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Research Paper

In situ construction of hierarchical WO_3/g-C_3N_4 composite hollow microspheres as a Z-scheme photocatalyst for the degradation of antibiotics

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ABSTRACT

Elegant Z-scheme WO_3/g-C_3N_4 composite hollow microspheres (CHMs) were constructed through precisely controlled in situ hydrolysis and a polymerization process consecutively. The formation of intact and well-defined hollow microspheres can be realized through optimizing the ratio of precursors for WO_3 and g-C_3N_4. The shell of these hollow microspheres consist of well-distributed WO_3 and g-C_3N_4 nanoparticles, and excellent heterojunctions with numerous interfaces and highly exposed oxidation-reduction active sites have thus been built. By virtue of this special architecture, more incident photons are expected to be trapped in the hollow cavities, which contribute to more electrons and holes available for photocatalytic reactions. Moreover, these photoinduced hole-electron pairs could be effectively separated, and the lifetime of charge carriers reaches 2.23 ns, which is obviously prolonged compared with the WO_3. WO_3/g-C_3N_4 CHMs as an optimized Z-scheme system retains the original oxidation and reduction abilities for the components without change of the oxidation and reduction potential. Combined with the long survival time of holes and electrons, this photocatalyst showed enhanced degradation rates towards tetracycline hydrochloride (TC-HCl) and ceftiofur sodium (CFS).

1. Introduction

The discovery and utilization of antibiotics was a significant step forward for mankind, allowing us to contend with bacterial infections, which are regarded as the first threat to human health. Until recent years, the problem of the misuse of antibiotics has attracted scientific and public attentions. The phenomenon of antibiotic resistance has become more and more evident, and residues of antibiotics are found in a variety of environmental matrices, including surface and groundwater, soils, waste and even the food on our table [1,2]. The quantities of these pharmaceuticals presented only increase and never decrease, which directly threatens the life conditions of the whole ecosystem. The well-known controversy surrounding DDT helped to first put antibiotics disposal on the public agenda.

In the past few years, various technologies for environmental contaminant abatement have being used to treat the antibiotics, including physical adsorption [3–5], biological treatment [6,7] and chemical degradation [8]. The latter is regarded as an effective and thorough solution. Chemical methods oxidize the antibiotics to substances that are easily biodegradable and less toxic, and even transform them into harmless compounds [9]. Among many advanced oxidation processes, photocatalysis has been descried as one of the most promising due to its energy-savings, environmental friendliness and low cost [10,11]. Semiconductors illuminated by renewable solar energy that exceed the band gap energy produce amounts of electrons (e^-) and holes (h^+). The electrons and holes could react respectively with oxygen and hydroxyl ions (OH^-) adsorbed on the catalyst surface to generate hydrogen peroxide and hydroxyl radicals ($\cdot OH$), and they are strong oxidants for the degradation of organics. Metal oxides, including TiO_2 [12–14], ZnO [15–17], SnO_2 [18], WO_3 [19,20], and others have been widely investigated for the photodecomposition of pollutants with the aid of light irradiation. Among them, tungsten oxide (WO_3) shows excellent visible-light-driven photocatalytic activity due to its narrow band gap energy of approximately 2.7–2.8 eV [21]. As visible light occupies 45% of the entire solar spectrum, WO_3 has great potential for environmental remediation with low resource consumption. Moreover, the position of the valance band for WO_3 is relatively high, and the holes generated on WO_3 therefore have intense capability for oxidizing

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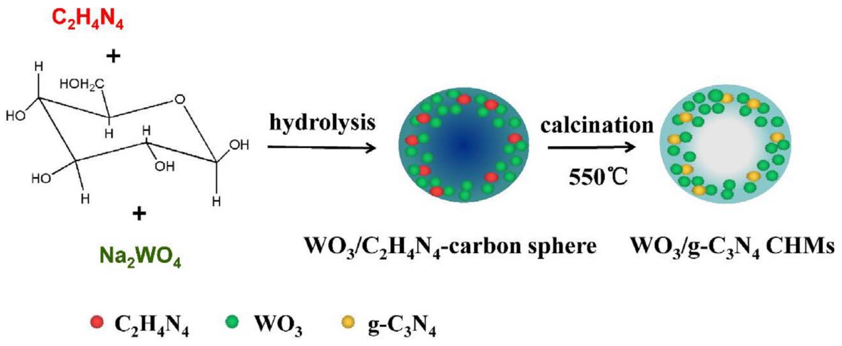

Scheme 1. Schematic representation of in situ construction of WO_3/g-C_3N_4 composite hollow microspheres (CHMs).

OH^- into ·OH, which has been demonstrated to be a vital intermediate step in the process of photodecomposition. Due to the rapid recombination of photoinduced hole-electron pairs, however, there are few instances for the utilization of WO_3 in the treatment of antibiotics.

