Designed synthesis of a p-Ag$_2$S/n-PDI self-assembled supramolecular heterojunction for enhanced full-spectrum photocatalytic activity†

Jun Yang, Hong Miao, Wenlu Li, Huiquan Li and Yongfa Zhu$^{a,b}$

Herein, an efficient full-spectrum responsive p-Ag$_2$S/n-PDI (perylenediimide) heterojunction was successfully constructed. The self-assembled PDI nanostructure was formed via hydrogen bonding and π–π stacking. Ag$_2$S quantum dots were tightly loaded onto the surface of PDI nanofibers via a two-step electrostatic process. When the mass ratio of Ag$_2$S to PDI was 1 : 0.6, the p-Ag$_2$S/n-PDI heterojunction showed optimum photocatalytic properties. The full-spectrum photocatalytic activity of p-Ag$_2$S/n-PDI was found to be 5.13 and 1.79 times higher than pure PDI for phenol degradation and O$_2$ evolution, respectively. The results showed that Ag$_2$S quantum dots promoted the well-organized π–π stacking degree of the self-assembled PDI, which was helpful for the migration of photo-generated electrons along the quasi-one-dimensional π–π stacking of PDI. Simultaneously, Ag$_2$S quantum dots were found to enhance the light absorption of Ag$_2$S/PDI. More interestingly, the p-Ag$_2$S/n-PDI heterojunction exhibited excellent photoelectric properties, indicating more effective separation of carriers, which arose as a result of the built-in electric field between the Ag$_2$S and PDI. Besides this, the p-Ag$_2$S/n-PDI heterojunction produces more active species than pure PDI, resulting in a much stronger oxidation ability. This work details some interesting ideas for designing efficient heterojunction photocatalysts that have a supramolecular organic nanostructure.

1. Introduction

Invigorated by the present worsening of the environment and serious energy crisis, efficient use of sustainable energy sources is becoming more and more important. Among all of the renewable energies, solar energy has been widely used due to its non-pollution, cleanliness and abundance. In consideration of making the most of solar energy, it is one of the most challenging missions to search for photocatalysts with a broad spectral response. The solar spectrum consists of about 5% UV and 95% visible and near-infrared light. At present, most photocatalysts, represented by titanium dioxide, can only absorb ultraviolet light. For this reason, researchers have put a lot of effort into developing visible light catalysts, such as C$_3$N$_4$, Bi$_2$WO$_6$ (ref. 4) and BiVO$_4$. Unfortunately, their photocatalytic performance is very poor under full spectrum light. It is the ultimate aim to realize the conversion of light and chemical energy by using the full solar spectrum in photocatalysis.

Therefore, it is indisputable that searching for full-spectrum-response photocatalysts is crucial.

At present, organic photocatalytic materials are widely used.$^{6,7}$ Unlike inorganic semiconductors, organic semiconductors have many preponderances, such as various structural modifications, tunable optical and electronic properties, low cost, and rich element resources. Organic catalysts mainly comprise three types: organometallic complexes,$^{8,9}$ covalent organic polymers$^{10-12}$ and non-covalent self-assembled supramolecular organics.$^{13,14}$ Recently, a representative n-type organic semiconductor, PDI-based materials (PDI = perylenediimide), have been used in photocatalytic degradation and light-driven water splitting.$^{15,16}$ Due to them having high electron affinity, superior photo-thermal stability, and excellent charge mobility properties, PDI-based semiconductors are responsive to visible light. However, PDI-based materials have very weak photocatalytic properties under UV light and in the full spectrum region. Besides this, they are confronted with the easy recombination of photo-induced carriers. Many modification methods have been reported in order to improve the photocatalytic properties of PDI-based semiconductors, which have generally intended to increase the internal electric field of PDI. The modification methods include forming a π–π stacking structure,$^{17}$ adjusting the electron acceptor-donor units$^{18}$ and introducing functional groups.$^{19}$ These methods can improve the electron transfer rate to different degrees, but their effects
are negligible in terms of the utilization of ultraviolet and infrared light to realize full-spectrum-response photocatalysis. As a result, it is very significant to explore an effective way to improve the full spectrum photocatalytic properties of PDI-based semiconductors.

