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Visible/Near-Infrared-Light-Induced H_2 Production over g-C_3N_4 Co-sensitized by Organic Dye and Zinc Phthalocyanine Derivative

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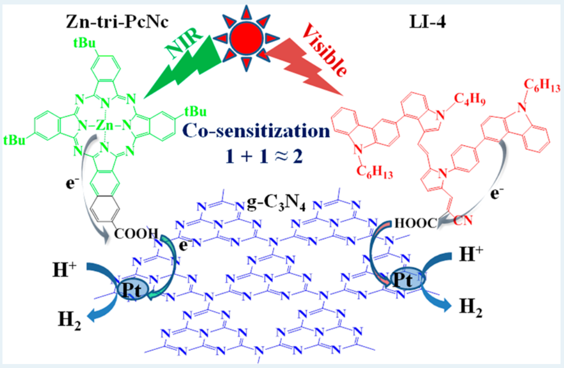
ABSTRACT: A new route is carried out to achieve broad spectral responsive photocatalytic H_2 production over g-C_3N_4 co-sensitized by an indole-based D-π-A organic dye (LI-4) and an asymmetric zinc phthalocyanine derivative (Zn-tri-PcNc) with complementary absorption spectra. Experimental results indicate that both LI-4 and Zn-tri-PcNc are efficient photosensitizers of g-C_3N_4 for H_2 production, and their co-sensitized g-C_3N_4 (LI-4/g-C_3N_4/Zn-tri-PcNc) exhibits an extremely high H_2 production activity (371.4 μmol h^{-1}) under visible/near-infrared (NIR) light ($\lambda \geq 420$ nm) irradiation, which approximates the summation of the H_2 production activity of LI-4/g-C_3N_4 (233.8 μmol h^{-1}) and Zn-tri-PcNc/g-C_3N_4 (132.3 μmol h^{-1}), although LI-4 and Zn-tri-PcNc can just absorb the light in the range of 400−600 and 600−750 nm, respectively. Moreover, the co-sensitized catalyst shows a broad visible/NIR light responsive range (400−800 nm) with impressively high apparent quantum yields (AQY) of 16.3, 7.7, and 1.75% at 420, 500, and 700 nm monochromatic light irradiation, respectively. The present work gives a new advance toward panchromatic light responsive photocatalytic application by combining the photosensitization of two different dyes with complementary absorption spectra on one kind of semiconductor.



KEYWORDS: *co-sensitization, photocatalytic H_2 production, metal-free organic dye, asymmetric zinc phthalocyanine, broad spectral responsive range*

■ INTRODUCTION

In the past decades, a photocatalytic procedure for clean hydrogen energy production has become one of the hottest research topics due to the increasingly serious energy and environment crises.[1−5] Typically, titania (TiO_2), the most widely used photocatalyst, is limited by its wide bandgap (~3.20 eV), which leads to low visible light utilization and quantum efficiency, and thus the development of photocatalysts that can effectively harvest visible light is indispensable for an efficient photocatalytic H_2 production. For example, many strategies, such as coupling with a narrow bandgap semiconductor (e.g., CdS and WO_3), doping metal, or nonmetal element or dye sensitization, have been established to improve the visible-light-driven photoactivity of TiO_2.[6−10] As a strategy for effectively utilizing visible light, dye sensitization has been studied extensively in dye-sensitized solar cells (DSSCs), and a great photovoltaic conversion efficiency (>15.0%) has been made.[11] However, the photocatalytic H_2 production efficiency based on dye-sensitized semiconductor is still insufficient, and there is a long way to go for improving the light-to-hydrogen energy conversion efficiency.[8−10]

Typically, Ru-bipyridyl complexes are the most popular dyes utilized for the photocatalytic H_2 production due to their great success in the field of DSSCs. However, those Ru complexes suffer from some obvious defects such as high cost, noble metal, and limited light absorption range (mostly <600 nm),[8,12,13] and therefore Ru complexes are replaced by some metal-free organic molecules such as xanthene dyes (mostly eosin Y, eosine bluish, etc.), which show efficient photosensitization but with narrow and limited visible light utilization.[14,15] Recently, various D-π-A organic dyes have been successfully utilized in DSSCs with impressive conversion efficiency.[16] Moreover, their absorption region can be flexibly adjusted to satisfy the solar light absorption requirement by changing molecular structures.[8−10] Nevertheless, a few investigations have been focused on photocatalytic H_2 production based on this type of organic dye-sensitized semiconductor.[17−20] For example, Kang et al.[17,18] reported the effect of organic dye's hydrophilic character on the H_2 generation over TiO_2. Park et al.[19] investigated the effect of the number of anchoring groups in a simple D-π-A dye on the photosensitization for H_2 production over TiO_2. However, these organic dyes investigated still have significant defects such as limited visible light absorption (mostly <550 nm) and unsatisfactory sunlight utilization coefficient.

