

Supporting Information

For

Nanostructured g-C₃N₄/AgI composites assembled by AgI nanoparticles-decorated g-C₃N₄ nanosheets for effective and mild photooxidation reaction

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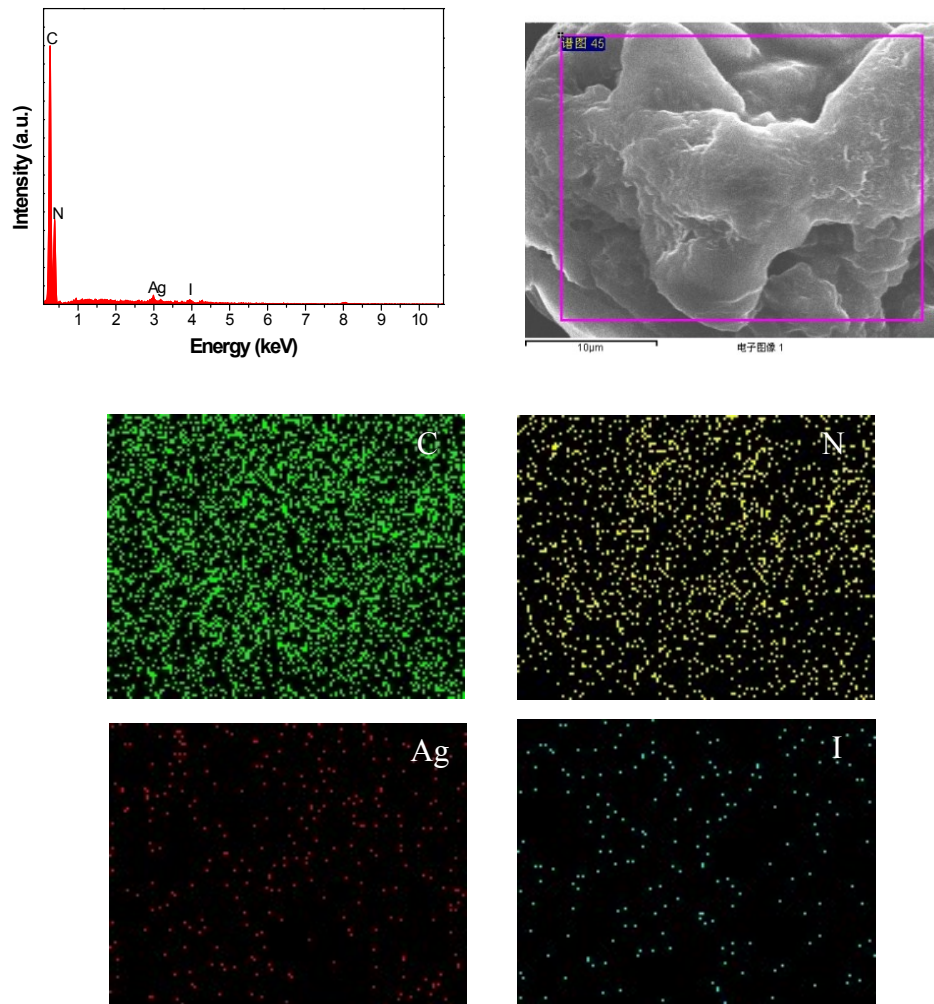


Fig. S1 The EDS spectrum of the g-C₃N₄/AgI-30% composite and the corresponding EDS elemental mapping of C, N, Ag and I.

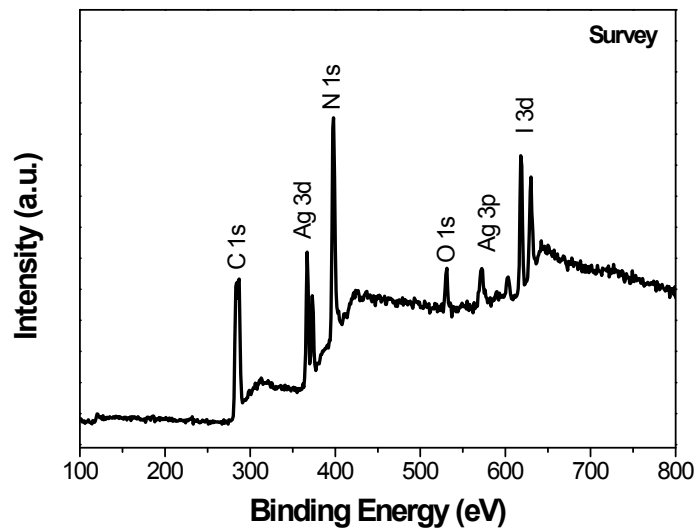


Fig. S2 The survey XPS spectrum of the g-C₃N₄/AgI -30% composite sample.

