



# Construction of heterostructured MIL-125/Ag/g-C<sub>3</sub>N<sub>4</sub> nanocomposite as an efficient bifunctional visible light photocatalyst for the organic oxidation and reduction reactions



Zhiwang Yang\*, Xueqing Xu, Xixi Liang, Cheng Lei, Yuhan Cui, Wenhua Wu, Yaoxia Yang, Zhe Zhang, Ziqiang Lei\*

Key Laboratory of Polymer Materials of Gansu Province, Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University Lanzhou 730070, China

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## ABSTRACT

Photocatalytic synthesis using visible light is a desirable chemical process because of its potential to utilize sunlight. A heterostructured MIL-125/Ag/g-C<sub>3</sub>N<sub>4</sub> nanocomposite was implemented as an efficient bifunctional visible-light response catalyst for the photoreduction of nitrocompounds and the oxidation of alcohols. The photocatalyst was prepared via an accessible method and characterized by XRD, SEM, TEM, XPS, FT-IR, N<sub>2</sub> adsorption–desorption isotherm, UV–vis DRS, PL and EIS. The reactive efficiency of the photocatalyst depends on two primary factors, one is the light adsorption of catalysts, Ag nanoparticles (NPs) were photodeposited on the surface of g-C<sub>3</sub>N<sub>4</sub> and MIL-125 to increase visible-light absorption via the surface plasmon resonance. And the other is the separation efficiency of the photogenerated charge carrier. As an electron–conduction bridge in the interface between MIL-125 and g-C<sub>3</sub>N<sub>4</sub>, Ag NPs could facilitate the direct migration of photoinduced electrons from g-C<sub>3</sub>N<sub>4</sub> to MIL-125 and retard the recombination of electron–holes. Therefore, the MIL-125/Ag/g-C<sub>3</sub>N<sub>4</sub> sample shows highest photocatalytic activity compared with MIL-125, g-C<sub>3</sub>N<sub>4</sub>, MIL-125/Ag and MIL-125/g-C<sub>3</sub>N<sub>4</sub>. A corresponding photocatalytic mechanism of these reactions was discussed in detail. Moreover, the photoreduction of nitrocompounds and oxidation of the alcohols with superior conversions and selectivities were obtained, and the catalyst can be recycled four times. It is concluded that MIL-125/Ag/g-C<sub>3</sub>N<sub>4</sub> would be a promising visible light photocatalyst in the field of selective organic transformations.

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## 1. Introduction

Metal organic frameworks (MOFs), also called porous coordination polymers (PCPs) are self-assemblies obtained via metal-oxide units joined by organic linkers through coordination bonds [1]. It was used for applications in H<sub>2</sub> storage [2], carbon dioxide capture [3] catalysis [4,5], optical materials [6] et al. Recent researches suggest that MOFs have the ability to behave as semiconductors when exposed to light [7,8], making them unique platforms for light harvesting and photoinduced catalysis [9–11] for hydrogen evolution [6], carbon dioxide reduction [12], degradation of the organic pollutants [9] and transformation of organic compounds [13]. A case in point, MIL-125 (MIL = Materials of Institut Lavoisier)

is composed of basic units of Ti<sub>8</sub>O<sub>8</sub>(OH)<sub>4</sub>-(O<sub>2</sub>C-C<sub>6</sub>H<sub>5</sub>-CO<sub>2</sub>)<sub>6</sub>, constructed from corner or edge sharing octahedral titanium units and led to a porous three-dimensional quasi-cubic tetragonal structure [14]. Nevertheless, pure MIL-125(Ti) has a bad gap within ultraviolet region at about 3.6 eV. So it is related to the reduction of Ti (IV) to Ti (III) under UV irradiation, which accounts for only 3–5% of the solar spectrum [15]. Therefore, it is extremely important to develop the visible light responded MIL-125 based catalysts. Numerous attempts have been dedicated to increasing the photocatalytic efficiency of MIL-125. For example, noble metal deposition [16], coupled with inorganic semiconductor [17] and introduction of organic chromophores, NH<sub>2</sub>, in the linker [18] et al. To date, the heterostructures integrating MOFs with other functional materials such as CdS [19], Fe<sub>3</sub>O<sub>4</sub> [20], ZnO and C<sub>3</sub>N<sub>4</sub> [21] etc acted as catalysts show great advantages due to their synergism effect [22]. Especially, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) [23,24], a metal-free polymer semiconductor, possesses stacked two-dimensional struc-

\* Corresponding authors.

