

Article

Self-Assembled PDI-COOH/PDINH Supramolecular Composite Photocatalysts for Highly Efficient Photodegradation of Organic Pollutants

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Abstract: Photocatalytic degradation of organic pollutants is one of the green ways to solve environmental problems. In this study, the PDI-COOH/PDINH composite photocatalysts were successfully synthesized by electrostatic self-assembly. Under visible light irradiation, the degradation efficiency of the optimal PDI-COOH/PDINH sample reached 67%, which was 1.7 and 1.6 times higher than that of the self-assembled PDINH supramolecule and PDI-COOH supramolecule, respectively. The excellent photocatalytic performance of PDI-COOH/PDINH can be attributed to the enhancement of the separation and transport efficiency of photogenerated carriers by the construction of a hetero-junction and the expanded electronic conjugated structure by the combination of organic–organic semiconductors. This study offers a new idea for the preparation of organic–organic composite photocatalysts.

Keywords: self-assembly PDI supramolecular; photocatalytic degradation; composite semiconductor photocatalytic



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1. Introduction

Water is a core element of sustainable development and is critical for economic development, energy and food production, ecosystem health, and human survival. A large number of toxic dyestuff molecules are present in industrial wastewater. These dyestuff molecules must be removed from the system by degradation to protect the environment. Compared with traditional methods such as adsorption and osmosis, molecules must be removed from the system, e.g., by adsorption or degradation processes, to protect the environment, which has the advantages of gentle reaction conditions [1–7], relatively low price, and simple operative procedures [8,9]. The photocatalytic reaction mainly relies on semiconductor catalysts; therefore, designing and preparing highly active catalysts is the key to improving degradation efficiency. In the past, research on catalysts has focused on inorganic semiconductors, while organic semiconductors have received less attention [10–12]. Compared with high-cost inorganic semiconductors, organic semiconductors have a lot of advantages: abundant raw materials, environmentally friendly, gentle preparation conditions, easy structural modification, good photobleaching resistance, and better chemical stability [13–22].

The absorption of photons by organic semiconductor photocatalysts will cause the electrons in the HOMO orbitals to jump to the LUMO orbitals while leaving photogenerated holes in the HOMO orbitals. The photogenerated holes and electrons migrated to the surface can participate in a series of redox reaction processes, thus realizing the

photochemical energy conversion process. The organic supramolecule perylene-3,4,9,10-tetracarboxylic diimide (PDINH) is a typical n-type semiconductor whose molecules rely on π - π interactions to form a giant π -conjugated structure [23]. The conjugated system gives it excellent charge carrier mobility, photothermal stability, and electron affinity [24–27]. These advantages make PDINH supramolecules widely used in organic solar cells [28,29], photodynamic therapy (PDT) [30], and light-emitting diodes (LEDs). Meanwhile, the band electronic structure of a specific bandwidth enables them to degrade phenol [31,32], purify wastewater [33], generate hydrogen peroxide [34], and decompose water [35] under visible light. However, self-assembled PDINH supramolecules have the disadvantages of fast electron–hole complexation, high electrical resistance, and weak electrical conductivity [36–39], which limit their applications in photocatalysis. Fortunately, the composite of PDINH supramolecules with narrow bandgap materials for establishing heterojunctions can improve their photocatalytic activity.

Replacing the side chain of the PDINH molecule with -COOH yields a new organic semiconductor, PDI-COOH. A narrow band gap of ~ 1.7 eV allows it to combine with the PDINH molecule to form heterostructures. On the one hand, the PDI-COOH molecule is soluble in water, and the complexation with the PDINH molecule can increase the overall solubility of the composite in aqueous system. It can also be utilized to self-assemble through non-covalent interactions by taking advantage of the solubility difference in different solutions to achieve solid-state precipitation [40]. On the other hand, the heterostructures formed significantly improve the separation efficiency of photogenerated electron holes and exhibit higher redox capacity.

On the basis of these considerations, in this paper, two self-assembled supramolecules, PDINH and PDI-COOH, were composited, and their photocatalytic properties, stability, and photocatalytic mechanisms were investigated. SEM and TEM tests were employed to characterize the microscopic morphology, while XRD, FT-IR, UV-Vis and electrochemical tests were employed to characterize the materials' composition, structure and photoelectrochemical features. The research on PDINH and PDI-COOH heterojunctions in organic photovoltaic materials and devices has made remarkable progress, especially in the fields of organic solar cells and photocatalysis. However, future studies still need to make more explorations in the direction of molecular design, interfacial optimization and stability enhancement to promote the wide application of these materials.

2. Results

2.1. XRD Analysis

The crystal structures of PDINH, PDI-COOH, and PDI-COOH/PDINH were analyzed by X-ray diffraction (XRD) (Figure 1a). The self-assembled PDINH supramolecule shows a characteristic reflection at 12.5° , corresponding to the (020) crystal plane of the PDINH molecule. Remarkably, the composite photocatalyst at 12.5° coincides with the (020) plane of PDINH [40]. Meanwhile, the reflections between 24° and 28° in the self-assembled PDI-COOH supramolecule were considered to be the characteristic reflections of the π - π stacking structure, which corresponded to π - π stacking layer spacings of 3.34–3.55 Å [41]. The reflection intensity was almost unchanged after the composite, which proved that the composite photocatalyst had a similar degree of π - π stacking, indicating the successful preparation of PDI-COOH/PDINH composite photocatalysts.

