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Pyrene-functionalized polymeric carbon nitride with promoted aqueous-organic biphasic photocatalytic CO₂ reduction[†]

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We have demonstrated a simple copolymerization process to covalently graft pyrene-functional groups on the polymeric carbon nitride (PCN) surface. The resulting pyrene functionalized carbon nitride (Py-PCN) exhibits unique biphasic photocatalytic activities, which enable efficient CO_2 photoreduction in aqueous solution with simultaneous alkene (C=C) oxidation in the organic phase. The great biphasic activities are attributed to the increased lipophilicity from surface pyrene-functional groups, which allows the hydrophobic alkene molecules to readily approach the PCN surface and react with the hydroxyl radicals created from -OH oxidation by photogenerated holes. In this way, the alkene compounds indirectly consume the photo-holes from excited Py-PCN, promoting the overall photocatalytic process. Our study provides a new strategy for solar fuel production with simultaneous organic synthesis by the oxidation power of photo-holes on amphiphilic metal-free semiconductors.

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1. Introduction

Considering the increasing CO₂ concentration in the atmosphere and overconsumption of fossil fuels, photocatalytic CO₂ conversion to value-added fuels is believed to be an effective way to alleviate the energy crisis and environmental issues.1 Among all the semiconductors that are capable of reducing CO₂, polymeric carbon nitride (PCN) has attracted much research interest due to its perfect band structure.² Specifically, its high conduction band with respect to the CO₂ reduction potentials provides thermodynamic driving force. And the versatile strategies for PCN structure modification, such as copolymerization,³ introducing a heterojunction,⁴⁻⁶ and elemental doping,⁷ can be smoothly applied to functionalize PCN for boosting its photocatalytic activity for CO2 reduction. Moreover, PCN features amphiphilic properties owing to its terminal amine groups,8 enabling excellent affinity for the absorbates in aqueous solution for surface reaction.

To date, most photocatalytic CO₂ reduction tests have been carried out in aqueous suspensions, in which H₂O is expected to serve as the electron donor.^{9,10} In principle, the potential of the photohole ($E_{vb} = +1.4$ V, *vs.* NHE) of PCN is capable of oxidizing water into O₂ ($E_{H_2O/O_2} = +1.23$ V, *vs.* NHE). However, the large overpotential for O₂ evolution makes the real O₂ generation on

the PCN surface very difficult. Therefore, some sacrificial reagents, such as triethanolamine (TEOA), were commonly used for the photocatalytic CO₂ reduction.¹¹ Further, in terms of photocatalytic pollutant degradation, PCN was capable of oxidizing phenol,¹² bisphenol A¹³ and some organic dyes by hydroxyl radicals and/or superoxide radicals.¹⁴ Considering the π -conjugated units in the PCN backbones,¹⁵ the π -conjugated molecules (*e.g.*, alkenes, alkynes and aromatics) could be preferably adsorbed *via* interfacial π - π conjugation. Nevertheless, this requires that the PCN is capable of dispersing in organic solvents in order to achieve optimal adsorption of those π -conjugated molecules.

Co-polymerization of PCN precursors with co-monomers (*e.g.*, 2-aminobenzonitrile, aniline, benzonitrile, *etc.*) was commonly used to obtain functionalized PCN.^{16–18} However, the co-polymerization usually inserted the functional group into the PCN matrix, which significantly altered the PCN band structures besides the surface properties. An alternative strategy is post-calcination of PCN mixed with functional molecules, which is not effective with non-uniform surface functionalization. The required high temperature calcination restricted the available range of monomers in particular with large conjugated units that may decompose or carbonize.

According to our previous studies, PCN can be formed through a solvothermal process, which allows covalent attachment of triazine-based oligomers on the surface.¹⁹ Such oligomers can be further condensed upon mild annealing.²⁰ These observations suggest that the conjugated functional groups on triazine-based molecules can be covalently linked onto the PCN surface *via* post-polymerization to modulate the surface properties.