E-mail addresses: [yangzw@nwnu.edu.cn](mailto:yangzw@nwnu.edu.cn) (Z. Yang), [leizq@nwnu.edu.cn](mailto:leizq@nwnu.edu.cn) (Z. Lei).

ture, with tris-triazine building units connected with planar amino groups in each layer and weak van der Waals force between layers. It has attracted a focus of attention for photocatalytic reactions, because this material is cheap, easy to synthesize, and environmental friendly [25,26]. It is more important that  $g\text{-C}_3\text{N}_4$  owns relatively narrow band gap of 2.45 eV and the energy position of CB and VB is at -0.85 and 1.6 eV vs normal hydrogen electrode (NHE), respectively [27]. More recently, Hou W and his colleagues was reported that  $g\text{-C}_3\text{N}_4/\text{MIL-125}$  heterostructured photocatalyst exhibited an improved photocatalytic performance for the degradation of Rhodamine B under visible-light irradiation [28]. Nonetheless, bulk  $g\text{-C}_3\text{N}_4$  suffers the predicament of limited photocatalytic activity due to low quantum yield and high recombination rate of photo-generated charges [29]. Recent research shows that layer  $g\text{-C}_3\text{N}_4$  nanosheets with high specific surface area exhibit many intriguing properties different from bulk  $g\text{-C}_3\text{N}_4$ . Therefore, the  $g\text{-C}_3\text{N}_4$  nanosheets could effectively improve the photocatalytic activity.

Besides, it is well-known that for semiconductor-based photocatalysts, the separation efficiency of the photogenerated charge carriers is an important factor in determining their photocatalytic performance [30]. To further overcome the fast recombination process of the photocatalyst, considerable researches have been carried out using a noble metallic combination of semiconductors [31,32]. Ag nanoparticles (Ag NPs) can act as efficient electrons traps to suppress photoinduced electron-hole recombination at a certain extent. In addition, Ag NPs formed on the surface of semiconductors could strongly absorb visible light because of the surface plasmon resonance of Ag atom [22,33,34].

Based on the above discussion, to improve the photocatalytic activity of the MIL-125, herein we report a new hybrid photocatalyst made by heterostructured MIL-125/Ag/ $g\text{-C}_3\text{N}_4$  nanocomposite. It was primarily focused on its dual applications in the photocatalytic synthesis including the reduction of nitrocompounds into aromatic amine and the selective oxidation of alcohols.

The green chemistry involving photocatalytic synthesis, where photon is used as one of the reactants of chemical reactions, is a growing field. Moreover, the photocatalytic oxidation and reduction progress have carried out using the mild experimental conditions [35,36]. For example, photocatalytic reduction of nitrobenzene into aniline using photocatalytic technology has been reported in some literatures [37,38]. Theoretically, when the conduction band (CB) potential of photocatalyst is lower than -0.486 V, nitrobenzene (NB) can be photocatalytically reduced into aniline (AN) ( $E(\text{C}_6\text{H}_5\text{NO}_2/\text{C}_6\text{H}_5\text{NH}_2) = -0.486 \text{ V}$ , vs NHE), the methanol or isopropyl alcohol provide the proton and the photoinduced electrons were used as the reducing agent, so the whole process is eco-friendly and economical. Moreover, aromatic nitro-compounds reduction will produce aromatic amines that are valuable intermediate materials for production of dyes, pharmaceuticals, agro-chemicals, cosmetics, and chelating agents [39]. Therefore, photocatalytic reduction of nitrobenzene into aniline is significant. Again for instance, aromatic aldehydes and their derivatives are important fine chemical intermediate. Nowadays, photocatalytic aerobic alcohols to the aldehydes or ketones with molecular oxygen as oxidant have caused the extensive concern. Because, its providing of an economical and green way for this type of transformation [18,40].

According the experimental results, it was found that the MIL-125/Ag/ $g\text{-C}_3\text{N}_4$  composite has exhibited much higher photocatalytic activity for reduction of nitrobenzene into aniline and aerobic alcohols to the aldehydes or ketones than the bare MIL-125 or  $g\text{-C}_3\text{N}_4$  under visible-light irradiation ( $> 400 \text{ nm}$ ), distinctly demonstrating that the existence of a synergistic effect among Ag,  $g\text{-C}_3\text{N}_4$  and MIL-125. The low recombination of the photoinduced electron-holes of the prepared MIL-125/Ag/ $g\text{-C}_3\text{N}_4$  nanocomposites was confirmed based on a photoluminescence (PL) and electro-

chemical impedance spectroscopy (EIS) technique. In addition, the possible photocatalysis mechanism of MIL-125/Ag/ $g\text{-C}_3\text{N}_4$  under visible light was also discussed.

