Supporting Information: Photocatalytic reduction of aqueous nitrate with hybrid Ag/g-C₃N₄ under UV and visible light

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Materials:

Urea (Sigma-Aldrich, > 98%), NaNO₃ (Sigma-Aldrich, >99%), Methanol (Fisher chemical, HPLC grade, 0.2 micron filtered), and Silver nitrate (Alfa Division, 99.9 %) were used as supplied.

g-C₃N₄ Preparation:

We adopted previously reported methods for the synthesis of g-C₃N₄.¹ In brief, 10 g of ground urea was placed in a ceramic crucible and heated in a tube furnace under ambient atmosphere. The furnace was held at 550 °C for 3 hours after heating with a ramp rate of 5 °C/min. After the furnace cooled to room temperature, the yellow-colored products were collected and ground into a fine powder.

Ag/g-C₃N₄ Preparation:

Silver metal nanoparticle were deposited onto g-C₃N₄ by photoreduction.² ³ 50 mg of the above-synthesized g-C₃N₄ was dispersed into 50 mL of millipore water (18.2 MΩ) in a 100 mL round bottom flask. The suspension was ultrasonically treated for 3 hrs. Then, depending on the desired silver loading, 5, 10, 46.2, or 92.4 mg of AgNO₃ and 5 mL methanol were added to the suspension. The reported mass percentage of silver for the hybrid Ag/g-C₃N₄ were calculated based on these initial amounts. After an additional 15 min sonication, the flask was sealed with a rubber septum and purged with N₂ gas for one hour. The mixture was then irradiated with UV light in a photoreactor for two hours while continually stirring. The reaction mixture was centrifuged at 3900 rpm for 8 minutes and the precipitated Ag/g-C₃N₄ washed four times with Millipore water (18.2 MΩ) and once with methanol. Finally, the washed samples were dispersed in methanol, the
methanol was evaporated, and the remaining Ag/g-C₃N₄ powder was dried in an oven at 60 °C overnight.

**Nitrogen analysis**

For PNR studies, an aliquot of the sample (~ 2mL) was withdrawn from the reactor using a 5 mL glass syringe at regular sampling intervals. The aliquot was immediately transferred into a microcentrifuge tube and centrifuged at 15,000 rpm for 3 minutes to separate the catalyst. A 1.0 mL aliquot of the supernatant (sample) in the centrifuge tube was collected and diluted by adding 5.0 mL of millipore water. Concentrations of NO₃⁻ and NO₂⁻ were determined using a flow injector analysis LACHAT instrument (QuikChem 8500), and NH₄⁺ concentration was determined via Timberline Instruments TL-2800 Ammonia Analyzer. Gas analysis was performed by gas chromatography (GC) using an Agilent Technology 6850A GC system equipped with a Supelco 10 ft x 1/8 in Carbosieve S-II stainless steel packed column with Ar as the carrier gas.

**Sample preparation for optical study**

Approximately, 4 mg of photocatalyst sample (g-C₃N₄ or Ag/ g-C₃N₄) was transferred into ~5 mL millipore water and the mixture was sonicated for 3 hours. After sonication, the mixture was centrifuged at 3500 rpm for 3 minutes and the supernatant collected. This process was repeated three additional times (until there was no visible precipitate). The transparent supernatant was collected and diluted to the desired optical density.
Figure S1. UV Vis. absorption spectra of g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$. Spectra were obtained immediately after 5 minutes of ultrasonication of 1 g/L of each catalysis solution, using a 2 mm cuvette. The solution contains 16.67% v/v methanol as it is used in the actual photocatalysis study (10 mL MQ water + 2 mL Methanol. As can be inferred from the variable amounts of scattering observable at wavelengths longer than 500 nm, sample to sample variability in particle size prevents formation of uniform suspensions of the reaction mixture despite identical preparation (sonication, centrifugation) methods.

Instrumentation

Transmission Electron Microscopy (TEM) images were obtained using a FEI/Philips CM 200 with a LaB6 filament operating at 200 kV. Powder X-ray Diffraction (PXRD) was performed with SCINTAG X1 with Cu Kα radiation. The Jade 9.0 software package was used for XRD data analysis. X-ray photoelectron spectroscopy data was collected by Physical Electronics 5600 using an Al Kα source (1486.6 eV). UV-vis absorption spectra of the dispersed samples were measured with a Shimadzu UV-3101PC in a 1 cm cuvette. A Horiba Fluorolog-3 was used to measure photoluminescence spectra ($\lambda_{ex}$ = 310 nm) of the water-dispersed samples.
**Figure S2.** TEM images of (a) 58.4% Ag/g-C₃N₄ and (b) 117.5% Ag/g-C₃N₄

