Highly-crystalline Triazine-PDI Polymer with an Enhanced Built-in Electric Field for Full-Spectrum Photocatalytic Phenol Mineralization

Hanjie Zhang\textsuperscript{a}, Xianjie Chen\textsuperscript{a}, Zijian Zhang\textsuperscript{b}, Kunyi Yu\textsuperscript{c}, Wei Zhu\textsuperscript{d}, Yongfa Zhu\textsuperscript{a,∗}

\textsuperscript{a} Department of Chemistry, Tsinghua University, Beijing, 100084, PR China
\textsuperscript{b} Tsinghua University, Beijing, 100084, PR China
\textsuperscript{c} Affiliated Baoan Hospital of Shenzhen, Guangdong Medical University, Shenzhen, 518000, Guangdong, PR China
\textsuperscript{d} College of Environmental and Chemical Engineering, Xi’an Polytechnic University, Xi’an, 710048, Shaanxi, PR China

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\textbf{A B S T R A C T}

Herein, a conjugated triazine-perylene diimide (triazine-PDI) polymer photocatalyst is prepared, and its full-spectrum photo-oxidative activity is evaluated. Enhanced dipole promotes the generation and separation of photo-induced charges, while its high degree of crystallinity results in a strong built-in electric field, which provides channels for the rapid transfer of the photo-generated charges. The advantageous structural characteristics enable a phenol degradation rate constant of 0.191 h\textsuperscript{−1}, which is which is 12.7 and 2.2 times greater than bulk g-C\textsubscript{3}N\textsubscript{4} and supramolecular PDI, respectively. Besides, triazine-PDI’s deep VB position led to a high rate of mineralization, i.e., a 79% total organic carbon removal rate in 24 h, which is 38% higher than that of self-assembled PDI. In summary, this work demonstrates the critical influence of crystallinity and built-in electric field adjustments for PDI photocatalytic activity.

1. Introduction

Photocatalysis, a promising method for the purification of environmental pollutants, have numerous advantages, including clean energy utilization, reusability, and low energy consumption \cite{1}. In particular, inorganic metal oxide compounds (most commonly TiO\textsubscript{2} \cite{2}) have been studied and applied extensively throughout the past several decades. However, further development of such catalysts has been restricted because the transition metal resources are typically non-renewable, and the modifiability of functional groups and properties is limited. Therefore, organic photocatalysts \cite{3} have gradually become a preferred choice for photocatalytic environmental remediation \cite{4} because of featuring various chemically-modifiable sites huge elemental reserves.

Perylene diimide (PDI) materials have been investigated for applications in fluorescence imaging \cite{5}, sensors \cite{6}, solar cells \cite{7}, electroluminescence \cite{8}, and photocatalytic materials \cite{9} owing to excellent visible light harvesting capabilities \cite{10}, thermal and chemical stabilities \cite{11}, and chemical modification capacities \cite{12}. Our research group first reported \cite{13} that self-assembled PDI supramolecular structures (SA-PDI) could be used for the degradation of environmental pollutants such as phenol, and could form composite systems with other inorganic \cite{14} or organic materials \cite{15} to enhance the activity of PDI photocatalysts. PDI-based photocatalysts have a deep valence band (VB), which effectively enables degradation of a variety of organic pollutants; even oxidize water to evolve O\textsubscript{2} \cite{16}. Supramolecular PDI is assembled based on \pi-\pi conjugated stacking and hydrogen bonding interactions. The latter easily dissociates in alkaline or neutral environments \cite{17}, thus destroying the structure of the supramolecular assembly. Therefore, we aimed to employ covalent attachments to improve the stability of PDI photocatalysts.

Using perylene dicarboxylic dianhydride and an amine to prepare photocatalysts via a polycondensation reaction is a common and effective approach for covalently connecting PDIs \cite{18}, and these materials have applications in the fields of gas adsorption \cite{19} and lithium batteries \cite{20}. However, the polymerization reaction with imidazole, N-methyl pyrrolidone, or dimethylformamide (DMF) solvents requires high temperature and other harsh conditions. In addition, it is difficult to control the crystallinity of the product \cite{21}, and the resulting material often exhibits a micron-level strip or block shape \cite{22}. Even if the product has a relatively large molecular dipole \cite{23}, the photocatalytic

\textit{Abbreviations: PDI, perylene diimide; VB, valence band; CB, conduction band; SA, self-assembled; DBU, 1,8-diazabicyclo[5.4.0]-undec-7-ene; TMAH, tetramethylammonium hydroxide; DMAc, N,N-dimethyl acetamide; PTFE, polytetrafluoroethylene; NHE, normal hydrogen electrode.}

\textsuperscript{*} Corresponding author.

