



## Insight into the dual-channel charge-carrier transfer path for nonmetal plasmonic tungsten oxide based composites with boosted photocatalytic activity under full-spectrum light

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### ABSTRACT

The photocatalytic activities of the semiconductor-based photocatalysts are often practically limited by the insufficient photoinduced charge-carrier separation, so the construction of efficient charge transfer path is vital for highly efficient photocatalysis reaction system. In this study, we reported a rational designed novel hierarchical  $W_{18}O_{49}/g-C_3N_4$  composite with boosted photocatalytic activity through the manipulated flow of dual-channel charge-carrier separation and transfer process. Due to the efficient strategy about the combination of the morphology structure and the regulation of band structure, the prepared composites present enhanced photocatalytic performance in both full-spectrum light and near-infrared (NIR) light irradiation. Under the optimum condition, the prepared  $W_{18}O_{49}/g-C_3N_4$  composites show high degradation efficiency for both colorful methylene blue (MB) and colorless ciprofloxacin (CIP). Mechanistic characterizations and control experiments demonstrate the cooperative synergy effect of dual-channel charge-carrier transfer path in such  $W_{18}O_{49}/g-C_3N_4$  composites, including Z-scheme charge transfer and surface plasmon resonance effect, which interactively leads to the boosted photocatalytic performance. The match of the band gap results in the Z-scheme reaction mechanism and brought both the strong redox ability and promotion of the transfer rate of the photogenerated charges; the LSPR effect of nonmetal plasmonic  $W_{18}O_{49}$  can broaden the light response of the prepared  $W_{18}O_{49}/g-C_3N_4$  to NIR region, leading to enhanced utilization of solar energy. Moreover, the oxygen vacancies in this reaction system which played important role in the photocatalytic process have been fully studied by the appropriate design of the control experiments.

### 1. Introduction

Photocatalysis technology based on semiconductor materials aiming at solving the global environmental pollution and energy crisis has become one of the most promising avenues in the worldwide [1–4]. Thus, various high-efficient and environmental-friendly photocatalysts have been designed and employed [5–9]. However, the photocatalytic activity of most single-component photocatalysts is still far from satisfactory due to the fast recombination efficiency of the photoinduced charge carriers, which inhibits the migration of these charges to reach the semiconductor surface to participate in the redox reactions [10,11]. To solve this dilemma, various approaches have been explored to promote the transfer rate of the photogenerated charge-carrier.

Rational construction of heterostructure with band matchable

semiconductors is commonly regarded as an efficient way to impede the recombination of the charge-carrier by space separation of photo-generated holes and electrons [12,13]. But traditional heterojunctions would reduce the redox ability of photogenerated charges due to the ineluctable charge transfer process from high band level to relative low band level. On the contrary, new types of Z-scheme photocatalysts can effectively avoid the above problems, retaining the strong redox ability of the photogenerated charges with improved photocatalytic activity [14,15]. Therefore, designing new Z-scheme photocatalysts via the proper combination of different semiconductors is fascinating. Additionally, the use of local surface plasmon resonance (LSPR) would be another efficient strategy to promote the charge transfer in the composite, and many researchers prefer it [16–18]. However, to maximize the charge transfer rate and separation efficiency, promotion strategy

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just via only one charge-carrier transfer channel is difficult to achieve the goal. Therefore, it is important to optimally integrate different charge separation strategy in a well-designed hybrid photocatalysts to synergistically improve the photocatalytic performance.

Graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ), a stable and nontoxic polymeric semiconductor, has attracted great attentions as a visible-light excited photocatalysts for photocatalytic degradation [19–24]. Tremendous interests have focused on the combination of  $g\text{-C}_3\text{N}_4$  with inorganic semiconductors, especially for the construction of Z-scheme reaction mechanism, to achieve spatial separation of charge carriers and improve photocatalytic performance [25–27]. Unfortunately, due to that the intrinsic strong coulomb interactions of single Frenkel excitons in  $g\text{-C}_3\text{N}_4$  resulted in sluggish exciton dissociation, the photocatalytic performance of these  $g\text{-C}_3\text{N}_4$  based photocatalysts needs to be further improved [28–30].