Generally, single dye sensitization cannot reach a broad spectral photosensitization in the visible/near-infrared (NIR) light region because each dye possesses only its own characteristic absorption band, which covers only a several

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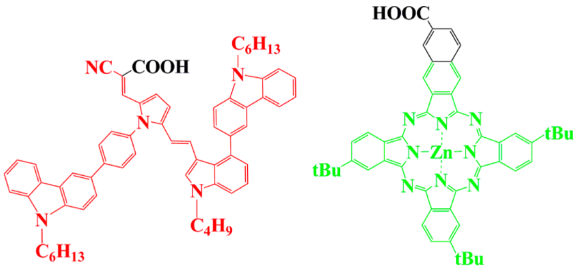
hundred nanometer wavelength region. The corresponding problem has been successfully solved to some extent in DSSCs by co-sensitization of two or more dyes.[21,22] Nevertheless, a co-sensitized semiconductor for visible/NIR-light-induced H_2 production has not been reported, although two kinds of monochromatic lights (520 and 550 nm) were utilized for photocatalytic H_2 production by Lu et al.[23] On the other hand, the recent breakthrough of zinc phthalocyanine (ZnPc) derivatives as efficient red/NIR light (600−900 nm) sensitizers in DSSCs also makes them a practical dye in dye-sensitized photocatalytic systems,[24] and a series of ZnPc derivatives have been synthesized and successfully applied in photovoltaic conversion and photocatalytic H_2 production for utilizing the red/NIR light.[25,26] Moreover, an asymmetric ZnPc derivative (Zn-tri-PcNc) with intense red/NIR light (600−750 nm) absorption was used as sensitizer of a polymeric graphitic carbon nitride (g-C_3N_4), and a record apparent quantum yield (AQY, 1.85%) was obtained under 700 nm monochromatic light,[26] much higher than that (0.07% at 660 nm) of the MgPc-sensitized g-C_3N_4 reported previously.[26c]

Herein, we report a new work on broad visible/NIR light (400−800 nm) induced H_2 production based on g-C_3N_4 co-sensitized by two different dyes: indole-based D-π-A organic dye (LI-4) and asymmetric ZnPc derivative (Zn-tri-PcNc). Different from the commonly used D-π-A dyes, LI-4 is a novel indole-based organic dye constituted by the order of triphenylamine (D)−thiophene (π)−cyanoacrylic acid (A). Its electron donor moiety is changed as carbazole moieties bonded to an indole group and another carbazole group so as to suppress the dye aggregation; simultaneously, the thiophene-based conjugate bridge is substituted by pyrrole (see Scheme 1). This kind of organic dye has been proven to be an efficient sensitizer of DSSCs.[27] The results indicate that LI-4 can also be used as sensitizer of g-C_3N_4 for efficient visible-light-driven H_2 production in the range of 400−600 nm, and a higher photoactivity and border spectral responsive range for H_2 production can be obtained when Zn-tri-PcNc (see Scheme 1) with a complementary spectral absorption region (600−750 nm) is used as co-sensitizer of LI-4 loaded on g-C_3N_4. Moreover, the present dye co-sensitized g-C_3N_4 (LI-4/g-C_3N_4/Zn-tri-PcNc) shows a perfect combination of the photosensitization of two different dye components with complementary absorption spectra loaded on g-C_3N_4.

Scheme 1. Molecule Structures of D-π-A Organic Dye (LI-4) and Asymmetric Zinc Phthalocyanine Derivative (Zn-tri-PcNc)



LI-4

Zn-*tri*-PcNc

EXPERIMENTAL SECTION

Material Preparation. g-C_3N_4 was synthesized according to our previous paper.[26] Typically, the precursor (urea) was kept in a crucible with a cover and heated at 580 °C for 3 h at a heating rate of 5 °C min^{-1}. The product was washed with HNO_3 solution (0.1 M) and water and then dried at 70 °C overnight to obtain the product (g-C_3N_4). Pt/g-C_3N_4 was prepared by adding 0.2 g of g-C_3N_4 into 50 mL of methanol/water (v/v = 1:4) solution containing H_2PtCl_6 solution (0.077 M) and then exposed to a 500 W Hg lamp for 3 h under stirring. The product was separated by centrifugation, washed with water and ethanol, and then dried at 70 °C overnight to obtain 0.5 wt % Pt/g-C_3N_4.

Indole-based D-π-A organic dye (LI-4) and asymmetric ZnPc derivative (Zn-tri-PcNc) were prepared according to our previous publications,[25,27] and their molecule structures are shown in Scheme 1. Dye-sensitized g-C_3N_4 was prepared by stirring 0.1 g of Pt/g-C_3N_4 in 3 mL of dye ethanol solution (0.17 mM) for 12 h in dark condition, then filtered and washed with ethanol, and dried at 70 °C overnight. As for the Zn-tri-PcNc sensitization, CDCA is used as co-adsorbent to reduce the molecule agglomeration of Zn-tri-PcNc.[25,26] In the present work, all dye molecules (LI-1 and Zn-tri-PcNc) containing a carboxyl group can quantitatively adsorb on Pt/g-C_3N_4, and the UV−vis spectra showed no sign of dyes existing in the filtrate. The dye-adsorbed amount can be calculated as 5.0 μmol g^{-1} on Pt/g-C_3N_4. Co-sensitized g-C_3N_4 (LI-4/g-C_3N_4/Zn-tri-PcNc) was prepared through a similar procedure except for the two dyes (LI-4 and Zn-tri-PcNc) added simultaneously.