\textsuperscript{E-mail address: zhuyf@mail.tsinghua.edu.cn (Y. Zhu).}

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activity will be greatly reduced due to poor crystallinity and rapid photo-generated electron-hole recombination \cite{24}. To our knowledge, there are almost no reports describing the generation of nano-scale PDI polymer photocatalysts. Preparation of nano-scale highly-crystalline PDI polymers can be expected to lead to enhanced catalytic activity for the degradation of environmental pollutants.

Intrinsic electric field of photocatalysts is the key factor to promote the charge separation \cite{25}. A strong built-in electric field relies on two characteristics: specifically, high crystallinity is necessary for highly-ordered structures \cite{16}, and molecular dipole guarantees its capability for photo-generated charge separation. The molecular dipole of PDI is very small, resulting in an insufficient driving force for photo-induced charge generation and separation \cite{26}; therefore, it is crucial to incorporate linkers to increase the dipole. There are many potential options for such linkers \cite{27}, but if the linker disrupts the crystallinity of the PDI, the larger molecular dipole alone will not be able to induce a strong built-in electric field. Considering that, we choose triazine as the linker in this work because its rigid planar structure helps to retain the π-π stacking of PDI as much as possible \cite{28}. Additionally, cyanuric chloride is used as an electrophile \cite{29} because of its high reactivity, which guarantees that the low-temperature polymerization reaction proceeds normally without requiring severe conditions like high temperature. Employing these reagents is expected to be beneficial for increasing the built-in electric field and improving photocatalytic activity.

In this work, we prepared a full-spectrum PDI polymer photocatalyst linked by triazine (triazine-PDI). Triazine-PDI exhibits a high degree of crystallinity, which enhances the transfer efficiency of photo-generated charges and improves the photocatalytic activity. Under the same visible light conditions, the catalytic rate constant of phenol degradation is 2.2 times that of SA-PDI, and it has strong mineralization ability. Furthermore, the VB of triazine-PDI is located at a deeper position (1.66 V vs. NHE) than that of SA-PDI supramolecular photocatalyst. In addition, the reaction proceeds normally without requiring severe conditions like high temperature, and filtered through a PTFE membrane. The residue was washed thoroughly with dimethyl sulfoxide (DMSO) and methanol, and dried at 80 \textdegree C under vacuum overnight to afford the desired product (yield 80%).

For the preparation of other photocatalysts, please see Supplementary Materials.

### 2. Characterisation

Transmission electronic microscopy (TEM) images were obtained using a Hitachi HT7700 microscope. Scanning electronic microscopy (SEM) images were obtained using a Hitachi SU8000 microscope instrument. Solid-state \textsuperscript{13}C nuclear magnetic resonance (NMR) spectra (150 MHz) were recorded using a JEOL JNM-ECP600MR spectrometer. Ultraviolet-visible-near infrared diffuse reflectance spectroscopy (UV-vis-NIR DR) spectra were used to record absorption and transmittance spectra on Agilent Cary 5000 spectrophotometer. Fourier transform (FT)-IR spectra were obtained using a Bruker V70 spectrometer. X-ray diffraction (XRD) patterns were recorded on a Rigaku (Japan) Smart-Lab X-ray diffractometer using Cu K\textsubscript{α} (\(λ=1.54 \text{ Å}\)). X-ray photoelectron spectra (XPS) were recorded using Thermofisher ESCALAB 250Xi spectrometer. The Brunauer-Emmett-Teller (BET) surface area and pore distributions were measured using a JEOL FA-200 spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL FA-200 spectrometer using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping probe. Surface photovoltage (SPV) spectra were acquired on an Edinburgh FLSP920 fluorescence spectrometer. Electrochemical measurements were conducted using a CHI660E electrochemical workstation at room temperature in a 3-electrode cell, with Pt wire as the counter electrode, saturated Ag/AgCl as the reference electrode, and 0.1 mol/L NaCl aqueous solution as the electrolyte. The working electrodes were prepared by dispersing each sample (2.0 mg) via sonication in isopropanol (400 \textmu L) with 5 wt.% Nafion added, then coating them onto indium tin oxide (ITO) glass (2 cm x 4 cm) and drying overnight at 80 \textdegree C. The ITO glass slides were pretreated according to a reported method \cite{31}.
2.4. Measuring pollutant degradation

