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# g-C<sub>3</sub>N<sub>4</sub> Sensitized by an Indoline Dye for Photocatalytic H<sub>2</sub> Evolution

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**Abstract:** Protonated g-C<sub>3</sub>N<sub>4</sub> (pCN) formed by treating bulk g-C<sub>3</sub>N<sub>4</sub> with an aqueous HCl solution was modified with D149 dye, i.e., 5-[[4[4-(2,2-diphenylethenyl) phenyl]-1,2,3,3a,4,8b-hexahydro-cyclopent[b]indol-7-yl] methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-thiazolidin-2-ylidenerhodanine, for photocatalytic water splitting (using Pt as a co-catalyst). The D149/pCN-Pt composite showed a much higher rate (2138.2  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) of H<sub>2</sub> production than pCN-Pt (657.0  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>). Through relevant characterization, the significantly high activity of D149/pCN-Pt was linked to improved absorption of visible light, accelerated electron transfer, and more efficient separation of charge carriers. The presence of both D149 and Pt was found to be important for these factors. A mechanism was proposed.

Keywords: g-C<sub>3</sub>N<sub>4</sub>; D149 dye; photocatalyst; visible light; H<sub>2</sub> production



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# 1. Introduction

Photocatalysis is an important branch of catalysis. Compared with traditional thermal catalysis, photocatalysis can only work in a narrower range of reactions, but it usually operates under milder conditions, consumes no thermal energy, and thus is of low cost [1]. Research into photocatalysis originated from the discovery of photocatalytic water splitting on TiO<sub>2</sub> electrode [2]. H<sub>2</sub> in industry is generally produced via steam reforming of CH<sub>4</sub> and the water-gas shift reaction. Without relying on fossil fuels, photocatalytic water splitting is promising for producing clean H<sub>2</sub> [3,4]. Many photocatalysts, such as CdSe/ZnSe [5], Ag/TiO<sub>2</sub> [6], NiO/TiO<sub>2</sub> [7], TiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> [8], MoS<sub>2</sub>/CdS [9], ZnS/Cu<sub>3</sub>P [10], Co<sub>2</sub>P/ZnIn<sub>2</sub>S<sub>4</sub> [11], Bi<sub>2</sub>WO<sub>6</sub>/ZnIn<sub>2</sub>S<sub>4</sub> [12], and BaTaO<sub>2</sub>N/Pt [13], were used for photocatalytic H<sub>2</sub> evolution under visible light.

Graphitic carbon nitride  $(g-C_3N_4)$  is a metal-free semiconductor photocatalyst with a suitable band gap (~2.7 eV) and high chemical stability [14–16]. However, pristine  $g-C_3N_4$  exhibits weak visible light absorption. One of the prerequisites for photocatalysts to exhibit superior performance under visible light is sufficient absorption of visible light. Therefore, several approaches have been used to enhance the visible light absorption of  $g-C_3N_4$ . For instance,  $g-C_3N_4$  has been modified by doping with metal or nonmetal ions [17–20], forming heterojunctions [21–26], and being photosensitized with dyes [27–31].

Dye sensitization is a simple and effective method to broaden the response range of materials under visible light because dyes can absorb visible light [32]. For a dye-sensitized photocatalyst, the dye molecules adsorbed on the surface of a semiconductor can be excited after absorbing visible light, thus injecting electrons into the conduction band of the semiconductor. MK2/TiO<sub>2</sub> [33], Eosin Y/TiO<sub>2</sub> [34], N749/rGO [35], GS12/TiO<sub>2</sub> [36], PY-1/g-C<sub>3</sub>N<sub>4</sub> [37], PY-2/g-C<sub>3</sub>N<sub>4</sub> [37], ZnPy/g-C<sub>3</sub>N<sub>4</sub> [38], chlorin e6/g-C<sub>3</sub>N<sub>4</sub> [39], protoporphyrin/g-C<sub>3</sub>N<sub>4</sub> [40], mTHPC/g-C<sub>3</sub>N<sub>4</sub> [41], Ppa/g-C<sub>3</sub>N<sub>4</sub> [42], N3/g-C<sub>3</sub>N<sub>4</sub> [31], and N719/g-C<sub>3</sub>N<sub>4</sub> [31] exhibited enhanced performance in H<sub>2</sub> evolution. How-

ever, more studies are needed to enrich the family of dye-sensitized  $g-C_3N_4$ , to find more efficient catalysts for water splitting, and to understanding fundamental aspects of these photocatalytic systems.