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Specifically, in this work, we introduce surface pyrenefunctionalization on PCN through a solvothermal process by using 1-(4,6-dichloro-1,3,5-triazin-2-yl)pyrene (PyCC) as the monomer and pre-synthesized PCN microspheres as the matrix. The heptazine units in PCN are naturally hydrophilic, which allows it to readily disperse in water. However the pyrene-moiety supplies hydrophobic sites that allow affinity for nonpolar solvents for adsorption and reaction of organic compounds.

Therefore, the pyrene-functionalized polymeric carbon nitride (Py-PCN) can act as an aqueous-organic biphasic photocatalyst, which enables photoreduction of bicarbonate in the aqueous phase and simultaneous oxidation of organic compounds in a nonpolar solvent. Here, for proof-of-concept, we demonstrate that the photogenerated holes of PCN can lead to the oxidation of the C=C bond of alkene compounds, while the pyrene groups on Py-PCN can greatly enhance the affinity for alkene compounds in the organic phase and enables more effective oxidation reaction. This work provides valuable guidance for the design and preparation of multifunctional PCN photocatalysts for not only CO_2 reduction but also simultaneous organic synthesis in nonpolar organic solvents.

2. Experimental

2.1 Chemicals

All the chemical reagents were used as received without further purification. Cyanuric chloride (99%), cyanamide (99%), 1-(4,6-dichloro-1,3,5-triazin-2-yl)pyrene (\geq 85%), sodium bicarbonate (99.5%), cyclohexene (\geq 99.7%), 2-methyl-2-butene (\geq 99.0%), acetonitrile (anhydrous, 99.8%), and toluene (HPLC Plus, \geq 99.9%) were all purchased from Sigma-Aldrich.

2.2 Synthesis of polymeric carbon nitride

The raw PCN was synthesized through a solvothermal approach. Typically, 360 mg of cyanuric chloride (CC) and 168 mg of cyanamide (CA) were dissolved in 15 ml of acetonitrile through sonication, and the mixture was transferred to a 40 ml Teflon-lined autoclave. Afterwards, the autoclave was sealed, put into an oven, and maintained at 200 $^{\circ}$ C for 24 h. The obtained product was washed with acetonitrile, DI water and absolute ethanol in sequence, and finally dried at 80 $^{\circ}$ C. This raw PCN sample is denoted as CN0.

2.3 Synthesis of pyrene-functionalized polymeric carbon nitride (Py-PCN)

The synthesized CN0 (100 mg) was dispersed in acetonitrile to form a homogeneous suspension. Different amounts of 1-(4,6-dichloro-1,3,5-triazin-2-yl)pyrene (PyCC) were added to the suspension together with CC and CA. The molar ratio of PyCC : CC : CA is 1:1:5. The mixture was transferred to a Teflon-lined autoclave that was placed in an oven maintained at 200 °C for 24 h. The obtained products were washed with acetonitrile, DI water and absolute ethanol in sequence and finally dried at 80 °C. The final Py-PCN samples were labelled 2.5% Py-PCN, 5% Py-PCN, 10% Py-PCN and 20% Py-PCN based on the mass ratio of PyCC to CN0. As a control sample, CN0 was

treated with the same solvothermal process in acetonitrile with only CC and CA (no PyCC), which is considered as the bare PCN and denoted as 0-PCN.

2.4 Characterization

SEM images were obtained using an FESEM 7600F scanning electron microscope with the acceleration voltage set at 5 kV. Fourier transform infrared spectra (FTIR) were obtained from a Perkin Elmer Fourier Transform Infrared Spectrometer GX. The XRD patterns of all samples were collected on an XRD-6000 X-ray diffractometer (Cu K_{α} source) at a scan rate of 5° min⁻¹. UV-Vis diffuse reflectance spectra (DRS) were measured with a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin-Elmer, USA) using BaSO₄ as a reference. Photoluminescence (PL) spectra were obtained in the solid state with a Shimadzu RF5301 Spectrofluorophotometer. The specific surface area was calculated from N2 adsorption-desorption isotherms measured using a surface area and porosity analyzer (Micromeritics, ASAP 2020) by using the Brunauer-Emmett-Teller (BET) equation. The surface hydrophilicity was measured by contact-angle (CA) measurement (Data Physics, OCA 15 Pro); the samples were pressed into tablets for measurement.

