Short-Range $\pi-\pi$ Stacking Assembly on P25 TiO$_2$ Nanoparticles for Enhanced Visible-Light Photocatalysis
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ABSTRACT: Utilization of the renewable solar fuel based on a perylenetetracarboxylic acid diimide (PTCDI)–semiconductor composite represents an effective method to solve the energy crisis; however, most applications have focused on dye sensitization of the monomolecular layer. Here the synergy effect of PTCDI self-assembly and P25 nanoparticles (NPs) has been elucidated systematically from the PTCDI stacking structure on P25 NP and electron transfer (ET) mode, for which the visible-light photocatalytic activity of PTCDI self-assembly through the assistance of P25 has been acquired and enhanced, even up to 7 times with the addition of EDTA. It has been found that self-assembly of PTCDI nanowires (NWs) as building blocks has been reconstructed on P25 NP via arrangement of short-range $\pi-\pi$ stacking that is important for high photocatalytic activity. We inferred that the indentation plays a key role in the formation of the short-range $\pi-\pi$ stacking mode on the basis of the results of XRD, photoluminescence, transient decay spectroscopy, and photocurrent measurements. In addition to that, a substantial part of the electrons excited in the interfacial layer of the PTCDI shell are injected into the conduction band of P25, thus preventing charge recombination. Our findings will provide guidance for photocatalytic enhancement of the organic self-assembly.

KEYWORDS: hybrid, photocatalysis, visible light, stacking reconstruction, electron transfer

INTRODUCTION

As a n-type organic semiconductor, perylene diimide derivatives possess many outstanding merits, such as high molar extinction coefficient and electrical conductivity, fluorescence emission, exceptional thermal and photochemical stability, and structural modifiability. Hence, PTCDI derivatives have attracted much attention in supramolecular systems to construct various functional materials initiated by visible light, as they provide potential in solar cells, sensors, fluorescence probes, and n-transistors. Recently there have been two technological difficulties in visible-light utilization of photocatalysts: one is low visible-light utilization, and the other is high $e^-/h^+$ recombination. Usually modification to the semiconductor is adopted to solve these problems, including surface doping, surface defects, metal deposition, and complexation with other semiconductors, but only for inorganic semiconductors.

Photocatalysts have been applied in effective utilization of solar fuel (environmental treatment, selective organic reaction, and water splitting). Enhancement of visible-light collection and utilization in photocatalytic H$_2$ evolution and photocatalytic degradation has been achieved by PTCDI/ C$_3$N$_4$ and PTCDI/semiconductors. Importantly, PTCDI derivatives can act on ET that mainly depends on intermolecular interaction in the form of $\pi-\pi$ interactions, hydrogen bonds, or covalent bonds combined with other semiconductors. Photoinduced ET originating in the PTCDI molecule determines the photocatalytic activity; for example, Ghosh revealed that photoinduced ET makes PTCDI cause bond scission to catalyze reduction of aryl halides; Duan’s group created a highly effective photocatalyst (Zn-PTCDI) to oxidize benzyl alcohols and amide, due to photoinduced ET between PTCDI molecules. In addition, under the noncovalent interaction of $\pi$-conjugation between perylene rings and van der Waals forces between side chains, PTCDI molecules can spontaneously aggregate into disklike, spiral, fiber, etc. morphologies in specific disperse media. The self-assembly process presents essentially a dynamic balance between gel and sol; therefore, environmental factors are of utmost importance to achieve a pathway-controlled self-assembly of well-defined structures. It has been reported that self-assembled supramolecular species can form bandlike energy levels and contribute to photoinduced charge delocalization along the $\pi-\pi$ stacking direction. However, except for changing the entire morphology of the nanosized self-assembly, it is difficult to regulate microscopic molecular stacking modes between PTCDI chromophores due to the unique equilibrium state under fixed environmental conditions, which can tune the mode of photoinduced ET and enhance the photocatalytic activity.

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activity. The choice is limited to the introduction of a
substituent, such as covalently linked acceptor−donor dyads20
or nonvalently linked acceptor−donor dyads;21 however, due to
the bulk mixed stacking phase resulting from a strong charge
transfer interaction between acceptor and donor,22 a rapid
charge recombination dominates the major loss of energy
transfer and charge transfer.23 Another choice is combination
with inorganic semiconductor NPs, but the photocatalysis of
PTCDI self-assembly on inorganic semiconductor NPs has
been rarely studied systematically. On the other hand, PTCDI
self-assembly working as a hybrid agent and photocatalyst
simultaneously has not yet been studied.

In this study, a PTCDI/P25 hybrid has been constructed to
enhance the visible-light photocatalytic activity of PTCDI for
degradation of dyestuff and phenol, especially for the
mineralization of organic molecules upon addition of EDTA.
The relationship between the intermolecular π−π stacking
structure and charge transfer mode within the hybrid has been
analyzed systematically. This self-assembled PTCDI exhibited a
novel stacking mode in the existence of P25 NP and favored
effective charge transfer with less charge recombination in
PTCDI self-assembly. Furthermore, a C=O−−Ti “bridge” was
put forward to explain ET in the interface. Here we provide
novel insight and guidance into the synergy effect between
TiO2 and PTCDI self-assembly.