D149 dye, namely, 5-[[4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-3-thiazolidineacetic acid, is a typical indoline dye (Figure S1) [43]. D149 dye has been found to exhibit remarkable performance in dye-sensitized solar cells (DSSCs), such as D149/TiO<sub>2</sub> [44], D149/BiVO<sub>4</sub> [45], D149/SnO<sub>2</sub> [46], and D149/ZnO [47]. D149/BiVO<sub>4</sub> with enhanced performance in photocatalytic degradation of methylene blue was also developed [48]. However, D149/g-C<sub>3</sub>N<sub>4</sub> hybrid used for H<sub>2</sub> production has not been reported.

Herein, D149/pCN-Pt was developed and found to be highly active for photocatalytic water splitting. The catalysts with and without Pt were systematically tested and characterized to understand the role of D149 and Pt. Previous studies using Pt as a cocatalyst demonstrated the presence of Pt particles on g-C<sub>3</sub>N<sub>4</sub> by using TEM and EDX mapping [31,40–42]. The presence of Pt particles was found to enhance the absorption of visible light and photocatalytic activity [31,40–42]. However, the effect of Pt particles on transient photocurrent density, electronic impedance, and photoluminescence properties of the catalysts have not often been studied. Our current work provided clear evidence for the beneficial effect of both D149 and Pt particles for enhancing the photocatalytic activity.

#### 2. Materials and Methods

## 2.1. Materials

Melamine, HCl solution (36.0–38.0 wt%), and ethyl alcohol ( $C_2H_6O$ , >99.7%) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 5-[[4[4-(2,2-diphenylethenyl) phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7yl] methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-thiazolidin-2-ylidenerhodanine (D149 dye, 95%, LC) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China).

# 2.2. Preparation of Protonated g- $C_3N_4$ (pCN)

To synthesize bulk g-C<sub>3</sub>N<sub>4</sub> (bCN), 10 g of melamine was heated at 550 °C for 2 h at a rate of 5 °C ·min<sup>-1</sup> in a muffle. Then, 1 g bCN was put into 200 mL of HCl solution (1 M) for exfoliation. The slurry was magnetically stirred for 4 h. The sediment was collected by centrifugation for 16 min, washed with deionized water, and dried at 80 °C for 15 h [42]. The powders (pCN) were prepared for further use.

## 2.3. Preparation of D149/pCN

First, 0.5 g pCN was added into 25 mL ethanol solution, then the turbid liquid was magnetically stirred to make it mix evenly. Subsequently, 50 mg D149 dye was added into the slurry, and the suspension liquid was magnetically stirred rapidly overnight. Then, the sediment was collected by centrifuging and drying in an oven. The obtained powders (D149/pCN) were collected.

#### 2.4. Characterization

XRD patterns were measured by Ultimate IV powder X-ray diffractometer (Rigaku, Tokyo, Japan) using Cu K $\alpha$  radiation. FT-IR spectra were measured by Thermo Scientific Nicolet IS5. TEM and EDX mapping images were collected by a JEM-2100plus electron microscope (JEOL, Tokyo, Japan). N<sub>2</sub> adsorption-desorption isotherms were used to measure Brunauer-Emmett-Teller (BET) specific surfaces by an ASAP2460 instrument (Micromeritics Instrument Corp., Norcross, GA USA). XPS data were recorded on an ESCALAB 250XI instrument (Thermo Fisher Scientific Instrument Corp., Now York, USA).

Ultraviolet-visible diffuse reflection spectra (UV-vis DRS) were recorded by UV-3600 (Shimazu, Kyoto, Japan) to evaluate the optical properties of catalysts. In order to collect plentiful samples containing Pt for other characterizations, the samples here were

magnified. An amount of 100 mg D149/pCN was put into an aqueous solution (180 mL) containing 8.1 mg  $H_2PtCl_6 \cdot 6H_2O$ , and 20 mL triethanolamine (TEOA) was added as a sacrificial agent. The slurry was irradiated under a 300 W Xe lamp for 4 h and was stirred magnetically. Finally, D149/pCN-Pt was collected by centrifugation and drying. pCN-Pt was prepared with the same method described above.