2.2. FT-IR Analysis

The FTIR spectra of the prepared photocatalysts were compared in the wave number range of $4000\sim 1300$ cm^{-1} . The peaks located at $3500\text{ cm}^{-1}\sim 3300\text{ cm}^{-1}$ belong to the stretching vibration of N-H [33], the peak located at about 1680 cm^{-1} belongs to the C=O stretching vibration, and the peaks at $1750\text{ cm}^{-1}\sim 1300\text{ cm}^{-1}$ correspond to the asymmetric secondary contraction, symmetric stretching and bending vibrational absorption peaks of C=O in the five-membered imine ring, respectively. The characteristic peaks of the self-assembled PDINH supramolecule and self-assembled PDI-COOH supramolecule were

both present in the composite photocatalysts, and these results further indicated that these two materials were successfully composited.

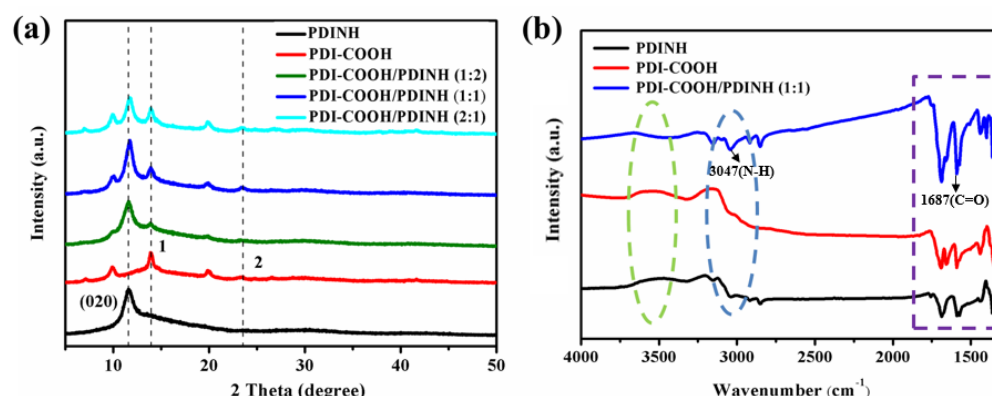


Figure 1. Self-assembled PDINH supramolecules, PDI-COOH supramolecules, and composite photocatalysts with (a) XRD and (b) FT-IR (measured under anhydrous conditions).

2.3. SEM Analysis

The SEM characterization technique was used to understand the morphology of catalytic materials. As shown in Figure 2, the PDINH supramolecule was a nanosheet morphology, and the width of the nanosheets was 400–600 nm. PDI-COOH supramolecules were formed by stacking short fibers to form a dense morphology. The average length of such short fibers was about 500 nm, and the width of such short fibers was about 50 nm. It can be observed from the figure that the composite photocatalyst PDI-COOH/PDINH (1:1) has a more compact nanosheet morphology.

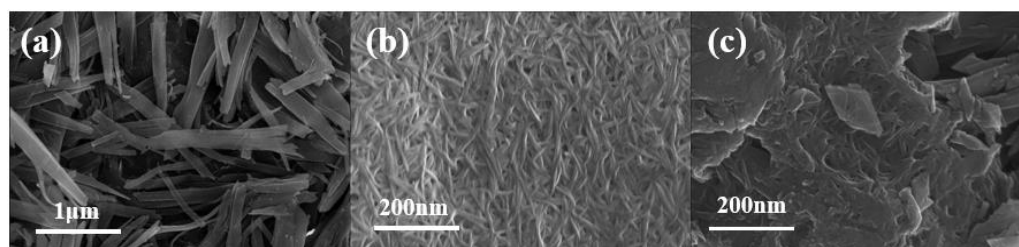


Figure 2. SEM images of self-assembled PDINH supramolecules (a), self-assembled PDI-COOH supramolecules (b), and composite photocatalysts PDI-COOH/PDINH (1:1) (c).

2.4. TEM Analysis

Figure 3 shows the TEM images of self-assembled PDINH supramolecule, self-assembled PDI-COOH supramolecule, and composite photocatalyst PDI-COOH/PDINH (1:1) samples. The PDINH supramolecule formed a nanosheet morphology with a width of about 80–100 nm. Meanwhile, the PDI-COOH supramolecule formed a nanofiber morphology with a higher aspect ratio than the PDINH supramolecule. The PDI-COOH/PDINH (1:1) showed a nanosheet morphology. In summary, it can be seen that the morphologies of PDINH, PDI-COOH, and PDI-COOH/PDINH (1:1) are all regular two-dimensional shapes.

2.5. UV-Vis DRS

The photocatalytic materials were characterized using UV-Vis diffuse reflectance spectroscopy. The spectral data in Figure 4a show that these materials exhibit distinct absorption peaks in the 200–750 nm wavelength range. PDINH and PDI-COOH showed different absorption edges at 430 nm and 660 nm. PDI-COOH/PDINH showed a slight redshift of the absorption edge compared to PDINH supramolecules (~425 nm), and the absorbance range was in between that of the self-assembled PDINH supramolecule and that of the

self-assembled PDI-COOH supramolecule, which indicated an enhanced light-absorbing ability [42]. The corresponding Tauc plots are shown in Figure 4b; the band gap energies (E_g) of self-assembled PDINH supramolecules, self-assembled PDI-COOH supramolecules, and PDI-COOH/PDINH (1:1) were 2.27 eV, 1.76 eV, and 2.10 eV, respectively. Based on the above results, it is hypothesized that the two molecules interacted with each other during the self-assembly process of the composite photocatalyst, making the formed supramolecular structure irregular, which ultimately led to a smaller light absorption range than that of the self-assembled PDI-COOH supramolecule.