Silver sulfide (Ag$_2$S) is a p-type semiconductor, which is responsive to solar light due to its narrow band gap. The reported exciton Bohr radius of Ag$_2$S is 2.2 nm. When the radius of Ag$_2$S is larger than the exciton Bohr radius, it has a continuous band structure. Ag$_2$S has been widely applied in photovoltaic cells, photoconductors, and superionic conductors because of its good chemical stability, excellent optical properties and electronic transport. In addition, photocatalysts modified with Ag$_2$S have been reported, such as Ag$_2$S/Bi$_2$WO$_6$, ZnO/Cds/Ag$_2$S, and Ag$_2$S/TiO$_2$. The conduction band (CB) of Ag$_2$S is at around 0 eV vs. NHE, which means that it can absorb ultraviolet, visible and infrared light. As a result, silver sulfide has great potential to be applied in full spectrum photocatalysis. However, there is also the issue of the easy recombination of photoinduced carriers on account of the narrow band gap energy.

Considering the disadvantages of PDI and Ag$_2$S, we thought that it was worth constructing a novel inorganic/organic hybrid heterojunction p-Ag$_2$S/n-PDI to investigate its photocatalytic ability. On the one hand, Ag$_2$S can broaden the absorption of light, which is conducive to forming a full spectrum-responsive composite photocatalyst. On the other hand, the p-n heterostructure forms a build-in internal electric field, directed from the PDI (n-type) to Ag$_2$S (p-type), facilitating the transfer of holes and electrons in opposite directions. Simultaneously, Ag$_2$S contributes to hole transfer, which is conducive to the separation of photo-generated charge carriers. Furthermore, the photo-induced charge behavior of a p-n-type heterojunction containing self-assembled PDI has scarcely been reported. Herein, a novel composite p-Ag$_2$S/n-PDI photocatalyst was successfully designed, which exhibits satisfactory photocatalytic activity under ultraviolet, visible and full spectrum light. The work presents a new viewpoint for constructing p-n heterojunctions based on self-assembled organic catalysts.

2. Experimental section

2.1 Sample preparation

The bulk PDI was synthesized according to a reported method, the details of which can be found in the ESI.

2.2.1 Preparation of the self-assembled nano PDI. 0.5432 g of bulk PDI was dispersed in deionized water (200 mL). Then, triethylamine (800 μL) was added under vigorous stirring. After stirring for 1 hour, hydrochloric acid (4.0 M, 35 mL) was added and then the mixture was stirred again for 3 hours to form the self-assembled PDI nanofibers as a dark red solid, which was fully washed. When the pH value of the filtrate became neutral, the wet red solid was collected through a 0.22 μm filter membrane and was then placed in a vacuum drier at 70 °C.

2.2.2 Preparation of the p-Ag$_2$S/n-PDI composite. Ag$_2$S/PDI composites were obtained via an in situ precipitation method. Firstly, different quality of self-assembled PDI was dispersed in a definite volume of AgNO$_3$ solution (0.025 mol L$^{-1}$), stirred for 60 min, and then sonicated for 30 min. Secondly, the mixture was stirred for 180 min after adding a certain volume of 0.025 mol L$^{-1}$ (NH$_4$)$_2$S dropwise, and was then subjected to ultrasonic treatment for 180 min. The final solid was fully washed with deionized water and dried at 70 °C in a vacuum oven. The series of photocatalysts prepared were labelled as AP (1 : x), where AP is the abbreviation for Ag$_2$S/PDI and 1 : x represents the mass ratio of Ag$_2$S to PDI for x = 0.2, 0.4, 0.6, 0.8, 1, 1.4, 2. The pure Ag$_2$S was prepared in the same way without adding nano PDI.

2.2 Characterization of the materials

The X-ray powder diffraction (XRD) spectra were obtained on a Bruker D8 Advance X-ray diffractometer. The morphology of the materials was observed by transmission electron microscopy (TEM, Hitachi HT 7700 electron microscope). High-resolution TEM (HR-TEM) was carried out using a JEM 2010F electron microscope. The UV-vis diffuse reflection spectra (DRS, Hitachi U-3010) were recorded to investigate the light absorption capacity of the materials. A Bruker VERTEX 700 spectrometer was used to record Fourier-transform infrared (FT-IR) spectra. Raman spectra were recorded on a HORIBA HR800 spectrometer. Solid photoluminescence spectra (PL) were recorded using a Bruker D8 Advance X-ray diffractometer. Electron paramagnetic resonance (EPR, JEOL FA200) spectroscopy was used to detect active species.