■ RESULTS AND DISCUSSION

Structure of the Hybrids. The morphologies and sizes of
PTCDI/P25 hybrids (4-methoxyl benzyl PTCDI) were
characterized by transmission electron microscopy (TEM)
and scanning electron microscopy (SEM). The diameter of the
TiO2 nanocrystal was ca. 19 nm (calculated by the Scherrer
formula on the basis of the results of X-ray diffraction), and the
shape of P25 performs an irregular nanoparticle of ca. 25 nm.24
The PTCDI building block mainly presented a morphology of
50−200 nm NWs (Figure 1a). Each perylene diimide
chromophore grows longitudinally along the long axis of the
NWs,25 similarly to the ET direction within the PTCDI self-
assembly. Negative charges revealed by its ζ potential of −50
mV were carried to maintain its nanosized morphology (Figure
S1a in the Supporting Information). Importantly, by adjust-
ment of the pH value, the self-assembly process can be
controlled to fabricate a larger aggregation, such as a PTCDI
rod with a length of 3 um and a width of 250 nm (Figure 1b).
The hybrid photocatalyst was obtained through an economical
method of pH-induced thermal treatment. The results of
nanoparticle size distribution (Figure S1b ) displayed the
volume distribution of PTCDI/P25 hybrid of mixture
(without H+) and mixture 2 (with H+) in comparison with
P25 NPs. (Note that a pure PTCDI self-assembly cannot be
detected with 532 nm laser light.) The larger diameters of the
mixtures were ascribed to the adsorption of PTCDI NWs due
to electrostatic attraction and the H+-induced PTCDI
aggregation on P25 NPs, respectively. After it was freeze-
dried under vacuum, the photocatalyst formed with structural
features assignable to a hybrid of PTCDI NWs and P25 NPs.
As can be seen in the high-resolution TEM (HRTEM) images
(Figure 1c,d), the structure of the hybrid consisted of a P25
core with 0.33 nm interplanar spacing of the TiO2 (101) crystal
face and PTCDI shell with 3−6 nm thickness; a close contact
between the P25 core and PTCDI shell is conductive to ET,
which will be discussed in the following section. Upon an
increase in the PTCDI amount, due to the cohesive interaction
in the drying process, the hybrid extends to an irregular large-
scale agglomerate of micrometer size which consists of more
PTCDI moieties around P25 (Figure S2 in the Supporting
Information). For n% PTCDI/P25 in the following discussion,
the percentage refers to the weight percent of PTCDI self-
assembly with respect to P25.

Figure 1. TEM images of (a) PTCDI NWs and (b) a 1D PTCDI self-assembly rod (some branched NWs can be seen in the two ends). (c, d)
HRTEM images of 8% PTCDI/P25 hybrid.
X-ray diffraction (XRD) of PTCDI in the hybrid was totally different from that of pure PTCDI self-assembly (Figure 2a). The 1D PTCDI self-assembly presented two peaks of π−π stacking distances with a d spacing of 3.3 Å which is attributed to the cofacial π−π stacking distance and 3.5 Å corresponding to a twisted arrangement. The side-chain-dependent interaction

Figure 2. (a) XRD pattern. (b) Absorption spectra of PTCDI (0.4 mmol L⁻¹) suspended in H₂O or EtOH and UV–visible diffuse reflectance spectra of 8% PTCDI/P25 hybrid. (c) UV–vis DRS of PTCDI/P25 hybrids. (d) Normalized absorption (solid line) and emission spectra (dashed line) of PTCDI/P25 hybrids (λex 560 nm).

Figure 3. Rearrangement stacking mode of PTCDI self-assembly of PTCDI/P25 hybrid in the X, Y, and Z directions, with the X axis as the π−π stacking direction, the Y axis as the edge-to-edge stacking direction, and the Z axis as the side-chain interaction direction. (a) 3D PTCDI/P25 core–shell model. (b) Stacking model along the Y axis. (c) Optimal conformation of the isolated molecule obtained from DFT calculations at the B3LYP/6-31G* level. (d) π–π stacking model at the same radius, with the disordered structure displayed with the dihedral angle (θ) between two PTCDI molecules. (e) Staggered π–π stacking mode, which fabricates the short-range structure.
determines the molecular packing along one dimension. The steric effect of the benzene ring in the optimal conformation calculated through density functional theory (DFT) would lead to inhomogeneous strain, resulting in diﬀuse diﬀraction broadening at 40−45° in the XRD pattern (Figure S3 in the Supporting Information). The sharp diﬀraction peak at 12.55 Å is absent in the hybrid, which was assigned to the diﬀraction of the (010) plane, indicating the destruction of long-range periodicity and the existence of short-range π−π stacking on the surface of P25 NPs. PTCDI/P25 hybrids have been induced to rearrange in three stacking directions, resulting in edge-to-edge disordered alignment, and exhibited short-range π−π stacking aggregation.

The π−π stacking mode of the hybrids was monitored by UV−visible diffuse reﬂectance spectra (UV−vis DRS) spectra. PTCDI was dissolved in concentrated sulfuric acid in the state of individual molecules, as reﬂected in the absorption spectra (Figure S4 in the Supporting Information). In Figure 2b, two bands in the visible region (499 and 550 nm) are present. The absorption band at 499 nm is assigned to electronic transitions in individual molecules, and the latter 550 nm band is due to the π-electron delocalization between PTCDI chromophores. The relatively enhanced peak (550 nm)/peak (499 nm) in the hybrid with respect to the PTCDI aggregation suspended in ethanol or H2O can be interpreted as relatively stronger π−π stacking in the longitudinal and transverse directions. Optical absorption spectra of Figure 2c showed that the hybrid noticeably absorbed visible light of less than 750 nm. Absorption bands at 535 nm in 2% hybrids also emerged in the spectra; however, with an increase in the PTCDI amount, the absorption peak of J band was red-shifted, due to distorted π−π stacking. The relatively broad band at long wavelength in 40% and 80% hybrids was in accordance with the aggregation state owing to extended π−π stacking interactions.

PTCDI self-assembly usually represents a J-type aggregation with lower stacking Gibbs energy in comparison to H-type aggregation. Pure PTCDI self-assembly easily adsorbed H2O molecules which were diﬃcult to remove completely if only heated to 573 K, while the hybrid would easily desorb its hydration shell under the thermal treatment, as shown by thermogravimetric analysis (Figure S5 in the Supporting Information). The stacking state between PTCDI molecules may be associated with the hydration shell on the surface of the PTCDI self-assembly. Therefore, in combination with an analysis of the XRD pattern, the PTCDI self-assembly of the hybrid should be in the disordered state of long-range stacking.