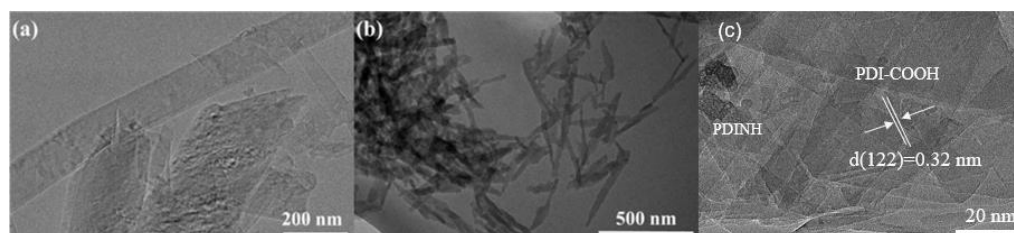


Figure 3. TEM images of self-assembled PDINH supramolecules (a), self-assembled PDI-COOH supramolecules (b), and composite photocatalysts PDI-COOH/PDINH (1:1) (c).

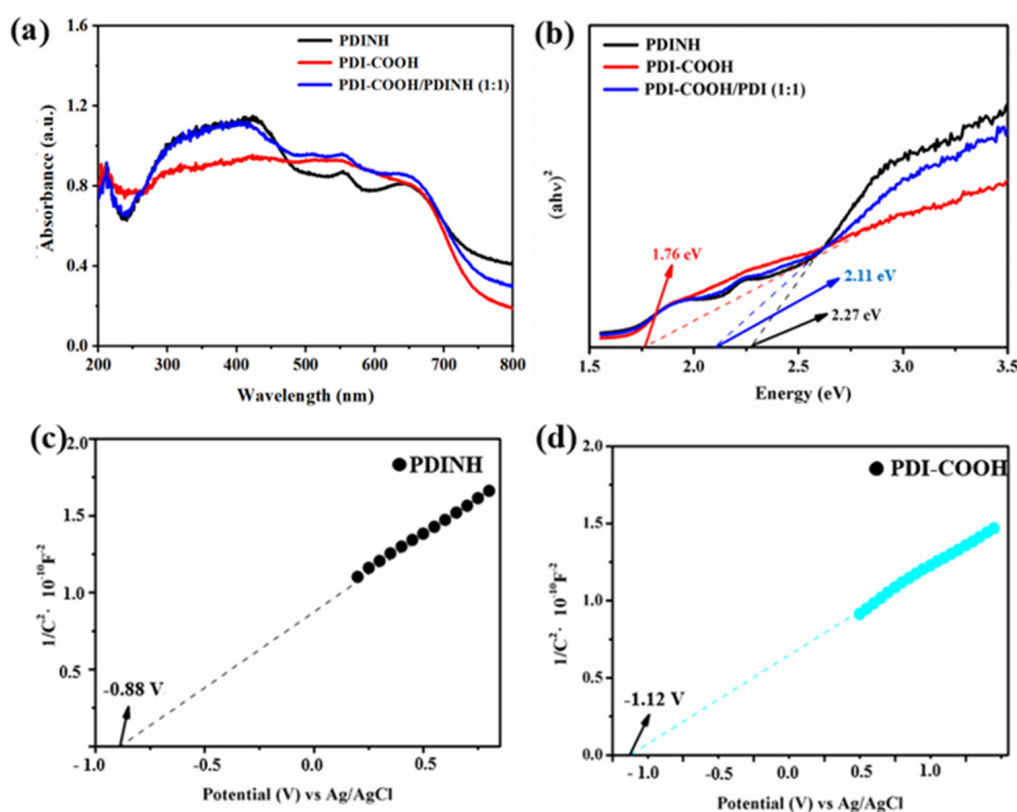


Figure 4. Self-assembled PDINH supramolecules, self-assembled PDI-COOH supramolecules, and composite photocatalysts with (a) ultraviolet–visible diffuse reflectance (UV-vis DRS); (b) bandgap diagrams; (c) Mott–Schottky plot of PDINH supramolecule; (d) Mott–Schottky plot of PDI-COOH supramolecule.

2.6. Photoelectrochemistry Analysis

Electrochemical experiments were performed to further understand the process of electron–hole separation and transfer. The carrier separation performance of all photocatalytic materials is shown in Figure 5a, and the photocurrent response curves of the composite samples were all enhanced under visible-light irradiation. The above results indicated that the heterogeneous structures of the PDINH supramolecule and PDI-COOH supramolecule significantly enhanced the electron–hole separation ability. Figure 5b shows the impedance plot; the shorter the arc diameter, the smaller the charge transfer resistance. The results showed that the self-assembled PDINH supramolecule had the most significant impedance, and the impedances of the composite photocatalysts were all smaller than that of the self-assembled PDINH supramolecule, which was consistent with the photocurrent results. Figure 5c shows the steady-state photoluminescence spectra of the samples. A broad fluorescence peak at 485 nm is observed in the three samples. The results indicated that after the heterostructure formation, the intensity of the concentration peak of PDI-COOH/PDINH (1:1) was significantly reduced, and the probability of electron–hole complexation was lowered, realizing the effective separation of the electron–hole. Using cyclic voltammetry (CV) curves it is possible to quantify the active surface area of heterojunction catalysts and to assess the efficiency of electron transfer at the interface (Figure S1).

