Facile synthesis of phosphorus doped graphitic carbon nitride polymers with enhanced visible-light photocatalytic activity

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ABSTRACT

Phosphorus-doped carbon nitride materials were prepared by a one-pot green synthetic approach using dicyandiamide as the monomer and a phosphorus-containing ionic liquid as precursors. The as-prepared materials were subjected to several characterizations and investigated as metal-free photocatalysts for the degradation of organic pollutants (dyes like Rhodamine B, Methyl orange) in aqueous solution under visible light. Results revealed that phosphorus-doped carbon nitride have a higher photocatalytic activity for decomposing Rhodamine B and Methyl orange in aqueous solution than undoped g-C3N4, which was attributed to the favorable textural, optical and electronic properties caused by doping with phosphorus heteroatoms into carbon nitride host. A facile post-annealing treatment further improved the activity of the photocatalytic system, due to the higher surface area and smaller structural size in the postcalcined catalysts. The phosphorus-doped carbon nitride showed high visible-light photocatalytic activity, making them promising materials for a wide range of potential applications in photochemistry.

1. Introduction

Semiconductor-mediated photocatalysis has become the current topic of intensive interest because of its potential applications in solar energy conversion and environmental purification [1,2]. Much effort has been devoted to the development of photocatalysts capable of utilizing visible light, which accounts for about 43% of the incoming solar energy [3–6]. Among various semiconductor materials in present research, graphitic carbon nitride (g-C3N4), a metal-free organic semiconductor material, is recently recognized as a very promising candidate for visible-light photocatalyst. The metal-free material possesses a very high thermal (up to 873 K) and chemical (e.g. acid and base) stability and an appealing electronic structure with appropriate band positions and gaps (2.7 eV), which is suitable for a variety of relevant chemical reactions [7,8]. As a result of its unique surface and electronic structures, carbon nitride can catalyze Friedel–Crafts reactions [9] and CO2 reduction [10]. Moreover, some studies have highlighted that the defect, polymeric version of g-C3N4 was able to split water photochemically into hydrogen or oxygen in the presence of external redox agents and decompose organic dyes like Rhodamine B (RhB) to CO2 under visible light illumination [11,12]. However, the photocatalysis quantum efficiency of pure carbon nitride remains to be improved for large-scale industrial application. So far, some methods have been reported to improve the photocatalytic performance of g-C3N4, such as, by introducing an appropriate textural porosity [13,14], dye-sensitization [15], doping [16–19], transition metal-modification [20,21], combination of carbon nitride with metals [22], or coupling with inorganic semiconductor (ZnO) [23,24].

Generally, chemical doping with foreign anion elements is an effective strategy to modify the electronic structures of semiconductors as well as their surface properties, thus improving their photocatalytic performance. Chemical doping strategy to enhance photocatalytic efficiency, for example, doping of anion elements with sulfur, boron or fluorine, has been proven recently for g-C3N4 [16–19] and also for conventional photocatalysts (e.g. TiO2) by others [25,26]. Recently, it was reported that phosphorus can be introduced into the structural framework of graphitic carbon nitride, leading to tuned electronic properties and enhanced ion conductivity [27]. This suggested that introducing phosphorus into the structural framework of g-C3N4 might favor the photocatalytic efficiency. However, to the best of our knowledge, there are no reports on the application of phosphorus doped g-C3N4 for photocatalytic degradation of organic pollutants.

Phosphorus-doped g-C3N4 catalysts could be synthesized by using dicyandiamide and 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF6) as precursors, in combination with a thermal-induced polycondensation at 550 °C [27]. This one-pot
synthetic approach, successfully making phosphorus homogeneously distributed in the carbon nitride host, is not only low-cost, but also easy to scale-up. Thus, this abundant, stable, and metal-free polymeric solid could fulfill the requirements for use as an industrial catalyst. An inherent disadvantage to such synthetic approach is that the high degree of polycodensation of monomers during the synthesis at 550 °C renders the carbon nitride materials with low surface area (~10 m² g⁻¹ for pure g-C₃N₄). It is well known that a large surface area would be favorable for photocatalytic reaction by providing more possible reaction sites, enhancing mass transfer, and improving light-harvesting. To obtain carbon nitride materials with large surface area, some synthetic strategies have been used. Hard templates such as silica particles [13,14], anodic aluminum oxides [28] and TiO₂ spheres [29] have been used to improve the surface area of g-C₃N₄. However, these methods required additional strong acid (NH₄HF₂ or HF) or strong base (NaOH) treatment to remove hard templates, which are not only complicate but also not environmentally benign. Thus, it is highly desirable to develop a simple and template-free strategy to improve the surface area of phosphorus-doped carbon nitride material.