Material Characterization. UV−vis spectra and UV−vis diffuse reflectance absorption spectra (DRS) were obtained with a Shimadzu UV-3600 UV−vis-NIR spectrophotometer equipped with an integrating sphere. Photoluminescence (PL) spectra were determined by using a Hitachi F-4500 fluorescence spectrofluorophotometer. Time-resolved fluorescence spectra (TRFS) were obtained on an Edinburgh FES 920 with an excitation wavelength of 377 nm. The photocurrent behaviors of the dye-sensitized semiconductor systems were investigated on a CHI618C electrochemical analyzer with a three-electrode (Pt wire, Pt plate, and Ag/AgCl as working, counter, and reference electrode, respectively) system immersed in the suspension containing 10 mL of catalyst (1 g L^{-1}), 5 mg of methyl viologen (MV), and 1.0 M NaOH solution, which was continuously purged by N_2 to remove O_2 before irradiation.[26,28]

Photocatalytic Property Tests. H_2 production reactions are performed at room temperature in an outer irradiation-type photoreactor (Pyrex glass) connected to a closed gas-circulation system.[26] A 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co. Ltd., China) was used as light source, which was collimated and focalized into 5 cm^2 parallel faculae. A series of cutoff filters (such as $\lambda \geq 420$ nm) or band-pass filters (such as $\lambda = 500$, 600, or 700 ± 10 nm) are employed to obtain visible light or monochromatic light. Typically, the photoreaction is performed in 10 mL of aqueous suspension containing 15 mg of catalysts and 10 vol % of triethanolamine (TEOA) or ascorbic acid (AA) as sacrificial reagent. Prior to irradiation, the suspension of the catalyst was dispersed in an ultrasonic bath for 5 min, and then the reactor was irradiated from the top with visible light irradiation after air had been thoroughly removed. H_2 evolution rate was analyzed with an online gas chromatograph (GC, SP6890, TCD detector, 5 Å molecular sieve columns, and Ar carrier). The pH values of the reaction solution were determined with an FE20/EL20 model pH meter (Mettler-Toledo Instruments Co., Ltd.).

The turnover number (TON) is usually defined by the number of reacted molecules and the number of active sites. In the present work, we assumed that H_2 production takes place when two electrons injected from the excited dye molecules react with two protons. One dye molecule can produce only one photogenerated electron, which can be injected into the conduction band (CB) of g-C_3N_4; therefore, two dye molecules are needed to react with two H^+ and produce one H_2 molecule. Hence, the TON for H_2 evolution with respect to the sensitizer was estimated as eq 1.

$$\mathrm{TON} = \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of dye molecules adsorbed}} \qquad (1)$$

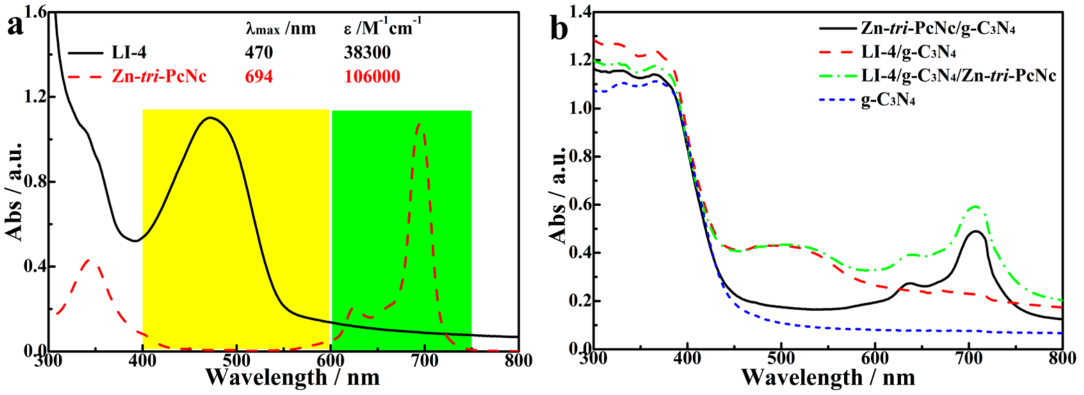


Figure 1. (a) UV−vis absorption spectra of LI-4 and Zn-tri-PcNc ethanol solution; (b) DRS spectra of g-C_3N_4, LI-4/g-C_3N_4, Zn-tri-PcNc/g-C_3N_4, and LI-4/g-C_3N_4/Zn-tri-PcNc.

Apparent quantum yield (AQY) was measured under the same photoreaction condition but with monochromatic light irradiation obtained from band-pass filter (for example, $\lambda = 700 \pm 10$ nm) and was estimated as eq 2.

$$\text{AQY (\%)} = \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}} \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Photosensitization of LI-4 on g-C_3N_4. Figure 1a shows the UV−vis absorption spectra of LI-4 and Zn-tri-PcNc solutions. LI-4 shows a strong visible light absorption with a molar extinction coefficient (~38300 M^{-1} cm^{-1}) in the range of 400−600 nm centered at ~470 nm,[27] and Zn-tri-PcNc has an absorption property complementary to that of LI-4 and shows a strong red/NIR light absorption with a high molar extinction coefficient (~106000 M^{-1} cm^{-1}) in the range of 600−750 nm centered at ~695 nm.[25] UV−vis diffuse reflectance absorption spectra (DRS) of g-C_3N_4 and its sensitized products (LI-4/g-C_3N_4, Zn-tri-PcNc/g-C_3N_4, and LI-4/g-C_3N_4/Zn-tri-PcNc), shown in Figure 1b, indicate that g-C_3N_4 absorbs limited visible light with wavelength <450 nm due to its large bandgap (2.70 eV),[26a] whereas the light-harvesting ability of g-C_3N_4 can be efficiently extended to ~600 nm by LI-4 sensitization and Zn-tri-PcNc/g-C_3N_4 shows obvious red/NIR light (600−800 nm) absorption ability. Moreover, the characteristic absorption bands of LI-4 and Zn-tri-PcNc show ~35 and ~10 nm red shifts with obvious broadening when adsorbed on g-C_3N_4, which is ascribed to the dye molecules' aggregation (a common phenomenon in dye-sensitization systems).[18,19] The co-sensitized catalyst (LI-4/g-C_3N_4/Zn-tri-PcNc) exhibits obvious visible/NIR light (400−800 nm) absorption ability, which combines the characteristic absorption band of the single dye-sensitized g-C_3N_4.

