



## Research Paper

# One-pot synthesis of metakaolin/g-C<sub>3</sub>N<sub>4</sub> composite for improved visible-light photocatalytic H<sub>2</sub> evolution

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## ABSTRACT

The conversion of solar energy to chemical energy via photocatalysis is a potential pathway for future energy supplying, and the development of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) for visible-light photocatalytic hydrogen evolution reaction (HER) has attracted increasing attention. In this work, raw kaolinite was used to enhance the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> by constructing the metakaolin/g-C<sub>3</sub>N<sub>4</sub> composites. A facile one-pot method, heat-treating their mixed precursors, was employed. The as-prepared MK/CN-70.4% exhibits a favorable hydrogen evolution rate of 288 μmol g<sup>-1</sup> h<sup>-1</sup>, which is 1.5 times that of bulk g-C<sub>3</sub>N<sub>4</sub>. The improved HER benefits from both the electronegativity of metakaolin and the nanosizing of g-C<sub>3</sub>N<sub>4</sub>. The proposed strategy has the potential to inspire the utilization of other clay minerals to improve the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>.

## 1. Introduction

Currently, fossil fuels such as oil and coal are still the main energy sources. Facing the problem of energy depletion and environmental pollution stemmed from fossil fuels, hydrogen energy has gradually drawn widely attention due to its cleanliness of non-pollution after combustion. Semiconductor photocatalysis technology is extensively attractive because of its ability to utilize inexhaustible solar energy to split water into hydrogen and/or to degrade pollutants. Developing an environment-friendly photocatalyst with response to visible light has become a hot research topic (Chen et al., 2017).

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has attracted increasing attention since it was, for the first time, reported by Wang et al. in 2009 as a metal-free photocatalyst for hydrogen evolution by water splitting under visible light (Wang et al. 2009). The features such as appropriate valance band and conduction band positions, metal-free composition and favorable thermal/chemical stability, endow it with extensive applicability in hydrogen production (Su and Zhang 2017), CO<sub>2</sub> reduction (Xu et al. 2016) and pollutant degradation under visible light irradiation (Pi et al. 2015). Nevertheless, the pristine bulk g-C<sub>3</sub>N<sub>4</sub> synthesized by thermal polycondensation of cyanamide (Tan et al. 2017),

dicyandiamide (Lv et al. 2017) or melamine (Huang et al. 2015) is still dissatisfactory in photocatalysis owing to its limited efficiencies of visible light absorption and photogenerated electrons and holes separation (Jing et al. 2017; Wei et al. 2018). Several strategies have been developed to improve the photocatalytic performance of pristine g-C<sub>3</sub>N<sub>4</sub>, such as, structural nanosizing (Shu et al. 2018; Wang et al. 2018; Zheng et al. 2015), element doping (Zhang et al. 2015; Zhu et al. 2017) and composite construction (Tan et al. 2018; Wang et al. 2014; Wang et al. 2017). Among them, compositing g-C<sub>3</sub>N<sub>4</sub> with other materials is a promising technique to promote the photogenerated carrier separation for improving photocatalytic activity. For instance, Z-scheme porous g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite (Zhang et al. 2017) and Ta<sub>3</sub>N<sub>5</sub>/g-C<sub>3</sub>N<sub>4</sub> metal/non-metal nitride hybrid (Jiang et al. 2017) have been synthesized to achieve enhanced photocatalytic hydrogen evolution efficiency. However, most of the used reinforce-phase are synthetic and costly, which is unfavorable for large-scale application. Thus, the development of low-cost and environmental-friendly reinforce-phase to modify g-C<sub>3</sub>N<sub>4</sub> is of great interest.

Raw clay minerals, such as kaolinite (Dong et al. 2018; Li et al. 2018; Fida et al. 2015), attapulgite (Zhang et al. 2016), montmorillonite (Liu et al. 2015) and halloysite (Li et al. 2015), are abundant in