2.5 Photocatalytic CO₂ reduction in biphase

For the photocatalytic activity measurement, 3.0 wt% Pt as a cocatalyst was loaded through a wetness impregnation process. Typically, the prepared sample (100 mg) was mixed with H_2PtCl_6 (1.0 mg mL⁻¹) solution, followed by ultrasonic treatment for 5 min to form a slurry. After 2 hour impregnation under vigorous stirring, excess water was removed by drying at 70 °C in an oven. Afterwards, the obtained solid sample was treated by NaBH₄ reduction. The final product was washed thoroughly with distilled water to completely remove ions, separated via centrifugation, and dried at 70 °C. In a quartz reactor, 10 mg of the catalyst was dispersed in a mixture of 1 ml aqueous solution of NaHCO₃ (3 M) and 9 ml cyclohexene (or 9 ml toluene containing 2 mmol of 2-methyl-2-butene). After sonication the mixture became a milky suspension, which was sealed with rubber and purged with N2 for 30 min to drive away the inside air. Afterwards, the reactor was placed under illumination of a xenon lamp (300 W, MAX-302, Asahi Spectra, USA). Reaction kinetics were monitored via analyses of the withdrawn gaseous samples at a given period using a GC (Shimadzu 2010) equipped with FID and TCD detectors. The liquid product was determined and analyzed at the end of reaction using a GC-MS (Agilent 5977B GC/MSD).

3. Results and discussion

3.1 Preparation and characterization of Py-PCN

The synthetic procedure of Py-PCN is illustrated in Scheme 1. The raw PCN (denoted as CN0) microspheres were synthesized through a solvothermal process at 200 °C by using cyanuric chloride (CC) and cyanamide (CA) as precursors. The surfaces of these microspheres are enriched with 1,3,5-triazine based oligomers that are not fully condensed,¹⁹ which allows PyCC to



Scheme 1 Illustration of carbon nitride synthesis *via* solvothermal and further functionalization.

be grafted onto the microsphere surface through further polymerization and condensation together with CC and CA in the secondary solvothermal process. Therefore, the final pyrenemoiety is expected to covalently link with the tri-*s*-triazine structure on the PCN surface, giving the product Py-PCN.

SEM images (Fig. 1a) indicate that the PCN products from the first solvothermal process are irregular spheres with diameters of 0.5–2.5 µm. After pyrene-functionalization, the morphology did not show obvious change, as shown in Fig. 1b. The XRD patterns (Fig. 2) of the obtained samples show a clear peak at 27.3° ($d \approx 0.323$ nm) corresponding to the (002) interlayer of graphitic carbon nitride. It indicates that the PCN product has a well stacked conjugated hexatomic heterocyclic system.²¹ The FT-IR spectra (Fig. S1†) also show the characteristic peaks of aromatic C–N heterocycles and the *s*-triazine ring.

However the microspheres do not show the characteristic peak of in-planar repeat packing at $\approx 13^{\circ}$, suggesting the imperfect and disordered crystal structure of the PCN microspheres.¹⁹ Functionalization of pyrene on the PCN surface by a secondary solvothermal process did not clearly change the XRD pattern.

The solid-state ¹³C NMR spectra (Fig. 3) of Py-PCN show two peaks at 154.0 and 162.3 ppm corresponding to the sp²hybridized carbon atoms of $-CN_2(NH_x)$ and $-CN_3$ in the CN network, respectively, which indicates the existence of the characteristic tri-*s*-triazine structure.²² Besides, the weak shoulder at ~157.6 ppm may be attributed to the junctional carbon atoms bridging the pyrene-moiety and two nitrogen atoms.²² The signal at 123.1 ppm can be assigned to the aromatic carbon from pyrene moieties,²³ proving successful pyrene-functionalization. Elemental analysis results (Table S1†) also indicate higher C/N ratio for Py-PCN compared to 0-PCN.



Fig. 1 SEM images of (a) CN0, (b) 0-PCN and (c) Py-PCN. The scale bar is 1 $\mu m.$









Fig. 3 Solid-state ¹³C NMR spectra of Py-PCN.