The primary result indicates that there is no H_2 production over g-C_3N_4 or Pt/g-C_3N_4 from pure water; that is, the presence of sacrificial reagent is necessary in the present system. Figure 2 shows the H_2 production activity of Pt/g-C_3N_4 and its LI-4 sensitized product (LI-4/g-C_3N_4) under visible light ($\lambda \geq$ 420 nm) by using triethanolamine (TEOA) as electron donor. It should be noted that the reaction condition is not optimized and just similar to our previous works.[8a,26] g-C_3N_4 gives only an average H_2 production activity of 19.8 μmol h^{-1} in 4 h of visible light irradiation due to its limited visible light responsive ability. After sensitization with LI-4, the photoactivity of g-C_3N_4 is dramatically enhanced to 138 μmol h^{-1}. To further confirm the dye molecules on g-C_3N_4 dominate the enhancement of the photoactivity, the wavelength-dependent AQY values based on H_2 production are shown in Figure 3a. The variation tendency of AQY curves of g-C_3N_4 and LI-4/g-C_3N_4 are very similar to their respective DRS curves, and LI-4/g-C_3N_4 gives impressive AQY values of 11.7, 5.0, and 2.2% under λ = 420, 475, and 550 nm light irradiation, respectively. Those AQY values of LI-4/g-C_3N_4 are much higher than that of g-C_3N_4, indicating that the H_2 production in the range of 400−600 nm light irradiation is mainly governed by the photosensitization of LI-4 on g-C_3N_4. Moreover, the long-term stability of LI-4/g-C_3N_4 is conducted under λ = 420 and 475 nm light irradiation, and the corresponding results are shown in Figure 3b. As can be seen, LI-4/g-C_3N_4 exhibits excellent stability for H_2 production, which shows just a slight decrease in the second 10 h compared with the first 10 h of irradiation. This indicates the excellent recycling performance of the present organic dye-sensitized catalyst.

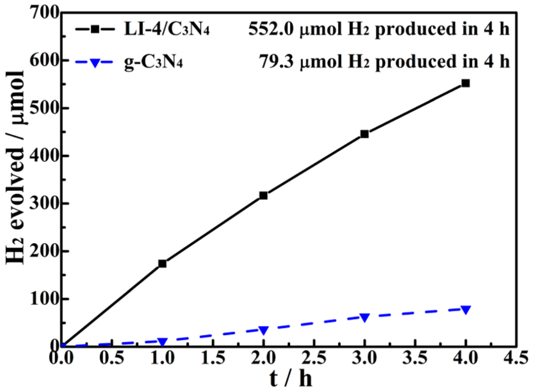


Figure 2. Photoactivity for H_2 production over Pt/g-C_3N_4 and LI-4/g-C_3N_4 under $\lambda \geq$ 420 nm light irradiation. Conditions: 15 mg of catalyst suspension containing 10 vol % TEOA, pH ~10.5 without adjustment, and 5.0 μmol g^{-1} dye on 0.5 wt % Pt/g-C_3N_4.

Photocatalytic Mechanism of LI-4 on g-C_3N_4. The electron transfer between LI-4 and g-C_3N_4 can be observed by the photoluminescence (PL) spectra shown in Figure 4a. The strong PL of LI-4 solution indicates the fast carrier recombination, and an obvious quenching effect can be observed with the addition of g-C_3N_4, implying that the photogenerated electron of the excited LI-4 can be efficiently transferred to the conduction band (CB) of g-C_3N_4 because there is no overlap between the absorption band of g-C_3N_4 and

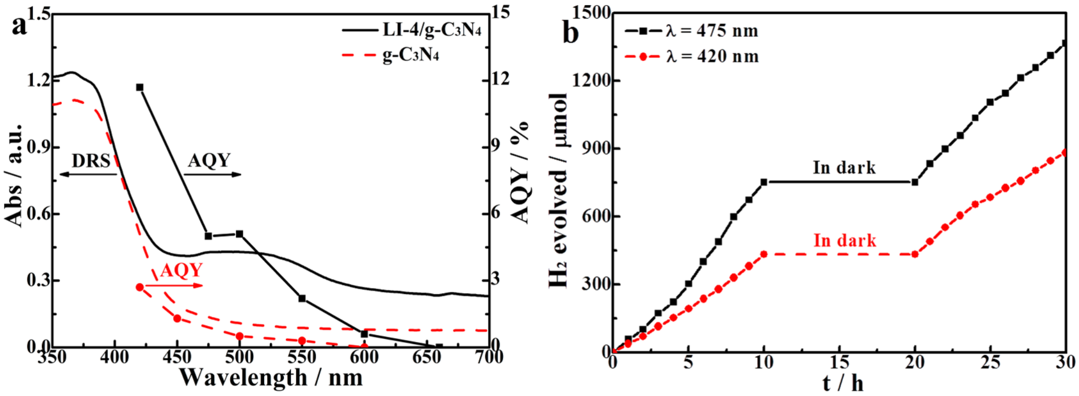


Figure 3. (a) Wavelength-dependent AQY and DRS spectra of Pt/g-C_3N_4 and LI-4/g-C_3N_4; (b) long-term stability of LI-4/g-C_3N_4 under 420 and 475 nm light irradiation.