Photoelectrochemical measurements are detailed in the ESI.

2.3 Photocatalytic performance evaluation

The catalytic performance was evaluated via phenol degradation (5 ppm) under visible light (500 W xenon lamp, 420 nm cut-off filter), ultraviolet light (ultraviolet lamp, 254 nm), and full spectrum light (500 W xenon lamp, without filter), respectively. Specifically, photocatalyst (25 mg) and phenol solution (5 ppm, 50 mL) were firstly dispersed in a quartz tube via ultrasonic treatment. The solution was stirred without light for 1 hour to achieve adsorption and desorption equilibrium. Then, the quartz tubes were irradiated by light (ultraviolet light, visible light, full spectrum light) and the reaction solution (2.5 mL) was extracted every 20 minutes. The concentration of phenol was detected by high performance liquid chromatography (HPLC) at 270 nm. Besides this, a 500 W xenon lamp with different bandpass filters (350 ± 15 nm, 380 ± 15 nm, 420 ± 15 nm, 450 ± 15 nm, 500 ± 15 nm, 550 ± 15 nm, 600 ± 15 nm, 650 ± 15 nm, 700 ± 15 nm) was used to research the relationship between the photocatalytic properties and the light absorption of the samples.

The photocatalytic water oxidation experiments are detailed in the ESI.
3. Results and discussion

3.1 The structure of the p-Ag$_2$S/n-PDI heterojunction composite

The preparation of the p-Ag$_2$S/n-PDI composite is presented in Scheme 1 and the morphologies of the obtained catalysts were analysed by TEM (Fig. 1). In detail, the formation of the PDI nanowires can be attributed to hydrogen bonding and π–π stacking (pH = 4.2). The length of nano PDI was 100–300 nm and the width of nano PDI was approximately 20 nm (Fig. 1A). Ag$_2$S/PDI composites with different mass ratios were synthesized via a two-step electrostatic process. As can be seen in Fig. S1 and Table S1, the average zeta potential ($\xi$) of nano PDI was $-85.0$ mV. Obviously, the surface of the self-assembled PDI is negatively charged, making it easy for positively charged silver ions (Ag$^+$) to adsorb to the surface of nano PDI via electrostatic interactions. After adding sulfides (S$_2^-$), silver sulfide (Ag$_2$S) immediately formed on the surface of the PDI nanowires. The average zeta potential ($\xi$) of Ag$_2$S/PDI was around $-79.3$ mV, with a surface charge more positive than that of PDI. The change in the surface charge indicated that Ag$_2$S successfully combined with PDI to some extent. As shown in Fig. 1B, the average particle size of the pure Ag$_2$S nanoparticles is in the range of 7–10 nm and there is no obvious aggregation. The radius of Ag$_2$S is large compared with the reported exciton Bohr radius of Ag$_2$S, indicating that the as-prepared Ag$_2$S has continuous energy levels. Furthermore, the morphology of the Ag$_2$S/PDI composite is shown in Fig. 1C, where it can be seen that the Ag$_2$S quantum dots are closely combined with nano PDI. The HR-TEM image of p-Ag$_2$S/n-PDI is shown in Fig. 1D. A tightly integrated interface was obviously formed between the PDI and Ag$_2$S and the two phases of Ag$_2$S and PDI can be clearly distinguished. The fringe interval of 0.244 nm is in accordance with that of the (121) plane of Ag$_2$S. The effective interface integration of p-Ag$_2$S and n-PDI helps to form an internal electric field directed from the PDI (n-type) to the Ag$_2$S (p-type), which is conducive to the migration of photon-generated carriers. According to the above analysis, the Ag$_2$S/PDI heterojunction (p–n type) was successfully constructed.