Transient photocurrent density curves and EIS data were recorded by a CHI 760E electrochemical workstation (CH Instrument Company, Shanghai, China) under visible light ( $\lambda > 420$  nm). The details of electrode fabrication were given elsewhere [40–42]. Briefly, 0.09 g sample power, 0.01 g polyvinylidene fluoride (PVDF), and 20 drops N-methylpyrrolidone were homogenously mixed and spread (1 × 1 cm<sup>2</sup>) on a 1 × 2 cm<sup>2</sup> indium tin oxide (ITO) glass. Photoluminescence (PL) spectra were measured by Edinburgh FLS1000 (Edinburgh Instruments Livingston, Edinburgh, UK) under 300 nm excitation at room temperature.

#### 2.5. Photocatalytic Activity

Photocatalytic H<sub>2</sub> production was tested under visible light (300 W Xe lamp,  $\lambda > 420$  nm). The light intensity was 120 mW cm<sup>-2</sup>. The distance from the reaction instrument to the light source was 4 cm.

The procedure for testing H<sub>2</sub> evolution yields was as follows [40–42]: 10 mg samples were put into an aqueous solution (18 mL) containing 0.81 mg H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O, and then 2 mL of triethanolamine (TEOA) was added as a sacrificial agent. The sealed quartz reactor was subjected to ultrasonic treatment for 10 min. Pure N<sub>2</sub> was blown into the reactor to remove the remaining air. Afterwards, the system was treated by ultrasound for 10 min. Eventually, the photocatalytic reaction system (PerfectLight, Labsolar-IIIAG, Beijing, China) was irradiated by a light source (PerfectLight, PLS-SXE300C, Beijing, China) with a filter ( $\lambda > 420$  nm), and operated at 12 °C. The production of hydrogen was analyzed by an online gas chromatograph (GC9200, Tian Mei, shanghai, China), with the help of a circulating pump. The schematic hydrogen production system is shown in Figure S2.

## 3. Results

#### 3.1. Regular Characterization

Figure 1 shows XRD patterns. pCN shows peaks at  $13.1^{\circ}$  and  $27.3^{\circ}$ , corresponding to the (100) and (002) planes of g-C<sub>3</sub>N<sub>4</sub> (JCPDS No.87-1526), respectively [49]. D149 dye shows a few distinct peaks. D149/pCN shows the peaks of pCN and some tiny peaks corresponding to D149 dye.



Figure 1. XRD patterns of pCN, D149, and D149/pCN.

Figure S3 shows FT-IR spectra. The cuspidal peak at 807 cm<sup>-1</sup> represents the tris-triazine structure of g-C<sub>3</sub>N<sub>4</sub> [50]. The peaks at 1250, 1330, 1413, 1575, and 1645 cm<sup>-1</sup> correspond to the stretching vibration modes of C–N and C=N bonds of the heptazine heterocyclic ring (C<sub>6</sub>N<sub>7</sub>) [51]. A broad peak located from 2800 to 3600 cm<sup>-1</sup> signifies the existence of abundant –NH<sub>x</sub> [52]. As for D149 dye, the peak at 1128 cm<sup>-1</sup> corresponds to a C–O bond. The peaks at 1240, 1547, and 1697 cm<sup>-1</sup> can be classified with N–C=, C=C, and C=O bonds, respectively [53]. The D149/pCN pattern is highly similar to the pCN pattern. The presence of D149 on pCN can be seen from the differential spectrum by subtracting the spectrum of pCN from D149/pCN (Figure S4). There, the positive peaks ranging from 700~1200 nm labeled by a red dotted line are consistent with the peaks in D149 (Figure S3), whereas the negative peaks between 1150 and 1900 nm are due to the decrease in pCN content after loading D149.

Figure S5 shows TEM images of pCN and D149/pCN. g- $C_3N_4$  treated with hydrochloric acid has a porous ultrathin structure (Figure S5A). Nonetheless, D149 dye loading can not be observed on the surface of pCN (Figure S5B), which is because that TEM is unable to detect organic dye molecules. STEM-EDX mapping images certify the existence of C, N, O, and S elements, indicating that D149 dye has been loaded on pCN (Figure 2).