The optimal conformation of the isolated PTCDI molecule shown in Figure 3c via DFT calculation favors the π−π cofacial stacking mode. For materials self-organized by aromatic molecules, the mobility of charges becomes maximized along the π−π cofacial stacking direction. However, large oscillator strength of the ET process in organic semiconductors can prevent long-range electron migration, especially for H-aggregate NWs. It has been proposed that, by distorting its cofacial stacking structure, the electron lifetime can be enhanced significantly, such as topological wire defects introduced by atomic force microscopy. In addition to that, the orientation of the growth of organic semiconductors on a bare gold surface would inhibit the evolution of the ordered stacking into larger aggregations. Similarly, with the stacking rearrangement on the surface of P25 NPs, only short-range cofacial stacking was maintained due to the formation of indentation in the long-range π−π cofacial stacking structure by staggered stacking and dihedral angle between PTCDI molecules. The corresponding structure is shown in Figure 3. The short-range stacking can
reduce the strong aggregation effect between PTCDI molecules, thus enhancing electron diffusion and dissociation.\(^{10}\) In transient fluorescence spectra (Figure S6 in the Supporting Information), the saturated fluorescence intensity with less PTCDI aggregation gave a higher value that represented the maximum of excitation states, indicative of more excitation states. Short-range aggregation promoted photon absorption and charge separation, whereas long-range aggregation led to more energy loss due to the longer ET distance which more easily resulted in quenching and thermal relaxation. With an increase in the radius of the PTCDI shell, the length of PTCDI self-assembly along \(\pi-\pi\) cofacial stacking may increase so that the fluorescence lifetime was decreased, for the lack of excitons which were concentrated in a specific exciting state of PTCDI.

The self-quenching behavior during the light irradiation would inhabit its photocatalytic activity, especially for a quite long stacking queue. ET progress in PTCDI self-assembly competes with the self-quenching progress,\(^{33}\) codetermining the photocatalytic activity of PTCDI self-assembly. Effective ET usually occurs in a certain range: namely, the electron mean free path.\(^{38}\) Within its mean free path, the rate-determining step (RDS) refers to the charge transfer, while beyond the path, RDS may turn to the self-quenching progress. In the self-quenching progress, absorbed light energy is mainly converted into heat rather than available chemical energy.\(^{33}\) As a consequence, the ET efficiency was decreased, thus resulting in two subsequent problems: one was a decrease in the quantity of reactive oxidative species (ROS), including superoxide radical\(^{36}\) and hole,\(^{37}\) because self-quenching behavior decreases the lifetime of photoinduced electron and holes.\(^{38}\) The other problem was a decrease in the quantity of exposed active site of unit mass. The radical cation PTCDI*\(^+\) acts as an active site, and thus influences adsorption and catalytic reaction on the surface of PTCDI self-assembly. However, the self-quenching progress resulting from the electrostatic interaction between PTCDI*\(^+\) and PTCDI*\(^-\) would decrease the quantity of PTCDI*\(^+\) sites.

Photoluminescence spectroscopy is a powerful analytical tool to study \(e^-/h^+\) separation and recombination (Figure 2d). The intermolecular \(\pi-\pi\) interaction induces electronic transition bands at 434, 503, and 543 nm that correspond to 0–2\(^*\), 0–1\(^*\), and 0–0\(^*\) transitions.\(^{39}\) The fluorescence intensity of PTCDI depends on the density of transition carriers; on the other hand, PTCDI aggregation and doping agents are the direct factors that increase nonradiative transition, thus leading to energy loss and inhibiting radiative transition.\(^{40}\) It was observed that the emission of 22% PTCDI/P25 hybrid reached a maximum intensity at 550 nm, indicative of the highest density of transition carriers. The absorption bands of 2% and 8% hybrids were relatively lower, while the intensity of the emission was higher than that of the 40% hybrid; such stronger emission of 22% PTCDI/P25 hybrid reached a maximum and thus in

**ET Process of the Hybrid.** A combination of PTCDI and P25 is the prerequisite for intermolecular ET from PTCDI to TiO\(_2\). The interaction mode of PTCDI/P25 was analyzed by FT-IR spectra, as shown in Figure 4a. The common adsorption mode, monodentate linkage via \(-\text{C}==\text{O}\), was detected according to the blue shift from 1688 cm\(^{-1}\) for the 80% hybrid to 1699 cm\(^{-1}\) for the 2% hybrid. It has been reported that, when dyes are adsorbed on the semiconductors via the binding of polar groups (such as carboxyl and sulfonyl groups), the adsorption mode is switched due to the electrostatic interaction.\(^{32}\) Preadsorption of CO also induces this adsorption mode.\(^{43}\) Similarly, there must exist an interaction between PTCDI and P25. The blue shift of the bands indicated that the strength of the C==O bond was enhanced. It has been reported that an H bond to the carbonyl oxygen on P25 allowed the carbonyl group to be more consistent in comparison to that of free-stated group\(^{44}\) and a perylene ring without the interaction of \(-\text{C}==\text{O}\) could hardly realize ET to the semiconductor system;\(^{36}\) therefore, an H-bond interaction with \(-\text{OH}\) of P25 and the perylene ring was excluded. In the field of DSSC, the interaction of a carboxylic group and titanium oxide can affect the electronic coupling mode with the Ti (3d) conduction band orbital.\(^{45}\) It may be more possible that the electrons of the nonbonding orbital of \(-\text{C}==\text{O}\) coordinated with Ti\(^{4+}\) empty d orbitals and s orbitals, as a consequence, the enhancement of the strength of \(\sigma\) bond (C==O−Ti) and inductive effect of Ti\(^{4+}\) promoted electrons enriched in the \(-\text{C}==\text{O}\) due to the weakening of a conjugated effect between th perylene ring and \(-\text{C}==\text{O}\). The bonding interaction was in favor of the intermolecular charge transfer. The relative location of the frontier orbital of PTCDI was calculated at the B3LYP/6G(d,p) level\(^{36}\) to acquire the HOMO (−6.2 eV) and LUMO levels (−3.7 eV). The conduction band of TiO\(_2\) (rutile, −4.8; anatase, −5.1 eV)\(^{47}\) is just located between the HOMO and LUMO levels of PTCDI. Such a relative location favors ET from the LUMO level of PTCDI to the conduction band of P25. Therefore, the effect of \(-\text{C}==\text{O}--\text{Ti}\) should be valid for the photoinduced ET. Other semiconductor-mediated hybrids were prepared to analyze the interaction mode by Fourier transform infrared (FT-IR) spectra. The 8% TiO\(_2\)/PTCDI and ZnO/PTCDI hybrids presented only one peak at 1695 cm\(^{-1}\) (Figure S7a in the Supporting Information). The valence orbitals of Ti\(^{4+}\) and Zn\(^{2+}\) correspond to 3d\(^{4}4s^{0}\) and 3d\(^{10}4s^{0}\), respectively, which indicated that, in addition to the 3d orbital, 4s orbital could also play a role in the bonding interaction. Interestingly, the C==O vibrations of ZrO\(_2\)/PTCDI (with the Zr\(^{4+}\) orbital 4d\(^{5}5s^{0}\)), Cd\(_2\)/PTCDI (with the Cd\(^{2+}\) orbital 4d\(^{10}5s^{0}\)), and B\(_2\)/PTCDI (with the B\(^{3+}\) orbital 6s\(^{6}6p^{3}\)) were split into two bands (Figure S7b). The 4s orbital played a more important role in accepting electrons from -C==O than the d orbital and other s orbitals. Also, the electrons of the 4s orbital have been detected via X-ray photoelectron spectroscopy (XPS). As can be seen, with an increase in the PTCDI amount, the Ti\(_{2p}/O_{1s}\) intensity ratio decreased (Figure S8 in the Supporting Information) due to the covering effect of PTCDI layer, but the relative intensities of Ti\(_{4p}/O_{2p}\) and Ti\(_{3d}/O_{2p}\) in the hybrids were enhanced (Figure 4b), indicative of interfacial ET from the oxygen atom of PTCDI to the 4s orbital of titanium.