In addition, the XRD patterns are shown in Fig. 2A, which were measured to determine the phase composition. The P1 peak of nano PDI was around 3.34–3.55 Å, corresponding to the d-spacing of π–π stacking. The intensity ratio of P1 to P0 ($I_{P1}/I_{P0}$) is usually used to evaluate the degree of the self-assembly of PDI. Obviously, the value of $I_{P1}/I_{P0}$ here (the line of pure PDI) is greater than 1 and this indicates that the PDI has highly ordered π–π stacking, which is helpful for electron delocalization and conducive to the transfer of photo-induced electrons. All of the peaks of Ag$_2$S here are in accordance with those of monoclinic Ag$_2$S, matching the No. 14-0072 JCPDS card. The characteristic peaks of Ag$_2$S/PDI with different mass ratios all indicated the coexistence of PDI and Ag$_2$S. No other diffraction peaks were detected, showing that Ag$_2$S does not react with PDI. In
addition, the typical P1 peak of Ag2S/PDI shifts toward high angles in comparison to that of pure PDI, indicating that Ag2S/PDI has a smaller d-spacing of the π-π stacking, which means a higher electron cloud overlap density, which is beneficial for the efficient transfer of carriers. The results showed that the Ag2S quantum dots enhanced the π-π stacking density of PDI, which was probably caused by the built-in potential between the two phases. The results showed that the Ag2S quantum dots enhanced the π-π stacking density of PDI, which was probably caused by the built-in potential between the two phases.

3.2 Photocatalytic performance of the samples

The photocatalytic properties were investigated via phenol degradation. As shown in Fig. 3A, the catalytic performance of the p-Ag2S/n-PDI heterojunction was obviously enhanced under visible light (λ > 420 nm). The corresponding first order kinetics curve fitting is exhibited in Fig. S6B. The photocatalytic process was found to be in accordance with pseudo first order kinetics. When the mass ratio of Ag2S to PDI was 1 : 0.6, the composite exhibited the optimum catalytic activity with a rate constant k (0.0259 min\(^{-1}\)) 6.93 times that of pure PDI (0.00374 min\(^{-1}\)). The Ag2S/PDI (1 : 0.6) composite degraded 94.48% of the phenol after visible light irradiation for 120 min.

![Fig. 2](image-url) (A) XRD patterns of Ag2S, PDI, and Ag2S/PDI; (B) UV-vis diffuse reflection spectra (DRS) of the self-assembled PDI and Ag2S/PDI (Ag2S/PDI is abbreviated as AP, 1 : x represents the mass ratio of Ag2S to PDI).

![Fig. 3](image-url) Photocatalytic degradation of the rate constants k of samples under (A) visible light irradiation (where B-PDI represents bulk-PDI, N-PDI represents nano-PDI, 1 : x represents the mass ratio of Ag2S to PDI), (B) ultraviolet irradiation, (C) full spectrum irradiation and (D) wavelength-dependent photodegradation results of Ag2S/PDI (1 : 0.6).
Furthermore, the novel p-Ag2S/n-PDI exhibited more excellent photo-degradation activity in comparison with some existing visible-light photocatalysts, such as Bi2WO6,17 commercial self-assembled PDI,17 and g-C3N4.41 The related photocatalytic performance data are listed in Table S2.† HPLC was used to detect the intermediates (Fig. S5A†). The peak intensity (3.106 min) of phenol was observed to gradually decrease with irradiation. In addition, several speculated intermediate products were detected (Fig. S5B†). The peaks at 2.363 and 1.112 min may be attributed to p-benzoquinone and maleic acid, respectively.17 Besides these, the peaks at 0.392 and 0.778 min may be related to the small molecule dissolution of nano PDI.

The ultraviolet-light (UV-light) photocatalytic performance of pure AgS, bare PDI and the Ag2S/PDI (1 : 0.6) composite is shown in Fig. 3B. Dramatically, the p-Ag2S/n-PDI (1 : 0.6) showed optimal photocatalytic properties ($k = 0.0142 \text{min}^{-1}$) of around 8.07 times higher than those of nano PDI ($k = 0.00176 \text{min}^{-1}$). The full spectrum photocatalytic performance is shown in Fig. 3C. It is obvious that the Ag2S/PDI (1 : 0.6) composite exhibited the best activity, with an apparent rate constant ($k = 0.0298 \text{min}^{-1}$) 5.13 times higher than that of pure PDI ($k = 0.00581 \text{min}^{-1}$).

Simultaneously, as shown in Fig. 3D, the photo-degradation results alongside the wavelength indicated that the photocatalytic degradation rate may be connected to the optical absorption. The trends in the phenol degradation of Ag2S/PDI (1 : 0.6) were positively related to its optical absorption properties, implying that optical absorption played a key role in the photocatalytic degradation. Furthermore, the UV-vis DRS spectra manifested that the Ag2S/PDI heterojunction has more efficient light absorption compared with pure PDI (Fig. 2B). It is worth noting that even under 380 ± 15 nm UV-light and 700 ± 15 nm visible light (band-pass filter), Ag2S/PDI showed considerable photocatalytic activity, suggesting that p-Ag2S/n-PDI has an extended spectral response that nearly covers the whole UV and visible spectrum.