Photocatalytic degradation of organic pollutants (OPs) was carried out under the irradiation of a 500 W Xe lamp with a 420 nm cutoff filter. Photocatalysts (10 mg) were dispersed in an aqueous solution of OPs (10 mg/L, 50 mL) by sonication. Prior to irradiation, the reaction mixture was stirred in the dark for 1 h to reach adsorption-desorption equilibrium [32]. At 1 h intervals during the photocatalytic reaction, 3 mL aliquots were taken from the mixture, centrifuged, and filtered through a PTFE membrane to remove the photocatalysts. The supernatant was analyzed via high performance liquid chromatography (HPLC; Shimadzu LC-20A) equipped with a UV detector through a Restek C-18 column (length = 150 mm) using water and acetonitrile (v/v = 60/40) as the mobile phases. The total organic carbon (TOC) was measured on a Jena Multi N/C 2100 TOC/TN spectrometer.

The degradation rate and TOC removal rate were evaluated using the formula in Eq. 1,

\[ r = \frac{(c_0 - c)}{c_0} \]  

where \( r \) represents the degradation or TOC removal rate, \( c \) represents the detected concentration of phenol in the aliquot, and \( c_0 \) represents the initial concentration of phenol.

HPLC-UV detection wavelengths for the pollutants are: phenol = 270 nm [33]; 2,4-dichlorophenol = 284 nm [34]; bisphenol A = 270 nm [35]; and ciprofloxacin = 276 nm [36]. Particularly for ciprofloxacin, pure water with 0.1 v.% formic acid was used in place of deionized water to prevent the peaks of HPLC spectra from tailing behind.

3. Result and discussion

3.1. Construction of highly-crystalline triazine-PDI polymer photocatalysts

Ethylenediamine, hydrazine, and cyanuric chloride were selected as the linkers, and the polymeric PDI photocatalytic materials were prepared by a polycondensation reaction. To determine the chemical environment of carbon atoms, solid-state \( ^{13} \text{C} \)-NMR experiment is carried out. As Fig. 1a depicts, the carbonyl peak at 162.92 ppm is observed. Also, peak at 166.75 ppm is attributed to the carbon atoms on the triazine moiety, which proves that the triazine structure has been successfully introduced into the product. Due to the conjugation of the carbon atoms on the PDI aromatic motif and the delocalization of electrons, several peaks at 120–135 ppm cannot be accurately identified [16]; however, the presence of PDI structural units in the product can still be confirmed. The purpose of treating PDINH with sulfuric acid is to purify this starting material, to ensure cyanuric chloride reacts completely with PDINH to form the polymer, triazine-PDI, particles of which are approximately 50 nm wide (Fig. 1c).

The \( \pi-\pi \) stacking structure is reflected in the XRD pattern (Fig. 1b) by the sharp peak at 27°. High-resolution (HR) TEM results (Fig. 1d) show that the triazine-PDI has clear lattice fringes, suggesting good crystallinity. The stripe width in the HR-TEM image is 0.33 nm, which corresponds to the \( \pi-\pi \) stacking between PDI layers [13]. The observed spots in the electron diffraction image also confirm the crystallinity of the product. The above experimental results indicate that triazine-PDI has enhanced crystallinity. This is because ethylenediamine is a flexible aliphatic carbon chain, which has no tendency to form a co-planar stacked structure, whereas hydrazine and triazine are rigid linkers, which are more conducive to the formation of a co-planar stacked structure in the product, thus promoting improved crystallinity.