The frontier orbital of the PTCDI molecule should overlap with the conduction band of TiO\(_2\) to promote ET to reactive sites on P25 surface.\(^{46,48}\) Photoinduced charge redistribution has been directly observed by using Kelvin probe force microscopy.\(^{49}\) Direct evidence for ET was provided by the fluorescence lifetime using time-resolved diffuse reflectance spectroscopy (Figure 4c). The transient absorption trace was fitted to a one-exponential function to calculate the average fluorescence lifetime of PTCDI (0.893 ± 0.033 ns), 2% (32.258 ± 1.068 ns), 8% (21.154 ± 0.486 ns), 40% (6.521 ± 0.182 ns), and 80% PTCDI/P25 (1.597 ± 0.056 ns). Generally the fluorescence lifetime of dyestuff rarely exceeds 10 ns in aqueous solution due to rapid fluorescence quenching.\(^{50}\) It has been reported that the lifetime for separated PTCDI chromophores

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can only reach 4.45 ns, while the lifetime of the PTCDI/CB(8) host–guest complex increases to 7.11 ns upon the limitation of the macrocycle. For the 2% hybrid, the electron lifetime was 30 times higher than that of pure PTCDI self-assembly. The addition of P25 would decrease e−/h+ recombination in the interfacial layer of the PTCDI shell due to an ultrafast ET process, thus extending significantly the fluorescence lifetime of the hybrid. For the 8% hybrid the lifetime of emission was longer than the fluorescence lifetime of isolated PTCDI chromophores, in contrast to the case for the 80% hybrid. As shown in Figure S2, in the proposed mechanism based on the photoinduced ET process in the literature, photoinduced ET contributed to the formation of the radical anion PTCDI− and cation PTCDI+. In conjugation with the two integrals with opposite charges, the long-range charge separation would be inhibited by Coulombic forces.

PTCDI possessed a very small reorganization energy (0.15 eV; see the Experimental Section) in the ET reaction, which renders this material appealing in the application of energy conversion and storage. On the basis of Marcus theory, a smaller reorganization energy can assist in decreasing the energy-wasting charge recombination. In time-resolved diffuse reflectance spectroscopy (Figure S9 in the Supporting Information), it was observed that the photoinduced ET for 8% PTCDI/P25 takes place within 3 ns. For a time scale of 3–20 ns, the concentration of the electrons in PTCDI underwent an exponential decrease due to the coupling process between the radical anion and cation. At 20 ns, the concentration of electrons was detected to be 1% of the maximum, indicative of the fluorescence lifetime. As shown in Figure S10 in the Supporting Information, the concentration of the electrons in 80% PTCDI/P25 decreased more quickly than that in 8% PTCDI/P25. At 7.2 ns, the electron concentration in 80% PTCDI/P25 decreased to ~3%, indicative of a faster rate of the coupling process in comparison to that in 8% PTCDI/P25.

There are three steps in the right part from radical anion to ground state of PTCDI molecule: (1) neutral PTCDI accepts an electron of the LUMO level of one excited adjacent PTCDI*; (2) PTCDI* absorbed one visible-light photon to form PTCDI*++; (3) the excited PTCDI*++ that would contribute to subsequent ET to next PTCDI; (4) the excited PTCDI*++ was quenched by the next PTCDI to give PTCDI* and regenerate the neutral PTCDI, which is equal to the reaction PTCDI1 + PTCDI*++2 → PTCDI*−1 + PTCDI2. There are three alternative ET reactions:

$$\text{PTCDI}_1 + \text{PTCDI}^{*+}_2 \rightarrow \text{PTCDI}^{*+}_1 + \text{PTCDI}_2$$

$$(1)$$

$$\text{PTCDI}_1 + \text{PTCDI}^{*+}_2 \rightarrow \text{PTCDI}^{*+}_1 + \text{PTCDI}_2$$