In this paper, phosphorus-doped g-C₃N₄ was synthesized via a facile heating method with a phosphorus containing ionic liquid as precursors. The obtained doped materials showed enhanced visible light photocatalytic activity than pure g-C₃N₄. The effect of phosphorus contents on the efficiency of photocatalytic degradation of dyes is investigated and discussed in detail. Moreover, in attempts to further improve the physicochemical property, the as-prepared materials were further annealed at 550 °C in sufficient air. This work clearly presents a promising metal-free photocatalyst for environmental purification.

2. Experimental

2.1. Catalyst preparation

Phosphorus-doped g-C₃N₄ samples were synthesized by mixing dicyandiamide (3 g) and different amounts (0.05 g, 0.1 g, 0.3 g) of BmimPF6 in 15 mL water with stirring at 100 °C to remove water. The white mixtures were put into a crucible with cover and heated at 550 °C for 4 h in air. The obtained samples were denoted as xCNP (x = the initial amount of BmimPF6). The resultant xCNP samples were milled into powder and put into a crucible without cover, and then annealed at 550 °C for 4 h in air atmosphere. The CN catalysts postannealed at 550 °C were denoted as xCNP550. The pure carbon nitride sample without and with post-treatment were designated CN and CN550, respectively.

2.2. Characterization

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.54178 Å). Elemental analysis was performed with a vario EL cube from Elementar Analysensysteme GmbH. FTIR spectra were recorded on a Thermo Nicolet FTIR Spectrometer. X-ray photoelectron spectra (XPS) data were obtained on a Thermo ESCALAB250 instrument with a monochromatized Al Kα line source. The binding energies were calibrated to the C 1s peak at 284.6 eV. UV–vis spectra were recorded on a HITACHI U-4000 Spectrophotometer equipped with a Labsphere diffuse reflectance accessory. Photoluminescence (PL) spectra were measured on the Fluoro-max-4 spectrofluorometer. All the measurements were performed at room temperature. Nitrogen adsorption-desorption isotherms were collected at 77 K on a micromeritics ASAP 2020 m+ sorptometer. Before measurement, the samples were degassed in a vacuum at 150 °C for 6 h. The Brunauer–Emmett–Teller method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.4. Transmission electron microscope (TEM) images were taken using a field emission H-7600 electron microscope. Energy dispersive X-ray spectroscopy (EDS) and elemental mapping were measured on a Hitachi S-4800 instrument.

2.3. Photocatalytic experiments

The photocatalytic activity was evaluated by the degradation of RhB and MO under visible light irradiation. In each experiment, 50 mg of catalyst was initially suspended in a RhB (or MO) aqueous solution (50 mL, 10 ppm). A 500 W Xe lamp together with a 420 nm cut-off filter was used as a visible-light source for the irradiation of the reaction system. Prior to irradiation, the suspensions were stirred in the dark for 12 h to assure adsorption equilibrium. At a given reaction time, the solution (1.5 mL) was sampled and centrifuged, and then the UV–vis spectra were obtained using a Lambda 25 spectrometer. The concentration of RhB and MO was determined by monitoring the changes in the absorbance maximized at ca. 554 nm and ca. 464 nm, respectively.

3. Results and discussion

3.1. Characterizations of phosphorus-doped g-C₃N₄

The structures of phosphorus-doped g-C₃N₄ hybrid materials were investigated by XRD. Fig. 1 shows the XRD patterns of the bulk g-C₃N₄ and phosphorus-doped g-C₃N₄ samples. The XRD pattern supports the preservation of the graphite-like packing of practically all phosphorus-doped products, showing the typical (0 0 2) interlayer-stacking peak around 27.3° (d = 0.321 nm) and in-plane structural packing motif (1 0 0) peak at 13° (d = 0.669 nm) [8–11]. No peaks for phosphorus species were observed in all the phosphorus-doped g-C₃N₄ materials. In addition, the phosphorus-doped g-C₃N₄ samples showed a slight broad of (0 0 2) peak and a decrease of their relative intensities with increasing phosphorus content, indicating that the crystal growth of graphitic carbon nitride is inhibited by introduction of BmimPF₆ as precursor according to the Scherrer's formula [9].