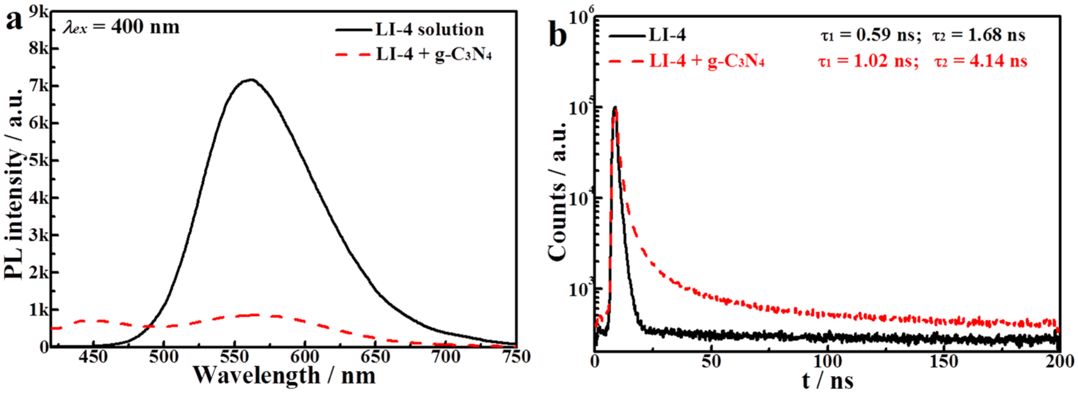


Figure 4. (a) PL spectra of LI-4 and the quenching effect of addition of Pt/g-C_3N_4; (b) time-resolved fluorescence spectra (TRFS) of LI-4 solution and its mixture with Pt/g-C_3N_4.

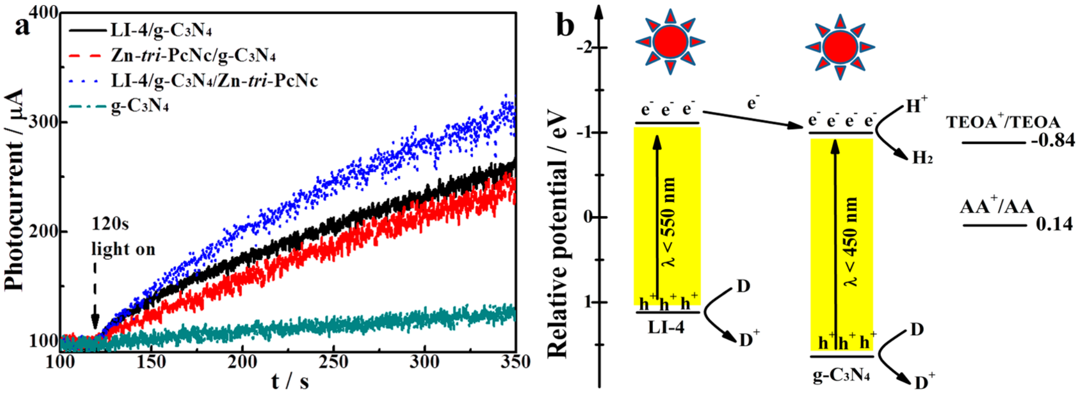


Figure 5. (a) Photocurrent−time curves of Pt/g-C_3N_4, LI-4/g-C_3N_4, Zn-tri-PcNc/g-C_3N_4, and LI-4/g-C_3N_4/Zn-tri-PcNc; (b) proposed mechanism for H_2 production over LI-4/g-C_3N_4.

the emission band of LI-4. Those electron injection dynamics from LI-4 and g-C_3N_4 can be further investigated by the time-resolved fluorescence spectra (TRFS) shown in Figure 4b.[27] The short fluorescence lifetime (0.59 ns, take τ_1 as example) of LI-4 is related to the fast charge recombination of the dye excited state, whereas the corresponding τ_1 value is prolonged to 1.02 ns with the addition of g-C_3N_4. It can be ascribed to the efficient electron transfer from the excited LI-4 to the CB of g-C_3N_4. Simultaneously, the fluorescence lifetime of LI-4 + g-C_3N_4 is increased by 73% compared to LI-4, also indicating the electron transfer from the excited LI-4 to g-C_3N_4 is fast, which might further lead to the enhanced photoactivity for H_2 production of LI-4/g-C_3N_4 as mentioned above. This conjecture on the photogenerated electron transfer can be validated by the photocurrent−time behaviors shown in Figure 5a. It can be observed that LI-4/g-C_3N_4 gives a much higher photocurrent value than g-C_3N_4 under visible light irradiation, also indicating the photogenerated electrons of LI-4 can be efficiently transferred to the CB of g-C_3N_4.