$$(2)$$

$$\text{PTCDI}^{*+}_1 + \text{PTCDI}^{*+}_2 \rightarrow \text{PTCDI}^{*+}_1 + \text{PTCDI}_2$$

$$(3)$$

The ET mechanism of the first alternative should be considered as follows. (1) The stronger reducing capacity of PTCDI*+ with more active electrons enabled the utilization of sufficient energy for ET and energy transfer; therefore, the reaction rate of the first alternative should be faster. (2) The PTCDI* singlet state exists in polar solvents while PTCDI*− exists in the form of a doublet. Although on the basis of the energy gap law the lifetime of PTCDI*− is shorter than that of PTCDI*, since the PTCDI triplet state would appear for a dendrimer-like compound or supramolecule, the nonradiative decay rate of intersystem crossing and internal conversion may become faster in PTCDI self-assembly for S1 → S0 transition than for D1 → D0 transition. Therefore, PTCDI* may have a shorter fluorescent lifetime than PTCDI*− in PTCDI self-assembly, as is the case for naphthalene diimide. (3) On the basis of minimization of Gibbs free energy, the second alternative is infeasible in thermodynamics and completely reversible; therefore, it would not contribute to net charge transfer. (4) For the third alternative, ET and energy transfer from PTCDI*− to PTCDI* would be inhibited due to electron repulsion in the semiﬁlled orbital of PTCDI*.

Photogenerated electrons transfer along the π–π stacking direction of PTCDI. ET in PTCDI self-assembly would favor the charge separation. In well-arranged supramolecule, the radical anion and cation moieties can be well-isolated spatially and electronically with high efﬁciency. Perylene diimides are electron-deﬁcient dyes, especially for the excited state of perylene diimide; hence, PTCDI* can be regarded as a reasonably stable radical, which has been identiﬁed. As a consequence, the progress involves the formation of the radical PTCDI− cation and PTCDI− anion, essentially belonging to a redox reaction between PTCDI molecules. Upon visible-light irradiation a few PTCDIs in the self-assembly form the radical anion PTCDI−; meanwhile a second excitation of PTCDI− can be considered in the process. As conﬁrmed by theoretical calculations (see the Experimental Section), to realize the charge separation—namely, the reaction PTCDI + PTCDI → PTCDI* + PTCDI− (−ΔG > −W)—it requires exactly two photons absorbed by one PTCDI that acts as catalyst. The progress of two-photon absorption contained two procedures: a transition from the singlet state to the singlet
state or the triplet state for PTCDI and a transition from the doublet state to the doublet state for PTCDI\(^{**}\). Under the \(\pi-\pi\) stacking interaction, the orbitals of perylene rings were well-overlapped; therefore, the mobility of photoinduced electrons in PTCDI self-assembly would be ultrafast.\(^{59}\) Usually the ET rate between two molecules with \(\pi-\pi\) interaction (such as PDI-\(C_{60}\))\(^{54}\) would be much higher than the fluorescence lifetime of excited state PTCDI,\(^{3,50}\) thus realizing the charge separation in PTCDI self-assembly. In the progress of electron transmission, only a few PTCDI molecules require two-photon absorption to induce continuing ET along the \(\pi-\pi\) stacking direction; however, a majority of PTCDI molecules may only absorb one photon in one ET process.

Photoresponse was evaluated by measuring on–off photocurrent (Figure 6a). During the light-on period, 2% PTCDI/P25 displayed a stationary positive photocurrent due to ultrafast interfacial ET, while the other hybrids first showed a sharp rise followed by decay to a near-stationary negative photocurrent which represented the dynamic equilibrium between charge separation and recombination. The inverted photocurrent may be attributed to a strong reduction in the formation of photogenerated electrons and electron flow to the Pt electrode.\(^{60}\) Upon the excitation of pure PTCDI self-assembly, the photocurrent density stayed at \(~0.2\ \mu A/cm^2\). The initial photocurrent of the 8% hybrid reached 1.7 \(\mu A/cm^2\) and then remained at a stationary value of \(~1.0\ \mu A/cm^2\), 5.0 times higher than that of pure PTCDI self-assembly, because of the reduced charge recombination. The spike peak at 30 s may result from charge recombination caused by long-range electron transmission.\(^{60}\) To enhance the conductivity between the hybrid and ITO glass, poly(vinylidene fluoride) (PVDF) and carbon black were mixed with the hybrid, and the plots are shown in Figure S11a in the Supporting Information. The total trend was the same as the result above.

According to the proposed electron transmission in PTCDI self-assembly (Figure 5), which essentially belongs to an oxidation–reduction reaction between PTCDI molecules, the ET process of different layers of the PTCDI shell is proposed in Figure 6c, which is in line with the account of the corresponding photocurrent measurement. In combination with P25 NP, long-range PTCDI aggregation could change into several short-range aggregations, due to the formation of indention which resulted from a staggered \(\pi-\pi\) stacking mode and the dihedral angle between PTCDI molecules mentioned above. As shown in Figure 6c, photogenerated electrons moving in the short-range aggregation recombined with holes in a lower probability, as the delocalization distance of electrons was shortened and fewer holes were accumulated in comparison to those in the long-range aggregation.

Electrochemical impedance spectroscopy (EIS) was analyzed on the basis of the Vorotynsev theoretical model\(^{65}\) (Figure 6b). For this system, electrochemical polarization and concentration polarization can be taken into account in EIS.\(^{66}\) The linear part refers to material transfer in the electrode/electrolyte interface, which indicated that diffusion became dominant in the electrode process.\(^{63}\) A smaller slope means a larger diffusion coefficient;\(^{64}\) hence, the diffusion coefficient of 22% PTCDI/P25 reached the largest value while its impedance of concentration polarization was the smallest. The impedance curve corresponding to the high-frequency region in the graph of complex function is an approximate semicircle (due to a half-circle rotation of impedance), indicating that the possible RDS was charge transfer.\(^{65}\) The radii of the curve corresponding to 2%, 8%, and 22% PTCDI/P25 were less than that of 40% and 80% PTCDI/P25, indicative of a faster kinetics of Faradaic reaction.\(^{65,66}\) Double-layer capacitance is inversely proportional to the resistance of charge transfer.\(^{66}\) An equivalent electronic circuit is shown in Figure S11b in the Supporting Information, and several parameters (\(R_C\), electrochemical impedance of ideal polarized electrode; \(C_D\), double-layer capacity; \(R_p\), charge transfer resistance) of the equivalent circuit were calculated by the fitting of the impedance curve (Figure S12 in the Supporting Information). ET to P25 could lower the interaction between electrons and holes, thus enhancing the
conductive properties. However, for 40% and 80% PTCDI/P25, $e^-/h^+$ recombination became predominant, thus resulting in an increase in the resistance.

