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Synthesis, characterization, and activity of a covalently anchored heterogeneous perylene diimide photocatalyst

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ABSTRACT

The consecutive two-photon photocatalytic behavior of perylene diimide (PDI) enables it to catalyze photoreduction reactions that are thermodynamically unfavorable via single-photon processes. In this work, we developed a heterogeneous PDI photocatalyst by covalently binding PDI molecules on the surface of nanosilica. This photocatalyst structure overcomes the intrinsic limitation of the low solubility of PDI, but retains its consecutive two-photon photocatalytic property. Detailed characterization of the photocatalyst by techniques such as thermogravimetric analysis, solid-state nuclear magnetic resonance spectroscopy, and Fourier transform infrared spectroscopy indicated that the PDI molecules were anchored covalently on the surface of nanosilica. The obtained photocatalyst reduced aryl halides under visible-light irradiation in polar organic solvent and in water. The present study provides a promising strategy to realize two-photon activity of PDI in common solvents for photocatalytic applications.

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1. Introduction

The photocatalyst is essential in photocatalytic reactions. Inorganic photocatalysts such as TiO₂ [1–3] have played a leading role in past photocatalysis studies. However, satisfactory photocatalytic efficiency has still not been reached even after a long, thorough investigation of inorganic photocatalysts. Therefore, many researchers have turned their attention to the development of organic photocatalysts [4]. Compared with inorganic photocatalysts, organic materials have many advantages, for example, their strong visible-light adsorption, cheap and abundant element resources, and structural tunability. Various organic photocatalysts have been reported including pure organic dyes [5], organometallic complexes [6,7], and

covalent organic polymers such as carbon nitride [8,9] and poly(*p*-phenylene) [10,11]. While each pure catalyst has associated limitations, they may be overcome by using a combination of catalysts [12–15].

Perylene-3,4,9,10-tetracarboxylic diimide (PDI) has unique optical and electronic properties, such as high oxidation potential, high molar extinction coefficient, and good thermal and photochemical stability [8,16], and thus has been widely used as a basic structural unit to fabricate organic photofunctional materials for applications such as fluorescent sensors [17–19]. PDI has also been used as a photocatalyst to realize photoinduced chemical transformation. It was recently reported that the excitation of PDI by visible light produces a PDI radical anion, which can absorb another photon [20]. The excited state of

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the radical anion accumulates the energy of two photons and can then reductively cleave the C–X bond of aryl halides. This consecutive two-photon reaction can promote photoreduction reactions that are thermodynamically unfavorable as a single-photon process (such as the cleavage of the C–X bond of stable aryl halides), making PDI promising as a visible-light photocatalyst for use in reactions with low activity. However, because of the intrinsic hydrophobicity of PDI, these reactions have to be carried out in organic solvents [21]. Most PDI derivatives have very low solubility and a strong tendency to aggregate in common organic solvents. Therefore, it remains desirable to realize photocatalytic reactions using PDI in common organic solvents, or even in water, which is the most environmentally friendly solvent. PDI may be loaded on semiconductor oxide (WO_3 , TiO_2 , or SnO_2) surfaces via aggregation/hydrophobic forces [22] or form self-assembled supramolecular nanostructures [23] to enable its photocatalytic reactions to be carried out in polar solvents or water. However, the two-photon activity of PDI is lost in such systems because of the electronic interactions of PDI and the semiconductor or between PDI molecules. To avoid these interactions, PDI has been incorporated into a metal–organic polymer [24]. This approach achieved efficient reduction of aryl halides by the consecutive two-photon process.

Herein, we develop a novel strategy to realize the heterogeneous two-photon photocatalytic activity of PDI by covalently anchoring PDI on non-conductive nanosilica (nano- SiO_2). In this hybrid photocatalyst (denoted as SN-PDI), the binding of PDI to the nano- SiO_2 surface avoids the interaction between PDI molecules. The high hydrophilicity of nano- SiO_2 makes the SN-PDI photocatalyst miscible with polar solvents. As a result, efficient photocatalytic reduction of aryl halides is achieved in aqueous solution.

