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Graphene oxide and carbon nitride nanosheets co-modified silver chromate nanoparticles with enhanced visible-light photoactivity and anti-photocorrosion properties towards multiple refractory pollutants degradation

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ABSTRACT

In this work, a ternary composite photocatalyst consisted of graphitic carbon (g-C_3N_4), graphene oxide (GO) and Ag_2CrO_4 was successfully synthesized through one-step chemical precipitation route. The GO/Ag_2CrO_4/g-C_3N_4 (GO/ACR/CN) nanocomposite exhibited superior photocatalytic performance towards dyes (rhodamine (RhB) and methylene blue (MB)) and two other refractory pollutants (phenol and oxytetracycline) degradation under visible light irradiation. The efficient photo-induced electron-hole pairs separation, multi-step charge transfer and enhanced visible light absorption should be concluded as the synergistic effects among three components, resulting in the improved photoactivity. The decreased degradation efficiency of RhB (MB) over bare ACR was about 25.74% (43.22%) after four times cycles, while insignificant loss was perceived over GO/ACR/CN. The corresponding anti-photocorrosion property was further confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). For in-depth insight into practical applications, the effects of initial concentration and different water sources were also taken into discussions. This work demonstrated that rational and design of ternary nanocomposites could provide a new approach for the development of more efficient visible-light photocatalysts for wastewater treatment and environmental remediation.

1. Introduction

Over the past decades, the increasing industrialization has brought out massive products of dyes, phenols, pesticides, antibiotics, solvents and other refractory organic contaminants with potentially carcinogenic intermediates in natural water resources [1–5]. In order to resolve the more and more serious water pollution crisis, semiconductor-based photocatalysis has attracted considerable attention as a potential and environment-friendly solution to decompose pollutants with high toxicity in wastewater by the utilization of solar light energy [6–10]. Among numerous semiconductor photocatalysts, graphic carbon (g-C_3N_4, CN) has been regarded as a promising photocatalyst for wastewater treatment because of its simple synthesis, superior photocatalytic performance, preferable photochemical stability and low toxicity [11–13]. However, there are still some drawbacks that restricted the applications of CN in environmental remediation, for example, the relatively wide bandgap (about 2.75 eV), low surface area of bulk CN, poor quantum yield and high recombination rate of photo-generated electron-hole pairs [14,15]. So appropriate modifications should be adopted to widen its visible light region absorption, enlarge surface area as well as charge transfer rate and separation efficiency. Up to now, continuous attempts have been devoted to improve the photocatalytic efficiency of bare CN, including doping metals or nonmetals [16,17], regulating shape [18,19] and constructing heterostructured photocatalysts between CN and another semiconductor with suitable band potential [20].

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Researches demonstrated that the construction of heterojunction photocatalyst is more effective since the photo-generated electron-hole pairs were effectively transferred and separated. As a result, strenuous efforts had been made to design CN-based binary heterojunctions, like CN/$BiVO_4$ [21], CN/BiOBr [22], CN/Ag_3PO_4 [11,13], CN/TiO_2 [23], CN/ACR [24,25], CN/$SmVO_4$ [26] and so on. In these binary systems, the recombination rate of photo-induced electron-hole pairs was significantly inhibited and the charge separation efficiency was also increased, so the corresponding visible light photoactivity was enhanced. In our work, Ag_2CrO_4 (ACR) was adopted to improve CN photoactivity, due to its strong visible light absorption (~720 nm [25]). The more negative conduction band of CN (−1.24 eV) was also beneficial to achieve stronger reducing characteristics and produce more active species. Recently, researches proved that layer CN nanosheets with higher specific surface area exhibited many intriguing properties, which are different from bulk CN [16]. Therefore, CN nanosheets were prepared in our work to provide greater reaction area and shorter photogenerated carrier diffusion length for reducing their photo-generated electron-hole pairs recombination efficiency and promoting higher pollutants removal rate.

However, the photocatalytic activity of these binary systems is still not sufficient in practical activity since the limited region of visible light response and relatively lower photo-induced electron-hole pairs separation efficiency [27,28]. In order to further promote the charge separation and transfer characteristics, ternary system construction was developed and confirmed as an effective method, which could lead to multistep charge transfer and remarkable enhancement of photocatalytic activity. For example, Wei and his co-workers designed TiO_2/rGO/Cu_2O ternary heterostructure to achieve more photoelectrochemical hydrogen production, and the synergistic effect of TiO_2, rGO and Cu_2O improved the absorption spectrum range and electron/hole separation, resulting in enhanced photocurrent intensity and incident photon-to-photocurrent efficiency [29]. Zhang et al. successfully introduced ZnO into CdS/TiO_2 system to construct ZnO/CdS/TiO_2 hybrid for refractory pollutants degradation and the anti-photocorrosion capacity of CdS was greatly strengthened because the outer ZnO acted as a solid sacrificial reagent in ternary ZnO/CdS/TiO_2 system [30]. According to previous studies [29], graphene oxide (GO) or reduced graphene oxide (rGO) has been identified as one of the most ideal supports for charge carriers separation and transfer for its large specific surface area, high stability and excellent charge carriers mobility. Considering above-mentioned advantages, CN and GO/rGO were simultaneously added into single semiconductor to fabricate novel ternary heterojunction photocatalysts, successful cases such as rGO/Bi_2WO_6/CN [31], rGO/ZnS/CN [28], rGO/TiO_2/CN [32], rGO/$(C_{16}H_{33}(CH_3)_3N)_4W_{10}O_{32}$/CN [33] and GO/$Ag_3PO_4$/CN [34]. Similarly, common problems of binary nanocmposites might exist in CN/ACR heterojunctions, thus it seemed to be feasible for assembling GO/ACR/CN ternary photocatalyst with enhanced photocatalytic activity and stability. To our knowledge, this type of ternary photocatalyst has not been reported yet.