The morphology and microstructures of 0.1CNP were studied by TEM and nitrogen adsorption. Fig. 2 shows the typical TEM images of 0.1CNP and CN. The TEM picture of 0.1CNP clearly reflects a two-dimensional structure consisting of small flat sheets with wrinkles and irregular shape, which is different from large sheets for bulk g-C₃N₄. The results of the BET surface area analysis
Condensation of C24/C3N4 as 0.1CNP ammonium fluoride vibrations overlapped samples playing important role in the processing of carbon nitride condensation and enlarging the surface area of g-C3N4, presumably due to the formation of gaseous species such as hydrocarbons and ammoniumfluoride acting as inflating medium by BmimPF6 reacting with amine groups during carbon nitride polymerization [30].

The molecular structure information of the phosphorus-doped g-C3N4 was further provided by FT-IR spectra and elemental analyses. The IR spectra of the as-prepared xCNP samples (Fig. S2) showed typical C–N heterocycle stretches in the region of ca. ~1100–1600 cm⁻¹ and the breathing mode of the tri-s-triazine units at 800 cm⁻¹ [8–11], similar to the results of undoped g-C3N4, evidencing that the original graphitic C–N network remained. The vibrations of P-related group were hardly observed in doped g-C3N4 as phosphorus content was low and its vibration was overlapped by that of C–N. Elemental analyses of all the xCNP samples (Table S1) revealed that the average C/N ratio value of ~0.66 for xCNP is similar to that of undoped g-C3N4 (~0.66).

Elemental analyses and IR were in good agreement and indicated that incorporation of phosphorus does not alter the bulk structure or the core chemical skeleton of g-C3N4 too much. The existence of phosphorus within the framework of phosphorus-doped g-C3N4 is clearly evidenced in the energy dispersive X-ray microanalysis. The phosphorus content as determined by EDS is ca. 0.5 at% for 0.1CNP, implying that phosphorus from BmimPF6 has been introduced into the g-C3N4 host. This result, together with the elemental mapping images (shown in Fig. 3), indicates that phosphorus is homogenously distributed in the whole host of doped g-C3N4 solid. The electronic state of phosphorus-doped g-C3N4 was further studied by XPS. Fig. 4 showed that the P 2p binding energy peak of 0.1CNP is centered at ca. 133.5 eV. The binding energy of P 2p in P–N and P–C bonds was found at ~133.5 eV and 131.5–132.5 eV, respectively [27]. Thus, the peak at 133.5 eV is reasonably considered to be originated from P–N bonds formed in phosphorus-doped g-C3N4. In addition, no fluorine could be detected in the doped materials. The XPS results support the view that phosphorus atoms have been incorporated into the CN matrix. Therefore, the ionic liquid template not only influences textural features but also enters the

![Fig. 2. Typical TEM images of CN (A) and 0.1CNP (B).](image)

![Fig. 3. Typical SEM images of 0.1CNP and corresponding elemental mapping images of C, N, and P.](image)
materials. Most probably, the phosphorus atoms replace the corner or bay carbon in polymeric C–N structures to form P–N bonding [27].

The incorporation of a low percentage of phosphorus heteroatoms into g-C₃N₄ changes structural and electronic aspects and consequently the optical/electronic properties of the resulting phosphorus-doped g-C₃N₄ polymers. The optical absorption spectra were used to investigate the effect of phosphorus doping on the electronic structure of g-C₃N₄. As shown in Fig. 5, pure CN exhibited the typical absorption pattern of a semiconductor with a band gap of 2.73 eV. The spectra of the phosphorus-doped g-C₃N₄ showed obvious red shifts in the band–gap transition with increasing phosphorus content, implying the electronic integration of the phosphorus-heteroatoms in the lattice of g-C₃N₄. A further observation indicated that the phosphorus-doped samples exhibit the absorbance in the visible region from 470 to 650 nm with increasing P content, in agreement with the color changing from pale yellow to brown (inset in Fig. 5).

The effect of incorporation of phosphorus into carbon nitride on the electronic properties was also checked by PL experiments. Fig. 6 depicts the PL spectra of 0.1CNP and CN under 400 nm excitation at room temperature. A broad visible PL band centered at approximately 470 nm is observed for CN, which can be attributed to the band-band PL phenomenon with the energy of light approximately equal to the band gap energy of g-C₃N₄. Doping with phosphorus heteroatoms of g-C₃N₄ led to obvious quenching of PL. It is well known that the PL spectra are closely related to the recombination of photo-induced electron and holes, free excitons, and self-trapped excitons. The lower intensity of the

Fig. 4. High-resolution XPS spectrum of P recorded from pristine surface of 0.1CNP.