Many studies have devised heterostructured photocatalysts with diverse models for WO_3 [22] and g-C_3N_4 [23–25]. Based on the heterojunctions, the effective separation of charge carriers is realized, and the photocatalytic activity and stability of photocatalysts are improved. Cui et al. [26] prepared WO_3/g-C_3N_4 photocatalysts via a facile one-step simultaneously heating procedure using urea and tungsten chloride as the precursors. WO_3 particles with the size of 30–50 nm were covered on the g-C_3N_4 surfaces or embedded in g-C_3N_4 layers. These composites showed significant enhancement in photodegradation of Rhodamine B by virtue of the heterostructures. Tsubota's group [27] synthesized the composite of g-C_3N_4 and WO_3 using a planetary mill, and the prepared photocatalyst showed high photocatalytic activity for acetaldehyde decomposition under visible-light irradiation as a result of Z-scheme charge transfer. Katsumata et al. [28] used g-C_3N_4 nanosheets for the preparation of a g-C_3N_4/WO_3 composite in which WO_3 particles were covered on the surfaces of g-C_3N_4. The composite exhibited enhanced photocatalytic activity for the degradation of acetaldehyde. Despite these exciting advances in the field of photocatalysis for WO_3, there are still problems regarding efficiency. The low utilization rate of photons and fewer surface active sites seriously restrict their practical applications [29]. Various morphologies of semiconductors are thus being designed, including nanosheets [30], nanorods [31], nanocubes [32], and others. Hollow structures have attracted intense attention for many years due to their special structural, physical and chemical properties [33–35]. This cavity structure endows the material with low density, high specific surface area, favourable efficiencies of mass transfer and utilization of photons. Our group has reported a variety of hollow spheres with different compositions for the photocatalytic reduction of CO_2, including $Ti_{0.91}O_2$/CdS hollow spheres with alternated multilayer structure [36], Au@TiO_2 yolk–shell hollow spheres with surface plasmon resonance effect [37], and GaN double-shelled hollow spheres with oxygen doping [38].

In this article, we demonstrate an in situ hydrolysis and polymerization process for the construction of WO_3/g-C_3N_4 composite hollow microspheres (CHMs). The formation of intact and well-defined hollow microspheres is realized when the ratio of the precursors for WO_3 and g-C_3N_4 is well optimized. The specific hollow structure allows the trapping of incident light for a long time, and provides high efficiency for photon utilization. Moreover, the shells of the microspheres are constructed by the well-distributed WO_3 and g-C_3N_4 nanoparticles. Numerous interfaces between WO_3 and g-C_3N_4 can thus be built, and the separation efficiency of photoinduced electron–hole pairs was improved. Compared with the WO_3, WO_3/g-C_3N_4 CHMs possesses a longer charge carrier lifetime of 2.23 ns and highly exposed oxidation-reduction active sites, which obviously improve the oxidation and reduction abilities of the catalyst. The powerful heterojunctions as a Z-scheme system retains the original oxidation and reduction abilities for the components without changing their oxidation and reduction potential, and the photodegradation rates towards tetracycline hydrochloride (TC-HCl) and ceftiofur sodium (CFS) are thus improved.

2. Experimental

2.1. Chemicals and materials

Sodium tungstate dihydrate (Aladdin, 99.5%) was used as a precursor for the preparation of WO_3. Dicyandiamide (Aladdin, 99%) was used as a precursor for the preparation of g-C_3N_4. Ceftiofur sodium ($C_{19}H_{16}N_5O_7S_3Na$, CFS) and tetracycline hydrochloride ($C_{22}H_{24}N_2O_8$·HCl, TC-HCl) obtained from Macklin were employed as the target organic pollutants. 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) purchased from Sigma-Aldrich was used as the trapping agent for investigation of ·OH and $·O_2^-$ radicals. Glucose was the product of Aladdin, and other chemicals used in the experiments were purchased from the Shanghai Chemical Reagent Company.

2.2. Preparation of WO_3/g-C_3N_4 composite hollow microspheres (CHMs)

As described in Scheme 1, WO_3/g-C_3N_4 CHMs were prepared using an in situ hydrolysis and polymerization process with a hydrothermal method combining calcination. In a typical procedure, 1 mmol Na_2WO_4 was added to 50 mL of deionized water while stirring to form a homogeneous solution. Subsequently, a certain amount of dicyandiamide and 25 mmol of glucose were introduced, and the resulting mixture was continuously stirred for 30 min. Afterwards, the homogeneous solution was transferred to a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was sealed and heated in an oven at 200 °C for 20 h. After naturally cooling to room temperature, the solid products were subjected to centrifugation, washed with distilled water and ethanol three times, and finally dried in air at 60 °C. In the next step, the as prepared dry products were annealed at 550 °C for 3 h in air. According to the above manner, a series of WO_3/g-C_3N_4 composites with different contents of g-C_3N_4 were prepared and labelled WO_3/g-C_3N_4-x for simplicity, where x represented the molar quantities of dicyandiamide added in the process of preparation.

WO_3 and g-C_3N_4 were prepared for comparison by using the same method. For the preparation of WO_3, 1 mmol Na_2WO_4 and 25 mmol of glucose were added to 50 mL of deionized water to form a homogeneous solution under stirring. Then, the products were obtained by following the abovementioned steps. Meanwhile, to obtain g-C_3N_4, 5 g dicyandiamide was put into an alumina crucible that was heated at 550 °C for 3 h with a temperature increase rate of 10 °C/min. After the reaction, the alumina crucible was cooled naturally to room temperature. The as-prepared g-C_3N_4 was collected and ground into powder for further use.

2.3. Catalyst characterization

The crystal structures were characterized using a Brucker-D8-Advanced X-ray diffraction equipped with Cu Ka radiation source. The