

Supplementary Information

Enhanced photocatalytic reduction of Cr(VI) to Cr(III) over g-C₃N₄ catalysts with Ag nanoclusters in conjunction with Cr(III) quantification based on operando low-field NMR relaxometry

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1. Experimental section

1.1 Chemicals

Urea ($\text{CH}_4\text{N}_2\text{O}$, 98%), mercaptosuccinic acid (H_2MSA , 98%), N-(2-mercaptopropionyl) glycine (MPGH, 98%), silver nitrate (AgNO_3 , 99%), diphenylcarbazide (DPC, 98%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99%), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 99%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, AR grade, 95%) were purchased from Shanghai Civi Chemical Technology Co., Ltd., China. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 99%), sodium hydroxide (NaOH , 96%), and sodium borohydride (NaBH_4 , 99%) was obtained from Sigma-Aldrich. All chemical reagents in this experiment are analytical and were used without further purification. Deionized water was used throughout the experiments.

1.2 Synthesis of pristine g-CN

We prepared g-CN powders according to a previously reported protocol ¹. Here, 10 g of urea powder was placed in a 50 mL closed ceramic crucible and then heated to 550°C at a ramp rate of $10^\circ\text{C}/\text{min}$ in a muffle furnace for 2 h in air.

1.3 Synthesis of Ag NPs, Ag(I)MSA, $\text{Ag}_9(\text{H}_2\text{MSA})_7$ NCs, and $\text{Ag}_{32}(\text{MPG})_{19}$ NCs

We prepared $\text{Ag}_9(\text{H}_2\text{MSA})_7$ and $\text{Ag}_{32}(\text{MPG})_{19}$ NCs via a previously reported solid-state synthesis route ^{2,3}. For $\text{Ag}_9(\text{H}_2\text{MSA})_7$ NCs, AgNO_3 (47 mg) was added to H_2MSA (187 mg), and the mixture was ground thoroughly in a mortar until obtaining an orange powder. Then, NaBH_4 (50 mg) was added and milling was continued until a brown powder was obtained. Deionized water was subsequently added dropwise (~ 15 mL) to the mixture to form a reddish brown solution. The solution was quickly added to excess ethanol to precipitate the NCs. The obtained precipitates were collected as powder by centrifugation, washed repeatedly with ethanol, and then dried. An equivalent synthetic procedure as that described above was employed for preparing $\text{Ag}_{32}(\text{MPG})_{19}$ NCs, except that the ligand and reagent doses were different. Here, the initial powder was formed by mixing AgNO_3 (47 mg) and MPGH (110 mg), followed by milling with NaOH (1.5 mg). Finally, NaBH_4 (25 mg) was added prior to the dropwise addition of deionized water (~ 10 mL). The Ag NPs were prepared by the chemical reduction method reported in the literature ⁴. Briefly, AgNO_3 (20 mL, 1 mmol) was mixed with $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (1.6 mL, 40 mmol) for 30 min under continuous stirring, and then, a freshly prepared solution of NaBH_4 (0.4 mL, 112 mmol) was added dropwise under vigorous stirring to obtain a yellowish-brown Ag hydrosol. The precipitates were collected by freeze-drying and used for further analysis. Ag(I)MSA was prepared according to the following procedure. AgNO_3 (47 mg) and H_2MSA (187 mg) were added

into NaOH solution (1 mL, 1.5 mol). The powder sample was obtained by freeze-drying.

1.4 Synthesis of AgNCs/g-CN

AgNCs/g-CN sample was prepared by an impregnation method.⁶ A mixture of a g-C₃N₄ powder and an aqueous solution of AgNO₃ was magnetically stirred and dried up, followed by calcination at 673 K for 2 h. The loading amounts of Ag were 0.1 wt%.