Fig. 5. UV–vis spectra of as-prepared xCNP and CN. Inset: photographs for as-prepared xCNP and CN samples.

Fig. 6. PL spectra of CN and 0.1CNP at 400 nm excitation at 298 K.

Fig. 7. (A) The photocatalytic degradation of RhB over as-prepared xCNP and CN photocatalysts under visible light irradiation. (B) The photocatalytic degradation of MO over 0.1CNP and CN as a function of reaction time.
PL band for the 0.1CNP probably suggested that phosphorus doping resulted in a decrease in the recombination of electron–hole pairs, which would be favorable for the photocatalytic process.

3.2. Photocatalytic activity of phosphorus-doped g-C₃N₄

Since the manipulation of textural and electronic structure demonstrated above has important consequences for the photocatalytic activity of the phosphorus-doped g-C₃N₄, the degradation of RhB in aqueous solution under visible light was investigated by using phosphorus-doped g-C₃N₄ with varying phosphorus content as metal-free catalysts. Fig. 7A shows comparison of photocatalytic activity of as-prepared xCNP and CN. xCNP samples show higher activity than pure CN. The degradation rate of RhB increased with x to a maximum at 0.1, beyond which the activity of the samples began to decrease. Control experiments indicated that no obvious activity was detected in the absence of either irradiation or photocatalyst, suggesting that RhB was decomposed via photocatalytic reactions. There is no measurable alteration in surface and local X-ray structures of the sample before and after the reactions, as reflected by XRD and FT-IR measurements (see Fig. S3). These results demonstrated that the presented 0.1CNP photocatalyst was stable under the experimental reaction conditions employed here.

Other organic pollutant like MO was also tested and found to be effectively degraded by phosphorus-doped g-C₃N₄ sample. As shown in Fig. 7B, 0.1CNP sample exhibited much higher photocatalytic performance than undoped g-C₃N₄ towards the degradation of MO. This fact further proved that doping with a low percentage of phosphorus heteroatoms indeed could enhance the photocatalytic performance of the resulting carbon nitride polymers. The enhanced activity of phosphorus-doped samples is considered to reflect a reduction in the probability of recombination between photogenerated carriers, due to the favorable textural, optical properties and electronic structure caused by doping with phosphorus heteroatoms into carbon nitride host.

3.3. Effect of postsintering on phosphorus-doped g-C₃N₄

In order to further enhance the activity of phosphorus-doped g-C₃N₄, the phosphorus-doped samples were further annealed at 550 °C in sufficient air, with CN annealed at similar condition as a comparison. The product yields of 0.1CNP and CN after calcination at 550 °C were near 54 wt% and 51 wt%, respectively, indicating that carbon nitride was partly decomposed during thermal treatment in the presence of oxygen. The XRD pattern of 0.1CNP550 and CN550 (Fig. 8) presented two feature diffraction peaks at 27.3° and 13°, indicating the original graphitic C–N network remained mostly unchanged after calcination at 550 °C. However, the postcalcined samples showed a lower intensity of (0 0 2) peak compared to as-prepared samples without postcalcination. This indicated that post-treatment could result in a decrease in particle size of carbon nitride induced by a reduced structural correlation length. The result is supported by the increased specific surface area from 10 m² g⁻¹ for CN to 21 m² g⁻¹ for CN550 and from 15 m² g⁻¹ for 0.1CNP to 31 m² g⁻¹ for 0.1CNP550, respectively (Fig. S1). This result suggested that a slight thermal decomposition of carbon nitride would result in small particle sizes and large surface area by self-introducing the nanostructure during the thermal treatment, which was in agreement with the earlier observations by others [31–33].