In addition, grafting plasmonic metal to semiconductors to employ the local surface plasmon resonance (LSPR) effect would be another efficient strategy to boost the charge-carrier separation of photocatalysts [31]. In the past decade, some conducting metals, such as Au, Ag and Pt have been applied into the photocatalysis process to obtain enhanced photocatalytic performance based on the LSPR effect [32,33]. The existence of these metals provides a unique pathway for solar harvesting, and the LSPR effect can broaden the light response range and promote the photogenerated charge transfer rate. However, the high-cost of noble metals limits their large-scale practical applications. Recently, new types of nonmetal semiconductors have been investigated, such as  $\text{WO}_{3-x}$ , [32]  $\text{Cu}_{2-x}\text{S}$ , [34]  $\text{MoO}_{3-x}$ , [35] and Sn-doped  $\text{In}_2\text{O}_3$ , [36]. These semiconductors also have LSPR effect due to the existence of element vacancies. The free charges on the surface of the vacancy-rich nanoparticles can be induced by the incident and cause collective oscillation, giving opportunities to design new kind of low-cost and noble-metal-free plasmonic semiconductor materials. Nevertheless, owing to the low density of free charges, the LSPR absorption of those nonmetal nanoparticles usually locates in the NIR region, which indicates that the combination with another proper semiconductor is necessary to obtain high photocatalytic performance. Among these nonmetal semiconductors,  $\text{W}_{18}\text{O}_{49}$ , as member of tungsten oxide, present unique characteristics, showing enhanced performance for photocurrent response and photocatalytic water oxidization due to its LSPR effect [28,37]. It has been demonstrated that the existence of oxygen vacancies on  $\text{W}_{18}\text{O}_{49}$  surfaces bring about the plasmon-driven activities under visible light and NIR light irradiation [38,39]. Some researchers have found that the LSPR effect can improve the photocatalytic activity of plasmonic tungsten oxides ( $\text{W}_{18}\text{O}_{49}$ ) in the full spectrum (UV–vis–NIR) region, and the oxygen vacancies can also serve as the reaction sites to improve the reaction process [32,40,41]. Considering the advantages of  $g\text{-C}_3\text{N}_4$  and  $\text{W}_{18}\text{O}_{49}$ , and combined with the investigations of the interfacial charge density migration and charge carrier effective masses, it is revealed that dual-channel charge-carrier transfer path would be established. One channel would be the direct Z-scheme electron transfer process between  $\text{W}_{18}\text{O}_{49}$  and  $g\text{-C}_3\text{N}_4$ . Another channel would be the LSPR effect caused by nonmetal plasmonic  $\text{W}_{18}\text{O}_{49}$  from its oxygen vacancies. The rapid electron transfer between  $\text{W}_{18}\text{O}_{49}$  and  $g\text{-C}_3\text{N}_4$  via the dual-channel charge transfer path would result in both slower recombination rate and prolonged lifetime of photogenerated charge carriers than that in the single component.

Thus, in this study, novel  $\text{W}_{18}\text{O}_{49}/g\text{-C}_3\text{N}_4$  nanograin composites with superior full-spectrum-light response ability have been synthesized successfully via facial hydrothermal supported self-assembly process. Benefit from the designed unique structure and match of the band gap, the photogenerated charges transfer of the prepared  $\text{W}_{18}\text{O}_{49}/g\text{-C}_3\text{N}_4$  nanograin composites have been greatly improved via dual-channel transfer path: Z-scheme charge transfer and surface plasmon resonance effect. Thus, the prepared  $\text{W}_{18}\text{O}_{49}/g\text{-C}_3\text{N}_4$  nanograin composites present enhanced photocatalytic degradation efficiency for both colored methylene blue (MB) and colorless ciprofloxacin (CIP).

Additionally, the role of oxygen vacancies in this reaction process have been fully investigated, and results show that due to the existence of LSPR effect, the hot-electrons can be injected into the conduction band of  $g\text{-C}_3\text{N}_4$ , and contribute to the enhanced photocatalytic performance. The reported highly efficient photocatalyst with unique charge transfer process provides a new insight into the design of photocatalyst.