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reserve, cheap and environmental-friendly. Construction of clay/g-C<sub>3</sub>N<sub>4</sub> composites has been reported to be efficient to improve the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>. For example, Shui-Lin et al (2016) synthesized g-C<sub>3</sub>N<sub>4</sub> from dicyandiamide first, and prepared a protonated g-C<sub>3</sub>N<sub>4</sub> (H<sup>+</sup>) via reacting the g-C<sub>3</sub>N<sub>4</sub> with HCl solution, then mixed it with kaolinite in methanol under ultrasonic and magnetic stirring. After drying, kaolinite/g-C<sub>3</sub>N<sub>4</sub> (H<sup>+</sup>) composites were obtained. Sun et al. (2016) prepared kaolinite/g-C<sub>3</sub>N<sub>4</sub> composites by synthesizing g-C<sub>3</sub>N<sub>4</sub> from dicyandiamide, then wet-grinding it with kaolinite and finally drying. Li et al. (2016) synthesized g-C<sub>3</sub>N<sub>4</sub>/montmorillonite composites via calcining the mixture of organic montmorillonite and melamine, which were previously mixed in ethanol and dried by rotary evaporation. Li et al. (2017) synthesized dark orange montmorillonite/g-C<sub>3</sub>N<sub>4</sub> composites by stirring the solution of dicyandiamide and montmorillonite, then drying and finally calcination. All the above clay/g-C<sub>3</sub>N<sub>4</sub> composites showed enhanced photocatalytic activity in the degradation of organic pollutants such as rhodamine B, methylene blue and tetracycline. Nevertheless, the reported processes for preparing clay/g-C<sub>3</sub>N<sub>4</sub> composites are relatively complex. They require multistep operations and follow the wet route containing water and/or organic solvent drying. Moreover, there is no report on the photocatalytic H<sub>2</sub> evolution properties of clay/g-C<sub>3</sub>N<sub>4</sub> composites yet.

In this work, we demonstrated a facile one-pot dry process to obtain metakaolin/g-C<sub>3</sub>N<sub>4</sub> composites by directly calcining the mixture of melamine and raw kaolin, and the photocatalytic H<sub>2</sub> evolution efficiency was improved. The detailed process was introduced and the mechanism for improving photocatalytic hydrogen evolution was also described.

## 2. Experimental

### 2.1. Materials synthesis

#### 2.1.1. Metakaolin/g-C<sub>3</sub>N<sub>4</sub> composites

Metakaolin/g-C<sub>3</sub>N<sub>4</sub> composites were facilely synthesized in one-pot. Typically, a mixture containing 6 g of melamine (A. R.) and certain amount of kaolinite (abbreviated as KA hereafter, China Kaolin Clay Co., Ltd.) was sealed in a crucible (300 mL) with aluminium-foil paper and calcined in a muffle furnace at 550 °C for 4 h with a heating rate of 15 °C/min. The resultant yellow-brown samples were ground into powder for further use and denoted as MK/CN-x, where x represents the mass fraction of g-C<sub>3</sub>N<sub>4</sub> in composite.

#### 2.1.2. Control samples

For comparison, bulk g-C<sub>3</sub>N<sub>4</sub> (denoted as bulk-CN) was synthesized via the same process in absence of kaolinite, while calcined kaolinite (denoted as MK) was obtained via the same process in absence of melamine. The nanosized g-C<sub>3</sub>N<sub>4</sub> phase (denoted as nano-CN) of metakaolin/g-C<sub>3</sub>N<sub>4</sub> composite was obtained by etching MK/CN-70.4% with 15 wt% hydrofluoric acid at room temperature to remove the kaolinite phase. A physical mixture of nanosized g-C<sub>3</sub>N<sub>4</sub> and calcined kaolinite was prepared by mechanically mixing 0.296 g MK with 0.704 g nano-CN (denoted as MK/CN-70.4%-mix).

### 2.2. Characterizations

Thermogravimetric/differential thermal analyzer (TG-DTA) measurement was conducted on a NETZSCH STA 449 F5 with an air flow of 50 mL/min and a heating rate of 10 °C/min. The crystalline structure of samples was investigated by X-ray diffraction (XRD) on a Rigaku MiniFlex600 using Cu K $\alpha$  radiation at 45 kV and 15 mA. Fourier transform infrared (FTIR) spectra were carried using a Nicolet iS50 infrared Fourier transform spectrometer with scanning from 400 to 4000 cm<sup>-1</sup>. The internal and apparent structures of samples were obtained by transmission electron microscopy (TEM) on JEOL 200CX at 200 kV and scanning electron microscopy (SEM) on Magellon 400. For

