Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2018

#### **Support information**

# Combination of efficient charge-separation process with the assistance of novel dual Zscheme system: self-assembly photocatalyst of Ag@AgI/BiOI modified oxygen-doped carbon nitride nanosheet with enhanced photocatalytic performance

# Chao Liang,<sup>a</sup> Cheng-Gang Niu, <sup>a\*</sup> Hai Guo, Da-Wei Huang,<sup>b</sup> Xiao-Ju Wen,<sup>a</sup> Shi-Feng Yang<sup>a</sup> and Guang-Ming Zeng<sup>a\*</sup>

a College of Environmental Science Engineering, Key Laboratory of Environmental Biology Pollution Control, Ministry of Education, Hunan University, Changsha 410082, China

b South China Institute of Environmental Sciences, Ministry of Environmental Protection of

PRC, Guangzhou 510655, China

\*Corresponding Author: Cheng-Gang Niu; E-

mail address: cgniu@hnu.edu.cn, cgniu@hotmail.com; Guang-Ming Zeng; E-mail address: zgming@hnu.edu.cn

# 1. Fabrication mechanism of oxygen-doped ultrathin micropore g-C<sub>3</sub>N<sub>4</sub> material

The oxygen-doping micropore ultrathin nanosheet  $g-C_3N_4$  material was obtained through modified nitric acid-assisted hydrothermal method and calcination procedure. As is well known, the  $g-C_3N_4$  exhibited high chemical and thermodynamic stability owing to the melon units with tri-s-triazine structures.<sup>1, 2</sup> The melon structures staked together with hydrogen bonds in terms of strand nitrogen atoms and NH/NH<sub>2</sub> groups. Also, the melon units own a large amount of active sites acting as proton acceptors, demonstrating that the protonation and depolymerization reactions can be formed with assistance of some strong oxidants, such as KMnO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>.<sup>1, 3</sup> After complete removal of strong oxidants, the repolymerize reaction can be reestablished. In our work, we chose HNO<sub>3</sub> as the strong oxidant contributed to the strong oxidization ability of  $NO_3^-$  and large amount of protons in the nitric acid. The protons can easily insert into the layer structure of g-C<sub>3</sub>N<sub>4</sub>, and further immobilizing to the strand nitrogen atoms. Additionally, the hydrothermal procedure can accelerate the depolymerization as well as exfoliation reaction and form numerous micropores on the surface of g-C<sub>3</sub>N<sub>4</sub> with nitric acid assistance. Through calcination treatment at high temperature, the nitric acid was completely removed and the unique structure was formed. Interestingly, the oxygen atoms were doped into melon structures possibly owing to the strong oxidation ability.



Fig. S1 Nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution plots (inset) for (a) CN, (b) CN-500, (c) CN-520 and (d) CNH-500 composites



Fig. S2 (a) The XRD patterns; (b) The enlarge view of Ag(111) peak; (c) The survey of XPS spectra; (d) Ag 3d; (e) DRS spectra for the fresh and used CBI composites



Fig. S3 (a) Photoluminescense spectra of CNH-520, CB, BiOI/AgI and CBI composites, (b) the fresh and used CBI composites



Fig. S4 The ESR spectra of hydroxyl radicals trapped by DMPO under dark and visible light illumination



Fig. S5 TOC removal ratio of TC over CBI composite under visible light irradiation



Fig. S6 Elements mapping images of CBI composite: (a) Bi, (b) O, (c) C, (d) N, (e) Ag, (f) I



Fig. S7 XPS spectra of CB composite: (a) survey, (b) O 1s, (c) Bi 4f, (d) C 1s, (e) N 1s and (f) I 3d



Fig. S8 The trapping experiments for degradation of TC molecules over BiOI composite

#### 2. Photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> material

The photocatalytic activities of g-C<sub>3</sub>N<sub>4</sub> materials were first evaluated by dyes degradation under visible light irradiation ( $\lambda > 420$  nm). Fig. S9a presented the variation of RhB concentration with irradiation time increasing over different catalysts. The blank experiment confirmed that the photolysis of RhB molecules could be neglected under the identical condition. It could be observed that the photocatalytic performance of CNH-520 was the highest among all the catalysts. The RhB molecules could be decomposed completely only in 10 min of visible light time. Remarkably, about 44.9 % of RhB could be decomposed over the bulk CN catalyst after illumination for 25 min. The orders of degradation efficiency for all the catalysts could be listed as follows: CNH-520 > CNH-500 > CN-520 > CN-500 > CN. Additionally, it was clear that the adsorption ability of CNH-520 was stronger than that of other catalysts, which was possibly closely related to the relatively high surface area. The large surface area means more active species and reactants could be absorbed on the surface of catalyst, which was favorable for the photocatalytic activity. The results of adsorption test were well identical with BET analysis. Also, similar phenomenon could be observed in degradation of MB molecules in Fig. S9b.