**Figure 2.** A typical STEM image of D149/pCN (**A**) and EDX mapping images of C (**B**), N (**C**), O (**D**), and S (**E**).

Figure S6 shows N<sub>2</sub> sorption data. The N<sub>2</sub> adsorption-desorption isotherms of pCN and D149/pCN can be classified as a type IV hysteresis loop (Figure S6A), indicating that both pCN and D149/pCN have mesoporous structure. D149/pCN has a lower BET surface area (14.7 m<sup>2</sup>·g<sup>-1</sup>) than pCN (15.3 m<sup>2</sup>·g<sup>-1</sup>), probably because the covering of pCN by D149 could block some pores of its surface. The mean pore diameter of D149/pCN is 23.5 nm, less than that of pCN (37.8 nm). The total pore volumes of D149/pCN and pCN are 0.09 and 0.10 cm<sup>3</sup>·g<sup>-1</sup>, respectively (Table S1).

Figure 3 and Figure S7 show XPS spectra. XPS survey spectra show that pristine pCN mainly consists of C, N, and O elements, and D149/pCN has an extra S element (Figure S7). Figure 3A shows the C 1s spectra of pCN and D149/pCN. The peaks at 284.40 eV and 287.91 eV are C–C and N–C=N bonds, respectively [54]. In addition, there are three main peaks in N 1s spectra (Figure 3B). The peak at 398.42 eV in the spectra of the two samples represents C–N=C bonds and the two smaller peaks at 399.80 and 400.90 eV can be classified

as N–(C)<sub>3</sub> and C–N–H, respectively [55]. Moreover, O 1s spectra of pCN and D149/pCN are shown in Figure 3C. Three main peaks at 531.40, 532.00, and 533.30 eV can be observed in pCN, assigned to O–C=O, N–C–O, and C=O, respectively [56,57]. However, these three characteristic peaks of D149/pCN have slight blue shift, pointing to 530.70, 531.90, and 533.20 eV, respectively. This result may be attributed to the interaction between D149 dye and pCN. The position of S 2p peak of D149/pCN is located at 161.40 and 163.60 eV, corresponding to S  $2p_{3/2}$  and S  $2p_{1/2}$ , respectively [58,59]. In addition, the peak at 164.90 eV corresponds to C=S bond [60], further confirming the presence of D149 dye (Figure 3D). Overall, the XPS data confirm that D149 dye has been loaded on pCN successfully.



Figure 3. High-resolution XPS data of (A) C 1s, (B) N 1s, (C) O 1s, and (D) S 2p of pCN and D149/pCN.

## 3.2. Photocatalytic Performance

Visible-light-driven H<sub>2</sub> production was used for assessing photocatalytic performance. The in situ formed Pt was used as a co-catalyst. TEOA was used as an electron donor. As can be seen in Figure 4A, both pCN and D149 dyes have low activity of H<sub>2</sub> production. When loading D149 dye onto pCN, the activity of H<sub>2</sub> evolution increases slightly, indicating that D149 dye plays a role in the photocatalytic system. In addition, there has been a significant improvement after loading Pt onto the three catalysts, confirming the critical impact of Pt in the system of photocatalytic hydrogen production. The H<sub>2</sub> evolution yield in 4 h under visible light of D149/pCN-Pt is much higher than that of pCN-Pt. The average H<sub>2</sub> evolution rate of D149/pCN-Pt reaches 2138.2 µmol·h<sup>-1</sup>·g<sup>-1</sup> (Figure S8). The D149/pCN-Pt photocatalyst exhibits good recyclability (Figure 4B).



**Figure 4.** Photocatalytic  $H_2$  production of six samples (**A**), and cycling experiments of photocatalytic  $H_2$  production of D149/pCN-Pt (**B**).

#### 3.3. Reasons for Enhanced Activity

Figure S9 shows the XRD patterns of samples after reaction for 4 h. The pCN-Pt and D149/pCN-Pt samples here were magnified (see Section 2.4). There are characteristic peaks of Pt at 38.1° and 44.4°, confirming the existence of Pt particles (JCPDS 04-0802) [61]. In addition, the peaks corresponding to D149 dye in D149/pCN-Pt, ranging from 10° to 25°, become lower than those in D149/pCN. This is may be because a small part of the D149 dye is lost (possibly leached) after loading Pt. Figure 5 certifies the presence of D149 dye and Pt after loading Pt.