PDTs have been used in water splitting systems.42 Fig. 4 shows the amount of oxygen produced by PDI and Ag2S/PDI (1 : 0.6) under full spectrum irradiation. For Ag2S/PDI (1 : 0.6), the rate of oxygen production is 34.6256 μmol g−1 h−1, nearly 1.79 times higher than that of PDI (19.3312 μmol g−1 h−1).

As is well known, the stability of photocatalysts is a critical issue. As shown in Fig. S7† Ag2S/PDI (1 : 0.6) showed high photocatalytic stability in an acid environment (pH = 4.3). Besides this, the XRD and IR spectroscopic measurements of the p-Ag2S/n-PDI (1 : 0.6) composite showed no differences before and after reaction (Fig. S8†), manifesting that a stable structure of PDI was maintained after the catalytic reaction.

3.3 Mechanism of the enhanced photocatalytic activity

3.3.1 The photoinduced charge behavior analysis. The efficient separation of photo-induced charge carriers is beneficial for catalytic reaction. Therefore, photoelectric tests were performed to investigate the separation efficiency of the electron–hole (e–h+) pairs. The photocurrent response signal of p-Ag2S/n-PDI was much higher than that of PDI under visible light and UV light (Fig. 5A and B), indicating that p-Ag2S/n-PDI facilitates the separation of photo-induced charge carriers.

Besides this, Fig. 5C shows the results of electrochemical impedance spectroscopic (EIS) measurements. The diameter of the arc represents the charge-transfer resistance.43 The pure PDI and p-Ag2S/n-PDI composite showed smaller arc radii under visible light than in the dark, indicating that p-Ag2S/n-PDI and pure PDI could both be excited under visible light. At the same time, the arc radius of p-Ag2S/n-PDI was much smaller than that of nano PDI, suggesting that the p–n heterojunction decreased the charge transfer resistance. The EIS results show that there is a tight connection between PDI and Ag2S, which is beneficial for charge migration. This means that the p-Ag2S/n-PDI heterojunction facilitates the separation of photo-induced charge carriers. Fundamentally speaking, this is mainly due to the

![Figure 4](image_url) Amount of evolved oxygen in photocatalytic water oxidation with PDI and Ag2S/PDI (1 : 0.6) under full spectrum irradiation (the inset shows the rate of oxygen production).

![Figure 5](image_url) Photocurrents of PDI and Ag2S/PDI (1 : 0.6) under (A) visible light (>420 nm) and (B) UV-light. (C) Electrochemical impedance spectroscopic (EIS) Nyquist plots of pure PDI and p-Ag2S/n-PDI (abbreviation: AP) composite and (D) room temperature PL emission spectra of the as-prepared samples.
3.3.2 Active species involved in photocatalytic reactions. Active species play a critical role in photocatalysis, which mainly involves $\text{O}_2^-$, $\text{h}^+$, $\cdot\text{OH}$ and singlet oxygen ($\text{^1O}_2$). The dominant active species were detected via free radical trapping experiments. Fig. 7A and B respectively show the phenol degradation curves of Ag$_2$S/PDI (1 : 0.6) with the addition of formic acid ($\text{h}^+$ scavenger), p-benzoquinone ($\text{O}_2^-$ scavenger), $\text{t-BuOH}$ ($\cdot\text{OH}$ scavenger) and AgNO$_3$ (electron scavenger) under ultraviolet light and visible light. The catalytic properties were observed to obviously decrease after adding formic acid, indicating that the holes ($\text{h}^+$) are the main active species. The positive SPV signal (Fig. 6) also indicates that the holes participate in photocatalytic reaction. Besides this, the photocatalytic activity reduced after adding benzoquinone, demonstrating that superoxide radicals ($\text{O}_2^-$) also take part in the photocatalytic degradation. The hydroxyl radicals showed almost no obvious effect on the photocatalytic degradation. Simultaneously, the presence of $\text{O}_2^-$ and $\text{^1O}_2$ were also confirmed through EPR measurements. No signal response for $\text{O}_2^-$ was observed in the dark (0 min) upon the Ag$_2$S/PDI composite. However, obvious signals appeared after illumination. Simultaneously, the peak intensity increased with the continuous exposure of light, which further indicated that $\text{O}_2^-$ was generated in the photocatalytic process (Fig. 7C). Besides this, strong singlet oxygen signals were detected by EPR spectroscopy for the p-Ag$_2$S/n-PDI sample (Fig. 7D). Singlet oxygen also has a certain oxidation capacity, which can oxidize intermediate products. Furthermore, Fig. S10† shows a comparison of the EPR spectra of PDI and Ag$_2$S/PDI in terms of the detection of $\text{O}_2^-$, $\text{^1O}_2$, $\cdot\text{OH}$, respectively.