**Figure S3.** Size distribution of Ag nanoparticles of (a) 6.4% Ag/g-C₃N₄, (b) 12.7% Ag/g-C₃N₄, and (c) 58.4% Ag/g-C₃N₄

**XRD** Powder X-ray diffraction (XRD) patterns of g-C₃N₄ and the hybrid Ag/g-C₃N₄ materials are shown in **Fig. S4**. The diffraction pattern of g-C₃N₄ shows the presence of two characteristic peaks. The weak diffraction peak at 13.1° and the stronger peak at 27.3° are associated with (100) and the interlayer (002) planes, respectively.⁴,⁵ In the hybrid materials, the XRD data reveal the presence of both g-C₃N₄ and face-centered cubic (fcc) silver. The additional peaks at 38.1°, 44.3°, 64.4°, 77.4°, and 81.5° in the diffraction pattern from Ag/g-C₃N₄ are attributed to the (111), (200), (220), (311), and (222) planes of fcc metallic silver nanoparticles, respectively (JCPD-04-0783).
Note that on average, as the mass percentage of silver is increased, the (111) peak narrows, consistent with TEM images that show nanoparticle size increasing at higher loadings.

Figure S4. PXRD patterns of g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$

**XPS** Chemical composition and chemical states of g-C$_3$N$_4$ and Ag/ g-C$_3$N$_4$ were characterized using X-ray photoelectron spectroscopy (XPS). Figure S5(a) shows survey spectra of the g-C$_3$N$_4$ and different mass loaded Ag/g-C$_3$N$_4$ samples which indicate that pristine g-C$_3$N$_4$ and hybrid Ag/ g-C$_3$N$_4$ consists primarily of C, N, and a small amount of O elements while Ag/ g-C$_3$N$_4$ contains Ag in addition to the other elements. The presence of oxygen in both materials is likely due to surface adsorption and partial oxidation of silver nanoparticles into Ag$_2$O.$^{1,6}$
Figure S5. XPS survey spectra of g-C₃N₄ and Ag/g-C₃N₄ (a) and high-resolution spectra of C 1s (b), N 1s (c), and Ag 3d (d)

As shown in Fig. S5b, the high-resolution XPS spectrum of C 1s of g-C₃N₄ and 12.7% Ag/g-C₃N₄ consist of two distinct peaks at 284.6 eV and 288.0 eV which characterize the graphitic carbon C—C coordination of the surface adventitious carbon and sp² hybridized carbon in N = C—N in graphitic carbon nitride ring respectively.6-9 Figure S5c displays a high-resolution N 1s spectrum of g-C₃N₄ and 12.7 % Ag/g-C₃N₄. Peaks at 398.6 eV, 400.1 eV, 401.2 eV, and 404.2 eV correspond to sp² hybridized nitrogen in C—N = C, sp³ hybridized nitrogen in N—(C)₃, nitrogen in C—NH₂ (amino functional groups with hydrogen), and positive charge localization in the heterocycle respectively.7,8,10-16 Figure S5d shows the high resolution Ag 3d XPS spectrum of the 12.7% Ag/g-C₃N₄ sample, which can be fit with four peaks. The peaks at 368.2 eV and 374.2 eV can be assigned to Ag 3ds/2, and Ag 3d₃/₂ of Ag⁰ respectively, whereas the low amplitude peaks
at 366.1 eV and 372.1 eV likely arise from Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ of Ag$^+$. The presence of Ag$^+$ is likely due to trapped precursor Ag$^+$ ions or partially oxidized Ag nanoparticles as Ag$_2$O.

**Figure S6.** Emission spectra of both UV and LED lamps of the UV and Visible photocatalytic reactors.
**Table S1.** Raw data of nitrate reduction of pristine g-C₃N₄ and silver loaded g-C₃N₄ under UV light irradiation

| Catalyst      | Reactions | Time (hrs.) | NO₃⁻ (µmol N) | NO₂⁻ (µmol N) | NH₄⁺ (µmol N) | N₂ (µmol N) |
|---------------|-----------|-------------|----------------|----------------|----------------|-------------|
| g-C₃N₄        | 1         | 0           | 3.636          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 3.190          | 0.254          | 0.200          | 0.000       |
|               | 2         | 0           | 3.571          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 2.831          | 0.575          | 0.194          | 0.000       |
| 6.4%Ag/g-C₃N₄ | 1         | 0           | 3.987          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.349          | 2.706          | 0.119          | 0.813       |
|               | 2         | 0           | 3.758          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.188          | 2.463          | 0.045          | 1.062       |
| 12.7%Ag/g-C₃N₄| 1         | 0           | 3.684          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.000          | 1.721          | 0.942          | 1.021       |
|               | 2         | 0           | 3.447          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.005          | 1.915          | 0.716          | 0.811       |
| 58.4%Ag/g-C₃N₄| 1         | 0           | 4.360          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.492          | 2.945          | 0.622          | 0.301       |
|               | 2         | 0           | 4.192          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 1.348          | 2.113          | 0.408          | 0.324       |
| 117.5%Ag/g-C₃N₄| 1        | 0           | 4.104          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.107          | 2.072          | 1.179          | 0.747       |
|               | 2         | 0           | 4.150          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.219          | 2.481          | 0.913          | 0.536       |