**Enhancement in Visible-Light Photocatalytic Activity.** Photocatalytic activity was evaluated by measuring the decomposition of methyl orange (MO). The degradation experiment must be carried out in acid solution to prevent the disaggregation of PTCDI on the surface of P25 NPs by neutralizing negative charges of PTCDI $\cdot^-$. As can be seen in Figure 7a, the UV photocatalytic activity of the hybrids was lower than that of pure P25, which may result from the difference in oxidation capabilities between PTCDI and P25. However, PTCDI/P25 hybrids exhibited more excellent visible-light photocatalytic activity in comparison to pure PTCDI self-assembly (Figure 7b). The rate constant $k$ increased when the PTCDI/P25 ratio increased from 1% to 22%. At a ratio of 22%, the value of the rate constant reached the optimal value ($0.076 h^{-1}$), suggesting that 22% PTCDI/P25 hybrid exhibited the highest photocatalytic activity due to the existence of short-range $\pi-\pi$ stacking PTCDI self-assembly. However, with a continuous increase in the PTCDI amount, the photocatalytic activity decreased, probably attributable to the change from short-range $\pi-\pi$ stacking to long-range $\pi-\pi$ stacking. With the addition of EDTA (EDTA concentration of 0.01 M), the $k$ value reached a maximum of $0.35 h^{-1}$, 8 times higher than that in the absence of EDTA (Figure 7c). It has been reported that EDTA as an effective sacrificial reagent could improve the photocatalytic activity of the hybrid. Even the pollution and intermediate were completely degraded in the presence of EDTA, as shown in HPLC tests (Figure S13 in the Supporting Information), which may be explained by the electrons from EDTA consuming most of the radical cation PTCDI$^+$ in PTCDI self-assembly (Figure S14 in the Supporting Information), contributing to the formation of excess PTCDI$^-$ and thus preventing the charge recombination. The photocatalytic activity was higher than that of C$_3$N$_4$ as a visible-light catalyst. PTCDI/P25 was also used to degrade methyl blue (MB) and phenol (Figure 7d), which proved that the catalyst can be applied widely in photocatalytic degradation.

Usually dyes may directly absorb visible light and thus undergo self-sensitized degradation. To avoid the possible light sensitization of the target molecule, an organic substrate which does not absorb visible light (e.g., phenol or formic acid) was employed to perform degradation experiments as a function of the percentage of PTCDI. As reflected by Figure S15a in the Supporting Information, different hybrids adsorbed similar amounts of phenol due to weak adsorption to phenol. In Figure 8 and Figure S15b, the $k$ values for 2%, 8%, and 22% hybrids increased, while the values for 22%, 40%, and 80% PTCDI/P25 trended to be numerically similar. This could be explained to the notion that if the amount of adsorbed phenol molecules was constant, the former can be attributed to an increase in active sites while the latter can be due to excess underutilized active sites. Because titanium oxide can catalyze the dehydration of formic acid, the reduction of the photocatalytic activity of PTCDI/P25 can be seen in Figure S15c in comparison with P25. Capturing ROS revealed the photocatalytic mechanism, proving that superoxide radicals and holes were the main ROSs (Figure S16 in the Supporting Information). The catalytic activity of hybrids may result from

**Figure 7.** Photocatalytic degradation of MO over P25 and PTCDI/P25 hybrids under the irradiation of (a) UV ($\lambda <365$ nm) and (b) visible light ($\lambda >450$ nm). The percentage $w$(PTCDI)/$w$(P25) refers to the quality percent of PTCDI self-assembly with respect to P25. The photocatalytic degradation process was fitted to a pseudo-first-order kinetic process; the reaction rate constant $k$ was used to reflect the reaction rate. (c) Photocatalytic degradation of MO over PTCDI/P25 hybrids or C$_3$N$_4$ upon the addition of EDTA under the irradiation of visible light ($\lambda >450$ nm) for 7 h. In the inset, the final state of the degradation upon the addition of EDTA (0.01 mol L$^{-1}$) is shown. (d) Photocatalytic degradation of MO, MB, and phenol over PTCDI/P25 hybrids under visible-light irradiation ($\lambda >450$ nm).
two opposite effects: one is visible-light photocatalytic activity of the short-range PTCDI self-assembly (8% and 22% PTCDI/P25) and the hybridizing effect with P25 in the interfacial layer of PTCDI shell (2% PTCDI/P25), enhancing the photocatalytic activity; the other is charge recombination resulting from the long-range stacking mode (pure PTCDI self-assembly), reducing the photocatalytic activity.

