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Full Length Article

Constructing effective photocatalytic purification system with P-introduced g-C_3N_4 for elimination of UO_2^{2+}

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ABSTRACT

Due to the inherent defects of precursor molecular structure, the limited effect of structure in the formed g-C_3N_4 will weaken the extension of delocalization of π electrons between the adjacent tri-s-triazine or heptazine units of g-C_3N_4, which thus leads to poor visible-light absorption, low utilization efficiency of charge carrier. Herein, P-introduced g-C_3N_4 (PC_3N_4) photocatalysts were constructed by partially replacing C with tributyl phosphate as precursor, and the as-designed PC_3N_4 photocatalysts were used to eliminate aqueous uranyl ion by photocatalytic reduction technology under visible-light irradiation. Experimental and DFT revealed that introduction of P into g-C_3N_4 significantly modified its electronic structure, as reflected by the narrowed band gap, enhanced visible-light absorption as well as improved transfer capability of photogenerated charge. Therefore, photocatalytic activity of PC_3N_4 was much better than that of pristine g-C_3N_4 and conventional reducing-type photocatalysts. This study suggests an efficient strategy for construct effective visible-light-responsive photocatalysts for radioactive environmental remediation.

1. Introduction

With the rapid growth in nuclear energy application, uranium pollutant is becoming the severe environmental and public health problems because of the chemical and radiological toxicity, thus how to remove uranium pollutant is an urgent problem to be solved [1–3]. Study has revealed that remediation of radioactive contamination is decided by reducing mobility and biosorption, which is subject to valence of uranium [4–6]. It is known that there is various uranium valence, e.g., U^{3+}, U^{4+}, and U^{6+}. Among these ions with different valences, soluble U^{6+} and insoluble U^{4+} have been determined as major uranium species in the water [5,7,8]. Therefore, reduction of U^{6+} to U^{4+} has been suggested as an ideal strategy to eliminate radioactive uranium pollutant. Photocatalytic reduction approach over semiconductor photocatalysts is widely used for detoxification of heavy metal pollutants including radioactive uranium due to green, environmentally friendly, efficient, and convenient advantages, which is conventionally photocatalyzed on TiO_2 photocatalysts [9–12]. TiO_2 photocatalyst holds excellent photocatalytic performance, nevertheless, it can be only activated under UV irradiation. Therefore, great efforts have been devoted to developing efficient visible-light photocatalysts for large-scale application of photocatalytic reduction technology.

The sp^2 π-conjugated polymers carbon nitride (g-C_3N_4) is a visible-light-driven material with bandgap of ~2.7 eV, appropriate conduction and valence band potentials, which make it candidate photocatalyst for photocatalytic poisonous pollutant elimination, H_2O splitting, and CO_2 reduction [13–23]. However, sp^2 π-conjugated system of g-C_3N_4 in the pristine form usually suffers intrinsic shortcomings, i.e., fast recombination of photo-charge carriers, relatively poor absorption and utilization of sunlight as well as low surface area due to imperfect structure in the polymerization [24,25]. Therefore, it is urgently desirable to improve the electronic structure and photocatalytic performance of g-C_3N_4 by developing effective strategies. Generally, some strategies have been considered to enhance the photocatalytic properties of g-C_3N_4, e.g., doping metal or nonmetal atoms, designing mesoporous thin layer, and introducing structure-matching aromatic groups or structures, etc [26–36]. Study has revealed that delocalization of π electrons extends by the C—N—C-N—C bonds in the tri-s-triazine or heptazine units, which is actually not so smooth due to the limited effect of bridge N atom of C—N—C-N—C chain [25,37]. Theoretical study shows the limited effect of bridged N can be reduced by introducing heteroatom to partially replace C atom of the chain [37], nevertheless, it has been reported that N atoms in the tri-s-

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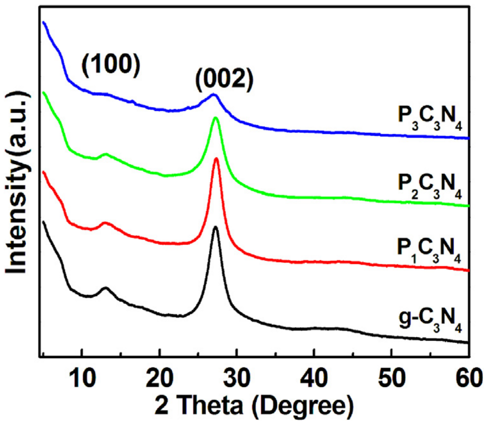

Fig. 1. XRD diffraction patterns of PC_3N_4 photocatalysts.

triazine or heptazine units are preferentially replaced by most of heteroatoms.