2. Experimental

2.1. Materials

Aminopropyltriethoxysilane (APTES), 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA), triethylamine (TEA), decabromodiphenyl ether (BDE 209), and 4-bromoacetophenone (4-BCP) were purchased from Alfa Aesar. Tetraethoxysilane (TEOS) was obtained from Xilong Chemical Co., Ltd. Sodium sulfide (Na_2S) was supplied by J&K. All materials were used as received.

2.2. Synthesis of nanosilica-supported PDI (SN-PDI) photocatalyst

2.2.1. Preparation of nanosilica with surface amino groups (SN- NH_2)

Nanosilica with surface amino groups (SN- NH_2) was synthesized by co-condensation of APTES and TEOS according to Rahman's method [25]. Briefly, TEOS (40.5 mmol) and APTES (162 mmol; molar ratio of 1:4) were added to ethanol (225 mL). After stirring magnetically for 10 min, H_2O (8 mL) was added to initiate the co-condensation by hydrolysis. Reaction

for 3 h led to the formation of a white suspension. The opaque suspension was filtered and washed three times with ethanol. Finally, the post-filtration product (SN- NH_2) was dried at 120 °C for 24 h [26].

2.2.2. Preparation of SN-PDI

A mixture of SN- NH_2 (0.7 g), PTCDA (0.5 g), and imidazole (5 g) was heated to 150 °C under nitrogen and stirred magnetically for 48 h. In this reaction process, the basic imidazole first catalyzes the cleavage of the anhydride groups of PTCDA, and then the formed diacid reacts with the amino groups on the nano- SiO_2 surface to generate an imide. As a result, PDI was anchored on nano- SiO_2 (Scheme 1). Upon cooling to room temperature, ethanol (50 mL) and concentrated hydrochloric acid (12 mol/L, 30 mL) were added to form diimide groups. After stirring overnight, a red powder was obtained following vacuum filtration through a 0.45- μm membrane filter. The powder was washed three times with 200 mL of an aqueous solution of potassium hydroxide (20 g) and potassium chloride (16 g) to remove the residual PTCDA. Subsequently, the red solid was added to 10% hydrochloric acid solution and stirred for 6 h to neutralize the residual base. The solid was filtered, washed with water, and then dried at 90 °C in a vacuum oven, providing 0.92 g of SN-PDI.

2.3. Characterization

Transmission electron microscopy (TEM; JEM-2010, JEOL, Japan) was conducted at an accelerating voltage of 120 kV. The TEM specimen was obtained by dissolving the sample in ethanol and added the solution dropwise onto a copper grid. Scanning electron microscopy (SEM; S-4300F, JEOL) was performed at 5 kV. The sample was dispersed in ethanol and added dropwise onto a conductive copper adhesive before sputtering approximately 3 nm of platinum on the surface. X-ray photoelectron spectroscopy (XPS; 220i-XL, ESCALab) was measured at a base pressure of 3×10^{-9} mbar.

Scheme 1. Synthetic route to SN-PDI.

Thermogravimetric analysis (TGA) was performed on Perkin-Elmer Pyris 1 and TGA 7 thermogravimetric analyzers in nitrogen and air atmospheres, respectively. Solid samples were heated from 100 to 750 °C at a rate of 20 °C/min. Brunauer-Emmett-Teller (BET) and total pore volume (TPV) analyses were conducted using Quantachrome Instruments software (version 11.0). Data acquisition and reduction were performed with NOVA Instruments equipment (1994–2010). Nitrogen was used as the analysis gas, the bath temperature was 77.3 K, and samples were analyzed for 567 min.

