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Enhanced photocatalytic activity of PTCDI-C_{60} via π–π interaction

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ABSTRACT

The π–π stacking of self-assembled PTCDI and π–π interactions between self-assembled PTCDI and C_{60} result in fast transfer of the photogenerated carriers and reduced carrier recombination. The π–π interaction lowers the position of valence band and narrows the band gap, thus leading to a stronger redox ability and a broad spectral response. The organic photocatalyst PTCDI-C_{60} can not only degrading phenol at a rate of $0.216\ h^{-1}$, which is 8.24 times higher than that of pure PTCDI, but also producing oxygen at a rate of $22.5\ \mu mol\ g^{-1}\ h^{-1}$. Moreover, the presence of C_{60} stabilizes the composite to decrease the accumulation of negative charge. The high catalytic activity can potentially be utilized in the fields of environmental and energy applications.

1. Introduction

The π-π interactions are generally defined as the attractive interactions that occur between the π-clouds of aromatic systems in a parallel, face-to-face orientation. It is, in fact, in the absence of spectroscopic evidence for HOMO-LUMO interactions [1]. They play a fundamental role in many aspects of chemistry and biochemistry [2–4], for example in the fields molecular recognition [5], self-assembly [6,7], supramolecular chemistry, and general host-guest interactions [8–11].

Mononuclear complexes containing aromatic ligands can be assembled into various supramolecular architectures by means of π–π interactions of the aromatic rings. It is worth mentioning that the non-covalent interactions lead not only to various supermolecules and solid-state architectures, but generate also interesting supramolecular properties, such as electrical, optical and magnetic ones [12].

Perylene tetracarboxylic diimide (PTCDI), a widely used n-type semiconductor, has attracted much attention because of its outstanding stability, excellent electron affinity, and chargecarrier migration arising from its π–π stacking [13]. On the strength of these properties, many applications have been investigated, such as organic field-effect transistors (OFETs) [14], solar cells [15], photon harvesting [16], sensors [17] and photoswitches [18].

Our group first presented an economical and rapid method to form a self-assembled nanophotocatalyst for the degradation of organic pollutants under visible light, and explained that the band-like electronic energy level structure of the PTCDI supramolecular system originating from orbital overlaps between PTCDI molecular units and long-range conjugated π-delocalization within the self-assembled PTCDI supramolecular system mainly contributes to its remarkable photocatalytic properties [19]. On this basis, we also reported that the TCNQ-PTCDI visible light catalyst, which is composed of PTCDI and TCNQ with a relatively large conjugate system, can formed a high-speed channel, which is advantageous to the separation and migration of photogenic carriers, and disadvantageous to the composite of photogenic electrons and holes because of the π–π interactions between TCNQ and PTCDI [20]. These related researches provide a new way to improve the separation and migration rate of photogenic carriers of organic photocatalyst.

Fullerenes(C_{60}) is an electronegative molecule and suitable for efficient electron transfer because π orbital of C_{60} is more out of the cage and the electronic structure of C_{60} has naturally focused on the surface 30 π-orbitals [21–24]. The symmetry of the C_{60}, the conical alignment of the conjugate large π bond system and the conical alignment of C atoms result in fast electron transfer and slow electron recombination. Photocatalysts/C_{60} have been prepared to improve the performance of photocatalyst [25–27].

On the basis of these concerns, PTCDI will also be able to combine well with C_{60} through strong π-π interaction between conjugated systems. The electrons are transferred through the π–π long-range transport pathway of self-assemble PTCDI and tend to transfer to C_{60}, then they will be transferred through the large π bond using C_{60} as an electronic separation center result in fast transfer of carriers and reduced carrier recombination. The photocatalytic performance of the catalyst will be enhanced.

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2. Experimental

2.1. Preparation of PTCDI-C_{60} photocatalyst

Perylene tetracarboxylic diimide (PTCDI) was purchased from Sinopharm Chemical Reagent Corp., Beijing, P. R. China. Fullerene(C_{60}) was purchased from Suzhou carbon Feng graphene Technology Co., Ltd. Sulfuric acid was purchased from Beijing Chemical Works. All reagents used in this research were commercially available and used without further purification.

The preparation of PTCDI-C_{60} photocatalysts was as follows: 50 mg C_{60} was dispersed in 100 ml concentrated sulfuric acid under ultrasonication for 5 h to form colloidal. 0.1 g PTCDI was dissolved with 2 mL of concentrated sulfuric acid, the appropriate amount of C_{60} colloidal according to the different mass ratio of the total mass of PTCDI and C_{60} was added into the above solution under ultrasonication for 3 h. The mixture was carefully added dropwise to 50 mL of water under stirring for 3 h, then, dark violet products were precipitated, washed several times. The product was then filtered and dried at 60 °C in a vacuum drying oven. In this way, composite photocatalysts with different C_{60} mass ratios ranging from 0.01% to 30% were synthesized. As shown in the optical photograph presented in Fig. S1, the final products were dark brown with a bit of metal luster before grinding.