On the bases of the above discussion, a proposed photosensitization mechanism of LI-4/g-C_3N_4 is given in Figure 5b. The relative positions of the redox potentials of TEOA, LUMO/HOMO of LI-4, and CB/VB energy levels of g-C_3N_4 are shown according to previous papers.[19,26,27] It can be

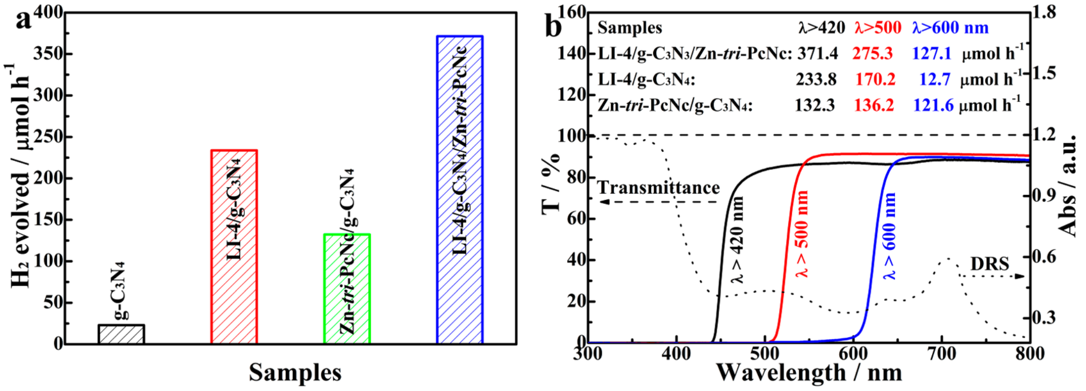


Figure 6. (a) Comparison of H_2 production activity over various dye-sensitized g-C_3N_4 under $\lambda \geq 420$ nm light irradiation; (b) wavelength-dependent H_2 production activity over sensitized catalyst under different irradiation conditions. Conditions: 10 mg of catalyst suspension (pH ~1.50) containing 10 mL of 50 mM AA and 5 μmol g^{-1} dye on g-C_3N_4. Inset data represent the H_2 production activities under $\lambda \geq 420$, 500, and 600 nm from left to right in sequence.

seen that the LUMO (−1.18 eV[27]) of LI-4 is more negative than g-C_3N_4 CB (−1.12 eV[26]), whereas its HOMO (1.09 eV[27]) is more positive than the redox potential of TEOA,[26] and therefore the overall charge transfers are allowed and consequently H_2 production is possible.[19] Both LI-4 and g-C_3N_4 can be excited by visible light; the electrons coming from the intrinsic excitation of g-C_3N_4 and injection from the excited LI-4 can be further trapped by Pt on g-C_3N_4 for H_2 production. Simultaneously, LI-4 and g-C_3N_4 can be regenerated by accepted electrons from TEOA for cyclic utilization.

Co-sensitization of LI-4 and Zn-tri-PcNc on g-C_3N_4. Although LI-4/g-C_3N_4 shows high H_2 production activity with impressive high AQY values, the photosensitization almost cannot work when the wavelength is >600 nm as shown in Figure 3a. According to the co-sensitization concept widely adopted in DSSCs,[21,22] a similar system based on g-C_3N_4 co-sensitized by LI-4 and Zn-tri-PcNc with complementary absorption spectral range is constructed for H_2 production. Zn-tri-PcNc exhibits excellent absorption ability in the region of 600−750 nm with high molar extinction coefficient (Figure 1a) and has already been proven to be an effective photosensitizer of DSSCs for solar conversion.[26,27] As mentioned above, the DRS spectrum (Figure 1b) shows the co-sensitized catalyst (LI-4/g-C_3N_4/Zn-tri-PcNc) exhibits obvious visible/NIR light (400−800 nm) absorption ability, which combines the characteristic absorption bands of the single dye-sensitized g-C_3N_4.

Figure 6a compares the photocatalytic H_2 production activities of various dye-sensitized g-C_3N_4 molecules. As can be seen, all dye-sensitized catalysts exhibit markedly enhanced photoactivity compared to the pure g-C_3N_4, indicating the efficient photosensitization of those dye molecules on g-C_3N_4. Typically, LI-4/g-C_3N_4/Zn-tri-PcNc gives a H_2 production activity of 371.4 μmol h^{-1} with TON of 7428 h^{-1} under visible/NIR light irradiation, which is approximately the summation of the two single-dye sensitized g-C_3N_4 molecules (233.8 μmol h^{-1} for LI-4/g-C_3N_4 and 132.3 μmol h^{-1} for Zn-tri-PcNc/g-C_3N_4). This result indicates the successful combination of the two different dyes (metal-free organic dye and zinc phthalocyanine) on one semiconductor for broad spectral responsive photocatalytic H_2 production. It should be noted that ascorbic acid (AA) instead of TEOA is adopted as sacrificial reagent in this section because Zn-tri-PcNc shows better photosensitization when AA is used as electron donor as reported in our previous work.[26] Moreover, LI-4/g-C_3N_4 also shows photoactivity (233.8 μmol h^{-1}) for H_2 production by using AA as electron donor, which is much better than that (138 μmol h^{-1}) of LI-4/g-C_3N_4 by using TEOA as electron donor as shown in Figure 2. Generally, it can be concluded that the regeneration of the oxidized dye can be more favored in TEOA solution due to its more negative redox potential than AA as sacrificial reagent by comparing their redox potentials and the HOMO level of LI-4 shown in Figure 5b.[26,27] However, AA as sacrificial reagent shows much better photoactivity than TEOA as mentioned above. This strongly suggests that the dye-sensitized system is sensitive not only to the relative energy levels but also to the electron transfer kinetics that are related to molecular interaction among dye molecules, g-C_3N_4, and electron donors.[19] The dye adsorption−desorption process on semiconductor surfaces is highly sensitive to pH value due to different acid-dissociation behaviors between dyes and semiconductor.[19] In this regard, the probable reason might be the differences in the acidity of the sacrificial reagent solutions, which may further influence the approach to the oxidized dye molecules because a pH-dependent H_2 production by using EDTA or TEOA as sacrificial reagent has been reported in a semiconductor system.[19]