Solid-state nuclear magnetic resonance (SSNMR) spectroscopy was conducted on a Bruker Avance III 400 NMR spectrometer. The samples were added into a zirconia rotor ($d = 4$ mm) and then the rotor was sealed and loaded in the spectrometer. ^{29}Si magic angle spinning (MAS) NMR spectra and ^{13}C cross-polarization (CP) MAS NMR spectra were measured. The spinning speed, pulse length, recycle delay, and accumulated number for ^{29}Si MAS NMR spectra were 8 kHz, 4 μs , 10 s, and 10240 times, respectively, while those for ^{13}C CP MAS NMR spectra were 8 kHz, 3.0 ms, 2.0 s, and 10240 times, respectively.

Fourier transform infrared (FT-IR) spectroscopy was performed using a Perkin-Elmer System 2000 spectrometer. The wavenumber range was 4000–650 cm^{-1} and the samples were dispersed in potassium bromide tablets. Ultraviolet-visible (UV-vis) absorption spectroscopy was carried out on a UV-vis spectrometer (Hitachi High-Technologies Corporation).

2.4. Determination of product distribution

BDE 209 and its reductive products were analyzed by electron capture detection gas chromatography (ECD-GC; Agilent Technology, 7890A) with an HP-5 column (30 m $\times$ 0.25 mm). Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The oven temperature was kept at 100 °C for 2 min, increased at a rate of 15 °C/min to 230 °C, then at 5 °C/min to 270 °C, and finally increased at 10 °C/min to 330 °C for 8 min. The amounts of 4-BCP and its reductive products were analyzed by high-performance liquid chromatography (HPLC; Agilent Technology, G1328B) with a Diamonsil C18(2) column (5- μm particles, 250 $\times$ 3.0 mm). The mobile phase was 45% water in acetonitrile, the flow rate was 0.2 mL/min, and the detector wavelength was 240 nm.

2.5. Photocatalytic activity experiments

Reaction dispersions were prepared by adding SN-PDI (10 mg) to DMF or water (10 mL) containing aryl halides in a Pyrex vessel. TEA (1 mmol/L) or another reductive agent was added to the dispersions as an electron donor. The Pyrex vessel was sealed and purged with argon gas for 30 min to remove oxygen and protected under argon atmosphere during irradiation. During the photoreaction process, the reactor was kept at 25 °C by a water circulating bath (HX-205, Beijing YKKY Technology Co., Ltd). A xenon lamp (PLS-SXE300, Beijing Trusttech Co. Ltd.) with a cut-off filter of $\lambda > 420$ nm was used as the light source. At given time intervals, 0.5-mL aliquots were removed, centri-

fuged, and then filtered through a Millipore filter (pore size: 0.20 μm) to remove the photocatalyst particles. The filtrates were analyzed by HPLC and ECD-GC.

3. Results and discussion

3.1. Characterization of SN-NH₂ and SN-PDI

The TEM and SEM images in Fig. 1 reveal that SN-NH₂ consists of irregular spherical particles with a diameter of about 40 nm. The energy-dispersive X-ray (EDX) profiles confirm the presence of C, N, O, and Si in SN-NH₂. Loading PDI did not appear to change the morphology of nano-SiO₂, implying that PDI was loaded as molecules on the surface of nano-SiO₂ rather than forming aggregates. The BET measurements show that SN-NH₂ has a surface area of 72.2 m^2/g , whereas that of SN-PDI is considerably lower (39.9 m^2/g , Table 1).

The XPS survey scans (Fig. 2(a) and (b)) contained peaks at binding energies of around 531, 399, 285, and 103 eV that are attributed to O 1s, N 1s, C 1s, and Si 2p, respectively. The main difference between the XPS scans for SN-NH₂ and SN-PDI is the shift in the N 1s binding energy from 399.1 to 399.9 eV (Fig. 2(c)), revealing that N is in different environments in the two samples. The XPS and EDAX analyses indicate that the atomic ratio of C in SN-PDI is larger than that in SN-NH₂, while that of Si decreases because of the presence of PDI (Table 2).