In addition, the main structure in the three synthesized polymers observed in the FT-IR spectra (Figure S3) is the PDI motif. In general, the characteristic C=O peak of perylene diacidic acid hydride (PTCDA) at 1700 cm\(^{-1}\) shifts to a lower wave number, and the sharp peak at > 3200 cm\(^{-1}\) disappears, indicating that the polymerization reaction is complete. However, in the case of triazine-PDI, after the cyanuric chloride is quenched by the alkaline solution, the Cl– moieties are replaced by –OH groups, leading to the detection of several sharp peaks.
around 3000 cm\(^{-1}\). Additionally, peaks at 812, 949, 1161 cm\(^{-1}\) are observed; 812 cm\(^{-1}\) corresponds to the semicircular stretching frequency of the triazine ring [28], and the latter two peaks are ascribed to the stretching vibrations of the C–N bonds of the triazine ring, overall confirming the integration of triazine in the product. In the case of XPS analysis (Figure S4), the C 1s spectrum of triazine-PDI is deconvoluted into three peaks at 286.9, 285.3 and 282.5 eV. The peak at 286.9 eV is assigned to C–O while the peak at 285.3 eV is assigned to C–N. The highest intensity peak at 282.5 is assigned to aromatic C–C. In a similar manner, the N 1s spectrum of triazine is deconvoluted into two peaks at 398.6 and 397.2 eV. The peak at 398.6 eV is assigned to N–C of the triazine ring while the higher intensity peak at 397.2 eV is assigned to imide N–C of perylene diimide. In O 1s spectrum, besides the peak at 528.8 eV, there is another peak at 530.9 eV which is assigned to –OH.

Furthermore, the results of the N\(_2\) isothermal adsorption-desorption experiment (Figure S5) reveal that the BET specific surface areas of ethylene-PDI, hydrazine-PDI, and triazine-PDI are 29, 16, and 76 m\(^2\)/g, respectively. The higher specific surface area of triazine-PDI is attributed to the fact that it has relatively smaller particles. The pore size of triazine-PDI is uniformly distributed from 5–30 nm, owing to secondary pore formation caused by stacking, and revealing important characteristics of the triazine-PDI nanoparticles. The results from the described structural characterization verify that triazine-PDI have the desired structure.

### 3.2. Degradation of phenol with high activity and stability

Phenol, which is a common industrial, biologically toxic pollutant in natural water bodies [37], is selected as the probe to conduct photocatalytic degradation experiments. The degradation of a very dilute (10 mg/L) phenol solution proceeds via a quasi-first order kinetic reaction process (Figure S6). As shown in Fig. 2a, the degradation rate constant of triazine-PDI is 0.191 h\(^{-1}\), which is 12.7, 3.9, and 2.2 times that of bulk g-C\(_3\)N\(_4\), self-assembled tetracarboxyphenylene porphyrin (SA-TCPP), and SA-PDI organic photocatalysts, respectively [13,38,39]. Dark adsorption experiment (Figure S8) reveals that the main decrease in phenol concentration is caused by photocatalytic degradation rather than physical adsorption. After 24 h (Fig. 2b), phenol degradation by triazine-PDI is as high as 100%, and the TOC removal rate reached 79%, which are both much higher than those obtained for the g-C\(_3\)N\(_4\) and SA-PDI photocatalysts. This enhanced activity is due to deeper VB potential of triazine-PDI, which enables complete degradation of phenol into harmless substances, such as small molecule fatty acids [40] (e.g., maleic acid) and CO\(_2\), to achieve water purification, thus verifying the strong ability of hole (h\(^+\)) generation by triazine-PDI, charge separation, and photocatalytic oxidation capabilities. Moreover, triazine-PDI exhibits full-spectrum activity, with strong absorption in the visible region, and demonstrated degradation rates that correlate with the light absorption behavior (Fig. 2c). Even at 650 nm, triazine-PDI performs degradation activity as high as 0.133 h\(^{-1}\), and there is also weak ultraviolet response, indicating that triazine-PDI has relatively low ultraviolet activity.

In addition to its phenol degradation performance, triazine-PDI has significant degradation activity towards other organic pollutants, such as bisphenol A, 2,4-dichlorophenol, and ciprofloxacin (Figure S6 and S7). These molecular pollutants are all larger than phenol, so they have stronger interactions with photocatalyst, which increases their degradation rates. This observation confirms that the triazine-PDI has the potential for wide practical application in environmental purification. It is worth noting that in the cyclic degradation experiment (Fig. 2d), triazine-PDI exhibits good stability by performing four catalytic cycles without a significant reduction in its performance. Compared with the SA-PDI catalyst, which is relatively unstable in a neutral environment, the covalent linkages that replaced the hydrogen bonds in triazine-PDI, made the photocatalyst more difficult to disintegrate, and greatly improved the stability of PDI in a neutral environment. Before and after catalytic cycling, the XRD pattern, XPS, FTIR and absorption spectra of triazine-PDI (Figure S9-S11) also verified the stability by showing that the catalyst did not undergo significant structural disintegration.