1.5 Material characterization

The powder XRD (PXRD) patterns of the samples were conducted on an X-ray diffractometer (Ultima IV) with Cu α radiation ($\lambda=1.54\text{\AA}$, 50kV, 40mA) to identify the crystal structure. The photoluminescence (PL) spectra were examined on a Hitachi F-4500 fluorescence spectrophotometer at an excitation wavelength of 360 nm. X-ray photoelectron spectroscopy (XPS) was performed using Thermo ESCALAB 250XI with a monochromatic Al α source operated at 150 W. All binding energies were calibrated by using the C 1s at 284.8 eV as an internal standard in this work. The morphology of the prepared catalysts was characterized by high-resolution transmission electron microscopy (HRTEM) using an FEI Tecnai G2 F20 microscope operated at the accelerating voltage of 200 kV. The UV-vis absorption spectra were carried out with a UV-vis spectrophotometer (UV-2700, Shimadzu) using BaSO₄ as a reflectance standard. The BET specific surface areas and porosity of the samples were estimated by a nitrogen adsorption-desorption method (Autosorb-iQ, Quantachrome). Before testing, all the samples were degassed at 120 °C for 12 h to remove adsorbed substances. The NMR experiments were acquired on 700 MHz Agilent NMR spectrometers at a magnetic field strength of 16.4 T to analyze the Ag NCs. The contents of Ag in the samples were determined by inductively coupled plasma optical emission spectrometer (ICP-OES).

1.6 Photocatalytic experiments

The photocatalytic activities of the as-prepared samples were evaluated by the reduction of aqueous Cr(VI) under the irradiation by the 300 W Xe lamp (Beijing Perfectlight Technology Co., China.) with a cut off filter ($\lambda>420$ nm). In detail, 20 mg of photocatalysts was suspended in 50 mL of 20 mg/L Cr(VI) solution (K₂Cr₂O₇) and 0.165 mL of 100 mg/mL citric acid as a sacrificial agent. The pH of the reaction solution was maintained at a constant 4.0 adjusted by adding 4 mol/L H₂SO₄. Prior to irradiation, the solutions were magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium between the photocatalysts and Cr(VI). During the visible light irradiation

treatment, about 1 mL aliquots were sampled from the reaction cell at given time intervals and then was extracted in the aid of the 0.45 μm PTFE membrane to remove the photocatalyst particles. The concentration of Cr(VI) was determined by a modified diphenylcarbazide (DPC) method with a UV-vis spectrophotometer at the maximum absorption wavelength at 540 nm for Cr(VI).

1.7 LF-NMR relaxometry measurements

The reaction solution containing 5 mg of a nanocomposite sample mixed with 1.5 mL of 20 mg/L $\text{K}_2\text{Cr}_2\text{O}_7$ and 5 μl of 100 mg/mL citric acid as a sacrificial agent was transferred to the NMR tube (20 mm in diameter and 100 mm in height). The pH of the reaction solution was maintained at a constant 4.0 adjusted by adding 4 mol/L H_2SO_4 . The solution temperature within the NMR tube was maintained at $32.0 \pm 0.1^\circ\text{C}$. The transverse relaxation time (T_2) measurements were conducted at 0.5 T (21.3 MHz for ^1H) in an NMI20-015V-I LF-NMR spectrometer (Shanghai Electronic Technology Co., Ltd. China) using a 15 mm diameter probe. The CPMG pulse sequence employed $\pi/2$ and π pulses of 7.4 and 14.64 μs , respectively, an echo time of 1 ms, recycle time of 8 s, 15000 echoes, and 4 scans. A 300 W Xe lamp without a cutoff filter ($\lambda > 420$ nm) was used as the light source during photocatalytic reduction testing of the nanocomposites. The light source beam was guided through a focusing lens device to converge on the entrance face of a custom made optical fiber bundle composed of seven quartz fibers with diameters of 3 mm. Then, the optical fiber bundle was introduced into the inside of the NMR tube. Prior to irradiation, the mixed solution was stabilized in the NMR tube for 10 min while obtaining a T_2 value every 5 min. The solution was then subject to irradiation for 60 min, and T_2 values were obtained at regular time intervals.