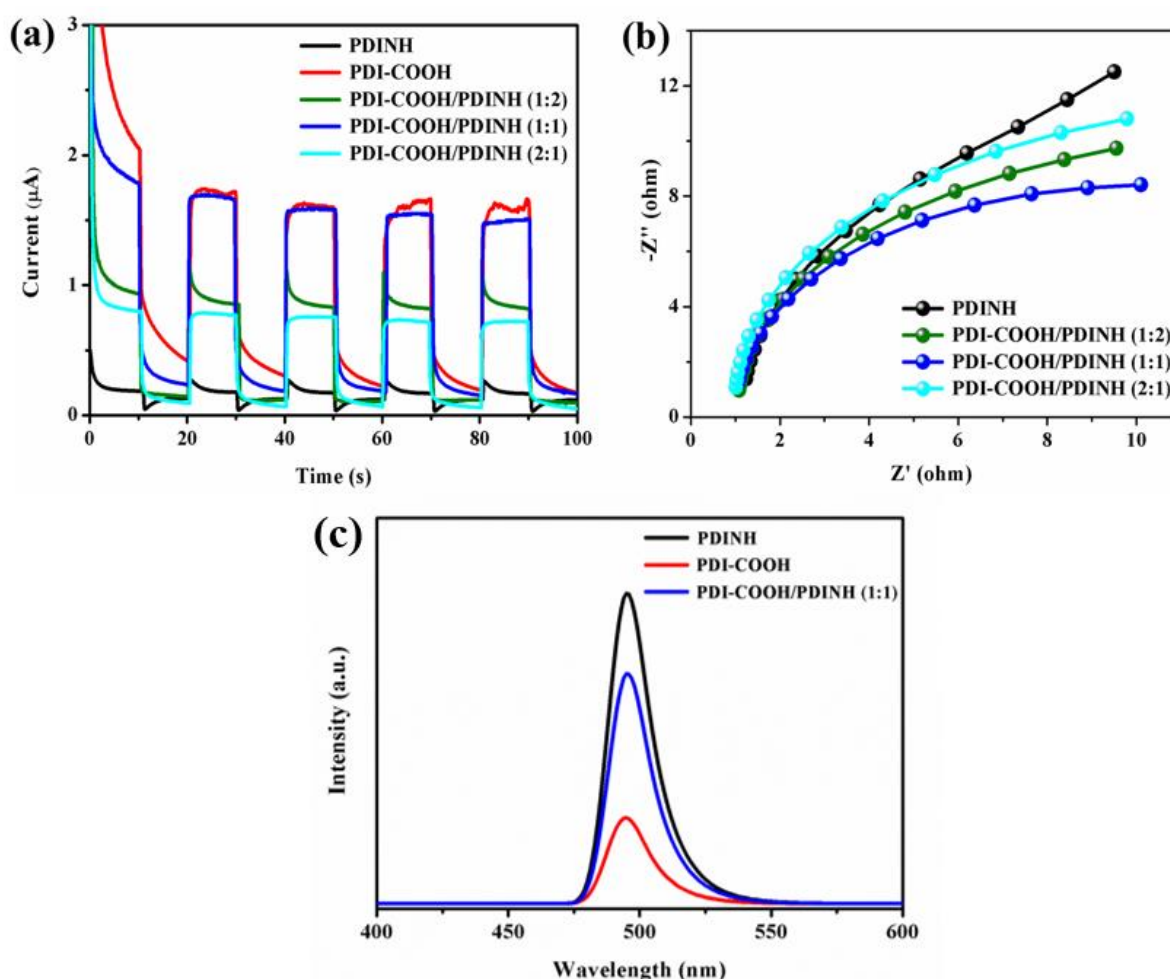


Figure 5. Self-assembled PDINH supramolecules, self-assembled PDI-COOH supramolecules, and composite photocatalysts with (a) transient photocurrent response maps, (b) electrochemical AC impedance spectra, and (c) steady-state fluorescence spectra (PL).

Additionally, the Mott–Schottky (MS) test calculated the samples' flat band potential (Figure 4c,d). The positive slope of the image indicated that PDINH is an n-type semiconductor. Also, it can be concluded that the flat band potential of PDINH was -0.88 V when Ag/AgCl was used as the reference electrode, which was converted to -0.68 V under the standard hydrogen electrode. According to the reported literature, the conduction band position of n-type semiconductors was deeper than the flat band potential (the difference was set to 0.2 eV in this paper), and the bottom of the conduction band of PDINH was obtained as -0.48 V. According to the equation " $E_{VB} = E_{CB} + E_g$ ", the valence band side of PDINH can be calculated as $(1.79$ V). The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) were commonly used in organic semiconductors when discussing the mechanism, so the LUMO and HOMO orbitals of PDINH were -0.48 V and 1.79 V, respectively. In the same way, the LUMO and HOMO orbitals of PDI-COOH could be obtained as -0.72 V and 1.04 V, respectively. Both supramolecules produced photogenerated electrons at reduction potentials lower than O_2/O_2^- (-0.33 V vs. NHE), demonstrating that photogenerated electrons could react with oxygen to form $\cdot O_2^-$.

3. Photocatalytic Performance

3.1. Photocatalytic Activity

Photocatalytic degradation experiments were performed under visible light ($\lambda > 420$ nm), and the oxidizing ability of the samples was evaluated by 20 ppm methylene blue. Compared with the single PDI supramolecular photocatalyst, the composite photocatalyst PDI-COOH/PDINH exhibited more robust photocatalytic performance. As shown in Figure 6a, PDI-COOH/PDINH (1:1) exhibited the best photocatalytic performance in degrading 20 ppm methylene blue over time. The degradation and corresponding kinetic curves were fitted, as shown in Figure 6b. The results showed that the photocatalytic degradation reaction conformed to the first-order reaction kinetics. The apparent rate constant K could be obtained from Figure 6b, and the magnitude of K is shown in Figure 6c. The degradation efficiency was obtained from Equation (1).

$$\eta = C/C_0 \quad (1)$$

where η was the photocatalytic performance efficiency, C_0 was the initial absorbance of the pollutant, and C was the absorbance of the pollutant at different times.

$$\ln(C_0/C) = kt \quad (2)$$

where C_0 was the initial absorbance of the pollutant, and C was the absorbance of the pollutant at different times. k was the reaction rate constant, and t was the reaction time.

The following values characterized the photocatalytic degradation reaction: PDI-COOH/PDINH (1:1) (0.35295 h^{-1}) > PDI-COOH/PDINH (1:2) (0.30127 h^{-1}) > PDI-COOH/PDINH (2:1) (0.28119 h^{-1}) > PDI-COOH (0.21838 h^{-1}) > PDINH (0.21129 h^{-1}), with PDI-COOH/PDINH (1:1) having the highest apparent rate constants, which are 1.7 and 1.6 times higher than those of the self-assembled PDINH and self-assembled PDI-COOH supramolecule, respectively. At the same time, the photodegradation performance under the same conditions without catalyst decreased only slightly. Figure 6d shows three cycling experiments under the same conditions.

