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Facile fabrication of mediator-free Z-scheme photocatalyst of phosphorous-doped ultrathin graphitic carbon nitride nanosheets and bismuth vanadate composites with enhanced tetracycline degradation under visible light

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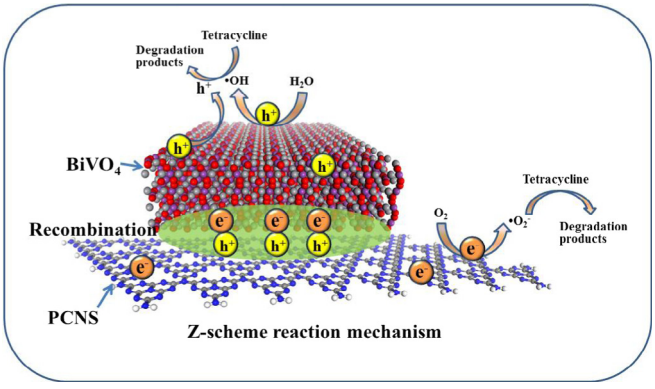
GRAPHICAL ABSTRACT



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ABSTRACT

To realize the sustainable employment of solar energy in contaminant degradation and environmental recovery, design and development of an efficient photocatalyst is urgently needed. Herein, a novel direct Z-scheme composite photocatalysts consist of phosphorous-doped ultrathin g-C_3N_4 nanosheets (PCNS) and bismuth vanadate ($BiVO_4$) are developed via a one-pot impregnated precipitation method. The as-prepared hybrid nanocomposite was utilized for the degradation tetracycline (TC) under visible light irradiation. Among the composites with various PCNS/$BiVO_4$ ratios, the prepared PCNS/BVO-400 photocatalyst presents the best performance, showing a TC (10 mg/L) removal efficiency of 96.95% within 60 min, more than double that of pristine $BiVO_4$ (41.45%) and higher than that of pure PCNS (71.78%) under the same conditions. The effects of initial TC concentration, catalyst dosage, pH value and different water sources have been studied in detail. The improved photocatalytic performance of the as-prepared PCNS/$BiVO_4$ nanocomposites could be attributed to the promoted separation efficiency of the photogenerated electrons and the enhanced charge carrier lifetime (1.65 ns) owing to the synergistic effect between the PCNS and $BiVO_4$. The degradation intermediates and decomposition pathway of TC were also

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analyzed and proposed. Additionally, radical trapping experiments and ESR measurement indicated that the photogenerated holes (h^+), superoxide radical ($\cdot O_2^-$) and hydroxyl radical ($\cdot OH$) all participated in the TC removal procedure in the reaction system. The high performance of PCNS/BVO-400 in real wastewater indicated the potential of the prepared composite in practical application. This work provides an efficient and promising approach for the formation of high performance Z-scheme photocatalyst and study the possibility for real wastewater treatment.

1. Introduction

Antibiotics have been widely employed to help human and animals fight for diseases. Tetracycline (TC), as one of the extensively used antibiotic in the world, plays great role on the field of both human therapy and animal husbandry owing to its broad-spectrum antimicrobial ability against various diseases [1–5]. However, owing to the essential characteristics of antibiotics, TC can only be partial metabolized by humans and animals, which causes the large release of the residues into wastewater [6–8]. Besides, traditional wastewater treatment cannot remove TC from aqueous solution efficiently due to its chemical stability and antibacterial nature. The released TC tends to accumulate in the environment and poses serious threat to human health and ecosystem by developing antibiotic resistant bacteria or pathogens [9–12]. Therefore, how to effectively eliminate TC from environment has become a necessary and urgent public issue.