CONCLUSION

In summary, a PTCDI/P25 photocatalyst was fabricated via pH-induced aggregation and performed higher visible-light photocatalytic activity for organic degradation in comparison to that of pure PTCDI self-assembly, especially for the addition of EDTA, owing to the synergetic effects of PTCDI and P25. Characteristic measurements showed that the short-range stacking mode of the PTCDI/P25 hybrid in the longitudinal and transverse directions originating in ineffectual orbital overlap between a few PTCDI chromophores differed from the long-range stacking mode of pure PTCDI self-assembly. The time constants for fluorescence and photocurrent in 2%, 8%, and 22% hybrids were significantly higher than those in 40% and 80% hybrids, which proved that short-range π−π stacking decreased the distance of charge migration along the π−π stacking direction in the 1D PTCDI structure and retarded charge recombination. It was concluded that the hybridizing effect in the interfacial layer and cofacial stacking mode together determined the optimal amount of PTCDI self-assembly on the surface of P25 NP. Additionally, as an electron acceptor, P25 contributed to effective charge separation in the interfacial layer of the PTCDI shell via an electron channel of the C=O...Ti "bridge" measured by FT-IR and XPS. The concept of short-range stacking structure and analysis of the relationship between the structure and charge transfer will provide new possibilities for photocatalytic enhancement of self-assembled PTCDI supramolecules.

EXPERIMENTAL SECTION

Materials. Commercially available P25 powder was purchased, which was prepared via the technology of German Degussa Corp., and the PTCDI derivative was synthesized by the reported procedures.

Synthesis of 4-Methoxylbenzylamino PTCDI (1). Perylene-3,4,9,10-tetracarboxylic dianhydride (5 g, 12.7 mmol) and p-methoxylbenzylamine (4.37 g, 31.9 mmol) were suspended in quinoline (65 mL). Under the protection of argon, the mixture was stirred at 160 °C. After it was heated for 6 h, the reaction mixture was cooled to room temperature and then quenched by adding hydrochloric acid (40 mL, 2 mol L−1) dropwise followed by stirring for 0.5 h. The residue was collected by vacuum filtration and washed with distilled water until the pH of the washings was neutral, followed by rinsing twice with alcohol and water successively. The filter cake was suspended in 1% hot KOH (30 mL) solution and stirred for 15 min. The mixture was filtered under vacuum. The filter cake was washed with a large amount of water until the pH of the washings was neutral and rinsed with alcohol and then dried under vacuum at 60 °C to give a dark green product (7.2 g) in a yield of 90%.

FT-IR: 1688 and 1652 cm−1 (s; νas (C=O)), 1590 cm−1 (m; ν (C=C)), 1322 cm−1 (s; νas (C=N)), 1437 cm−1 (m; CH3), 1367 cm−1 (s; CH3).

Self-Assembly Processing. Fabrication of PTCDI Self-Assembly. PTCDI self-assembly was fabricated by adding the molecules in a “good” solvent (such as concentrated sulfuric acid) to a “poor” solvent (such as H2O). 1 (1 mg) was dissolved in concentrated sulfuric acid (2 mL), and then H2O (2 mL) was added slowly to form two layers. About 3 days later, the mixture was centrifuged and washed with 10% HCl solution, followed by freeze-drying under vacuum for 24 h and drying under vacuum at 120 °C for 5 h.

Fabrication of PTCDI/P25 Hybrids. The percentage below refers to the weight percent of PTCDI self-assembly with respect to P25. P25 (100 mg) was suspended in distilled water with ultrasonic dispersion for 2 h. Samples of PTCDI (2, 8, 22, 40, and 80 mg) were dissolved in concentrated sulfuric acid (2 mL), and then H2O (2 mL) was added slowly to form two layers. About 3 days later, the mixture was centrifuged and washed with 10% HCl solution, followed by freeze-drying under vacuum for 24 h and drying under vacuum at 120 °C for 5 h.

Preparation of B3O3/PTCDI, CdS/PTCDI, TiO2/PTCDI, ZrO2/PTCDI, and ZnO/PTCDI Hybrids. The preparation was based on the method of the preparation of the PTCDI/P25 hybrid except that concentrated hydrochloric acid was replaced by MgSO4 as a precipitation reagent. Pure PTCDI with addition of MgSO4 was used as a reference sample.

Density Functional Calculations. DFT calculations were performed using Gaussian 09 and Gauss View 5.08 with the B3LYP hybrid DFT exchange-correlation function. The standard Gaussian basis function 6-31G* was used for PTCDI. The reorganization energy is equal to \( E^* - E + E^* - E (E^*, \text{energy of cation molecule in the neutral molecule geometry}; E^*, \text{energy of cation molecule in the cation} \).
geometry; $E^*$, energy of neutral molecule in the cation geometry; $E_0$, energy of neutral molecule in neutral molecule geometry. The redox reaction between two PTCDI is PTCDI + PTCDI $\rightarrow$ PTCDI + PTCDI. The thermal free energy change $\Delta G$ is equal to $G(\text{PTCDI}^+) + G(\text{PTCDI}^-) - 2G(\text{PTCDI})$. 

$\Delta G = -1330.976452 \text{ au} - 1330.616775 \text{ au} - 2(-1330.885577 \text{ au}) = 0.178323 \text{ au} = 468 \text{ kJ mol}^{-1}$; $W = N_\text{A}h\nu/\lambda (535 \text{ nm, } S_\text{B} \rightarrow S_{\text{HF}}) = 223 \text{ kJ mol}^{-1}$; $-\Delta G \approx -2W$.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). TEM was performed with a JEM 1010 electron microscope at an accelerating voltage of 100 kV. PTCDI self-assembly and PTCDI/P25 hybrid were examined suspended in 1% hydrochloric acid via ultrasonic methods. The dispersion sample (0.1 mL) was added to 230 mesh carbon support film/copper film and dried. High-resolution TEM (HRTEM) was performed with a JEM 2100F electron microscope at an accelerating voltage of 200 kV. SEM was performed with an SU8010 electron microscope (Hitachi) at an accelerating voltage of 5 kV. The PTCDI/P25 hybrid was observed directly using SEM.

X-ray Diffraction (XRD) Patterns. XRD pattern was recorded with a Bruker D8 advance diffractometer. The working potential and current were 40 kV and 40 mA, respectively. X-rays of wavelength 0.15406 nm were from Cu Kα radiation, and the whole scanning range was 5°–80° at a rate of 0.1°/s step.

