



Insight into highly efficient simultaneous photocatalytic removal of Cr(VI) and 2,4-dichlorophenol under visible light irradiation by phosphorus doped porous ultrathin g-C₃N₄ nanosheets from aqueous media: Performance and reaction mechanism

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ABSTRACT

Carbon nitride (g-C₃N₄) has attracted great attention for its wide applications in hydrogen evolution and photocatalytic degradation. In this study, phosphorus doped porous ultrathin carbon nitride nanosheets (PCN-S) were prepared successfully via the element doping and thermal exfoliation method. The prepared PCN-S was characterized by XRD, SEM, TEM, N₂-adsorption-desorption measurement, FT-IR, XPS, UV–vis diffuse reflectance spectra, photoluminescence (PL), photocurrent response (I-t) and EIS. The results show that PCN-S owns regular crystal structure of g-C₃N₄, large specific surface areas and nanosheet structure with lots of in-plane pores on its surface, excellent chemical stability, and broad light response to the whole visible light region, which was attributed to the doping of phosphorus element. Under visible light irradiation, the photocatalytic reduction of Cr(VI) over different samples indicated that the P doping and porous nanosheet structure play an important role for the enhanced performance of PCN-S. The reason was that P element doping can broaden the visible light response region, and large specific surface areas from the porous nanosheet structure can provide quantities of active sites for the photocatalytic reaction. Then the detailed study on the PCN-S for simultaneous photocatalytic reduction of Cr(VI) and oxidation of 2,4-dichlorophenol (2,4-DCP) was conducted. The experiments results show that low pH value and enough dissolved oxygen were found to promote Cr(VI) reduction and 2,4-DCP oxidation. The detailed photocatalytic mechanism was proposed. The strategies used in this study could provide new insight into the design of g-C₃N₄ based materials with high photocatalytic activity, and present potential for the treatment of Cr(VI)/2,4-DCP or other mixed pollutants in wastewater.

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1. Introduction

In this decade, photocatalytic degradation, as an economic efficient and environmental friendly advanced oxidation processes (AOPs), has been developed rapidly and widely. Various treatment approaches have been employed in the removal of harmful environmental contaminants, such as organic dyes, antibiotics, heavy metals and phenols [1–11]. Among the heavy metal pollutants, chromium is a common contaminant and widely exists in

industrial waste discharges, such as textile manufacturing, leather tanning, paint fabrication, steel fabrication, petroleum refining and so on [12–14]. Chromium mainly exists as Cr(VI) and Cr(III) in nature, and the features of these two states are very different. Cr(VI) has been demonstrated to be a highly toxic and mutagenic substance to environment and human beings [15]. However, Cr(III) is not only less harmful but also an essential trace metal in human daily life [16]. Therefore, the conversion of Cr(VI) to Cr(III) is usually considered to be an efficient method for wastewater treatment and environmental remediation. In addition to heavy metal pollutant, chlorophenols (CPs) also bring great threat to environment. Chlorophenols are widely used as flame retardants, biocides and wood treatment agents in synthetic chemistry. The wide distribution of these pollutants can cause chronic toxicity,

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mutagenicity and carcinogenicity [17,18]. 2,4-dichlorophenol (2,4-DCP), as one of the most abundant chlorophenols, often used as an important intermediate in the production of the herbicide 2,4-dichlorophenoxyacetate (2,4-D) [19,20]. Besides, due to the serious harmful effect to environment and humans, 2,4-DCP has been listed as one of the priority pollutants by the United States EPA and has attracted great attentions [21]. So it is an urgent need to find an efficient method for the treatment and removal of 2,4-DCP in ecosystems. So far, lots of researchers have been concentrating on the photocatalytic reduction of Cr(VI) and oxidation of 2,4-DCP [20,22–24]. For example, Cui and coworkers studied the removal of Cr(VI) by 3D TiO₂-graphene hydrogel via adsorption enriched with photocatalytic reduction, and they also investigated the efficient removal of 2,4-DCP by a stable Ag₃PO₄@PANI core@shell hybrid [25,26]. However, most of the photocatalytic system focused on the separate reduction of Cr(VI) and degradation of 2,4-DCP. In most cases, heavy metals and organic pollutants often co-exist in industrial wastewater and natural aqueous environment, and the wastewater containing both chromium and chlorophenol can easily be found, such as tannery effluents. Some researchers have studied the simultaneous Cr(VI) reduction and 4-chlorophenol (4-CP) oxidation using TiO₂ based composites [27,28]. But owing to the wide band gap of the TiO₂, the performances and applications are greatly limited. So it is important to develop more efficient and simultaneous photocatalytic treatment methods for the treatment of these mixed pollutants [19,29,30].

