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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 TiO_2 [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-perylenetetracarboxylic dianhydride (PTCDA), triethylamine (TEA), decabromodiphenyl ether (BDE 209), and 4-bromoacetophenone (4-BCP) were purchased from Alfa Aesear. 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)

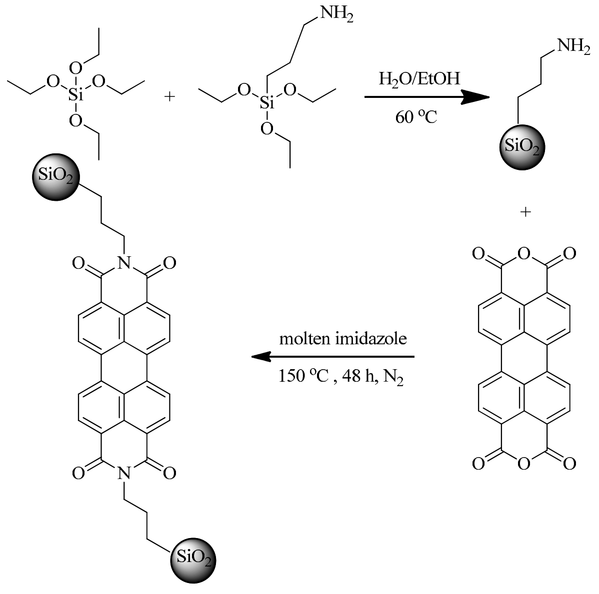
Nanosilica with surface amino groups (SN-NH_2) was synthesized by co-condensation of APTES and TEOS according to Rahman's method [25]. Briefly, TEOS (40.5 mmol) and APTES (162 mmol; molar ratio of 1:4) were added to ethanol (225 mL). After stirring magnetically for 10 min, H_2O (8 mL) was added to initiate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

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