Contact angle tests were also performed, which indicated the surface tension of the catalyst in contact with the reaction solution. The smaller the contact angle value, the higher the affinity between the solution and the catalyst, and the more favorable the degradation reaction (Figure S2).

Stability is used to determine whether a material has practical applications. Three cycling experiments were conducted under the same conditions to judge the composite samples' strength. As shown in Figure 6d, the degradation effect of PDI-COOH/PDINH (1:1) remained almost unchanged after three cycle tests, indicating that the PDI-COOH/PDINH (1:1) composite system has excellent stability.

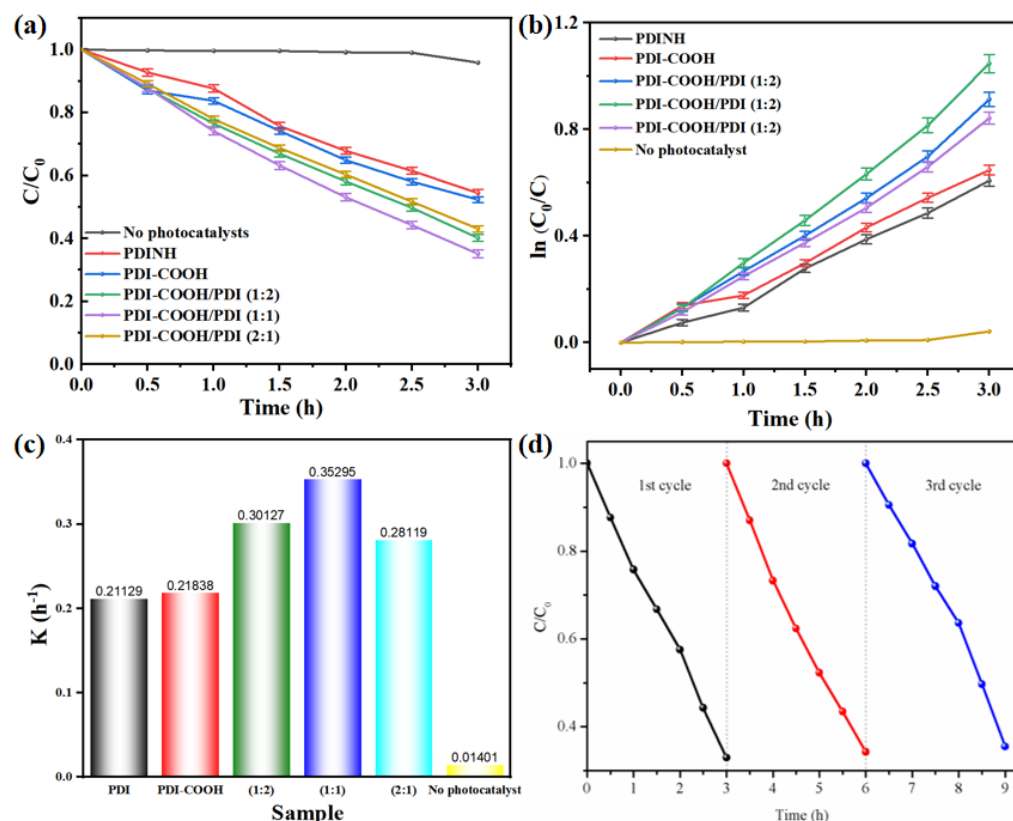


Figure 6. Degradation of 20 ppm methylene blue by visible light. (a) Degradation curve; (b) first-order kinetic curve fit; (c) apparent rate constant K value; (d) cycling experiments for the degradation of methylene blue by PDI-COOH/PDI (1:1) composite photocatalysts.

3.2. Capture Experiment

To identify the reactive groups generated during the degradation process, trapping experiments were carried out using different scavengers, see Figure 7a. The capture experiments were mainly performed for photogenerated holes (h^+), superoxide radicals ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$), and EDTA-2Na, p-benzoquinone (BQ), and isopropanol (IPA) were used as the scavengers for the groups mentioned above. This was done by quantitatively adding the various scavengers to the reaction system, keeping the experimental conditions consistent, and detecting the TC concentration at specified intervals to obtain the degradation efficiency. Three independent experiments were conducted with the three scavengers to maintain a consistent degradation environment and ensure experimental stability.

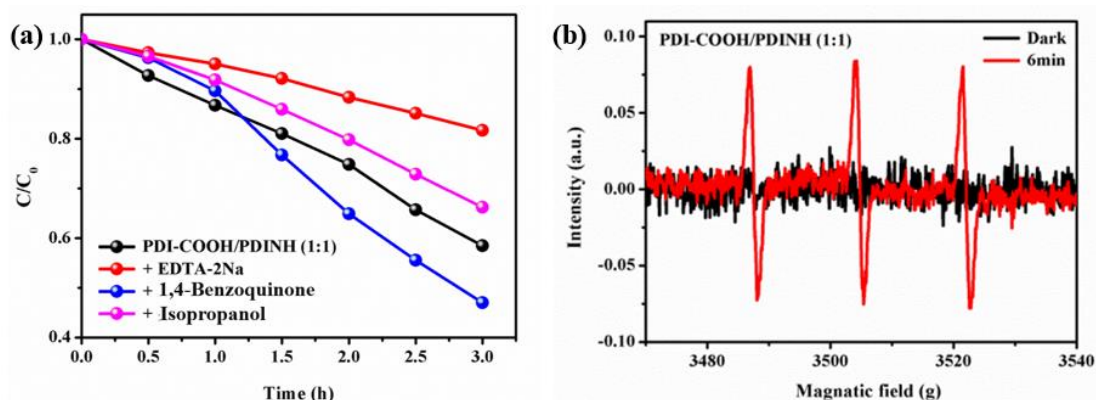


Figure 7. Capture experiment of PDI-COOH/PDI (1:1) degradation of 20 ppm methylene blue (a); PDI-COOH/PDI (1:1) for the detection of single-linear-state oxygen ($^1\text{O}_2$) in visible light (b).