UV–Vis Absorption Spectra and Optical Diffuse-Reflection Spectra (DRS). The spectra were recorded with a Hitachi U-3900 spectrophotometer. PTCDI powder was first dissolved in concentrated sulfuric acid, and then water was added to contribute to PTCDI self-assembly. Then the solid was suspended in alcohol or water and measurements were carried out from 250 to 800 nm. The solid of the hybrids was measured by the integrating sphere.

Photoluminescence Spectrometry (PL). PL was performed with an F-7000 FL spectrometer. Dispersions of 0.1 mg/mL for 2%, 8%, 22%, 40%, and 80% hybrids were prepared via ultrasound suspension. The distance between the front and back gratings was 5 nm, which may influence the intensity of luminescence. A photomultiplier (PMT) voltage of 400 V amplified the signal to detectable levels.

Fourier Transform Infrared Spectroscopy (FT-IR). FTIR spectra were obtained with a Bruker VERTEX 700 spectrometer. The datum were analyzed using Origin 8.0 software. A frequency resolution of 4 cm$^{-1}$ was chosen in the data range of 4000–600 cm$^{-1}$.

Transient Fluorescence Spectroscopy. The spectroscopy was carried out with a QY-2000 fluorescence spectrometer. The exciting wavelength was chosen as 470 nm. When 2% PTCDI/P25 was measured, a neutral density filter (OQFND 5010) was used to decrease the fluorescence intensity, which allowed for the transmission of 10% fluorescence. The data were analyzed using Origin 8.0 software, with which the count was converted into percentage ($\%$).

X-ray Photoelectron Spectroscopy (XPS). XPS was performed with a PHI quantra SXM spectrometer. Valence band spectra were recorded from 20 to 0 eV to detect the Ti$_{3p}$, Ti$_{4s}$, and O$_{2p}$ orbitals. The detection limit of the concentration reached 0.1 atom %. All of the hybrids and P25 were measured.

Electrochemical Measurements. Electrochemical measurements were performed with a CHI660B electrochemical workstation with a three-electrode system in which platinum wire acted as a counter electrode and the standard calomel electrode as a reference electrode. Na$_2$SO$_4$ (0.1 mol L$^{-1}$) solution was used as the electrolyte. The electrode surface was polished in a solution of H$_2$O$_2$/ammonia (6/1) at a temperature of 373 K and irradiated under ultraviolet light for 1 h. The photocatalyst (10 mg) was suspended in hexane/alcohol (1/1 v/v) with ultrasonic dispersion for 0.5 h and was spread on ITO glass. Before measurement, the films were dried at 25 °C for 12 h and under vacuum at 120 °C for 2 h. The other working electrode was prepared on the basis of the literature. The sample on ITO glass was a mixture of hybrid/poly(vinylidene fluoride) (PVDF)/carbon black (75/15/10), and the quality of the photocatalyst was 10 mg (area of ITO glass 2 × 4 cm$^2$, sheet resistance ≤15 Ω, transmittance ≥86%). PVDF was dissolved in DMSO. The mixtures were suspended in hexane/alcohol (1/1 v/v) with ultrasonic dispersion for 0.5 h and were spread on ITO glass. Before measurement, the films were dried at 25 °C for 12 h and under vacuum at 120 °C for 2 h. Under visible-light irradiation ($\lambda >420$ nm), the on–off photocurrent was measured at intervals of 30 s, and AC impedance was measured with an initial potential of 0.

Potential and Size Distribution. $\zeta$ potential and size distribution were measured with a Horiba SZ-100 Nano Particle analyzer with the temperature of the holder being 24.9 °C. PTCDI was treated with concentrated sulfuric acid and water, and the precipitate after centrifugation was suspended in H$_2$O to form a 0.2 mg mL$^{-1}$ colloid. Then the $\zeta$ potential was measured. The electrode voltage was set to 2.3 V, so that the conductivity was 0.493 mS cm$^{-1}$. When the size distributions of mixtures 1 and 2 were measured, the scattering angle was set to 173°, and the distribution mode was set to general mode and polydispersion mode. The scattering light intensity reached a count rate of ~1555 KCP.

Thermogravimetric Analysis (TGA). TGA was recorded with a Mettler Toledo TGA/DSC 1STAR® system. The samples were the prepared samples after drying treatment. Under an atmosphere of argon gas, the range of temperature was controlled between 303 and 1273 K, and the heating rate was set at 10 K min$^{-1}$. The quality of pure PTCDI self-assembly and 8% PTCDI/P25 hybrid corresponded to 8.5893 and 111.3490 mg, respectively.

High-Performance Liquid Chromatography (HPLC) and Liquid Chromatography Mass Spectrometry (LCMS). HPLC was performed on a LC-20AT chromatograph. The HPLC conditions were as follows: chromatographic column, C18 (150 × 4.6 mm, i.d. 5 μm); mobile phase, V(acetonitrile)/V(0.01 mol L$^{-1}$ ammonium acetate) = 24/76; flow rate, 0.8 mL min$^{-1}$; the wavelength channel was set at 500 nm. LCMS was performed on a IT-TOF spectrometer under the same conditions as for HPLC.
measure the maximum absorption value of MO at 506 nm. HPLC was used to measure the peak area of phenol at 270 nm (C18, 150 mm × 4.6 mm × 5 μm, 1 mL/min, H2O/MeOH = 45/55) and formic acid at 254 nm (C18, 250 mm × 4.6 mm × 5 μm, 0.5 mL/min, H2O/MeOH = 35/65).

The experiment of trapping active species was carried out using 1,2-benzoquinone (p-BQ) as a superoxide radical scavenger, methanol and formic acid as hole scavengers, and tert-butyl alcohol and isopropyl alcohol as hydroxyl radical scavengers. Concentrations or volumes of the reagents above were as follows: 1,2-benzoquinone (1 mmol L−1); methanol (4.8 μL); formic acid (4.8 μL); tert-butyl alcohol (4.8 μL), isopropyl alcohol (4.8 μL). The procedure was performed according to the above photocatalytic degradation.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b03064.

The authors declare no competing financial interest.

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