TEM testing, a certain amount of photocatalyst was dispersed in ethanol and then sonicated for 5 min. Subsequently, a small amount of the dispersion was dipped to a copper mesh with a diameter of 3 mm and then detected on JEOL 200CX at 200 kV. For SEM testing, a certain amount of photocatalyst was attached on the copper substrate by conducting resin, then sprayed with gold for 40 s. Afterward, the samples were detected on Magellon 400. Nitrogen adsorption/desorption isotherms were conducted using a Micromeritics TriStar 3020 porosimeter at 77 K, and specific surface areas ( $S_{\text{BET}}$ ) were calculated by the Brunauer-Emmet-Teller (BET) method. UV-visible diffuse reflectance spectra (UV-vis DRS) were recorded by a Shimadzu UV-2500PC UV-vis spectrometer with the wavelength range of 240–850 nm. The photocurrent analysis was measured using photocatalyst-coated fluorine-doped tin oxide (FTO) glass with repeated on-off cycles of Xenon lamp illumination ( $\lambda > 420$  nm), which was carried out using a computer-controlled potentiostat and a reference electrode of Ag/AgCl. Photoluminescence (PL) spectra were obtained on an F-4500 FL spectrometer (excitation wavelength = 350 nm).

### 2.3. Visible-light photocatalytic H<sub>2</sub> evolution test

Photocatalytic H<sub>2</sub> evolution by water splitting mainly reflects the photocatalytic reduction capability of photocatalysts. It was investigated in a sealable quartz vessel under simulated visible light (Fig. S1 in the Supporting Information). Typically, 0.1 g photocatalyst was dispersed in 90 mL deionized water and then sonicated for 10 min. Subsequently, 10 mL triethanolamine as sacrificial electron donor and 1 mL H<sub>2</sub>PtCl<sub>6</sub> aqueous solution were added to preset the mass ratio of Pt cocatalyst to photocatalyst at 3 wt%. Then, the vessel was purged for 15 min with high-purity N<sub>2</sub> and then sealed with a quartz cover equipped with a rubber stopper. Subsequently, it was irradiated vertically by a 300 W xenon lamp with a cut-off filter ( $\lambda > 420$  nm) at the fixed light-to-liquid distance (10 cm) to photo-reduce H<sub>2</sub>PtCl<sub>6</sub> into Pt co-catalyst. Afterwards, the vessel was thoroughly purged by N<sub>2</sub> again, sealed and irradiated under the same visible light for H<sub>2</sub> evolution. The reaction temperature was maintained at 10 °C by cyclical cooling water. 1 mL gas was sampled every 1 h and the H<sub>2</sub> content was analyzed by a gas chromatography (GC7900, Techcomp) equipped with 5A-zeolite column (3 m in length and 2.5 mm in diameter) and a thermal conductive detector (TCD). When analyzing H<sub>2</sub> content, high purity N<sub>2</sub> was used as carrier gas, and the column and TCD temperatures were set at 50 °C and 150 °C, respectively. After 4 h of reaction, the vessel was purged by N<sub>2</sub> and a new cycle was performed under the same conditions, repeating for three times.

## 3. Results and discussion

The crystalline composition of samples was investigated by XRD firstly. XRD reflections at 12.37°, 20.32°, 24.87°, 38.44° and 62.32° (Fig. 1a, sample KA) correspond to the (001), (020), (002), (003) and (060) lattice planes of kaolinite, respectively (Dong et al. 2018). The reflections of kaolinite are not observed in MK/CN-70.4% and MK (Fig. 1a), implying that there is dehydroxylated amorphous metakaolin instead of crystalline kaolinite in composite (Sudagar et al. 2018; Li et al. 2018). This is also proved by the TG test (Fig. S2 in the supporting Information). Specifically, there is a weight loss of ~10% around 500 °C for the dehydroxylation of kaolinite, which is not observed for composites or MK. The XRD reflection of MK/CN-70.4% accords well with that of bulk-CN (Fig. 2a), indicating the existence of g-C<sub>3</sub>N<sub>4</sub> in the composite. The diffraction peaks at 12.9° and 27.6° stem from the in-plane repeating tri-s-triazine units ((100) plane reflection) and interplanar stacking reflection of aromatic systems ((002) plane reflection) of g-C<sub>3</sub>N<sub>4</sub>, respectively (Zhao et al. 2017). When altering the g-C<sub>3</sub>N<sub>4</sub> content of the composite, the XRD reflection location hardly changes while the reflection intensity gradually grows as increased g-C<sub>3</sub>N<sub>4</sub> content (Fig. 1b). In short, the composites are composed of metakaolin

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