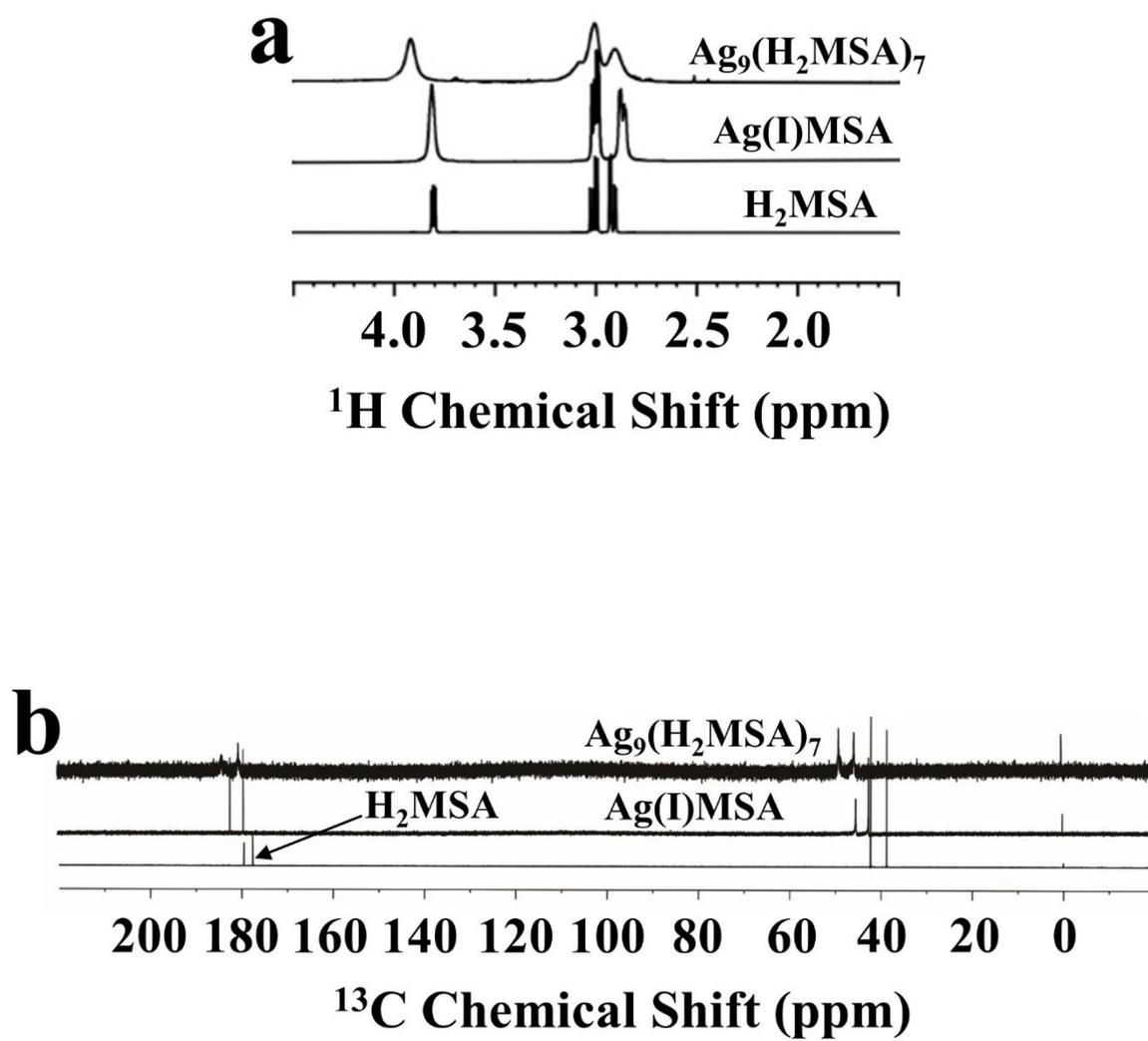


Figure S1. (a) ^1H and (b) ^{13}C NMR spectra of $\text{Ag}_9(\text{H}_2\text{MSA})_7$, H_2MSA , and $\text{Ag}(\text{I})\text{HMSA}$.