Figure 5 and Figures S10 and S11 demonstrate the presence of Pt particles on D149/pCN-Pt (collected after the recyclability test in Figure 4B) and pCN-Pt (collected after the activity test in Figure 4A), revealing that Pt was successfully loaded on the catalysts.

Figure 6 illustrates the UV-vis DRS. The absorption edge of pCN is located at 470 nm. Loading D149 onto pCN could distinctly boost the intensity of visible light absorption. Furthermore, the catalysts with Pt as a co-catalyst show stronger capacity of visible light absorption compared with those samples without Pt [26,42]. Additionally, there is an uplift from 450~700 nm in absorption line of D149/pCN. When Pt is loaded onto D149/pCN, the uplift decreases. This phenomenon is consistent with XRD results, showing the loss of some D149 (Figure S9).





**Figure 5.** A typical STEM image of D149/pCN-Pt collected after the recyclability test (**A**) and EDX mapping images of C (**B**), N (**C**), O (**D**), S (**E**), and Pt (**F**).



Figure 6. UV-vis DRS data of pCN, D149, D149/pCN, pCN-Pt, and D149/pCN-Pt.

Figure 7 displays the transient photocurrent density curves of the catalysts. The current density shows the order of pCN < D149/pCN < pCN-Pt < D149/pCN-Pt. The result illustrates that D149/pCN could produce more photogenerated electrons compared with original pCN. Moreover, the addition of Pt can make more photogenerated electrons transfer to the surface of the catalysts for redox reaction [62,63].

Figure 8 shows the EIS data. Smaller relative radius of the arcs can accelerate electrons transfer and make better separation efficiency of the photogenerated  $e^--h^+$  pairs, thus leading to a better photocatalytic performance [64]. In Figure 8, D149/pCN has smaller arc radius compared with pCN, showing that loading D149 dye onto pCN reduces the resistance to electron transfer and prevents the recombination of  $e^--h^+$  pairs. Adding Pt onto the two samples can significantly reduce the arc radius in EIS spectra, indicating

that pCN-Pt and D149/pCN-Pt have better capability of charge transfer and separation efficiency of the photogenerated  $e^--h^+$  pairs [62,63].



Figure 7. Transient photocurrent density of pCN, D149/pCN, pCN-Pt, and D149/pCN-Pt.



Figure 8. EIS spectra of pCN, D149/pCN, pCN-Pt, and D149/pCN-Pt.

Figure 9 shows the photoluminescence (PL) data. Apparently, the PL intensity of D149/pCN is lower than that of pure pCN, indicating that the recombination of  $e^--h^+$  pairs is confined due to the formation of D149/pCN. Furthermore, pCN-Pt and D149/pCN-Pt have much lower emission peaks compared with pCN and D149/pCN, which may be because Pt can not only restrict the recombination of  $e^--h^+$  pairs, but also accelerate charge transfer [65–67].



Figure 9. PL spectra of pCN, D149/pCN, pCN-Pt, and D149/pCN-Pt.

#### 3.4. Photocatalytic Reaction Mechanism

Based upon the above characterizations of the catalyst, a possible photocatalytic mechanism is proposed (Figure 10). The bandgap values of pCN and D149 dye can be calculated through the following equation [68]:

$$\alpha h \nu = A \left( h \nu - E_{\varphi} \right)^{n/2}$$

where  $\alpha$ , h,  $\nu$ , A, and E<sub>g</sub> represent the absorption coefficient, Plancks' constant, light frequency, proportionality constant, and bandgap energy, respectively. The n value is equal to 1 because g-C<sub>3</sub>N<sub>4</sub> is a direct bandgap semiconductor [69]. The E<sub>g</sub> of pCN and D149 are 2.50 and 1.58 eV, respectively (Figure S12). Obviously, the bandgap width of D149 is narrower than that of pCN. Moreover, the E<sub>VB</sub> of pCN and D149 dye obtained by XPS valence band spectra are 1.80 and 0.25 V, respectively (Figure S13). Consequently, the E<sub>CB</sub> values of pCN and D149 are -0.70 and -1.33 V, respectively.