Fig. 9 shows that RhB degradation under visible light over the as-prepared xCNP and the same materials after calcinations at 550 °C. It was found that postannealing has a great effect on the photocatalytic performance of carbon nitride for photodegradation of RhB in aqueous solution. All the postcalcined samples exhibited much higher activity than the as-prepared materials without postcalcination. Even for pure carbon nitride, the activity of CN550 can reach 64% after 1 h reaction, about 1.1 times higher than as-prepared CN sample. Similar to the trend of the activity of the as-prepared samples without postcalcination, the rates of RhB.
degradation over postcalcined samples also increased with increasing x to a maximum at 0.1. Among all the catalysts, 0.1CNP550 gave the best conversion of up to 98% for 1 h, about 0.8 times higher than that of as-prepared 0.1CNP. These results clearly indicate that postannealing can effectively enhance the photocatalytic activity of carbon nitride for RhB degradation under visible light, and phosphorus doping play an important role in enhancement of photocatalytic activity in the phosphorus-doped g-C3N4 photocatalysts. The high activity of postcalcined samples could be attributed to the small particle sizes and large surface area by self-introducing the nanostructure during the thermal treatment. Moreover, thermal decomposition would create surface sites to facilitate catalytic sorption and to promote the localization of light-induced electrons in the conjugated systems, which also favors for photocatalysis.

The photocatalytic stability of 0.1CNP550 was also checked by repeating the reaction five times under similar conditions (Fig. S4). The results showed that the catalyst can be reused for several cycles without loss of activity, reflecting sufficient stability of the carbon nitride based materials in decomposition of dyes, which is prerequisite for practical application. The excellent stability of catalytic activity during irradiation can be attributed to the strong binding of N in the covalent carbon nitride, which can also be supported by the unchanged structure and surface properties of these carbon nitride based photocatalysts after reaction (see Fig. S5).

3.4. Mechanism of photoactivity

It is important to detect the main oxidative species in the photocatalytic process for revealing the photocatalytic mechanism. The main oxidative species in the photocatalytic process could be detected through the trapping experiments of holes and radicals by using triethanolamine (TEOA, hole scavenger) and tert-butyl alcohol (TBA, radical scavenger), respectively. As shown in Fig. 10, in the CN550 system, the degradation of RhB was almost completely inhibited when the TEOA (10 vol%) was added into the reaction solution. On the contrary, the degradation of RhB was only partly depressed with the addition of TBA (10 vol%). These results suggested that free radicals were involved but not exclusively, and the photogenerated holes were the main oxidative species in CN550 system. During the photocatalytic process, the photogenerated hole can be directly transferred to the RhB dye, and then oxidize the dye. In the system of 0.1CNP550 system, the photocatalytic activity was also greatly suppressed by TEOA, while the degradation of RhB was partly depressed by the TBA, indicating the main oxidative species is the same as that of pure g-C3N4.

As mentioned above, the phosphorus-doped g-C3N4 exhibited the higher activity for decomposing RhB than undoped g-C3N4. Density functional theory calculations showed that the visible light response of carbon nitride originated from the electron transfer from the HOMO populated by N 2p orbitals to the LUMO formed by C 2p orbitals. As observed by UV–vis spectra, the phosphorus doping gives rise to a small decrease in the band gap. As the phosphorus is incorporated into the C sites by the form of P–N in g-C3N4, the small decrease in band gap by phosphorus doping originated from a decrease in the bottom of conduction band. This means that the oxidation ability of photogenerated hole was not decreased in the phosphorus-doped g-C3N4, while light absorption was increased in the visible light region, which is beneficial for the photodegradation reaction. Additionally, it is known that heterogeneous photocatalysis is a surface-based process. A large surface area not only facilitates mass transfer but also provides more activity sites for surface-dependent reactions, which would be favorable for photocatalytic reaction. Phosphorus heteroatoms doping into carbon nitride increased the surface area and decreased the structural size of g-C3N4, which also contribute to the improved activity.

4. Conclusions

In this paper, phosphorus was doped into polymeric g-C3N4 by a co-condensation strategy between dicyandiamide and a phosphorus-containing ionic liquid. The incorporation of phosphorus has a significant effect on the properties of the doped samples, including morphology, optical, and electronic nature as compared with undoped carbon nitride. Our results showed that the doped materials exhibit higher photocatalytic performances for decomposing dyes under visible light irradiation, which can be ascribed to the favorable textural, optical properties and electronic structure caused by doping with phosphorus heteroatoms into carbon nitride host. Moreover, the activity can be further improved by a facile postannealing treatment. This work demonstrates that the inexpensive metal-free phosphorus-doped graphitic C3N4 material is a very promising candidate for environmental application.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 20803038, no. 21003146 and no. 21201174), the Basic Research Project of the Qingdao Science
and Technology Program (12-1-4-9-(6)-jch), the Knowledge Innovation Program of the Chinese Academy of Sciences (no. KSCX2-EW-J-10).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.materresbull.2013.05.040.

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