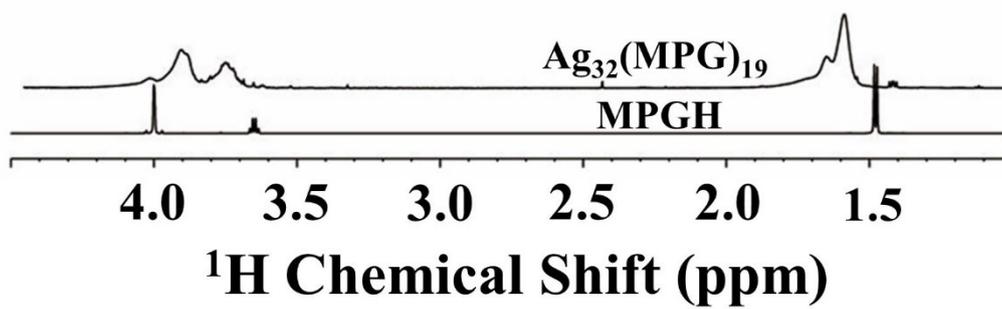


Figure S2. ^1H NMR spectra of $\text{Ag}_{32}(\text{MPG})_{19}$ and MPGH.

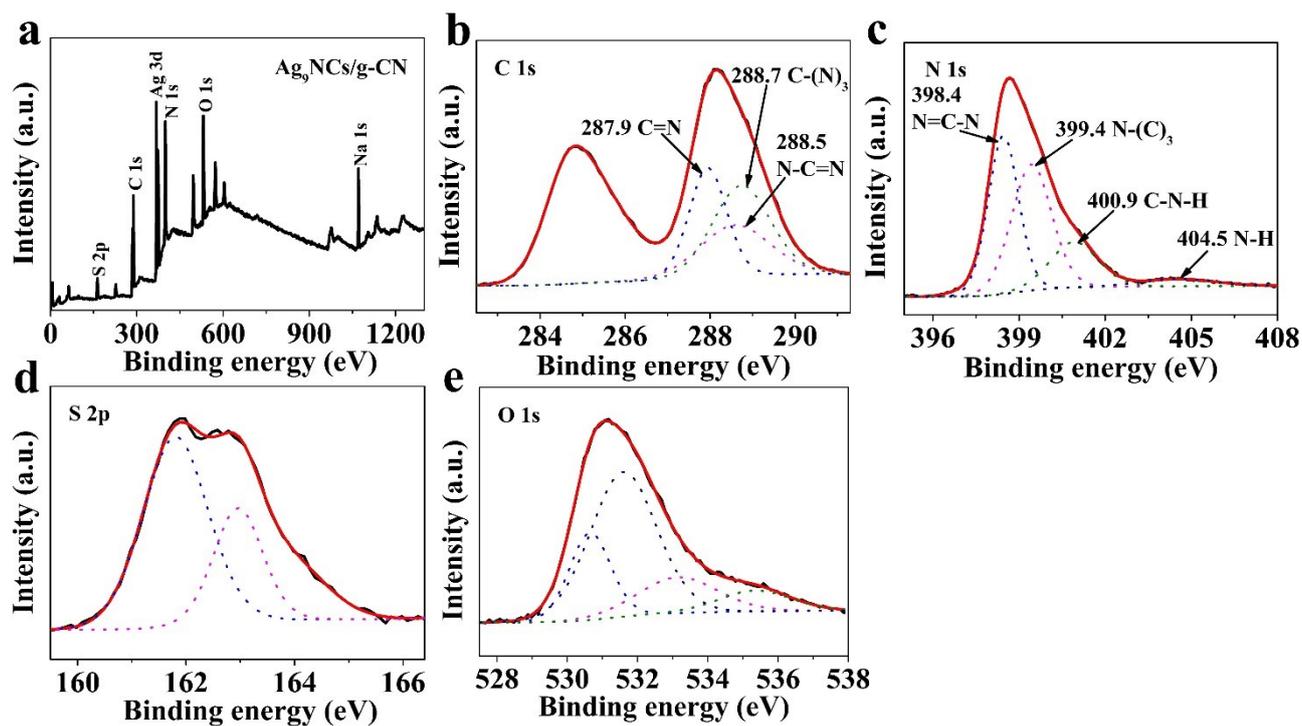


Figure S3. (a) XPS survey spectrum of the $\text{Ag}_9\text{NCs/g-CN}$ nanocomposite and corresponding high-resolution XPS spectra of (b) C 1s, (c) N 1s, (d) Ag 3d, (e) S 2p, and (f) O 1s.