When illuminated with visible light, the catalyst generates electrons (e<sup>-</sup>) on CB and holes (h<sup>+</sup>) on VB. Since electrons are inclined to migrate from negative to positive potential, the e<sup>-</sup> at the CB of D149 dye is more likely to transfer to Pt particles rather than transfer to the CB of pCN. Therefore, the e<sup>-</sup> at the CB of pCN recombined with the h<sup>+</sup> at the VB of D149 quickly due to the synergistic effect of internal electric field and electrostatic interaction [70]. Meanwhile, the h<sup>+</sup> and e<sup>-</sup> remain on the VB of pCN and CB of D149, respectively, to oxidize TEOA to TEOA<sup>+</sup> and reduce H<sup>+</sup> to H<sub>2</sub> [71,72]. A Z-scheme transfer mode is feasible for this photocatalytic system. This envisaged Z-scheme mechanism is in accordance with the mechanism proposed in previous photocatalytic works, involving PDIP/g-C<sub>3</sub>N<sub>4</sub> [73], PTCDI/g-C<sub>3</sub>N<sub>4</sub> [74], and O-CN/g-C<sub>3</sub>N<sub>4</sub> [75].



Figure 10. Mechanism of photocatalytic H<sub>2</sub> production by D149/pCN-Pt.

## 4. Discussion

Many studies have shown that Pt as a co-catalyst can effectively improve the performance of photocatalytic hydrogen production [27,76,77]. Some studies have also carried out the subsequent characterizations on samples containing Pt. For example, Mei et al. prepared TCPP/Pt/g- $C_3N_4$  and characterized the catalyst by PL, suggesting that the improved hydrogen production is because Pt inhibits the recombination of the photogenerated e<sup>-</sup>-h<sup>+</sup> pairs [66]. Ou et al. characterized  $Pt/g-C_3N_4$  with photocurrent, EIS, and PL, and revealed that introducing Pt onto g-C<sub>3</sub>N<sub>4</sub> leads to better charge transfer and higher efficiency in  $e^{-}$  h<sup>+</sup> pairs separation, thus to an improved H<sub>2</sub> evolution rate [62]. However, in many literatures, catalysts containing Pt have not been characterized in detail, and the reason why Pt improved the activity of photocatalytic  $H_2$  evolution has not been elaborated [31,39–42]. For instance, N3/pCN-Pt and N719/pCN-Pt were characterized by TEM and STEM-EDX mapping, indicating that Pt particles were loaded [31]. N3/pCN-Pt and N719/pCN-Pt were also characterized by UV-vis DRS, revealing that the absorbance of catalysts remained well after photocatalytic reaction [31]. However, the reason why Pt can improve the performance of photocatalytic H<sub>2</sub> production has not been explored. In this work, XRD and TEM were used to confirm that Pt was loaded onto the catalysts (Figures S9-S11, and Figure 4). UV-vis DRS, photocurrent density, EIS, and PL characterizations of catalysts with Pt were also performed (Figures 6–9).

The photocatalytic activity follows the order of pCN < D149/pCN < pCN-Pt < D149/pCN-Pt (Figure 4A). Here, the transient photocurrent density increase in the order of pCN < D149/pCN < pCN-Pt < D149/pCN-Pt (Figure 7). The relative radius of the arcs in EIS spectra decrease in the order of pCN > D149/pCN > pCN-Pt > D149/pCN-Pt (Figure 8). The sequence of PL intensity of the four samples from high to low is pCN > D149/pCN > pCN-Pt > D149/pCN-Pt (Figure 9). Based upon the above characterizations, it can be deduced that loading D149 dye on the pCN can improve the activity of photocatalytic hydrogen production to some extent. The reason may be attributed to increased absorption of visible light, better capability of charge transfer, and separation efficiency of the photogenerated  $e^-$ -h<sup>+</sup> pairs. However, it seems that the Pt can be a key factor to enhance the catalytic activity, which may result from a superior absorption of visible light and a faster electron transfer from pCN or D149 dye to Pt NPs and consequently contribute to higher activity of H<sub>2</sub> production under visible light [78].