3.3. Mechanism Analysis

A series of trapping experiments revealed that adding EDTA-2Na decreased the photodegradation rate after it trapped the hole, indicating that the photogenerated hole (h^+) was the active species in this degradation process. Adding p-benzoquinone (BQ) as a $\cdot O_2^-$ scavenger decreased the photocatalytic rate, indicating that $\cdot O_2^-$ was also an active species in this degradation process. However, the photocatalytic rate increased abnormally when isopropanol was added to the system as a $\cdot OH$ scavenger. There are two ways to produce $\cdot OH$; the first one was $h^+ + H_2O \rightarrow \cdot OH$ (+2.40 V vs. NHE), which was much higher than the photogenerated cavity redox potentials of PDINH and PDI-COOH supramolecules. It is hypothesized that $\cdot OH$ was generated as $e^- + O_2 \rightarrow \cdot O_2^-$, $\cdot O_2^- + e^- + 2H^+ \rightarrow H_2O_2$, $2e^- + O_2 + 2H^+ \rightarrow H_2O_2$, $H_2O_2 + e^- \rightarrow OH^- + \cdot OH$. $\cdot OH$ removal by the scavenger leads to an increase in $\cdot O_2^-$ and an improvement in photocatalytic degradation performance, and the main elements active in the system species are h^+ and $\cdot O_2^-$.

Meanwhile, to verify the existence of the energy transfer process during the reaction of this composite catalyst, electron paramagnetic resonance (ESR) was used to detect the presence of single-linear-state oxygen. The energy transfer process is prone to producing single-linear oxygen as an active species. Single-linear oxygen (1O_2) is a general name for the paramagnetic state of molecular oxygen, which belongs to the active oxygen and is the excited state of triple oxygen (3O_2), and 1O_2 is directly generated from 3O_2 by the energy transfer process. As shown in Figure 7b, the results indicate that single-linear oxygen exists in the composite photocatalyst. From the above investigation, the mechanism of degradation of methylene blue by the composite photocatalyst is shown in Figure 8. Under illumination, PDINH and PDI-COOH supramolecules absorbed light to generate electron-hole pairs and formed heterostructures to enhance the electron-hole separation efficiency.

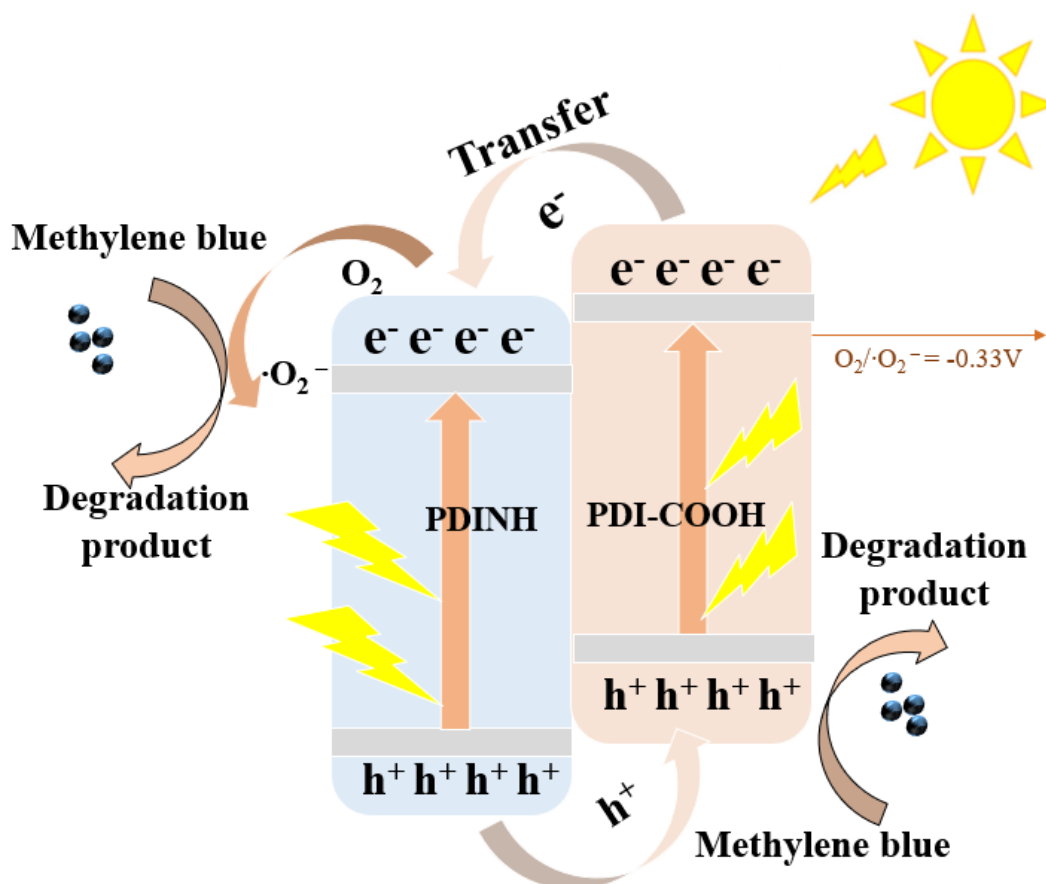


Figure 8. Mechanism of degradation of methylene blue by PDI-COOH/PDINH (1:1).