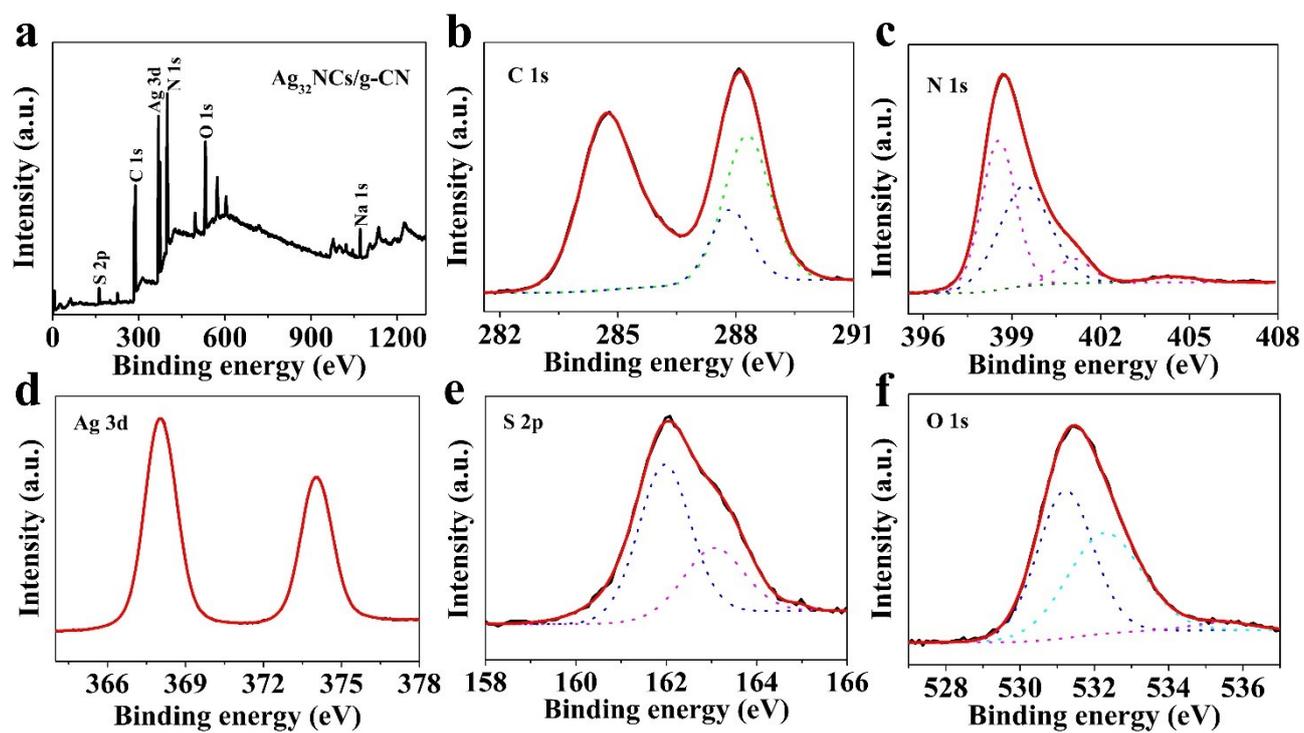


Figure S4. (a) XPS survey spectrum of the $\text{Ag}_{32}\text{NCs/g-CN}$ nanocomposite and corresponding high-resolution XPS spectra of (b) C 1s, (c) N 1s, (d) Ag 3d, (e) S 2p, and (f) O 1s.