The photocatalytic activities of as-synthesized g-C<sub>3</sub>N<sub>4</sub> samples were also investigated by control experiments of Cr(VI) solution reduction under visible light irradiation. As shown in Fig. S9c, nearly no obvious changes of Cr(VI) concentration in the absence of catalyst and EDTA-Na<sub>2</sub>. Noting that the hole scavenger make great contribution to the reduction of Cr(VI) solution. The CNH-520 composite exhibited poor photocatalytic performance in the absence of EDTA-Na<sub>2</sub>. However, the photoreduction process could be great accelerated with the increase in mount of EDTA-Na<sub>2</sub>, which was due to the reaction between holes and EDTA-Na<sub>2</sub>, suppressing the recombination of photoinduced electron-hole pairs. The control experiments showed that the addition amount of 10 mmol L<sup>-1</sup> was the most suitable, where the reduction ratio could reach to 98.6 %. Therefore, the following reduction experiments were carried out under the condition that the adding amount of EDTA-Na<sub>2</sub> was 10 mmol L<sup>-1</sup>. Also, the temporal concentration of Cr(VI) variation at different irradiation time was shown in Fig. S9e. As shown in Fig. S9d, among all the g-C<sub>3</sub>N<sub>4</sub> materials, CNH-520 exhibited the highest photocatalytic activity. While for other samples, the reduction efficiencies were 17.5 %, 23.6 %, 37.4 % and 80 % for CN, CN-500, CN-520 and CNH-500 composites, respectively.

The influence of pH value on the Cr(VI) reduction over CNH-520 composite were exhibited in Fig. S9f. It was clear that the reduction ratio was greatly improved along with the pH value decreasing, which was identical with other previous reports. Under lower pH condition, the  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  anions were the two main forms, and the reduction process could be described as following equation (1) and (2). Hence the reduction process could be accelerated due to the presence of a large amount of H<sup>+</sup>. Nevertheless, in alkaline condition, the reduced Cr(III) could combine with OH<sup>-</sup> to form Cr(OH)<sub>3</sub>, which would block the active sites of the catalyst, lowing the reduction efficiency.

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$
 (1)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
 (2)

In a summary, the enhanced photocatalytic performance of CNH-520 composite would be contributed to the unique structure and oxygen atoms doping. Firstly, the oxygen atoms doping into the melon units extend the wide spectrum absorption in above 460 nm regions, inhibiting the recombination of photo-induced electron-hole pairs. Additionally, the micropores are favorable for more light absorption owing to the synergistic effect of large surface area and multiple-reflection effect. Furthermore, the large surface area means more active sites for adsorption and degradation of organic pollutants.



Fig. S9 The photodegradation of (a) RhB, (b) MB and (d) Cr(VI) as a function of irradiation time over different g-C<sub>3</sub>N<sub>4</sub> materials under visible light irradiation; The effects of (c) EDTA-

 $Na_2$  and (f) pH for Cr(VI) photoreduction over CNH-520 composite; (e) The UV-vis absorption spectral changes at given time intervals over CNH-520 composite

# Table S1

Band gap energy (Eg), conduction band ( $E_{CB}$ ) and valence band ( $E_{VB}$ ) potentials of assynthesized composites.

Samples	Eg (eV)	E <sub>CB</sub>	$E_{VB}$
CNH-520	2.79	-1.18	1.61
BiOI	1.73	0.58	2.32
AgI	2.80	-0.55	2.25

#### Table S2

Surface area, pore size and total pore volume for a series of pristine g-C<sub>3</sub>N<sub>4</sub>, CB and CBI composites

Catalyst	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore width (nm)	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )
CN	12.25	7.79	0.02
CN-500	17.49	13.76	0.06
CN-520	36.87	11.55	0.11
CNH-500	137.58	10.63	0.36
CNH-520	160.01	9.48	0.38
CB	70.89	11.04	0.20
CBI	55.57	9.81	0.13

#### Table S3

The zeta potentials of CBI composite in different pH solution

рН	2	5	6.85	9	11
ξ-potential(mV)	-16.8	-21.9	-30.8	-39.8	-46.4

### Table S4

The inorganic ions concentration in 50 mL TC solution containing NaCl, Na<sub>2</sub>SO<sub>4</sub>, KBr and Na<sub>2</sub>S chemicals

Chemicals	Dose	Na <sup>+</sup>	Cl-	SO4 <sup>2-</sup>	$K^+$	Br−	S <sup>2–</sup>
	(mmol)	(mmol L <sup>-1</sup> )					
NaCl	0.1	2	2				
$Na_2SO_4$	0.05	2		1			
KBr	0.1				2	2	
Na <sub>2</sub> S	0.05	2					1

#### Reference

- 1. L. Ma, H. Fan, K. Fu, S. Lei, Q. Hu, H. Huang and G. He, *ACS Sustainable Chem. Eng.*, 2017, **5**, 7093-7103.
- J. Zhang, M. Zhang, L. Lin and X. Wang, Angew. Chem.Int. Edit., 2015, 54, 6297-6301.
- X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, 8, 76-80.