During the photocatalytic process, the performance of the photocatalyst determined the removal efficiency of pollutants, and it is necessary to design and fabricate stable and efficient photocatalysts [31–33]. Recently, graphitic carbon nitride (g-C₃N₄) has been rapidly developed and widely used in photocatalytic degradation and hydrogen evolution. g-C₃N₄ owns a band gap of 2.7 eV, which means the ability for the employment of visible light [34,35]. Compared with other photocatalysts, g-C₃N₄ has been regarded as an attractive metal-free visible-light photocatalyst owing to its unique characteristics, such as easy preparation, low cost, nontoxic and chemical stability [36,37]. Although g-C₃N₄ exhibits photocatalytic ability for the degradation of organics in some content, the performance of bare g-C₃N₄ are still far from satisfactory. The reasons can be summarized as the following three aspects: (i) limited response in visible-light irradiation; (ii) fast recombination of photogenerated electron-holes; (iii) relative low specific surface area [38].

To further improve the performance of g-C₃N₄, various modification strategies have been applied, such as coupling with other semiconductor materials [39–43], doping with other elements [38,44], exfoliating into two-dimensional nanosheets [45,46], as well as structure and surface adjustment [47,48]. Among these methods mentioned above, doping with other elements, especially with non-metal elements, has been considered as an efficient way. Because this strategy plays an important role in extending the light response region, increasing the charge transfer mobility and creating more active sites [38]. To date, some researchers have reported that P-doped g-C₃N₄ performed enhanced visible-light photocatalytic activity. For example, Zhou et al. prepared brand new P-doped g-C₃N₄ and presented improved photocatalytic for H₂ production and Rhodamine B degradation under visible light irradiation [49]. Hu and co-authors used (NH₄)₂HPO₄ as the source of phosphorous to prepare phosphorous modified g-C₃N₄ and presented enhanced performance for the degradation of Rhodamine B (RhB) [50]. Although the improved performance of the P-doped g-C₃N₄ was obtained, the specific surface areas of their prepared g-C₃N₄ were still very low. To increase the specific surface area of g-C₃N₄, converting the bulk g-C₃N₄ into nanosheets has been proved to be an efficient strategy. This strategy can provide large specific surface area, abundant active sites, short charge diffusion distance and enhanced redox abilities of photogenerated electrons and holes.

However, as for two dimensional g-C₃N₄ nanosheets, there exists one inevitable problem. That is the largely increased band gap due to the strong quantum confinement effects (QCE), which seriously inhibits their photocatalytic performance and practical application for solar energy conversion [45,51]. Besides, the strategies used in these studies just solved one or two impacts of the demerits that exist in pristine g-C₃N₄. Are there methods which can help to solve the above three problem at the same time? Will g-C₃N₄ prepared by the combination of P doping and thermal exfoliation have higher photocatalytic activity? Moreover, according to other researcher's works, the photocatalytic oxidation ability and reduction ability of g-C₃N₄ have both been separately demonstrated. Will the simultaneous band gap engineering and macropores created in 2D g-C₃N₄ nanosheets have good performance in synergistic photocatalytic reduction of Cr(VI) and oxidation of 2,4-DCP?

In this study, the P doping and thermal exfoliation strategies were combined for the synthesis of whole metal-free phosphorus-doped porous ultrathin g-C₃N₄ nanosheets (PCN-S). 2-aminoethylphosphonic acid (AEP) was used as the phosphorus source and for gas production to generate in-plane pores on the surface of g-C₃N₄ nanosheets. The prepared PCN-S with broad visible light response region, limited recombination efficiency of the photogenerated electron-hole pairs and large specific surface area, was applied in the simultaneous photocatalytic reduction of Cr(VI) and oxidation of 2,4-DCP to seek enhanced performance. To obtain deeper understanding of the synergistic effect between the reduction of Cr(VI) and oxidation of 2,4-DCP, systematical experiments have been conducted, including the control experiments performed to reveal the roles of Cr(VI), 2,4-DCP and g-C₃N₄ in the oxidation and reduction process. The effects of initial substrate concentrations, pH, dissolved oxygen and hole scavengers were also studied. A synergistic reduction-oxidation mechanism was finally proposed based on the experimental results.

2. Experimental

2.1. Materials

Melamine (>98.0%), 2,4-DCP (>99%) and disodium ethylenediamine tetraacetate (EDTA-Na₂, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 2-aminoethylphosphonic acid (AEP) (>99%) was purchased from Sigma-Aldrich (USA). All reagents were used as received from commercial suppliers without further purification. Deionized water (18.25 MΩ cm specific resistance) generated by an Ulupure (UPR-II-10T) laboratory water system was used to prepare all solutions.

2.2. Preparation of photocatalysts

Phosphorus doped porous ultrathin g-C₃N₄ nanosheets (PCN-S) were prepared according to the previous publication with some modifications [38]. In a typical synthesis, first of all, 2-aminoethylphosphonic acid (AEP) and melamine with a weight ratio of 1:60 were dissolved thoroughly in deionized water and heated to 80 °C, and kept stirring at 80 °C to evaporate the solvent completely. Then the remaining crystal complex was milled into powder and placed in a cover quartz container, and subsequently heated in a cube furnace under N₂ ambient from room temperature to 500 °C, and kept at this temperature for 3 h. Next the temperature was increased to 550 °C and continued to heat the sample for another 5 h. Finally the brown agglomerates were obtained and grounded into powder. The brown powder was labeled as PCN-B. To synthesize PCN-S, the thermal exfoliation process should be experienced. The above-obtained PCN-B was placed into an open crucible and heated at muffle furnace under static air from

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