4. Materials and Methods

4.1. Chemicals and Reagents

The chemical reagents 3,4,9,10-perylenetetracarboxylic diamide ($C_{24}H_{10}N_2O_4$, A.R.), β -alanine ($C_3H_7NO_2$, A.R.), and imidazole ($C_3H_4N_2$, A.R.) were purchased from Macklin Chemical Company, Ltd., Shanghai, China, and the reagents boric acid (H_2SO_4 , A.R.), hydrochloric acid (HCl, A.R.) and methylene blue ($C_{16}H_{18}N_3SCl \cdot 3H_2O$, A.R.) were purchased from Beijing Chemical Industry Group Co., Ltd., Beijing, China, melamine ($C_3H_6N_6$, C.P.) from Sinopharm Group Chemical Reagent Co., Ltd., Beijing, China, and anhydrous ethanol (CH_3CH_2OH , A.R.) from Beijing Yili Fine Chemicals Co., Ltd., Beijing, China. All the above chemical reagents were used directly, without further purification.

4.2. Preparation of Self-Assembled PDINH Supramolecules

Self-assembled PDINH supramolecules were prepared using a rapid-solution phase dispersion method. A total of 0.1 g of PDINH was dissolved in 10 mL of concentrated sulfuric acid and sonicated for 30 min, after which 100 mL of deionized water was added to the above solution at one time and allowed to stand overnight. The purplish-red solid was collected by filtration through a $0.45 \mu m$ hydrophilic filter membrane and repeatedly washed with deionized water until the filtrate was neutral. It was dried in a vacuum oven at $60^\circ C$ overnight to obtain the self-assembled PDINH supramolecule.

4.3. Preparation of Self-Assembled PDI-COOH Supramolecules

In the first step, the PDI-COOH molecule was prepared (Figure 9). Preparation of PDI-COOH molecule: 3.5 mmol of 3,4,9,10-tetracarboxylic dianhydride, 28 mmol of β -alanine, and 18 g of imidazole were mixed in a four-necked flask and heated up to $100^\circ C$ with a heating jacket, while argon was passed in to keep the whole reaction in an argon atmosphere, and the reaction was stirred for 4 h. The product of the response was naturally cooled down to room temperature, and the dark-red viscous substance was obtained. Then, 100 mL of anhydrous ethanol and 300 mL of 2.0 M hydrochloric acid (HCl) were added to the substance and stirred overnight to obtain a dark-red suspension. The above dark-red suspension was filtered through a hydrophilic filter membrane ($0.45 \mu m$) to obtain a dark-red solid. The dark-red solid was washed repeatedly with deionized water until the filtrate became neutral, and the obtained dark-red solid was dried in a vacuum oven at $60^\circ C$ for 24 h to obtain the molecule of PDI-COOH.

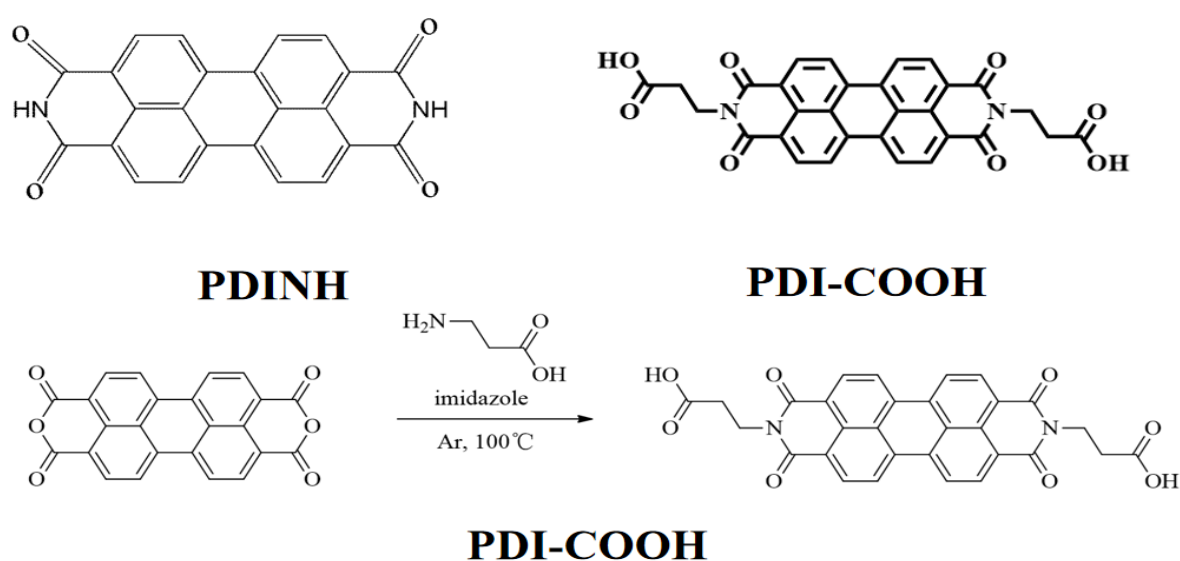


Figure 9. Flow chart of PDI-COOH molecule preparation.

Preparation of self-assembled PDI-COOH supramolecule: 0.1 g of the PDI-COOH molecule obtained in the above process was dissolved in 100 mL of deionized water, and at the same time, 800 μ L of the organic base triethylamine (TEA) was added to the solution to form a homogeneous red solution, which was stirred at room temperature for 1 h. After the stirring, 35 mL of 4.0 M hydrochloric acid was added dropwise to the solution. After the stirring, 35 mL of 4.0 M hydrochloric acid was added dropwise to the solution, and the solution was stirred for 3 h. After the stirring, the solution was allowed to stand for 12 h. A layered solution with a dark-red solid precipitated in the lower layer, and a clear transparent solution in the upper layer was obtained. After that, the above dark-red solid was filtered through a hydrophilic filter membrane (0.45 μ m), and then the above dark-red solid was washed repeatedly with deionized water until the filtrate was neutral, and the obtained dark-red solid was dried in a vacuum oven at 60 $^{\circ}$ C for 24 h to form a self-assembled PDI-COOH supramolecule.