The results indicate that the composite Ag$_2$S/PDI produces more $\text{O}_2^-$ and $\text{^1O}_2$ than pure PDI. In particular, the content of singlet oxygen in Ag$_2$S/PDI reached about 7 times higher than that in the pure PDI under light. In addition, the EPR measurements detected very weak hydroxyl radical signals in the presence of Ag$_2$S/PDI (1 : 0.6) under visible light irradiation and UV-light. (C) EPR spectra of the Ag$_2$S/PDI (1 : 0.6) composite for detection of $\text{O}_2^-$ under visible light irradiation ($\lambda > 420$ nm) and (D) EPR spectra of the Ag$_2$S/PDI (1 : 0.6) composite for detecting singlet oxygen.

As is well known, fluorescence emission arises as a result of the recombination of $e^-$–$\text{h}^+$ pairs. Thus, lower PL intensity indicates a lower recombination of $e^-$–$\text{h}^+$ pairs. As can be clearly seen from Fig. 5D, there is an obvious fluorescence signal at 728 nm for pure PDI. However, the intensity of the emission peak decreased after combination with Ag$_2$S, implying that the p-Ag$_2$S/n-PDI heterojunction facilitates the separation of $e^-$–$\text{h}^+$ pairs. Furthermore, the fluorescence emission peak of Ag$_2$S/PDI (at around 700 nm) shows a significant blue shift compared with that of pure PDI, indicating that the addition of Ag$_2$S prolonged the life of the $e^-$–$\text{h}^+$ pairs. The result demonstrates once again that there is a strong interaction between Ag$_2$S and PDI, that is, the built-in electric field from the n-type PDI to the p-type Ag$_2$S. The interaction redistributes the charge density at the interface.

Surface photovoltage (SPV) measurements were further used to research the separation process of the carriers. Fig. 6 presents the SPV spectra of Ag$_2$S/PDI and PDI. The SPV signal of PDI from 400 to 700 nm is caused by the transition of electrons from the valence band (VB) to the conduction band (CB). Obviously, the SPV signal of Ag$_2$S/PDI presents a much stronger response than that of pure PDI. The UV-vis absorption involves the absorption of a variety of photons, but the SPV is only influenced by electronic transitions. Therefore, the SPV results indicate that the charge carrier separation efficiency of Ag$_2$S/PDI is better than that of pure PDI. The SPV measurements were conducted under the same conditions, so the obvious difference between the SPV responses of the PDI and p-Ag$_2$S/n-PDI could be attributed to the interfacial interaction between the PDI and Ag$_2$S. It is speculated that a built-in electric field may have been formed at the interface of Ag$_2$S and PDI, which means that photon-generated carriers can be effectively separated. Besides this, the fluorescence lifetime provides direct evidence for electron transfer (Fig. S9†). The lifetime of p-Ag$_2$S/n-PDI was slightly longer than that of PDI, indicating that Ag$_2$S/PDI has more effective separation of the carriers.

Fig. 6 Surface photovoltage spectroscopy of PDI and Ag$_2$S/PDI (1 : 0.6).
both pure PDI and Ag₂S/PDI. The results demonstrated that hydroxyl radicals are not the dominant active species, which is consistent with the results of the free radical trapping experiment.