^{29}Si SSNMR spectroscopy is a frequently used technique to examine the chemical nature of Si atoms in SiO₂ [27–29]. As shown in Fig. 3, two peaks are observed in the ^{29}Si SSNMR spectrum of SN-NH₂. The peak around -110 ppm is assigned to Si atoms with hydroxyl groups. The peaks from Si atoms with no, one, and two hydroxyl groups appear at -109 , -100 , and -90 ppm, respectively [30]. In this case, only peaks at -109 and

Fig. 1. TEM images of SN-NH₂ (a) and SN-PDI (b), and SEM images (inset: corresponding EDX) of SN-NH₂ (c) and SN-PDI (d).

Table 1
BET and TPV of SN-NH₂ and SN-PDI.

Sample	BET (m^2/g)	TPV (cm^3/g)
SN-NH ₂	72.2	0.57
SN-PDI	39.9	0.52

Fig. 2. XPS scans of SN-NH₂ (a) and SN-PDI (b); (c) N 1s spectra of SN-NH₂ and SN-PDI.

–100 ppm are observed following peak deconvolution, indicating that the most of Si atoms have no or one hydroxyl group. This result means that most of the Si atoms are attached together to form a highly condensed network in SN-NH₂. The peak at –66 ppm is attributed to Si atoms connected to an amino group [30]. The percentage of Si atoms with an amino group estimated from the peak areas is 33% of the total Si atoms, which is similar to the result obtained by Suratwala et al. [31].

The ¹³C SSNMR spectrum of SN-NH₂ contains three signals at 44.2, 24.8, and 10.6 ppm that are assigned to the C_a, C_b, and C_c carbon atoms, respectively, of the alkyl chain attached to the amino group (the inset of Fig. 4). These C_a, C_b, and C_c signals move to 42.2, 22.7 and 10.0 ppm, respectively, in the spectrum of SN-PDI, indicating that the environment of the carbon atoms of the alkyl chain is changed when the amino group attaches to carbonyl groups. The overall shift of these three peaks indicates that most of the surface amino groups of silica react with PTCDA. The signal at 159.8 ppm in the spectrum of PTCDA,

which is assigned to the C_d carbon atom is shifted to 162.3 ppm in the spectrum of SN-PDI, indicating the oxygen atom in the acid anhydride is replaced by a nitrogen atom; that is, PDI bound covalently to the nano-SiO₂ surface.

The structures of the obtained SN-NH₂ and SN-PDI were further investigated by FT-IR spectroscopy. As shown in Fig. 5, for SN-NH₂, the absorptions near 1646 and 800 cm^{–1} are caused by the Si–OH vibration [31,32]. The absorption near 2940 cm^{–1} is attributed to the –CH₂ stretching vibration [31,32] and that near 1548 cm^{–1} is from the N–H bending vibration. The FT-IR spectrum of SN-PDI does not contain a peak at 1548 cm^{–1}, indicating that the reaction occurred between SN-NH₂ and PTCDA molecules. The FT-IR spectrum of PTCDA displays peaks near 1592 and 1500 cm^{–1} originating from skeleton vibrations of the aromatic structure; these absorptions are also observed in the FT-IR spectrum of SN-PDI. The FT-IR spectrum of PTCDA also exhibited peaks centered at about 1770 cm^{–1} attributed to the C=O vibration of acid anhydride and near 1300 cm^{–1} from the C–O vibration of acid anhydride. When PTCDA was loaded on SN-NH₂ to form SN-PDI, these characteristic absorptions of acid anhydride disappeared and characteristic amide C=O and C–N absorption peaks appeared at 1670 and 1274 cm^{–1}, respectively, indicating that the PDI structure formed. All of these results show that PDI was successfully anchored on silica through the one-step reaction of SN-NH₂ with PTCDA.

Table 2

Contents of Si, O, C, and N in SN-NH₂ and SN-PDI.

Sample	Atomic content (%)			
	Si	O	C	N
SN-NH ₂	19.7	35.67	35.64	8.99
SN-PDI	7.81	22.61	62.48	7.11

Fig. 3. ²⁹Si SSNMR spectrum of SN-NH₂.