Table S2 shows the comparison of the photocatalytic performance of H<sub>2</sub> production of g-C<sub>3</sub>N<sub>4</sub> sensitized by different dyes [27,31,37,39–42,79–81]. It is obvious that the range of H<sub>2</sub> evolution rates is from 39.0 to 6525.0  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>. This study obtained the H<sub>2</sub> evolution rate of 2138.2  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>, which is within a reasonable range. In particular, under similar conditions, the average HER of D149/pCN-Pt is higher than that of Ce6/pCN (1275.6  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [39], Pp/pCN (1153.8  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [40], mTHPC/pCN (1041.4  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [41], Ppa/pCN (1093.0  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [42], and N3/pCN (1490.7  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [31], although slightly lower than N719/pCN (2500.1  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [31]. In addition, the average HER of D149/pCN-Pt is also much higher than that of TiOF<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> (343.8  $\mu$ mol·h<sup>-1</sup>·g<sup>-1</sup>) [26], because dye-sensitized g-C<sub>3</sub>N<sub>4</sub> has a greater ability to absorb visible light.

It should be mentioned that if all the  $H_2PtCl_6$  can be reduced in situ upon visible-light irradiation and be deposited onto the catalyst surface, then the "theoretical" Pt loading should be 3 wt.%. However, the Pt content of the magnified D149/pCN-Pt sample contains 0.033 wt.% Pt, as analyzed by ICP-OES. This information thus shows that  $H_2PtCl_6$  in the slurry cannot be completely reduced under the adopted reaction condition. Even this is the case, the catalyst still shows obviously enhanced photocatalytic activity, underscoring the promoting role of Pt deposited onto the catalyst. In-depth analysis of the influence of Pt content on the activity may be conducted in the future.

## 5. Conclusions

In this study, we developed a novel dye-sensitized photocatalyst, and Pt was used as a co-catalyst (D149/pCN-Pt). In our study, D149 is a modena indoline dye; pCN stands for protonated g-C<sub>3</sub>N<sub>4</sub>. The photocatalyst shows better photocatalytic performance for H<sub>2</sub> production under visible light compared with pure D149 dye and pCN. Furthermore, we also conducted a control experiment to investigate the difference in hydrogen production of the catalysts with and without Pt. In particular, the addition of Pt nanoparticles as a co-catalyst can significantly increase the hydrogen evolution rate. Through a series of characterizations of catalysts with Pt, the possible reasons for improved performance of photocatalytic hydrogen production are ascribed to the observation that Pt has enhanced absorbance of visible light, and Pt particles can accelerate charge transfer and separation of photogenerated e<sup>-</sup>-h<sup>+</sup> pairs. This study revealed the possibility of achieving improved performance of photocatalytic hydrogen production by indoline dye-sensitized g-C<sub>3</sub>N<sub>4</sub> and discussed the reasons for enhancing the H<sub>2</sub> evolution activity by using Pt as a co-catalyst.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/ 10.3390/pr9061055/s1, Figure S1. Chemical structures of D149 dye. Figure S2. The schematic hydrogen production system. Figure S3. FT-IR spectra of pCN, D149, and D149/pCN. Figure S4. The differential spectra obtained by subtracting the spectrum of pCN from D149/pCN. Figure S5. TEM images of pCN (A) and D149/pCN (B). Figure S6. (A) N<sub>2</sub> adsorption-desorption isotherms and (B) pore diameter distribution curves from BJH adsorption curves of pCN and D149/pCN. Figure S7. XPS survey spectra of pCN and D149/pCN. Figure S8. average H<sub>2</sub> evolution rates of the three samples with and without Pt in 4 h under visible light ( $\lambda > 420$  nm). Figure S9. XRD patterns of pCN, D149, D149/pCN, pCN-Pt, and D149/pCN-Pt. Figure S10. TEM images of pCN-Pt collected after reaction for one time (A) and D149/pCN-Pt collected after the recyclability test (B). Figure S11. A typical STEM image of pCN-Pt collected after reaction for one time (A) and EDX mapping images of C (B), N (C), O (D), and Pt (E). Figure S12. Band gap curves of pCN and D149. Figure S13.  $E_{VB}$ values of pCN (A) and D149 dye (B). Table S1. BET surface area, mean pore diameter, and total pore volume of two samples. Table S2. Comparison of H<sub>2</sub> evolution rate of dye-sensitized g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation.

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