Simultaneously, the H_2 production activities of the catalysts under different cutoff wavelength light ($\lambda \geq 420$, 500, and 600 nm) irradiation are evaluated to investigate the main photosensitization region of the two dyes in the co-sensitized system, and the corresponding results are shown in Figure 6b. It can be concluded that Zn-tri-PcNc mainly works under $\lambda \geq 600$ nm light irradiation due to its photosensitization similar to that under $\lambda \geq 420$ and 500 nm light irradiation. Moreover, the photoactivity of Zn-tri-PcNc/g-C_3N_4 is almost unaffected by the co-sensitization of LI-4 because LI-4/g-C_3N_4/Zn-tri-PcNc and Zn-tri-PcNc/g-C_3N_4 show similar H_2 production activities under $\lambda \geq 600$ nm light irradiation. Simultaneously, LI-4 can work under 400−600 nm light irradiation due to its insignificant H_2 production activity (12.7 μmol h^{-1}) under $\lambda \geq 600$ nm light irradiation. On the whole, the H_2 production behavior of the catalysts accord basically with the visible/NIR absorption properties of the dyes, which govern the photocatalytic H_2 production of the catalyst. Moreover, the dye co-sensitized effect can also be observed from the transient photocurrent behaviors shown in Figure 5a. Typically, all dye-sensitized g-C_3N_4 molecules show much higher photocurrent values than the pure g-C_3N_4, indicating efficient photosensitization and electron injection after the dye sensitization, and the co-sensitized catalyst gives much higher photocurrent values than that of either LI-4/g-C_3N_4 or Zn-tri-PcNc/g-C_3N_4. The above results show the perfect combination of the two different dyes with complementary absorption spectra sensitized on one semiconductor.

To further investigate the endurance and stability of H_2 production over the present dye co-sensitized catalyst under visible/NIR light irradiation ($\lambda \geq 420$ nm), the H_2 production amount for every hour of light irradiation was determined. Figure 7 depicts the time course of H_2 production from LI-4/g-C_3N_4/Zn-tri-PcNc suspension in two consecutive runs of accumulatively 30 h. The photocatalyst was collected by filtration after 20 h (10 h of irradiation and 10 h in the dark), and then fresh sacrificial reagent solution and the separated photocatalyst were added again for the second run under the same photoreaction condition. As can be seen, the co-sensitized catalyst exhibits an average photoactivity of 332 μmol h^{-1} in the first run of 10 h of photoreaction, which then slightly declines to 290 μmol h^{-1} in the second run of 10 h. Namely, about 87.3% activity can be maintained in the second run, indicating the considerable stability of the dyes and their co-sensitized catalyst. Nevertheless, more efforts are necessary for further improving the stability of the present dye co-sensitized system for its practical application under visible/NIR light irradiation.

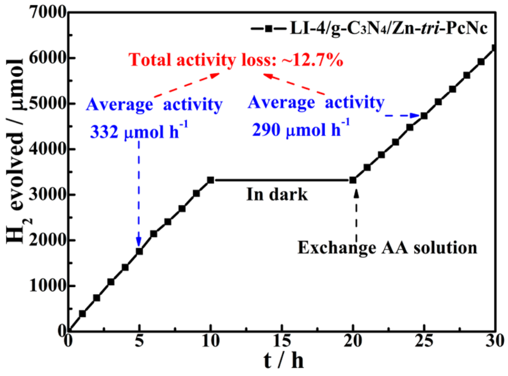


Figure 7. Photostability for H_2 production of the dye co-sensitized catalyst under $\lambda \geq 420$ nm light irradiation. Conditions: 10 mg of catalyst suspension (pH ~1.50) containing 10 mL of 50 mM AA and 5 μmol g^{-1} dye on g-C_3N_4.