Fig. 4. ¹³C SSNMR spectra of SN-NH₂ and SN-PDI. For comparison, the spectrum of PTCDA is also shown. Inset: the structure of SN-PDI.

Fig. 5. FT-IR spectra of SN-NH₂, SN-PDI and PTCDA.

The quantity of PDI in SN-PDI was determined by TGA. As shown in Fig. 6, PTCDA begins to lose weight at 550 °C. Nearly all the PTCDA disappeared after heating to 750 °C. The weight loss of SN-NH₂ began at 300 °C, and calcination at 750 °C led to the loss of 27% of its weight. After PDI loading, about 48% weight loss was observed at 750 °C for SN-PDI. These results indicate that PDI accounts for about 21% of the weight of SN-PDI.

Comparison on the fluorescence spectra of the supported PDI (SN-PDI) and molecular PDI shows that loading PDI on nano-SiO₂ slightly shifted its maximum emission wavelength from 578 to 574 nm (Fig. 7). This is probably because of the more polar environment of the PDI molecules on the surface of nano-SiO₂ than in solution.

3.2. Photocatalytic activity under visible-light irradiation

The photochemical reduction of SN-PDI was first examined using TEA as an electron donor in DMF. Before visible-light irradiation, the suspension of SN-PDI was yellow. After removing the SN-PDI by filtration, the solution was colorless, indicating that all the PDI was anchored on nano-SiO₂ and no PDI was released into the solution. After irradiation for 30 min, the sus-

Fig. 6. TGA curves of SN-NH₂, PTCDA, and SN-PDI.

Fig. 7. Fluorescence spectra of SN-PDI and molecular PDI in DMF.

pension became dark blue (Fig. 8), indicating the photochemical reduction of PDI to its radical anion (PDI^{•-}). The photochemical activity of the radical anion was investigated by its ability to catalyze the reductive debromination of BDE 209, an important environmental pollutant. It was found that the debromination reaction occurred quite quickly in the DMF solution containing SN-PDI. After irradiation for 0.5 h, all the BDE 209 was removed and polybromodiphenyl ethers with fewer bromine atoms were produced as intermediates (Fig. 9).

To verify the consecutive two-photon photocatalytic behavior of SN-PDI, we first irradiated a deaerated suspension of SN-PDI with TEA to transform the PDI into its radical anion. The subsequent addition of 4-BCP under argon protection did not change the color of the suspension and no 4-BCP was reduced in the dark, indicating that PDI^{•-} cannot directly reduce 4-BCP. However, subsequent irradiation by visible light led to the rapid reduction of 4-BCP, which suggests that the excited state of the radical anion can form through the reduction reaction.

To test the photostability of SN-PDI, we repeatedly added 4-BCP to the photocatalytic suspension. After adding 4-BCP three times, the removal rate of 4-BCP still exceeded 70% following irradiation for 1 h (Fig. 10), indicating the photocatalytic activity decreased somewhat. In addition, the color of the suspension did not change much, indicating the SN-PDI photocatalyst is quite stable under the photocatalytic conditions.

Fig. 8. Color change of a DMF suspension of SN-PDI in the presence of Na₂S during visible-light irradiation for 30 min.

Fig. 9. Photocatalytic reduction of BDE 209 by SN-PDI.

To test the photochemical activity of SN-PDI in water, we used 4-BCP as a substrate. In the presence of Na_2S as an electron donor, the photocatalytic debromination of 4-BCP occurred efficiently in aqueous solution. After irradiation for 2 h, about 60% of the original 4-BCP was debrominated to acetophenone. Control experiments in the absence of SN-PDI or Na_2S did not show any photochemical reaction under otherwise identical conditions (Fig. 11). This indicates that the debromination reaction is caused by the light absorption of SN-PDI and the electron donor is important to the photocatalytic reactions. Besides Na_2S , other common water-soluble electron donors such as methanol and TEA were also tested. However, at natural pH, none of these electron donors were active for the debromination reaction of 4-BCP. One possible explanation for the inertness of these electron donors is their different pH. The solution of Na_2S is basic with a high pH of 9.6 because of the hydrolysis of sulfide anions. To test whether the pH influenced the photocatalytic reaction, we adjusted the pH of the Na_2S solution. As shown in Fig. 11(b), when the pH of the suspension