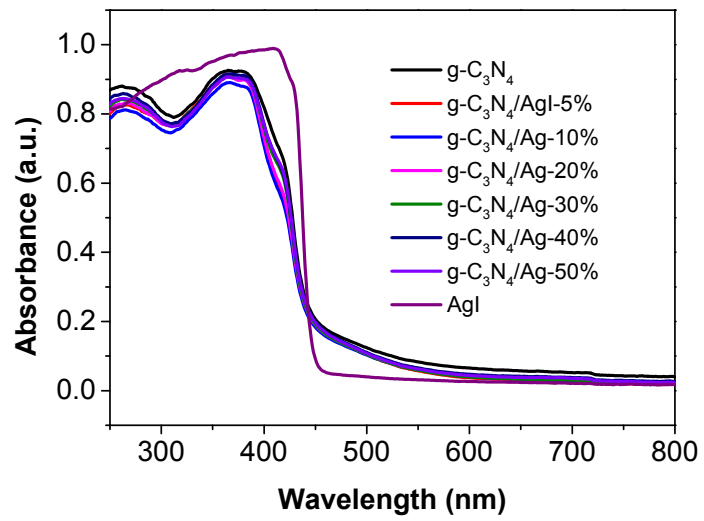


Fig. S3 The UV-visible diffuse reflectance spectra of g-C₃N₄, AgI and their composite samples.

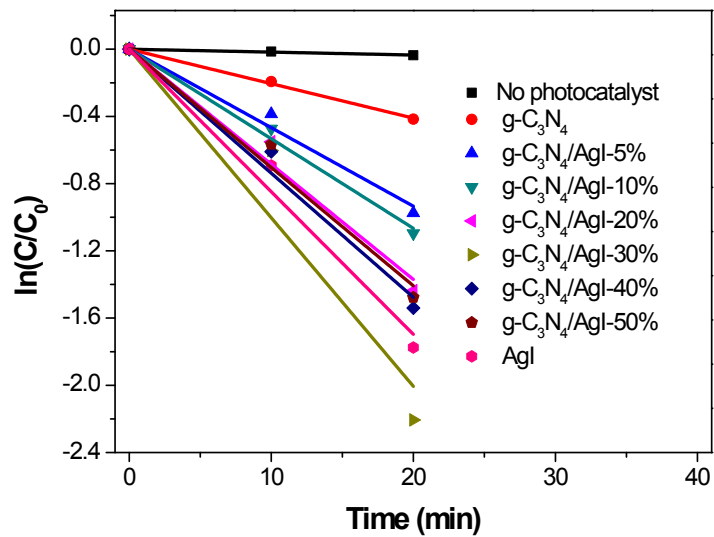


Fig. S4 Linear kinetics simulation of the photocatalytic performance of g-C₃N₄/AgI composites for the calculation of pseudo-first-order rate constant