**Table S2.** Raw data of nitrate reduction of pristine g-C₃N₄ and 12.7% silver loaded g-C₃N₄ under visible light irradiation

| Catalyst      | Reactions | Time (hrs.) | NO₃⁻ (µmol N) | NO₂⁻ (µmol N) | NH₄⁺ (µmol N) | N₂ (µmol N) |
|---------------|-----------|-------------|----------------|----------------|----------------|-------------|
| g-C₃N₄        | 1         | 0           | 3.637          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 3.637          | 0.000          | 0.000          | 0.000       |
| 12.7%Ag/g-C₃N₄| 1         | 0           | 3.331          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.056          | 2.328          | 0.363          | 0.584       |
|               | 2         | 0           | 3.246          | 0.000          | 0.000          | 0.000       |
|               |           | 8           | 0.000          | 2.694          | 0.227          | 0.326       |
Table S3. Raw data for the kinetic study of nitrate reduction of 12.7% silver loaded g-C₃N₄ under UV light irradiation

| Catalyst       | Reactions | Time (Min.) | NO₃⁻ (µmol N) | NO₂⁻ (µmol N) | NH₄⁺ (µmol N) | N₂ (µmol N) |
|----------------|-----------|-------------|----------------|----------------|---------------|--------------|
| 12.7%Ag/g-C₃N₄| 1         | 0           | 3.684          | 0.000          | 0.000         | 0.000        |
|                |           | 120         | 0.000          | 3.163          | 0.530         | 0.000        |
|                |           | 240         | 0.065          | 2.493          | 0.673         | 0.455        |
|                |           | 360         | 0.034          | 1.917          | 0.954         | 0.779        |
|                |           | 480         | 0.000          | 1.721          | 0.942         | 1.021        |
|                | 2         | 0           | 3.447          | 0.000          | 0.000         | 0.000        |
|                |           | 120         | 0.004          | 2.689          | 0.087         | 0.668        |
|                |           | 240         | 0.000          | 2.849          | 0.316         | 0.282        |
|                |           | 360         | 0.000          | 2.366          | 0.375         | 0.707        |
|                |           | 480         | 0.005          | 1.915          | 0.716         | 0.811        |
|                | 3         | 0           | 3.351          | 0.000          | 0.000         | 0.000        |
|                |           | 15          | 3.162          | 0.421          | 0.000         | 0.000        |
|                |           | 30          | 2.322          | 1.073          | 0.000         | 0.000        |
|                |           | 60          | 1.110          | 2.049          | 0.000         | 0.191        |
|                |           | 90          | 0.310          | 2.665          | 0.141         | 0.235        |
|                |           | 120         | 0.018          | 2.689          | 0.255         | 0.390        |

Table S4. Raw data for the kinetic study of nitrate reduction of 12.7% silver loaded g-C₃N₄ under visible light irradiation

| Catalyst       | Reactions | Time (Min.) | NO₃⁻ (µmol N) | NO₂⁻ (µmol N) | NH₄⁺ (µmol N) | N₂ (µmol N) |
|----------------|-----------|-------------|----------------|----------------|---------------|--------------|
| 12.7%Ag/g-C₃N₄| 1         | 0           | 3.331          | 0.000          | 0.000         | 0.000        |
|                |           | 120         | 0.797          | 2.568          | 0.000         | 0.000        |
|                |           | 240         | 0.127          | 3.105          | 0.000         | 0.099        |
|                |           | 360         | 0.000          | 2.844          | 0.191         | 0.296        |
|                |           | 480         | 0.056          | 2.328          | 0.363         | 0.584        |
|                | 2         | 0           | 3.246          | 0.000          | 0.000         | 0.000        |
|                |           | 120         | 2.254          | 1.071          | 0.000         | 0.000        |
|                |           | 240         | 1.022          | 2.137          | 0.000         | 0.088        |
|                |           | 360         | 0.350          | 2.640          | 0.049         | 0.207        |
|                |           | 480         | 0.000          | 2.694          | 0.227         | 0.326        |

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