## 2. Experimental section

### 2.1. Materials

Hexacarbonyltungsten ( $\text{W}(\text{CO})_6$ ) and Ciprofloxacin (CIP) were purchased from Aladdin Industrial Corporation. Melamine, absolute ethanol, Isopropanol (IPA), Ethylenediaminetetraacetic acid disodium (EDTA-2Na) and 1,4-benzoquinone (BQ) was purchased from Sinopharm Chemical Reagent Co., Ltd. Other reagents were of analytical grade and used as received without further purification. All solutions were prepared with deionized water (18.25 M $\Omega$  cm specific resistance), which was produced by an Ultrapure laboratory water system.

### 2.2. Preparation of the $\text{W}_{18}\text{O}_{49}/g\text{-C}_3\text{N}_4$ photocatalysts

First of all, the graphitic nitride ( $g\text{-C}_3\text{N}_4$ ) nanosheets were synthesized via a thermal polymerization method. Typically, 5 g of melamine was placed into an alumina crucible and covered to create semiclosed reaction environment. Subsequently, the alumina crucible was heated to 520 °C with a rising rate of 5 °C/min and kept at this temperature for 4 h, and then the yellow bulk  $g\text{-C}_3\text{N}_4$  can be obtained. To acquire  $g\text{-C}_3\text{N}_4$  nanosheets, the bulk  $g\text{-C}_3\text{N}_4$  was grinded into powder and placed into the alumina crucible for another thermal process, with the rising rate of 2.5 °C/min to 500 °C and kept for 2 h. Secondly, as for the synthesis of the  $\text{W}_{18}\text{O}_{49}/g\text{-C}_3\text{N}_4$  photocatalysts. 50 mg of  $\text{W}(\text{CO})_6$  was dissolved in 40 mL of absolute ethanol solution, and then certain amount of the prepared  $g\text{-C}_3\text{N}_4$  nanosheets was added into the above solution and stirred for 1 h to obtain the homogeneous mixture. Next, the mixture was sealed in a Teflon-lined autoclave and heated at 160 °C for 12 h. Finally, the yellow-blue precipitates were collected via centrifugation, and washed with ethanol for several time and dried in vacuum. By adjusting the addition dosage of  $g\text{-C}_3\text{N}_4$  nanosheets during the hydrothermal process, series of  $\text{W}_{18}\text{O}_{49}/g\text{-C}_3\text{N}_4$  photocatalysts can be obtained. For convenience, the added amount of  $g\text{-C}_3\text{N}_4$  in the reaction system with 50 mg, 80 mg, 100 mg, 120 mg and 150 mg for the synthesis of the photocatalysts were marked as WCN-1, WCN-2, WCN-3, WCN-4 and WCN-5, respectively. To make comparison, the pure  $\text{W}_{18}\text{O}_{49}$  were prepared by using the same route without the addition of  $g\text{-C}_3\text{N}_4$  nanosheets.

### 2.3. Characterization of materials

The Morphology structure of the samples was studied on a Hitachi S-4800 field emission scanning electron microscopy (FE-SEM Hitachi, Japan) with 5.0 kV scanning voltages. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy were obtained via an F20 S-TWIN electron microscopy (Tecnai G2, FEI Co.) at the acceleration voltage of 200 kV. The crystal structure characteristics of the prepared samples were measured via an X-ray diffractometer (XRD) (Bruker AXS D8 Advances) with Cu K $\alpha$  irradiation source at a scan rate (2 $\theta$ ) of 0.05 °s<sup>-1</sup>. FT-IR spectra were obtained on an IRAffinity-1 Fourier transform infrared spectrometer (Shimadzu, Japan) by the standard KBr disk method at room temperature. The X-ray photoelectron spectroscopy (XPS) of the prepared samples was carried out Thermo Fisher ESCALAB 250Xi spectrometer with Al K $\alpha$  source. The Ultraviolet visible near-infrared diffused reflectance spectra (UV–vis–NIR DRS) of the prepared samples were carried out via a UV–vis–NIR spectrophotometer (Hitachi U4100 UV Spectrometer)

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