2.2. Characterization of PTCDI-C_{60} photocatalyst

The crystallinity of the composites was determined on a Bruker D8 ADVANCE diffractometer under Cu Kα radiation. The structures and morphologies were examined by field-emission scanning electron microscopy (SEM, LEO-1530). High resolution transmission electron microscopy (HRTEM) images were obtained on a JEM 2010 F field-emission gun transmission electron microscope at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) measurements were carried out on an SPM-9700 scanning probe microscope (Shimadzu Corporation). Fourier transform infrared (FTIR) spectra were obtained using a Bruker V70FTIR spectrometer. UV–vis diffuse reflectance spectroscopy (UV-DRS) was performed on a Hitachi U-3010 UV–vis spectrophotometer with $BaSO_4$ as the reference. Raman spectra were obtained with a Horiba JY HR800 confocal microscope Raman spectrometer under an Ar-ion laser (514 nm). The photocurrent was measured on an electrochemical system(CHI-660B). Electron spin resonance (ESR) spectra were recorded from the sample mixture, containing spin-trapping probes such as 5,5- dimethyl-1- -N-oxide(DMPO), 2,2,6,6-tetramethyl-4-piperidone(TEMP), or 2,2,6,6-t pirroline etramethylpiperidine-1-oxyl (TEMPO) and products, after exposure to visible light for selected times using an electron–nuclear double resonance (ENDOR) spectrometer (JEOL ES-ED3X) at room temperature. X-ray photoelectron spectroscopy (XPS) was performed to estimate the VB positions of PTCDI, self-assemble PTCDI and 0.1%-PTCDI-C_{60} using a PHI 5300 ESCA system. PHI Quantera SXMTM system was used to get XPS spectra.

2.3. Photocatalytic evaluation

The photocatalytic degradation of phenol was conducted under visible light (> 420 nm). The light source was a 500-W Xe lamp with a 420-nm cutoff filter, produced by Institute for Electric Light Sources, whose average light intensity was 35 mW cm^{-2}. In the photocatalytic experiments, 25 mg of powder composite photocatalyst was dispersed in an aqueous solution of phenol (50 mL, 5 ppm). Before the light irradiation, the suspensions were stirred in the dark for 1 h to ensure absorption–desorption equilibrium. At intervals of 1 h, aliquots of 2 mL were withdrawn and centrifuged. The concentration of phenol was analyzed by high-performance liquid chromatography (Shimadzu LC-20AT) with UV detection (270 nm). A Venusil XBP-C18 (Agela Technologies Inc.) column was used, and the mobile phase consisted of methanol and pure water (55:45 for phenol, v/v) at a flow rate of 1 mL min^{-1}.

The photocatalytic water oxidation reaction was carried out with a Labsolar-IIIAG system (Perfect Light, Beijing) in the presence of 0.01 mol L^{-1} silver nitrate as an electron acceptor. The photocatalyst powders (50 mg) were added to 100 mL $AgNO_3$(aq) in the reaction cell with a magnetic stirrer. The light source was a 500-W xenon lamp with a 420-nm cutoff filter. The amount of evolved oxygen was determined using a gas chromatograph (GC 7920, thermal conductivity detector, Ar carrier).

2.4. Electrochemical measurement

To investigate the photoelectrochemical performance of the composites, a standard three-electrode cell was employed, with a composite as the working lectrode, a saturated calomel electrode (SCE) as the reference lectrode, and a platinum wire as the counter electrode. Na_2SO_4 was taken as the electrolyte solution. The working electrodes were repared as follows: A composite (5 mg) was suspended in 1 mL of pure/deionized water under grinding and ultrasonication. A dark purple slurry was obtained and dip-coated onto an indium tin oxide (ITO) glass electrode.

3. Results and discussion

3.1. Photocatalytic activity

Fig. 1 presents the photocatalytic activities of the photocatalysts under visible light (> 420 nm) in the degradation of phenol and the oxidation of water. Dramatically, the apparent rate constant of degradation for 5 ppm phenol first rose and then dropped with increasing C_{60} content (see Fig. 1a). When the mass ratio reached 0.1%, the apparent rate constant of degradation reached the maximum of 0.216 h^{-1}, nearly 8.24 times that of pure PTCDI (0.026 h^{-1}), and 2.27 times that of self-assemble PTCDI. However, when the ratio was over 0.1%, the phenol-degradation rate constant decreased notably. Furthermore, the highly efficient 0.1%-PTCDI-C_{60} catalyst could produce

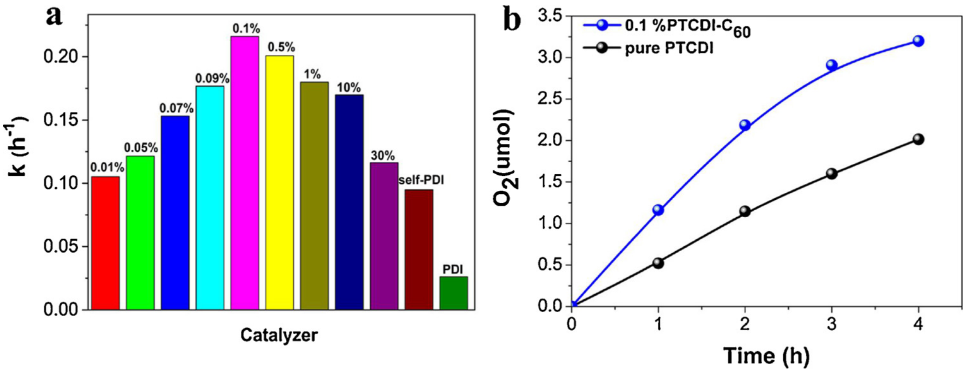

Fig. 1. Photocatalytic activities of PTCDI-C_{60} composite materials: (a) Apparent rate constants k of PTCDI-C_{60} composite photocatalysts for the degradation of 5 ppm phenol with different C_{60} mass ratios under visible light (λ > 420 nm); (b) amount of evolved oxygen in photocatalytic water oxidation with 0.1%-PTCDI-C_{60} under visible light (λ > 420 nm).