Fig. 10. Photostability of the SN-PDI photocatalyst tested by repeatedly adding BDE 209 to the same reaction mixture.

was adjusted from the natural pH (pH = 10) to pH = 6 or 8, the photocatalytic reaction was completely suppressed. In contrast, adjusting the pH of the suspension to 10 in the presence of methanol or TEA as an electron donor allowed the debromination reaction to occur smoothly. All these results suggest that basic conditions are needed for the successful photocatalytic reaction of SN-PDI in water.

To shed light on mechanism behind the effect of pH on the photocatalytic reaction, we investigated the change of visible light spectra after irradiation, which provided information about on the photochemical formation of $\text{PDI}^{\bullet-}$. As shown in Fig. 12, the irradiation of the deaerated aqueous suspension of SN-PDI in the presence of Na_2S at pH 10 leads to the appearance of a broad absorption peak around 750 nm, which is assigned to the formation of $\text{PDI}^{\bullet-}$. In addition, in the presence of 4-BCP, the peak from $\text{PDI}^{\bullet-}$ was not observed. By contrast, at pH = 8, no photochemical reaction was observed during the irradiation, even in the absence of 4-BCP, indicating that $\text{PDI}^{\bullet-}$ did not form under these conditions. It has been reported that the photocatalytic dehalogenation reaction by PDI proceeds through a two-proton, two-electron transfer process. In the

Fig. 11. (a) Photocatalytic reduction of 4-bromoacetophenone in the presence of SN-PDI (1 g/L) and Na_2S (1 mmol/L), only SN-PDI, and only Na_2S ; (b) The effect of pH on the photocatalytic reduction of 4-bromoacetophenone.

Fig. 12. Change in UV-vis absorption spectra of aqueous suspensions of SN-PDI in the presence of Na₂S at pH = 10 (a) and pH = 8 (b); (c) After 4-bromoacetophenone was added to the system in (a).

first step, PDI absorbs a photon and abstracts an electron from an electron donor to produce the relatively stable PDI^{•-}. In the second step, the formed PDI^{•-} is further excited by a second photon to produce an excited state with high enough reductivity to reduce the aryl halide. The observation that no PDI^{•-} is formed at pH = 8 suggests that the ineffectiveness of SN-PDI at low pH results from the prevention of the first step.

4. Conclusions

PDI was anchored on the surface of nano-SiO₂ by reaction of SN-NH₂ with PTCDA. Characterization of the SN-PDI photocatalyst showed that PDI was linked on the nano-SiO₂ surface through covalent chemical bonds. The SN-PDI photocatalyst retained the consecutive two-photon photocatalytic behavior of PDI, which enabled it to catalyze a photoreduction reaction that is thermodynamically unfavorable via a single-photon process. The present study provides a promising heterogeneous PDI photocatalyst that overcomes the intrinsic restriction of the low solubility of PDI while keeping its consecutive two-photon photocatalytic feature.