4.4. Preparation of Self-Assembled PDI-COOH/PDINH Supramolecules

A total of 0.1 g of purchased PDINH was dissolved in 10 mL of concentrated sulfuric acid and ultrasonicated for 30 min to obtain solution A. A total of 0.1 g of PDI-COOH supramolecular was dissolved in 100 mL of deionized water, and 800 μ L of an organic base, triethylamine (TEA), was added and stirred at room temperature for 1 h. Afterward, 35 mL of 4.0 M hydrochloric acid was added dropwise to the colored liquid and stirred again for 3 h. Solution B was finally obtained. The two precursor solutions were mixed and allowed to stand overnight in a three-layered solution with a floating purplish-red solid in the upper layer, a dark-red sediment in the lower layer, and a clarified clear solution in the center. The solids were filtered by 0.45 μ m hydrophilic filter membrane, rinsed with deionized water several times, and dried at 60 $^{\circ}$ C for 24 h in a vacuum oven to obtain the composite photocatalyst.

4.5. Photocatalytic Degradation

The catalyst performance test was carried out using the light-reaction apparatus of Beijing NBET Technology Co., Ltd. (Beijing, China) to conduct multi-tube parallel testing to ensure consistent experimental conditions for photocatalytic degradation. A water-cooling system was used to control the heat of the xenon lamp to reduce the thermal effect. The light source was an XQ 500 W high-pressure xenon lamp from the same company, and a >420 nm filter was added to eliminate the influence of ultraviolet light. The probe molecules for the photocatalytic degradation study were methylene blue with an initial concentration of 20 ppm; 35 mg of photocatalyst was added to 50 mL of methylene blue solution and stirred for 1 h to reach adsorption equilibrium. After the degradation started, every 30 min interval, 5 mL of the solution was taken out and centrifuged to precipitate the catalyst, and the clarified solution was taken for testing. To determine the accuracy of the experiments, degradation experiments were also carried out without the addition of the catalyst.

4.6. Characterization

A Bruker D8 Advance X-ray powder diffractometer (XRD) from Germany was used to determine the internal crystal structure of the substance and to analyze it qualitatively and quantitatively. A Hitachi SU-8010 cold field emission scanning electron microscope with an accelerating voltage of 100 kV from Hitachi Limited, Japan, was used to obtain the fine structure of the crystals. A Tecnai G2 F30 field emission projection electron microscope from FEI with an accelerating voltage of 200 kV was used to dissolve the powdered samples in anhydrous ethanol solution ultrasonically, and drop-coated on a copper sheet for testing. To test the nanomaterials' micromorphology, crystal structure, and elemental composition analysis, Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained by a Bruker spectrometer. A Hitachi U-3900 UV-Vis spectrophotometer with a scanning range of 200–800 nm was used, and the test was carried out using an integrating-sphere attachment. The samples were tested directly with BaSO₄ as a blank control to

determine the samples' light absorption properties. The instrument model was an FLS980 fluorescence spectrometer from Edinburgh, UK. Test conditions: excitation wavelength of 488 nm, resolution of 1.0 nm. The samples were further analyzed regarding fluorescence quantum yield, fluorescence lifetime, and fluorescence quenching. Meanwhile, the photoelectrochemical properties were characterized by the Shanghai Huachen Instrument Company model CHI760E electrochemical workstation. The photocurrent density, electrochemical impedance spectra, and model Schottky curve tests were accomplished using a three-electrode system in a quartz reactor: the platinum wire was the counter electrode, the electrode of the prepared sample material was the working electrode, and the silver electrode was the reference electrode. The light source was a xenon lamp light source or a UV lamp, and the electrolyte was 0.1 mol/L, pH 6.8 sodium sulfate solution.

4.7. Electrochemical Tests

An extensive three-electrode mode was used at the electrochemical workstation (Brilliance CHI-760E, Shanghai, China) with Na₂SO₄ solution at a concentration of 0.1 M as the electrolyte. A 500 W xenon lamp (Solar-500, Beijing NBET Technology Co., Ltd., Beijing, China) with a 420 nm cut-off filter was used to record the photocurrent response. The working electrode was prepared: 5 mg of catalyst was first mixed with 2 mL of deionized water.

A platinum electrode was used for the counter electrode, while a saturated Ag/AgCl electrode was used as a reference electrode. The Mott–Schottky test measured a voltage range between −0.8 and 1.5 V.

5. Conclusions

In summary, the organic supramolecules PDINH and PDI-COOH were composited by self-assembly, which enlarged the photoresponse range and enhanced the visible light absorption. The π - π conjugated structure of PDI polymers made it easier to precipitate electrons. In addition, the compact type II heterostructure also improves the photogenerated carrier mobility and reduces the complexation rate of electron–hole pairs. Under visible light irradiation, PDI-COOH/PDINH (1:1) showed the best degradation performance, 1.7 and 1.6 times higher than PDINH and PDI-COOH supramolecules, respectively. Capture experiments and ESR tests elucidated the catalytic mechanism and demonstrated the presence of active species such as h^+ , $\cdot\text{O}_2^-$, and $^1\text{O}_2$. The present research was conducted to improve the photocatalytic degradation performance of organic semiconductor materials by regulating the separation of electrons and holes. PDINH and PDI-COOH heterojunctions have shown good potential for photocatalytic CO₂ reduction and water decomposition. Future research can focus on developing more efficient and stable photocatalysts for carbon neutralization and environmental remediation through molecular design and modulation of catalytic reaction mechanisms.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14100696/s1>.

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