Herein, P-introduced g-C_3N_4 (PC_3N_4) samples were synthesized by partially replacing C with using tributyl phosphate as precursor, which strengthened absorption and utilization of visible light, and promoted photogenerated carriers transfer in the tri-s-triazine structures. Therefore, the obtained PC_3N_4 photocatalysts demonstrated superb photocatalytic performance in the photoreductive elimination of UO_2^{2+} pollutant, which is much better than pristine g-C_3N_4 and conventional reducing-type photocatalysts. The high photocatalytic activity is well-correlated with the desirable electronic structures and the improved surface structure properties, as revealed by experiment and theoretical calculation.

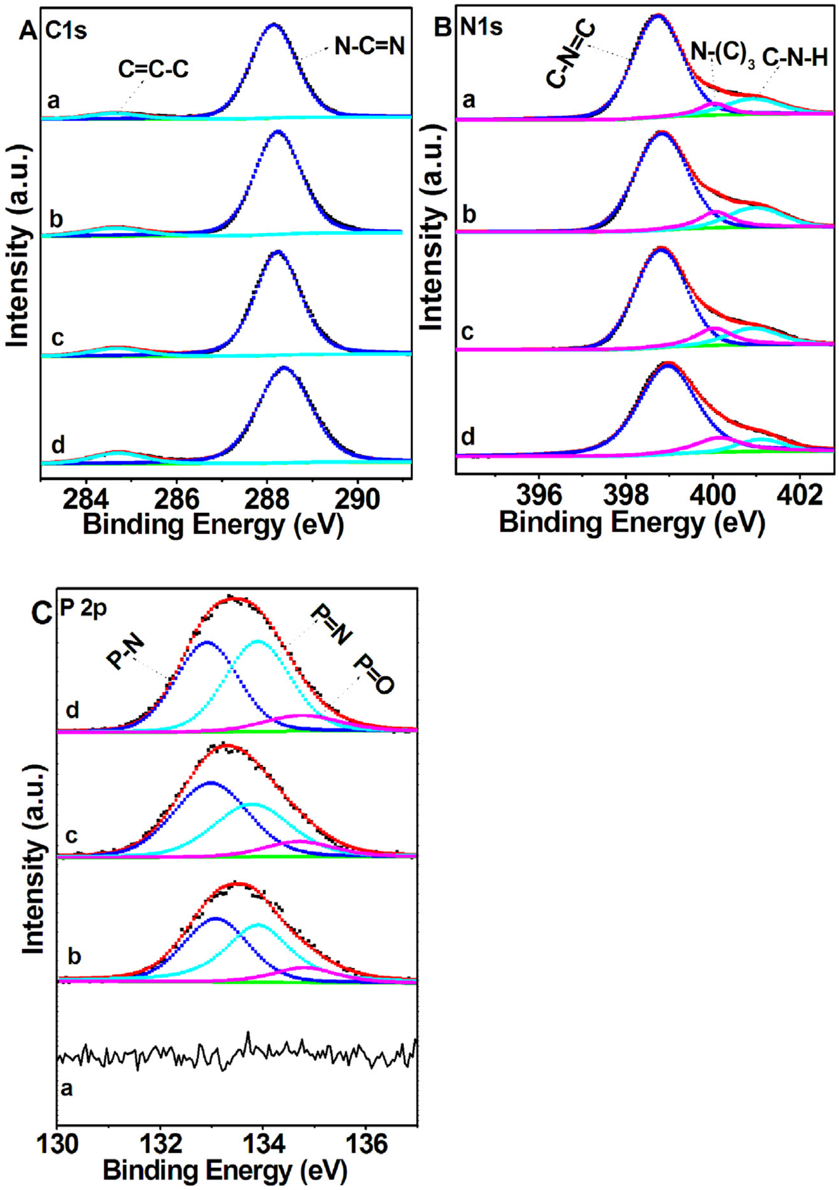

Fig. 2. XPS spectra of C 1s (A), N 1s (B), and P 2p (C) for g-C_3N_4 (a), $P_1C_3N_4$ (b), $P_2C_3N_4$ (c), and $P_3C_3N_4$ (d).

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