3.2 Photocatalytic CO₂ reduction

PCN based photocatalysts usually have a sufficient conduction band level for CO2 reduction into CO and various hydrocarbon products,² and have a suitable valence band level, allowing the photogenerated holes to oxidize many different organic compounds in aqueous solution. However, their capability of initiating reaction with alkenes (C=C) is rarely investigated as most C=C enriched compounds are not soluble in water. In this study, the pyrene-functionalized carbon nitride show affinity for both water and non-polar organic solvents. Therefore, we carried out photocatalytic tests in an aqueous-organic biphasic system by using bicarbonate in aqueous solution as the source for CO₂ reduction and alkene compounds in the organic phase for simultaneous reaction of the C=C bond. The prepared PCN and Py-PCN samples were loaded with 3.0 wt% Pt through a wetness impregnation process, and suspended in the biphasic liquid for the photocatalytic reactions.²⁴

3.2.1. Using cyclohexene. As a typical example, cyclohexene was used as both an organic solvent and a reactant. In this case, CO was the predominant gaseous product. As shown in Fig. 4, compared to the bare PCN sample (0-PCN), grafting with



Fig. 4 (a) CO evolution time course over 0-PCN and Py-PCN with different contents. Conditions: $[Cat.] = 1.0 \text{ g L}^{-1}$; 9 ml of cyclohexene as the solvent and 1 ml of 3.0 M NaHCO₃ as the CO₂ source; a 300 W xenon lamp. (b) The relationship between CO generation rate *versus* pyrene content.

pyrene-moieties greatly enhanced the CO evolution rate up to 4 times (0.28 μ mol h⁻¹ for 10% Py-PCN *versus* 0.07 μ mol h⁻¹ for 0-PCN). The pyrene-moieties afford the hydrophobic characteristic and thus allow the Py-PCN surface to be more approachable by the cyclohexene molecules for reactions. The enhanced reaction process of cyclohexene promotes the reduction of bicarbonate by the photoelectrons in the aqueous phase. Nevertheless, the excess pyrene-moieties would reduce the sample affinity for the aqueous phase. Thus we found that 10% Py-PCN is the optimal sample (Fig. 4b).

The control experiment (#1) showed no CO evolution over 4 hour irradiation when NaHCO₃ was absent in the aqueous phase. This indicates that the bicarbonate species serve as the source for CO production. We have also carried out an additional control experiment (#2) in aqueous solution only. As shown in Fig. 5, without cyclohexene, the CO evolution rate dropped more than 10 times, which proved that cyclohexene has significant contribution to the overall photocatalytic process.

Further, we have examined the liquid products using a GC-MS. Formic acid was the main product in the aqueous phase, and originates from HCO_3^- reduction by photoelectrons *via* a multi-step electron transfer process.^{25,26} Cyclohexanol was the main product in the organic phase, and possibly produced through the addition of water molecules. It is proposed that the



Fig. 6 Possible pathway of cyclohexene oxidation by hydroxyl radical addition to the C=C bond.

C=C bond was first attacked by the 'OH radical that was generated through the oxidation of chemisorbed –OH by photogenerated holes on the PCN surface, followed by proton addition.²⁷ The reactivity of 'OH radicals for addition to unsaturated C=C bonds has been extensively reported.^{28,29} A possible reaction pathway for cyclohexene is elucidated in Fig. 6.

The quantification results after 4 hour irradiation are shown in Fig. 7. The 10% Py-PCN sample still exhibits a much higher yield of formic acid (2.2 µmol) and cyclohexanol (3 µmol) than the bare PCN sample (0.37 µmol of formic acid and 1.1 µmol of cyclohexanol). Considering the CO evolution amount (0.76 µmol for Py-PCN and 0.3 µmol for the bare PCN), the amount of photoelectrons that are consumed for reduction ($2n_{\rm CO}$ + $2n_{\rm HCOOH}$) is 5.92 µmol over Py-PCN, which is close to the amount of photoholes for cyclohexene addition ($2n_{\rm cyclohexanol}$), 6.0 µmol. This indicates that CO₂ reduction and cyclohexene addition are initiated and driven by a photo-induced redox cycle. The small difference might be attributed to the trace amount of other liquid products, such as HCHO and CH₃CHO, which were hardly identified by our GC-MS.