Fig. 2. Photocatalytic phenol degradation performance ([phenol] =10 mg/L, \(\lambda > 420\) nm): (a) comparison of triazine-PDI activity with other reported photocatalysts; (b) mineralization of triazine-PDI; (c) UV-vis absorbance spectrum of water suspension and rate constant at different wavelength (using a monochromatic light emitting diode); (d) cyclic degradation runs in a neutral environment (pH = 7).
3.3. Enhanced activity and charge separation due to high crystallinity and increased electric field

The crucial factors related to the built-in electric field that influence the performance of triazine-PDI for the photocatalytic degradation of phenol are successively explored. Molecular dipole, which represents the internal essence of charge generation, is calculated using density functional theory (DFT); the theoretical calculation results are presented in Fig. 3a and Table S5. The dipole of triazine-PDI is 18.0 and 12.9 times that of ethylene-PDI and hydrazine-PDI, respectively, indicating that triazine-PDI can be expected to achieve dramatically increased photocatalytic activity.

A high degree of crystallinity (i.e., a highly-ordered structure), allow the catalyst molecules to arrange in an oriented space. The crystallinity of ethylene-PDI is poor due to its weakened π-π stacking structure, which hinders the transport channel for photo-generated charges and accelerates the recombination of photo-generated electrons and holes, leading to low degradation activity. Typically, carriers are generated under irradiation, and the photoelectrons and holes are partially transferred to the surface, forming a potential difference. The high degree of crystallinity and extended π-π stacking structure of PDI-triazine provide a channel for the rapid transfer of photo-generated charges, while also reducing defect centers and inhibiting the recombination of photo-generated electrons and holes. Therefore, more photo-generated carriers reach the surface of the catalyst and can participate in the reaction to improve catalytic performance.

A strong built-in electric field is supported by the enhanced dipole and high crystallinity characteristics. Based on the built-in electric field characterization method reported by Zhang et al. [41], we examine open circuit potential (vs. NHE) and zeta potential of the photocatalysts, which represent the surface voltage and surface charge density, respectively (Fig. 3b). The specific derivation process is described in the Supplementary Materials. Briefly, the relative built-in electric field intensity can be evaluated by multiplying the value of the open circuit potential and zeta potential for each sample. The open circuit potential of triazine-PDI is -0.135 V, and the zeta potential is -45.10 mV. If the built-in electric field of ethylene-PDI is normalized as 1.0, then the relative values for hydrazine-PDI and triazine-PDI are 1.7 and 10.3, respectively. This shows that triazine-PDI has a strong built-in electric field, which improves the photocatalytic activity by promoting photo-induced charge generation and separation. The results also indicate that the phenol degradation performance of triazine-PDI is 63.7 times greater than ethylene-PDI and 31.8 times greater than hydrazine-PDI (Fig. 3c), thus supporting our prediction. This result is also consistent with those provided by the photocurrent spectrogram (Figure S14). Specifically, under the same conditions, the photocurrent intensity of the three catalysts increase successively, such that the triazine-PDI photocurrent intensity is the largest. Meanwhile, other characterization experiments are conducted. Based on the surface photovoltage spectra (Fig. 3d), triazine-PDI has a clear, broad and positive peak, with a maximum photovoltage that is 77.4 and 32.1 times those of ethylene-PDI and hydrazine-PDI, respectively. This result indicates that in triazine-PDI, a large number of photo-generated holes have reached the surface to be detected, demonstrating its stronger photocatalytic oxidation capabilities and higher activity. The intensities of the photocurrent of the three catalysts increase in turn (i.e., ethylene-PDI < hydrazine-PDI < triazine-PDI), indicating that the charge separation and transport ability is sequentially enhanced, and the most carriers are transferred to the surface of the triazine-PDI. The results of transient fluorescence spectroscopy (Fig. 3e) showed that the lifetimes of ethylene-PDI, hydrazine-PDI, and triazine-PDI were successively increased (fitting results are listed in Table S3). The longer fluorescence lifetime of triazine-PDI (1.85 ns) means that exciton dissociation and diffusion distance are enhanced, so more photo-generated electrons and holes can be separated, thus extending the lifetime. From the electrochemical impedance spectroscopy (EIS; Fig. 3f) results, it is clear that the charge transfer impedance of triazine-PDI is the smallest (only 5.87 Ω/cm²), indicating that it can perform the fastest charge transfer, consistent with it having the strongest photoelectric conversion ability.

