, N.; Monai, M.; Montini, T.; Peri, F.; Angelis, F. D.; Fornasiero, P.; Abbotta, A. Dye-sensitized photocatalytic hydrogen generation: efficiency enhancement by organic photosensitizer–coadsorbent intermolecular interaction. ACS Energy Lett. 2018, 3, 85–91.

(30) Manfredi, N.; Cecconi, B.; Calabrese, V.; Minotti, A.; Peri, F.; Ruffo, R.; Monai, M.; Romero-Ocana, I.; Montini, T.; Fornasiero, P.; Abbotta, A. Dye-sensitized photocatalytic hydrogen production: distinct activity in a glucose derivative of a phenothiazine dye. Chem. Commun. 2016, 52, 6977–6980.

(31) Choi, S. K.; Yang, H. S.; Kim, J. H.; Park, H. Organic dye-sensitized TiO2 as a versatile photocatalyst for solar hydrogen and environmental remediation. Appl. Catal., B 2012, 121–122, 206–213.

(32) Han, W. S.; Lee, S.; Wei, X. S.; Lee, J. Y.; Yang, B.; Wang, Y. F.; Li, C. A.; Angelis, T.; Yamamoto, D.; Shimagishi, M.; Inoue, T.; Choi, J.; Cho, K.; Kang, S. Oxygen. Hydrophilic control of visible-light hydrogen evolution and dynamics of the charge-separated state in dye/TiO2/Pt hybrid systems. Chem. - Eur. J. 2012, 18, 15368–15381.

(33) Dessi, A.; Monai, M.; Bessi, M.; Montini, T.; Calamante, M.; Mordini, A.; Reginato, G.; Trono, C.; Fornasiero, P.; Zani, L. Towards sustainable H2 production: Rational design of hydrophobic triphenylamine-based dyes for sensitized ethanol photofermenting. ChemSusChem 2018, 11, 793–805.

(34) Manfredi, N.; Monai, M.; Montini, T.; Salamone, M.; Ruffo, R.; Fornasiero, P.; Abbotta, A. Enhanced photocatalytic hydrogen generation using carbazolebased sensitizers. Sustainable Energy Fuels 2017, 1, 694–698.

(35) Watanabe, M.; Hagiwara, H.; Ogata, Y.; Staykov, A.; Bishop, S. R.; Perry, N. H.; Chang, Y. J.; Ida, S.; Tanaka, K.; Ishihara, T. Impact of alkoxy chain length on carbazole-based, visible light-driven, dye sensitized photocatalytic hydrogen production. J. Mater. Chem. A 2015, 3, 21713–21721.

(36) Zhang, X. H.; Peng, T. Y.; Yu, L. J.; Li, R. J.; Li, Q. Z.; Li, Z. Visible/near-infrared-light-induced H2 production over g-C3N4 cosensitized by organic dye and zinc phthalocyanine derivative. ACS Catal. 2015, 5, 504–510.

(37) Yu, F. T.; Wang, Z. Q.; Zhang, S. C.; Yun, K.; Ye, H. N.; Gong, X. Q.; Hua, J. L.; Tian, H. N-Annulated perylene-based organic dyes sensitized graphitic carbon nitride to form an amide bond for efficient photocatalytic hydrogen production under visible-light irradiation. Appl. Catal., B 2018, 237, 32–42.

(38) Abe, R.; Shinmei, K.; Konuma, N.; Harai, K.; Ohtani, B. Visible-light-induced water splitting based on two-step photoexcitation between dye-sensitized layered niobate and tungsten oxide photocatalysts in the presence of a triiodide/iodide shuttle redox mediator. J. Am. Chem. Soc. 2013, 135, 16872–16884.

(39) Abe, R.; Shinmei, K.; Harai, K.; Ohtani, B. Robust dye-sensitized overall water splitting system with two-step photocatalysis of coumarin dyes and metal oxide semiconductors. Chem. Commun. 2009, 3577–3579.

(40) Lai, H.; Hong, J.; Liu, P.; Yuan, C.; Li, Y.; Fang, Q. Multi-carbazole derivatives: new dyes for highly efficient dye-sensitized solar cells. RSC Adv. 2012, 2, 2427–2432.

(41) Liu, X.; Lai, H.; Li, J. H.; Peng, G.; Yi, Z. Y.; Zeng, R. Y.; Wang, M. Y.; Liu, Z. B. Polyamine sensitized Pt@TiO2 for visible-light-driven H2 generation. Int. J. Hydrogen Energy 2019, 44, 4698–4706.

(42) Zhang, Q.; Zhu, W. J.; Fang, M.; Yin, F. F.; Li, C. Synthesis, photophysical and electrochemical properties of two novel carbazole-based dye molecules. Spectrochim. Acta, Part A 2015, 135, 379–385.

(43) Harai, K.; Sato, T.; Kato, R.; Furube, A.; Ohga, Y.; Shimo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. Molecular design of coumarin dyes for efficient dye-sensitized solar cells. J. Phys. Chem. B 2003, 107, 597–606.

(44) Wang, X. F.; Chen, S. H.; Zhang, M. M.; Huang, Y. V.; Feng, S. J.; Zhao, D. L. MoS2 quantum dots modified Ag/polyaniline composites with enhanced photogenerated carrier separation for highly efficient visible light photocatalytic H2 evolution performance. Catal. Sci. Technol. 2017, 7, 3531–3538.

(45) Zhang, X.; J.; Jin, Z. L.; Li, Y. Y.; Li, S. B.; Lu, G. X. Efficient Photocatalytic Hydrogen Evolution from water without an electron mediator over Pt-Rose bengal catalysts. J. Phys. Chem. C 2009, 113, 2630–2635.

(46) Bettucci, O.; Skalsas, T.; Calamante, M.; Dessi, A.; Bartolini, M.; Simicropi, A.; Filippi, J.; Reginato, G.; Mordini, A.; Fornasiero, P.; Zani, L. Combining dithienosilole-based organic dyes with a Brookite/platinum photocatalyst toward enhanced visible-light-driven hydrogen production. ACS Appl. Energy Mater. 2019, 2, 5600–5612.