Herein, GO/ACR/CN nanocomposite was fabricated by a facile precipitation route and employed in multiple pollutants degradation under visible light irradiation. Compared with ACR, CN, ACR/GO and ACR/CN, GO/ACR/CN ternary photocatalyst displayed the obviously enhanced photocatalytic performance. The improved photoactivity should attribute to the synergistic effect between ACR, CN and GO, including effective photo-induced electron-hole pairs separation, multistep charge transfer, enhanced surface area and visible light adsorption. The combination of ACR nanoparticles with GO and CN sheets might also effectively prevent the dissolution of ACR and thus improved its photostability, which could be confirmed by XRD, XPS and FTIR tests. The predominant active species were investigated by radicals trapping experiments and ESR measurements. A possible double Z-scheme degradation mechanism was also proposed. This work sheds light on a new kind of ternary photocatalysts with higher stability and visible light photocatalytic performance for organic pollutants decomposition, containing of one semiconductor, CN and GO/rGO.

2. Experimental section

2.1. Photocatalysts preparation

All chemicals were of analytical grade and without further purification before use. De-ionized water was employed throughout all experiments. The GO and CN nanosheets were prepared as our previous reports [8,27]. The GO/ACR/CN ternary composites were fabricated by a facile chemical precipitation method. Briefly, the prepared GO (0.010 g) and CN (0.300 g) nanosheets were separately dispersed in 50 mL de-ionized water by ultrasonication for 1 h. Simultaneously, $AgNO_3$ (0.307 g) and K_2CrO_4 (0.175 g) were dissolved in two 20 mL de-ionized water, respectively The forming $AgNO_3$ and K_2CrO_4 solutions were dripped into GO and CN suspension, respectively. After that, these mixtures were constantly stirred for 12 h under room temperature, so that Ag^+ and CrO_4^{2-} ions would be well adsorbed or dispersed on the surface of GO and CN, respectively. Then the obtained homogeneous suspension containing CN and K_2CrO_4 was added dropwise into GO mixture. After another 4 h stirring, the GO/ACR/CN ternary composites were collected by filtration, washed with ethanol and de-ionized water for several times and finally dried at 60 °C in an oven for 12 h. For comparison, ACR/GO and ACR/CN were also synthesized in the same way as the composite of GO/ACR/CN with the absence of CN and GO, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected using a Rigaka D/max 2500 v/pc X-ray diffractometer with Cu Kα irradiation. The morphologies investigation was performed by a field emission scanning electron microscope (FESEM, Hitachi S-4800) and a transmission electron microscope (TEM, FEI Tecnai G20). The X-ray photoelectron spectroscopy (XPS) was analyzed on a Thermo ESCALAB 250XI spectrometer with Al Kα source. Fourier transform infrared spectroscopy (FTIR) was measured on an IR Prestige-21 spectrometer (Shimadzu, Japan) with scan range from 400 to 4000 cm^{-1} after pressing into tablets with KBr powder. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were measured by the spectrophotometer (UV-4100, Shimadza) with $BaSO_4$ as reference. The total organic carbon (TOC) assays were tested using a Shimadzu TOC-VCPH analyzer. The Photoluminescence (PL) spectroscopy was obtained using a transient fluorescence spectrometer (Edinburgh FLsp920). The special surface area was detected by Brunauer-Emmett-Teller (BET) technology from the N_2 adsorption isotherm, which was evaluated at 77 K on a TRISTAR-3000 surface area analyzer. The electron spin resonce (ESR) signals were examined on a Bruker ER200-SRC spectrometer under visible light irradiation ($\lambda > 420$ nm). The electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation (CHI660C) in a typical three-electrode system.

2.3. Photocatalytic degradation experiments

The photocatalytic activities of the catalysts were investigated through the photodegradation of multiple refractory pollutants irradiated by a 300 W Xe lamp with a 420 nm UV-cutoff filter. In a typical experiment, 0.02 g photocatalyst was added into 100 mL of synthetic wastewater (15 mg/L rhodamine (RhB), 15 mg/L methylene blue (MB), 10 mg/L phenol or 10 mg/L oxytetracycline). Before