3.2.2. Using 2-methyl-2-butene. To further verify the hole oxidation capability of Py-PCN for the C=C bond, we have carried out photoreduction of NaHCO₃ in aqueous solution using 2-methyl-2-butene (2M2B) in toluene as the organic phase. In this case, both CO and CH₄ were the main gaseous products, and no liquid reduction product was detected. Notably, the yield of CO and CH₄ over 10% Py-PCN is about 4-fold and 7-fold higher than that over the bare PCN (Fig. 8). The main product in the liquid phase was identified as acetone, which is probably generated through oxidative addition of the C=C bond in 2M2B to a water molecule by the 'OH group created by the photogenerated holes on the PCN surface.^{30,31}



Fig. 5 Control experiments over 10% Py-PCN were carried out under identical conditions except for the absence of $NaHCO_3$ and cyclohexene, respectively.



Fig. 7 Comparison of gaseous and liquid products obtained over 0-PCN and Py-PCN when using cyclohexene as the substrate.

Fig. 8 CO (a) and CH₄ (b) evolution time course over 0-PCN and 10% Py-PCN, respectively. Conditions: [Cat.] = 1.0 g L⁻¹; 0.1 ml of 2-methyl-2-butene in toluene and 1 ml of 3 M NaHCO₃ as the CO₂ source; a 300 W xenon lamp.

The process should have generated acetaldehyde simultaneously with the same molar amount of acetone, but acetaldehyde could not be accurately quantified in our GC-MS. In this reaction, the total amount of electrons for reduction $(2n_{\rm CO} + 4n_{\rm CH_4})$ is almost equal to that of holes for addition $(2n_{\rm acetone})$ after 20 h irradiation (Fig. 9). Hence, it is reasonable to deduce such a reaction pathway as shown in Fig. 10.

The above photocatalytic experiments demonstrate that the C=C bond in organic alkenes can be indirectly reacted by the photogenerated holes of PCN when the photoelectrons are reducing HCO_3^- . Moreover, the pyrene-moiety grafted onto the PCN surface can promote adsorption of the hydrophobic organic alkenes as well as their addition with water, which enhances the overall photocatalytic activity.

Brunauer–Emmett–Teller (BET) surface areas of 0-PCN and Py-PCN are measured by using liquid nitrogen adsorption– desorption isotherms (Fig. 11). The specific surface area of the



Fig. 9 Comparison of gaseous and liquid products obtained over 0-PCN and Py-PCN using methyl-butene as the substrate. The products were accumulated after 20 h irradiation.



Fig. 10 The oxidation pathway of 2-methyl-2-butene by hydroxyl radicals.





Fig. 11 The BET surface area calculated from nitrogen adsorption-desorption isotherms.

Py-PCN was estimated as 2.11 m² g⁻¹, which is lower than that of 0-PCN (5.49 m² g⁻¹). The decrease of surface area after the attachment of pyrene-moieties can be attributed to the reduced surface roughness. The results further prove that the enhanced activity of Py-CN in the biphasic photocatalytic reaction is attributed to the surface pyrene-moieties, rather than the effect of surface area.

To clarify the effect of phase affinity on the photocatalytic activity, we have implemented a comparison experiment of photocatalytic H₂ generation in pure aqueous solution with 10% TEOA as a hole scavenger, which is one of the most common reactions for identifying photocatalytic activity. Interestingly, the H₂ generation rate over the bare PCN was obviously higher than that over Py-PCN (Fig. 12), which is an opposite trend to the activities for bicarbonate reduction in the biphasic system. The lower photocatalytic activity of Py-PCN in pure aqueous solution could be ascribed to the pyrene-moieties that restrict the free access of hydrophilic species, such as protons and TEOA, to the PCN surface, which reduces the rate of their redox reactions. The contact angle measurement confirmed that Py-PCN is more resistant to water (Fig. S2[†]). Therefore, we believe that the better performance of Py-PCN in the biphasic system would be more likely



Fig. 12 Photocatalytic H₂ generation over 0-PCN and Py-PCN in aqueous solution. [Cat.] = 1.0 g L⁻¹ with 3.0 wt% Pt *via* impregnation; 10% TEOA as the scavenger. Light source: a Xe lamp, 300 W.