Recently, many treatment methods have been employed for TC removal, such as adsorption, ozone oxidation, Fenton-like system and photocatalysis [13–15]. Among these methods, photocatalytic degradation of TC based on semiconductor reaction system is regarded as an efficient approach and has attracted great attentions [16–18]. Photocatalytic degradation of TC can be achieved based on the existence of photocatalysts under relative mild reaction conditions, some other advantages such as low toxicity, low cost, high degradation activity and complete mineralization ability are also included. As is known to all, the photocatalytic decomposition efficiency is greatly depended on the photocatalysts. However, the most widely studied and used photocatalyst is TiO_2, its employment is severely limited due to its wide band gap, which means that it can only be excited by ultraviolet light. Additionally, the fast recombination rate of photogenerated charges in TiO_2 also inhibits its photocatalytic activity greatly [19–22]. To overcome the drawbacks of TiO_2 based nanocomposites, many novel visible light response photocatalysts with high photocatalytic activity have been develop [23–29]. Among these new photocatalysts, bismuth-based photocatalysts are regarded as good candidates owing to the interaction between 2p O and 6s Bi orbital at the top of the valence band, and its potential visible light response ability [24]. Especially for monoclinic bismuth vanadate (m-$BiVO_4$), owing to its suitable bandgap (around 2.4 eV), excellent chemical stability and energy conversion, has attracted great attentions [30–33]. However, as for pristine $BiVO_4$, the relative photocatalytic activity still needs to be improved, because its weak transportation ability of photogenerated electrons and limited specific surface area for reaction targets adsorption hinder its photocatalytic performance greatly [34]. In the past decades, the couple of two or more semiconductors for the design of heterostructure photocatalytic system has been regarded an efficient method to overcome the problems that existed in single component reaction system and to acquire high photocatalytic performance [25,35,36]. But an unavoidable obstacle for traditional heterojunction is the reduced redox ability of the photogenerated charges due to the migration process [37], which means that it is difficult to realize the simultaneous acquisition of high photogenerated charge separation efficiency and strong redox ability. To solve this problem, Z-scheme photocatalytic reaction system has been put forwards and emphasized, and has been widely discussed for its ability in not only accelerating the migration of the photogenerated charges, but also keeping its strong ability without the transfer process [34]. In previous study, graphene was used as the bridged and electron mediator to form the Z-scheme Ag_3PO_4/Ag/$BiVO_4$ photocatalyst and present enhanced photocatalytic performance [38]. However, most of the Z-scheme reaction system based on two different semiconductors combined with an appropriate electron mediators, such as Au, Ag, Fe^{3+}/Fe^{2+}, IO^{3-}/I^- and graphene [38–42], which results in the difficulties for realistic application due to the complex reaction system. Therefore, to simplify the reaction system and achieve the same effect, the construction of direct Z-scheme photocatalysts without the need of mediator will be the most the promising candidate for realistic application.

Recently, graphite-like carbon nitride (g-C_3N_4) has attracted great attentions and been widely employed in photodegradation and hydrogen production field owing to its low coat, easy to prepared, excellent chemical stability and narrow band gap for visible light response [27,43–46]. However, due to the inherent defect of single component, the photocatalytic performance of pure g-C_3N_4 is unsatisfactory owing to the limited transfer rate of the photogenerated charges and relative low specific surface area. Strategies such as the constructed hybrid nanocomposites and the surface morphology adjustments have been demonstrated are efficient for promoting its photocatalytic performance [29,35,47–50]. In our group, Ag_2CrO_4/g-C_3N_4 Z-scheme has been synthesized and presents enhanced photocatalytic degradation activity towards dye pollutants [23]. We also prepared phosphorous-doped porous ultrathin g-C_3N_4 nanosheets and investigated its enhanced photocatalytic performance for simultaneous photocatalytic removal of Cr(VI) and 2,4-diclorphenol under visible light irradiation [51]. And we found that the prepared phosphorous-doped ultrathin g-C_3N_4 nanosheets show wide visible light absorption ability and fast transfer capacity of the photogenerated electrons and holes. Besides, considering that the suitable band structure of g-C_3N_4 and $BiVO_4$, the excited electrons produced in the conduction band of $BiVO_4$ tends to combine with the holes generated in the valence band of g-C_3N_4, which prefer to the formation of direct Z-scheme reaction process. So the combination of phosphorus doped ultrathin g-C_3N_4 nanosheets and $BiVO_4$ would present high photocatalytic activity, and the systematical study of its photodegradation activity towards TC removal will be favorable to understand its direct Z-scheme reaction mechanism.

In this work, a novel redox-mediator-free direct Z-scheme composite photocatalyst of phosphorus doped ultrathin g-C_3N_4 nanosheets/$BiVO_4$ (PCNS/BVO) is developed and applied for effective TC removal. To increase the efficiency, the band gap of g-C_3N_4 can be adjusted by phosphorus doping, and the relative specific surface area can be increased due to the formation of ultrathin g-C_3N_4 nanosheets. A composite photocatalyst with PCNS and $BiVO_4$ was simply synthesized via impregnated co-precipitation method. The improved photocatalytic performance of the prepared