The positions of the valence band (VB) and conduction band (CB) determine the photo-redox capacity of photocatalyst, which are essential thermodynamic parameters for mineralization. The Mott-Schottky [42] method is employed to measure the flat-band potential; the curve at the band is extended to the vertical axis, and the cross-sectional distance represents the flat-band potential. The flat-band potentials for the three catalysts are -0.48 V, -0.24 V, and 0.12 V (vs. NHE for ethylene-PDI.
tion spectrum, the absorption of the photocatalyst increased sharply as Kubelka-Munk formula [44]. In the UV potential [43]. In this work, we uniformly consider 0.2 V as the reference literature, the CB potential is 0.1~0.3 V higher than the flat-band potential [43]. Therefore, the proposed degradation process involves triazine-PDI generating charge separation under irradiation, and the $h^+$ and e– that reach the surface of the catalyst react respectively with organic pollutants and molecular O2 adsorbed on the surface of the catalyst. These reactions generate $O_2^-$, and some O2 is reduced to H2O2 to generate $\cdot OH$, which together attack pollutants and degrade them into small molecular fatty acids while successively oxidizing them to CO2. Overall, this system achieves the harmless treatment of pollutants (Fig. 5).

3.4. Degradation reaction mechanism

Finally, in order to confirm the main active species contributing to the pollutant degradation reaction, potassium iodide (KI) [47], p-benzoquinone (p-BQ) [48], and tert-butanol (TBA) [49] are used to quench the photo-generated holes ($h^+$), superoxide radicals ($O_2^-$), and hydroxyl radicals ($\cdot OH$), respectively. As illustrated in Fig. 4a, the degradation rate drops significantly upon quenching these species, indicating that $h^+$, $O_2^-$, and $\cdot OH$ are active species in the degradation reaction. And $h^+$, $O_2^-$ are more effective. Using DMPO as a probe [50], the EPR spectra of the sample solutions under light irradiation show the characteristic signals of $O_2^-$ [51] and $\cdot OH$ [52], which provides direct evidence for the existence of these active species (Fig. 4b). It is worth noting that H2O2 is also formed during the reaction, and is detected by a KI-starch experiment (Figure S18-S20), ultimately resulting in the formation of $\cdot OH$ as one of the reactive species.

In this work, a highly-crystalline triazine-PDI photocatalyst with strong oxidizing ability across the full spectrum was prepared. The molecular dipole of triazine-PDI was enhanced relative to similar catalysts, and its high degree of crystallinity provided a rapid transfer of charge separation under irradiation, and the $h^+$ and e– that reach the surface of the catalyst react respectively with organic pollutants and molecular O2 adsorbed on the surface of the catalyst. These reactions generate $O_2^-$, and some O2 is reduced to H2O2 to generate $\cdot OH$, which together attack pollutants and degrade them into small molecular fatty acids while successively oxidizing them to CO2. Overall, this system achieves the harmless treatment of pollutants (Fig. 5).

4. Conclusions

In this work, a highly-crystalline triazine-PDI photocatalyst with strong oxidizing ability across the full spectrum was prepared. The molecular dipole of triazine-PDI was enhanced relative to similar catalysts, and its high degree of crystallinity provided a rapid transfer channel for photo-generated charges, thus suppressing their recombination. Therefore, the built-in electric field is promoted, resulting in higher activity. The covalent linkage with triazine moieties prevents the structural disintegration and performance degradation of the SA-PDI supramolecular photocatalyst under neutral conditions caused by the dissociation of hydrogen bonds, thus greatly enhancing the catalytic stability of triazine-PDI. Its performance regarding the mineralization of phenol originates from the deep position of the VB, which enables strong oxidizing ability across the full spectrum was prepared. The molecular dipole of triazine-PDI was enhanced relative to similar catalysts, and its high degree of crystallinity provides a rapid transfer channel for photo-generated charges, thus suppressing their recombination. Therefore, the built-in electric field is promoted, resulting in higher activity. The covalent linkage with triazine moieties prevents the structural disintegration and performance degradation of the SA-PDI supramolecular photocatalyst under neutral conditions caused by the dissociation of hydrogen bonds, thus greatly enhancing the catalytic stability of triazine-PDI. Its performance regarding the mineralization of phenol originates from the deep position of the VB, which enables oxidizing pollutants to harmless products. This work demonstrates the importance of crystallinity and built-in electric field modifications for PDI-derived photocatalysts, and provides a new method for elevating the activity of total-organic photocatalytic materials.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare no competing financial interest.

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