Fig. 13 (a) UV-Vis diffuse reflectance spectra of 0-PCN and Py-PCN. (b) Plot of transformed Kubelka–Munk function *versus* energy of light.

due to the increased hydrophobicity by the incorporated pyrene-moieties, rather than the improvement of electronic properties.

To verify this, we have identified the band energy levels for Py-PCN and bare PCN (0-PCN). Fig. 13 shows the absorption spectra of 0-PCN and Py-PCN. According to the K–M plot, the bandgap energies are estimated as 2.27 and 2.31 eV for the bare PCN and Py-PCN, respectively. The Mott–Schottky plot (Fig. S3†) was used to estimate the flatband potential of 0-PCN and Py-PCN as -0.85 V (*vs.* Ag/AgCl) and -0.94 V (*vs.* Ag/AgCl), respectively, which could be approximately regarded as the conduction band.³² The detailed energy levels of the conduction band and valence band (*vs.* NHE) are listed in Table S2.† There is not much difference in the band structure between Py-PCN and bare PCN. And their conduction band potential is much more negative than that of the CO₂ reduction, and thus it is thermodynamically favorable to produce different products (Fig. S4†).

The PL spectra (Fig. 14, excitation at 360 nm) reveal a slight blue shift for the emission peak of Py-PCN (479 nm) compared to that of the bare PCN (485 nm), which is consistent with the slightly larger bandgap of Py-PCN.³³ Though the pyrene-CC precursor shows an intensive emission band at 488 nm, it is quenched in the Py-PCN sample, suggesting that strong π - π stacking exists between the pyrene and PCN. The results indicate that the pyrene-functionalization on the PCN surface resulted in little change in the PCN band structure, and had almost no effect on the charge separation and recombination on PCN.



Fig. 14 PL spectra of 0-PCN, Py-PCN and PyCC at an excitation wavelength of 360 nm.



Fig. 15 Illustration of photocatalytic simultaneous CO_2 reduction and organic alkene (C=C) oxidation.

3.3 Proposed reaction mechanism

The above results demonstrate that in the aqueous-organic biphasic system, the pyrene-functionalization of PCN provides certain lipophilic capability that enables the C=C bond of alkene compounds in the organic phase to readily approach the carbon nitride surface. Subsequently, the alkene molecules can sacrifice the 'OH radicals that are formed from oxidation of surface adsorbed -OH by the photogenerated holes (Fig. S5[†]). This process promotes hole consumption, and consequently the charge separation efficiency is greatly improved, which allows the photoelectrons to be more effectively accumulated on the attached Pt catalyst surface for reduction of HCO₃⁻. Therefore, Py-PCN showed much better activity in the photocatalytic reduction of HCO3⁻ in the biphasic system. In comparison, the bare PCN naturally has a more hydrophilic surface covered with a water layer, which inhibits adsorption of hydrophobic alkenes (Fig. 15). However, the capability of holes for water oxidation towards oxygen evolution is very limited, resulting in low overall photocatalytic activity. So the role of the pyrene-moiety is to optimize the interface of the photocatalystorganic solvent to promote the oxidation reaction, resulting in high charge separation efficiency for bicarbonate reduction. In addition, the cycling test (Fig. S6[†]) indicates very good stability of Py-PCN for bicarbonate reduction.

4. Conclusions

We have successfully grafted pyrene-functional groups on the PCN surface through a post co-polymerization strategy. Compared to the original bare PCN, the product, Py-PCN, exhibits greatly enhanced photocatalytic activities in an aqueous-organic biphasic environment, which enable efficient photoreduction of bicarbonate in the aqueous phase and simultaneous oxidation of alkenes in the organic phase. The enhancement is attributed to the increased lipophilicity from the surface pyrene-functional groups, which allows the hydrophobic organic molecules to readily approach the PCN surface, react and get converted to other molecules. This work is significant because of the unique promising advantages of biphasic photocatalytic reactions. Our study demonstrates a new strategy for solar fuel production with effective utilization of the oxidation power of photo-holes for organic synthesis with convenient separation of the product in the organic phase and economical solvent recovery.

Conflicts of interest

There are no conflicts to declare.

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