## 2. Experimental

### 2.1. Materials

All the used reagents and solvents were analytical grade and received from commercial sources without further purification. Titanium isopropoxide ( $\text{Ti}(\text{O-}i\text{Pr})_4$ ), 1,4-benzenedicarboxylic acid ( $\text{H}_2\text{BDC}$ ), benzyl alcohol, 4-methoxybenzyl alcohol were obtained from Aladdin Reagent Co., Ltd.  $N,N$ -dimethylformamide (DMF), melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ), concentrated hydrochloric acid (HCl, 36.0–38.0%), polyethylene glycol (PEG2000) and silver nitrate ( $\text{AgNO}_3$ ) were obtained from Shanghai Fine Chemical Materials Research Institution. 4-Nitrobenzyl alcohol, 2-methylbenzyl alcohol, 4-chlorobenzyl alcohol 2-methoxybenzyl alcohol, 4-hydroxybenzyl alcohol, benzhydrol, 4-chlorobenzhydrol, and 4-methoxybenzhydrol were obtained from the Beijing J&K Scientific Co. Ltd. 4-Methylbenzyl alcohol, 4, 4'-dimethylbenzhydrol, 4, 4'-dimethoxybenzhydrol and 4, 4'-dichlorobenzhydrol were obtained from Alfa Aesar Co. Ltd. Nitrobenzene and its derivatives were obtained from Aladdin Reagent Co., Ltd. or Beijing J&K Scientific Co., Ltd.

### 2.2. Preparation of photocatalysts

#### 2.2.1. Synthesis of MIL-125

MIL-125 was synthesized according to the literature [41]. In a typical synthesis procedure, a mixture of  $\text{Ti}(\text{O-}i\text{Pr})_4$  (1.60 mL),  $\text{H}_2\text{BDC}$  (3.00 g), 6 mL of  $\text{CH}_3\text{OH}$  and 56 mL of DMF were stirred at room temperature until it become a clear solution, then it was transferred into a 100 mL Teflon liner. After that, it was sealed in a stainless steel autoclave and heated at  $150^\circ\text{C}$  for 48 h. The resultant suspension was filtered, washed with DMF and  $\text{C}_2\text{H}_5\text{OH}$ , respectively. The white powder was collected by filtering and drying under vacuum at  $100^\circ\text{C}$  for 12 h.

#### 2.2.2. Synthesis of $g\text{-C}_3\text{N}_4$ nanosheets

Graphite-like  $\text{C}_3\text{N}_4$  ( $g\text{-C}_3\text{N}_4$ ) were synthesized on the basis of a procedure reported [33,42]. Specifically, 5.0 g of melamine was heated from room temperature to  $550^\circ\text{C}$  with a heating rate of  $3^\circ\text{C}/\text{min}$  and then calcined at  $550^\circ\text{C}$  for 4 h in a  $\text{N}_2$  furnace. The obtained yellow agglomerate was ground into powder. 1.0 g of the above powder was dispersed in 60 mL of 6 M HCl solution string for 1 h for protonation of  $g\text{-C}_3\text{N}_4$ . Then the suspension was transferred into a 100 mL Teflon liner. Then it was sealed in a stainless steel autoclave and heated at  $120^\circ\text{C}$  for 8 h. After cooled down to the room temperature, the suspension was filtered, washed with deionized water until the filtrate was close to neutral conditions. The collected  $g\text{-C}_3\text{N}_4$  was dried at  $100^\circ\text{C}$  in vacuum for 4 h. In order to conveniently use of the as-prepared  $g\text{-C}_3\text{N}_4$  subsequently, 100 mg of the protonated  $g\text{-C}_3\text{N}_4$  was ultrasonically dispersed in 100 mL of deionized water for 4 h to form a stable suspension of  $g\text{-C}_3\text{N}_4$  nanosheets.

#### 2.2.3. Synthesis of MIL-125/Ag/ $g\text{-C}_3\text{N}_4$ nanocomposite

A series of MIL-125/Ag/ $g\text{-C}_3\text{N}_4$  nanocomposite with different mass ratios of MIL-125 vs  $g\text{-C}_3\text{N}_4$  nanosheets were synthesized by a facile method as follows, the as-prepared MIL-125 power (200 mg) was mixed with 100 mL of deionized water by ultrasonication for 30 min. Then 1.0 mL of 5% PEG2000 was added and the dispersion was stirred for another 30 min. To deposit the Ag NPs on the surface of the MIL-125, a photodeposition method was applied. Firstly,

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