Photocatalytic Mechanism of Co-sensitization Catalyst. Figure 8a gives the AQY values of the three dye-sensitized g-C_3N_4 molecules under various monochromatic light irradiation with band-pass filters (λ = 420, 475, 500, 550, 600, 660, 700, 760 ± 10 nm). As can be seen, the variation tendencies of AQY curves are similar to their respective DRS spectra shown in Figure 1b. Metal-free organic dye-sensitized catalyst (LI-4/g-C_3N_4) gives high AQY in a wide range of 400−600 nm, and Zn-tri-PcNc/g-C_3N_4 mainly works under $\lambda \geq 600$ nm with impressive AQY values. Moreover, co-sensitized catalyst (LI-4/g-C_3N_4/Zn-tri-PcNc) exhibits a perfect summation of the two single dye-sensitized catalysts, which is accordance with the above result on H_2 production. Especially, LI-4/g-C_3N_4/Zn-tri-PcNc gives AQY values of 16.3, 7.7, and 1.75% under 420, 500, and 700 nm monochromatic light, respectively. All above results imply that the dye molecules adsorbed on g-C_3N_4 govern the broad visible/NIR light harvesting and conversion. Namely, the adsorbed LI-4 and Zn-tri-PcNc can be excited by corresponding light responsive region under the visible/NIR light, and then their photogenerated electrons are injected into the g-C_3N_4 CB for H_2 production at cocatalyst Pt sites and the oxidation state of dyes can be regenerated by accepting electrons from electron donors (such as AA) for recycling utilization.

On the bases of the above experimental results and discussion, a proposed photosensitization mechanism of H_2 production over LI-4/g-C_3N_4/Zn-tri-PcNc is given in Figure 8b. According to previous studies,[19,26,27] the relative positions of the CB of g-C_3N_4 as well as the HOMO/LUMO levels (for LI-4 and Zn-tri-PcNc) are shown in Figure 8b. As can be seen, the LUMO levels of Zn-tri-PcNc (−1.40 eV) and LI-4 (−1.18 eV) are more negative than CB of g-C_3N_4 (−1.12 eV), whereas their HOMO levels are more positive than the redox potentials of AA;[26] therefore, the overall charge transfers are allowed in the present co-sensitized photocatalytic system.[19] That is, all components (g-C_3N_4, LI-4, and Zn-tri-PcNc) in the co-sensitized catalyst can be excited by corresponding light responsive region under visible/NIR light irradiation, and both the photogenerated electrons from the intrinsic excitation of g-C_3N_4 and the injected electrons from the excited dyes (LI-4 and Zn-tri-PcNc) can be transferred to cocatalyst Pt loaded on g-C_3N_4 for H_2 production.

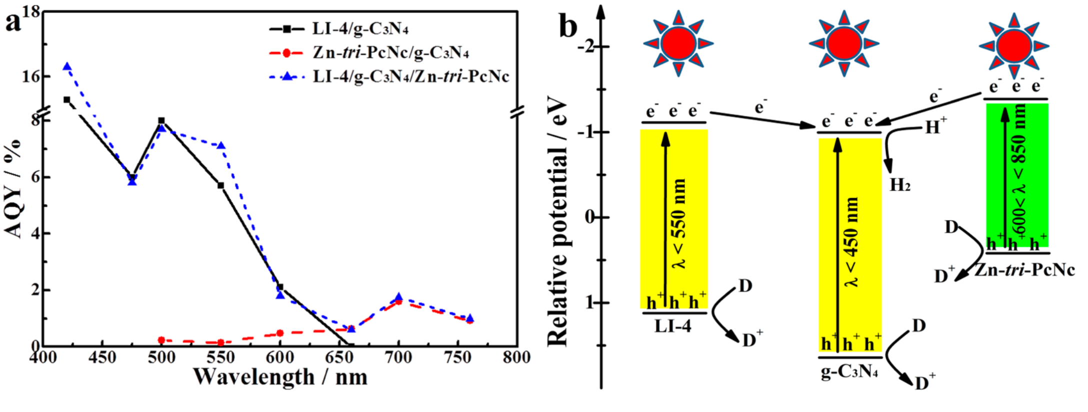


Figure 8. (a) Wavelength-dependent AQY curves of various dye-sensitized g-C_3N_4 under different monochromatic light irradiation; (b) proposed co-sensitization mechanism of g-C_3N_4 for photocatalytic H_2 production.

CONCLUSION

For the first time, a real sense of a dye co-sensitized system for panchromatic (including visible/NIR light region) responsive photocatalytic H_2 production has been successfully constructed. In this system, a novel indole-based organic dye (LI-4) that mainly absorbs 400−600 nm visible light is proved to be an efficient photosensitizer of g-C_3N_4 for H_2 production. Simultaneously, a highly asymmetric zinc phthalocyanine derivative (Zn-tri-PcNc) is taken as a complementary dye with a central absorption band of 600−750 nm. As a result, the co-sensitized catalyst LI-4/g-C_3N_4/Zn-tri-PcNc exhibits a H_2 production activity of 371.4 μmol h^{-1} with a TON of 7428 h^{-1} under visible/near-IR ($\lambda \geq 420$ nm) light irradiation, which approximates the summation of the H_2 production activity of Zn-tri-PcNc/g-C_3N_4 (132.3 μmol h^{-1}) and LI-4/g-C_3N_4 (233.8 μmol h^{-1}), although LI-4 and Zn-tri-PcNc can absorb the light in the ranges of 400−600 and 600−750 nm, respectively. Moreover, impressive AQYs of 16.3, 7.7, and 1.75% can be obtained under 420, 500, and 700 nm monochromatic light irradiation, respectively. The present work gives a clear advance toward panchromatic responsive photocatalytic application by combining the photosensitization of two different dyes with complementary absorption spectra on one kind of semiconductor.

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Notes

The authors declare no competing financial interest.

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