### 3.3.3 The separation process of photo-induced carriers and the catalytic process

Photocatalytic redox reactions and the formation of active species are thermodynamically related to the energy band structures of catalysts. Fig. S2† shows the band gaps of PDI, Ag₂S and Ag₂S/PDI, which were respectively confirmed to be 1.73 eV, 1.81 eV and 1.68 eV. Mott–Schottky tests were used to determine the semiconductor types of PDI and Ag₂S. A negative slope of the linear curve (1/C² vs. potential) represents a n-type semiconductor, and a positive slope represents a p-type semiconductor.

As shown in Fig. S11† the slopes of PDI (Fig. S11A†) and Ag₂S (Fig. S11B†) are positive and negative, respectively, indicating that PDI and Ag₂S are n-type and p-type semiconductors, respectively. The flat-band potential of pure PDI was found to be −0.24 eV vs. NHE (Fig. S11A†). According to previous reports, the CB positions of n-type semiconductors are deeper than the flat-band potential (0.1–0.2 eV). Therefore, the conduction band bottom of PDI was determined to be −0.34 eV vs. NHE (the difference value was set as 0.1 eV here). Thus, the valence band edge (1.39 eV) of PDI can be obtained using the equation “Eᵥ = E_C + E_g”. The potentials of the VB and CB of Ag₂S were confirmed using the Mulliken electronegativity theory (eqn (S1) and (S2)†). The obtained CB and VB edge potentials are as follows: PDI: E_CB = −0.34 eV, E_VB = 1.39 eV; Ag₂S: E_CB = −0.44 eV, E_VB = 1.37 eV. The interlaced band positions between the p-Ag₂S and n-PDI contribute to the transfer of photo-induced e⁻ and h⁺.

According to previous analysis, the separation process of carriers and the photocatalytic process are shown in Fig. 8. Firstly, the p-Ag₂S and n-PDI both absorb photons to generate e⁻ and h⁺ in the CB and VB, respectively. Next, the photo-induced electrons at the conduction band at the bottom of p-Ag₂S transfer to the CB of n-PDI. Based on the above study, the Ag₂S quantum dots can promote the ordered π–π stacking degree. As a result, this is helpful for electron delocalization and the migration of photo-generated electrons, leading to more photo-generated electrons that can transfer along the π–π stacking of PDI. The CB potential of PDI (−0.34 eV vs. NHE) is more negative than the E_p⁰ (O₂/O₂⁻) (−0.33 eV vs. NHE). Thus, O₂⁻ can be generated in the CB of PDI. This is consistent with the active species capture experiment and EPR results. Superoxide radicals [O₂⁻], as highly active oxidants, can decompose or even mineralize organic pollutants. In addition, the conduction band positions of PDI (−0.34 eV) and Ag₂S (−0.44 eV) are both above the E_p⁰ (O₂/O₂⁻) (+0.34 eV vs. NHE), so the p-Ag₂S/n-PDI heterojunction has the ability to generate ¹O₂. Besides this, the holes generated in the VB of PDI can easily transfer to the VB of Ag₂S, revealing the strong oxidation ability for the splitting of water and organic pollutants. It is worth noting that the built-in electrical potential in the direction of the PDI to the Ag₂S greatly facilitates the separation of photo-induced e⁻–h⁺ pairs. In short, the p–n heterojunction Ag₂S/PDI realizes high separation efficiencies of e⁻–h⁺ pairs and more efficient full-spectrum photocatalytic performance.

### 4. Conclusion

In conclusion, a novel effective self-assembled supramolecular heterojunction p-Ag₂S/n-PDI was successfully constructed via an in situ precipitation method. The p-Ag₂S/n-PDI heterojunction shows superior ultraviolet-light, visible-light and full-spectrum photocatalytic performance. The satisfactory photocatalytic properties can be mainly attributed to three factors: firstly, the π–π stacking degree of PDI is promoted by Ag₂S, which is helpful for the migration of photo-generated electrons along the quasi-one-dimensional π–π stacking. Simultaneously, Ag₂S enhances the absorption of light to facilitate the light–chemical energy conversion. Secondly, the built-in electrical potential between Ag₂S and PDI is conducive to more effective separation of photon-generated carriers. Finally, the p-

![Fig. 8](image_url) The separation process of photo-generated carriers and the photocatalytic process.
AgS/n-PDI heterojunction can produce more active species than pure PDI, resulting in much stronger oxidation ability. In short, the work provides some interesting ideas for designing efficient heterojunction photocatalysts with a supramolecular organic nanostructure.

Conflicts of interest
There are no conflicts to declare.

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Notes and references