References

- [1] M. S. Akple, J. Low, Z. Qin, S. Wageh, A. A. Al-Ghamdi, J. Yu, S. Liu, *Chin. J. Catal.*, **2015**, 36, 2127–2134.
- [2] Y. F. Li, W. P. Zhang, X. Shen, P. F. Peng, L. B. Xiong, Y. Yu, *Chin. J. Catal.*, **2015**, 36, 2229–2236.
- [3] T. J. Wu, X. D. Kang, M. W. Kadi, I. Ismail, G. Liu, H. M. Cheng, *Chin. J. Catal.*, **2015**, 36, 2103–2108.
- [4] M. L. Marin, L. Santos-Juanes, A. Arques, A. M. Amat, M. A. Miranda, *Chem. Rev.*, **2011**, 112, 1710–1750.
- [5] A. Graml, I. Ghosh, B. König, *J. Org. Chem.*, **2017**, 82, 3552–3560.
- [6] C. K. Prier, D. A. Rankic, D. W. MacMillan, *Chem. Rev.*, **2013**, 113, 5322–5363.
- [7] F. Teplý, *Collect. Czech. Chem. Commun.*, **2011**, 76, 859–917.
- [8] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [9] J. Zhang, X. F. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Fu, M. Antonietti, X. Wang, *Angew. Chem. Int. Ed.*, **2010**, 49, 441–444.
- [10] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.*, **1990**, 94, 5523–5527.
- [11] S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac, K. Yoshino, *J. Chem. Soc., Chem. Commun.*, **1985**, 474–475.

Graphical Abstract

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Synthesis, characterization, and activity of a covalently anchored heterogeneous perylene diimide photocatalyst

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By loading covalently PDI molecules on nano-silica, a heterogeneous PDI photocatalyst (SN-PDI) was developed, which can absorb two photons to reduce the halogenated substrates in common solutions, even in water.

- [12] B. Lin, C. Xue, X. Q. Yan, G. P. Yang, G. Yang, B. L. Yang, *Appl. Surf. Sci.*, **2015**, 357, 346–355.
- [13] C. J. Hao, J. Li, Z. L. Zhang, Y. J. Ji, H. H. Zhan, F. X. Xiao, D. Wang, B. Liu, F. B. Su, *Appl. Surf. Sci.*, **2015**, 331, 17–26.
- [14] S. Phanichphant, A. Nakaruk, D. Channei, *Appl. Surf. Sci.*, **2016**, 387, 214–220.
- [15] X. F. Wang, R. Yu, K. Wang, G. Q. Yang, H. G. Yu, *Chin. J. Catal.*, **2015**, 36, 1211–1218.
- [16] F. Würthner, *Chem. Commun.*, **2004**, 1564–1579.
- [17] K. Takahashi, I. Nakajima, K. Imoto, T. Yamaguchi, T. Komura, K. Murata, *Solar Energy Mater. Solar Cells*, **2003**, 76, 115–124.
- [18] L. Schmidt-Mende, A. Fichtenkötter, K. Müllen, E. Moons, R. H. Friend, J. MacKenzie, *Science*, **2001**, 293, 1119–1122.
- [19] X. W. Zhan, Z. A. Tan, B. Domercq, Z. S. An, X. Zhang, S. Barlow, Y. F. Li, D. B. Zhu, B. Kippelen, S. R. Marder, *J. Am. Chem. Soc.*, **2007**, 129, 7246–7247.
- [20] I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science*, **2014**, 346, 725–728.
- [21] S. Guha, F. S. Goodson, S. Roy, L. J. Corson, C. A. Gravenmier, S. Saha, *J. Am. Chem. Soc.*, **2011**, 133, 15256–15259.
- [22] F. Ronconi, Z. Syrgiannis, A. Bonasera, M. Prato, R. Argazzi, S. Caramori, V. Cristino, C. A. Bignozzi, *J. Am. Chem. Soc.*, **2015**, 137, 4630–4633.
- [23] D. Liu, J. Wang, X. J. Bai, R. L. Zong, Y. F. Zhu, *Adv. Mater.*, **2016**, 28, 7284–7290.
- [24] L. Zeng, T. Liu, C. He, D. Y. Shi, F. L. Zhang, C. Y. Duan, *J. Am. Chem. Soc.*, **2016**, 138, 3958–3961.
- [25] I. A. Rahman, M. Jafarzadeh, C. S. Sipaut, *Ceram. Int.*, **2009**, 35, 1883–1888.
- [26] H. X. Tang, P. Liu, M. Lu, Y. F. Ding, F. Wang, C. Gao, S. M. Zhang, M. S. Yang, *Polymer*, **2017**, 112, 369–376.
- [27] M. C. Brochier Salon, P. A. Bayle, M. Abdelmouleh, S. Boufi, M. N. Belgacem, *Colloids Surf. A*, **2008**, 312, 83–91.
- [28] K. Albert, R. Brindle, J. Schmid, B. Buszewski, E. Bayer, *Chromatographia*, **1994**, 38, 283–290.
- [29] R. Brambilla, G. P. Pires, J. H. dos Santos, M. S. Lacerda Miranda, *J. Colloid Interface Sci.*, **2007**, 312, 326–332.
- [30] S. Chen, S. Hayakawa, Y. Shirosaki, E. Fujii, K. Kawabata, K. Tsuru, A. Osaka, *J. Am. Ceram. Soc.*, **2009**, 92, 2074–2082.
- [31] T. I. Suratwala, M. L. Hanna, E. L. Miller, P. K. Whitman, I. M. Thomas, P. R. Ehrmann, R. S. Maxwell, A. K. Burnham, *J. Non-cryst. Solids*, **2003**, 316, 349–363.
- [32] T. Suteewong, H. Sai, M. Bradbury, L. A. Estroff, S. M. Gruner, U. Wiesner, *Chem. Mater.*, **2012**, 24, 3895–3905.