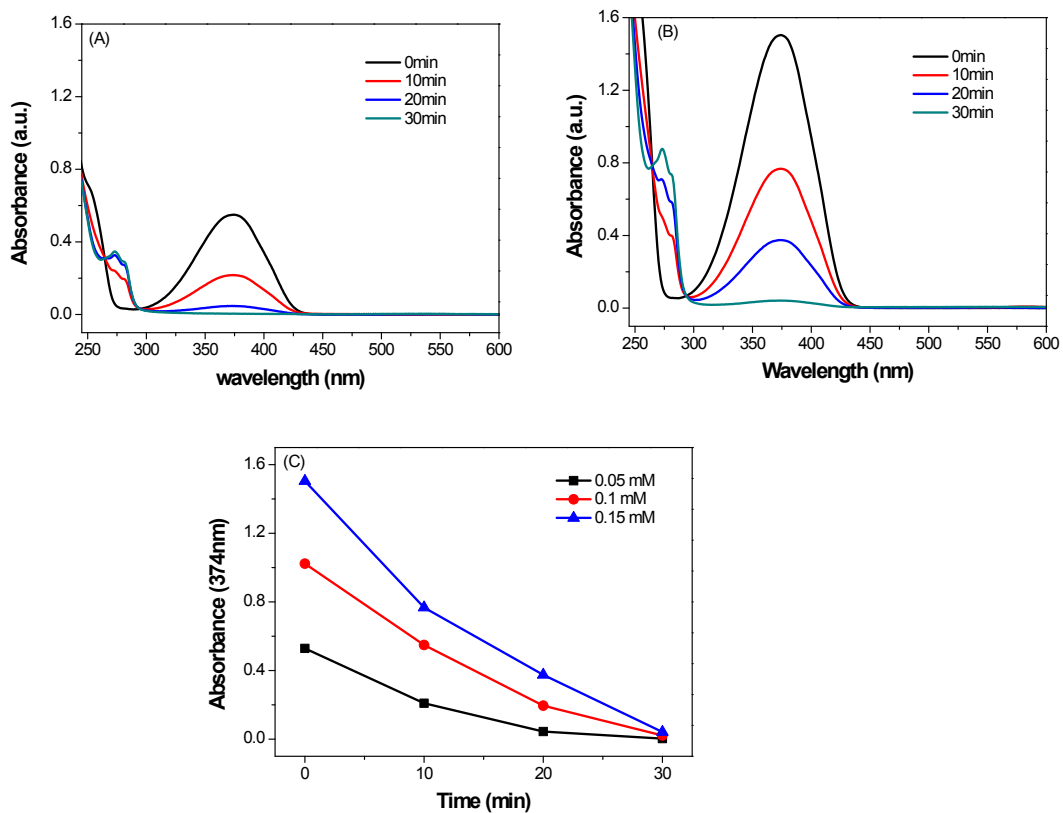


Fig. S5 The UV-visible spectral changes of different concentration of 1,4-DHP. (A) 0.05 mM, (B) 0.15 mM. (C) The absorbance (374 nm) changes of 1,4-DHP with different initial concentrations (0.05, 0.1 and 0.15 mM).

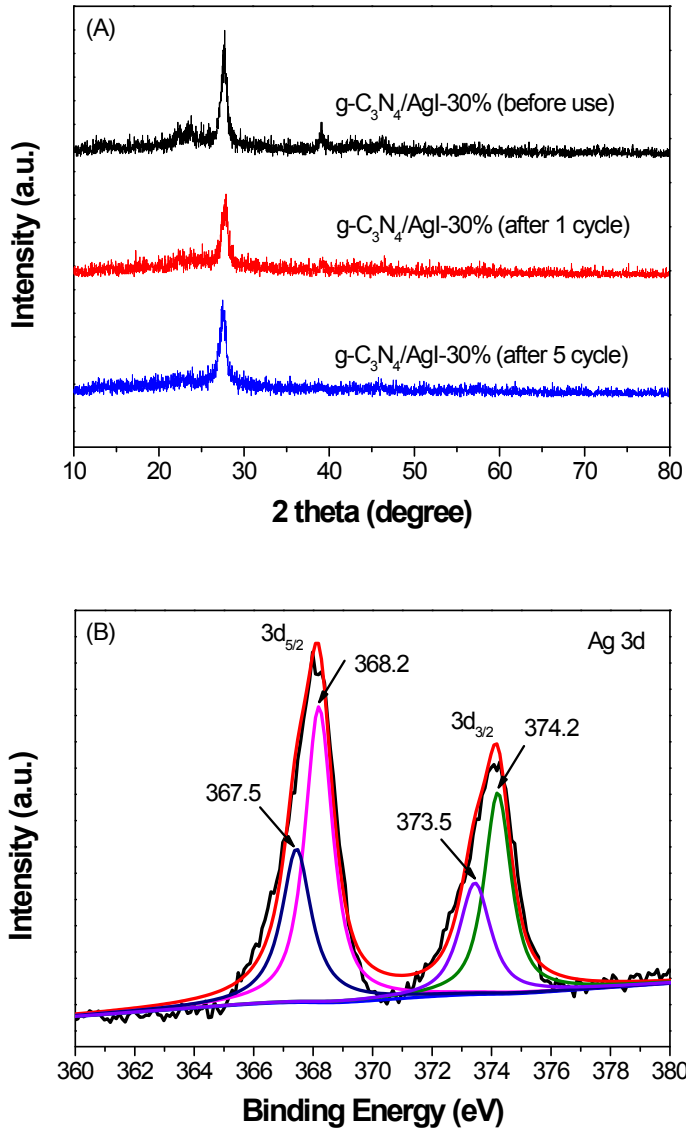


Fig. S6 The XRD patterns (A) and Ag 3d XPS spectrum of g-C₃N₄/AgI-30% sample after repeated use under visible light irradiation.