异相光催化剂苝酰亚胺的合成、表征及活性

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摘要: 光催化是催化反应中非常重要的一个领域, 其中可见光催化反应在实际应用中尤为重要. 近几十年, 众多研究者致力于可见光催化剂的研究, 如有机染料、有机金属复合物和共价有机聚合物等都是常见的可见光催化剂. 近年来, 人们发现苝酰亚胺(PDI)是一类活性非常高的可见光催化剂, 因为一个PDI分子可以连续吸收两个光子而积累足够的能量, 使得许多单光子过程能量不足以激发的反应能够顺利进行. 然而, 由于PDI结构中存在大共轭的苯环, 其在大部分溶剂中的溶解度都比较低, 尤其是在水相中很难溶解, 因此限制了它的应用.

本文将PDI分子通过共价键键合在纳米二氧化硅表面, 合成了一种新的多相PDI光催化剂(SN-PDI), 解决了PDI在很多溶剂中都难以分散的问题, 同时保留了它双光子吸收的光催化特性. 我们首先合成了表面修饰有氨基的纳米二氧化硅, 然后与苝酰反应, 从而将PDI键合在二氧化硅表面. 利用二氧化硅的亲水性使得PDI在水中以及大部分溶剂中很好地分散和分离, 从而充分发挥PDI的光催化还原性能.

通过²⁹Si固体核磁(NMR)、X射线光电子能谱(XPS)、¹³C固体核磁、傅里叶变换红外光谱(FT-IR)、紫外-可见吸收光谱以及热重分析等手段表征了合成后的SN-PDI. 其中²⁹Si固体核磁谱图中化学位移在-66 ppm处的峰证明了缩合形成的纳米二氧化硅中带有氨基, 根据峰面积得到其中33%的硅原子上连有氨基. XPS结果发现, N 1s轨道有明显位移, 说明合成后N原子的化学环境发生了明显变化. ¹³C NMR结果表明, 合成前后与氨基相连的几个碳也发生了较大位移, 与理论一致. FT-IR发现苝酰中酸酐特征峰消失以及亚胺特征峰出现, 证明PDI成功键合在了二氧化硅表面.

以十溴联苯醚和4-溴苯乙酮作为卤代底物, 分别在有机相和水相中采用SN-PDI光催化降解反应, 结果均得到了脱卤后的产物. 催化循环三次仍有较高活性. 可见, 键合在纳米二氧化硅表面的PDI确实具有光催化活性.

关键词: 可见光; 光催化; 纳米二氧化硅; 苝酰亚胺; 脱卤

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