The raw peak of Ag 3d_{5/2} can be further divided into two peaks at 367.5 and 368.2 eV, and the peak of Ag 3d_{3/2} can be further divided into 373.5 and 374.2 eV. The peaks appear at binding energy of 367.5 and 373.5 eV belongs to the monovalent silver (Ag⁺) in AgI. While the peaks with a binding energy of 368.2 and 374.2 eV were attributed to zero valent silver (Ag⁰) of metallic silver [1,2]

Estimation of the VB and CB of AgI and g-C₃N₄

The valence band (VB) and conduction band (CB) potential of a semiconductor can be theoretically calculated using Mulliken electronegativity and the bandgap of a semiconductor by the the following formulas [3]:

$$E_{VB} = X - E_e + 0.5E_g$$

$$E_{CB} = E_{VB} - E_g$$

where E_{VB} and E_{CB} are the top of the valence band and the bottom of the conduction band of the semiconductor, E_g is the band gap energy, E_e is the energy of free electrons on the hydrogen scale with a fixed value of 4.5 eV vs. NHE [3,4], and X is the geometric mean of the Mulliken electronegativity of the constituent atoms in the semiconductor. The Mulliken electronegativity of an atom is the arithmetic mean of the first ionization energy and the first electron affinity.

The detailed calculation steps for obtaining the Valence band and Conduction band of AgI was illustrated as follows:

The first ionization energy of silver element (Ag): $I_1 = 731.0 \text{ kJ}\cdot\text{mol}^{-1}$,

The first electron affinity of silver element (Ag): $E_1 = 125.62 \text{ kJ}\cdot\text{mol}^{-1}$,

The Mulliken electronegativity of silver element (Ag):

$$\chi = \frac{1}{2} (I_1 + E_1) = \frac{1}{2} (731.0 + 125.62) = 428.31 \text{ kJ}\cdot\text{mol}^{-1}.$$

Because: $1 \text{ eV} = 1.6022 \times 10^{-19} \text{ C} \times 1 \text{ V} = 1.6022 \times 10^{-19} \text{ J}$.

And the Avogadro constant (N_A) = $6.022 \times 10^{23} \text{ mol}^{-1}$.

Thus, the Mulliken electronegativity of a silver atom (Ag) can be calculated as follows:

$$\begin{aligned} \chi_{Ag} &= 428.31 \times 10^3 \text{ J}\cdot\text{mol}^{-1} \div (6.022 \times 10^{23} \text{ mol}^{-1}) \div (1.6022 \times 10^{-19} \text{ J}) \\ &= 4.439 \text{ eV}. \end{aligned}$$

For iodine (I): $I_1 = 1008.4 \text{ kJ}\cdot\text{mol}^{-1}$, $E_1 = 295.15 \text{ kJ}\cdot\text{mol}^{-1}$,

$$\chi = \frac{1}{2} (I_1 + E_1) = \frac{1}{2} (1008.4 + 295.15) = 651.78 \text{ kJ}\cdot\text{mol}^{-1}.$$

Thus, the Mulliken electronegativity of an iodine atom (I) is calculated as follows:

$$\chi_I = 651.78 \times 10^3 \text{ J}\cdot\text{mol}^{-1} \div (6.022 \times 10^{23} \text{ mol}^{-1}) \div (1.6022 \times 10^{-19} \text{ J})$$

$$= 6.755 \text{ eV}$$

The geometric mean of the Mulliken electronegativity for AgI (X) is calculated as follows:

$$X = \sqrt{\chi_{\text{Ag}} \times \chi_{\text{I}}} = \sqrt{4.439 \times 6.755} = 5.48 \text{ eV}$$

The bandgap (E_g) of AgI was obtained by the UV-visible diffuse reflectance measurement, and was determined to be 2.73 eV (Fig. 4B), i.e., $E_g(\text{AgI}) = 2.73 \text{ eV}$.

Therefore, The Valence band of AgI is calculated as follows:

$$\begin{aligned} E_{\text{VB}} &= X - E_c + 0.5E_g \\ &= 5.48 - 4.5 + 0.5 \times 2.73 \\ &= 2.35 \text{ eV} \end{aligned}$$

The conduction band of AgI is calculated as follows:

$$\begin{aligned} E_{\text{CB}} &= E_{\text{VB}} - E_g \\ &= 2.35 - 2.73 \\ &= -0.38 \text{ eV} \end{aligned}$$

The Valence band and Conduction band of g-C₃N₄ can be obtained with the similar method as that of AgI. The E_{VB} and E_{CB} of g-C₃N₄ were determined to be 1.56 and -1.09 eV, respectively [4,5].

References

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- [4] B. Lin, G. Yang, B. Yang, Y. Zhao, Construction of novel three dimensionally ordered macroporous carbon nitride for highly efficient photocatalytic activity, *Appl. Catal. B*, 198 (2016) 276-285.
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