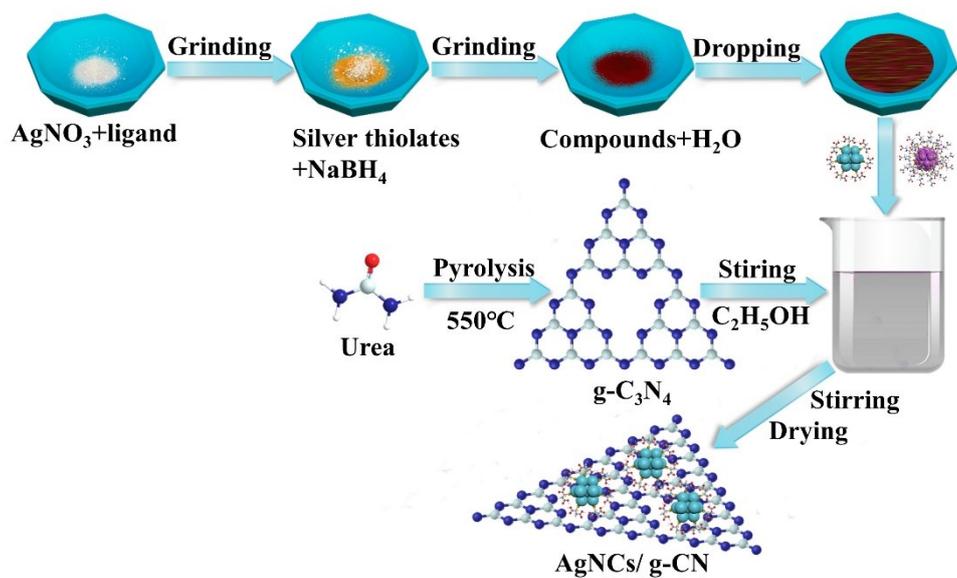


Figure S5. Schematic diagram of the fabrication process of the AgNCs/g-CN nanocomposite.

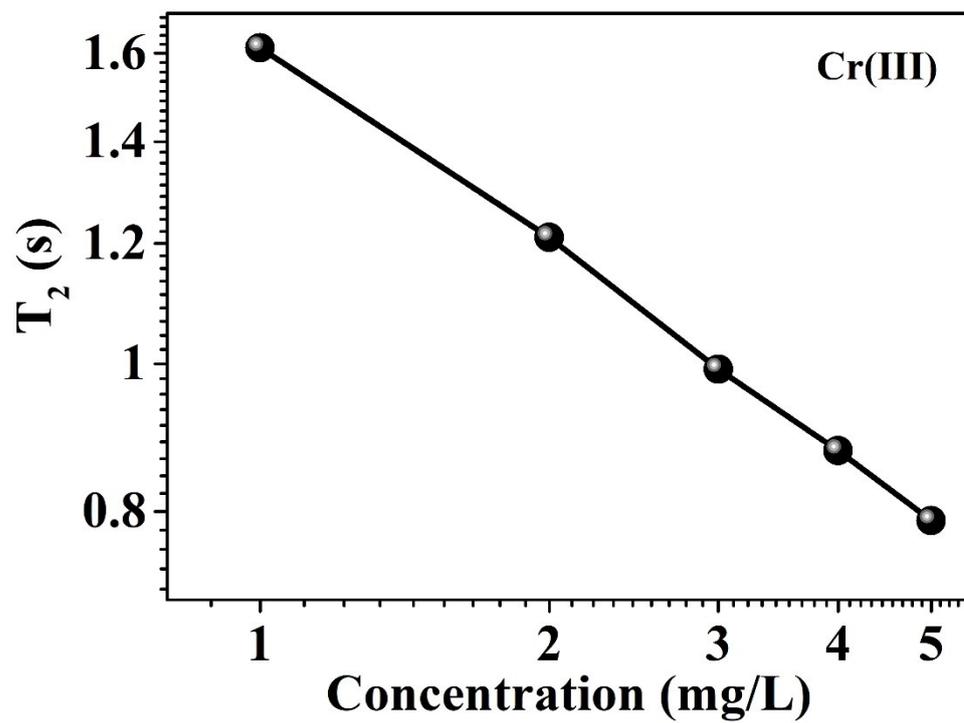


Figure S6. Variations in the transverse relaxation times (T_2) of Cr(III) versus concentration.

Table S1 Physicochemical characteristics of the as-prepared samples

Sample	S _{BET} (m ² /g)	Pore Volume (cc/g)	Pore Size (nm)	Amount of loaded NCs (wt%)
g-CN	74.469	0.244	3.830	-
Ag ₉ NCs/g-CN	65.400	0.230	3.420	11
Ag ₃₂ NCs/g-CN	42.517	0.178	3.416	8

Table S2 Reaction rate constants (p) and regression coefficients (R^2) of the as-prepared samples for the photocatalytic reduction of Cr(VI) to Cr(III) under visible-light irradiation.

Sample	p (min ⁻¹)	R^2
g-CN	0.026	0.9748
Ag ₉ NCs/g-CN	0.061	0.9588
Ag ₃₂ NCs/g-CN	0.054	0.9968

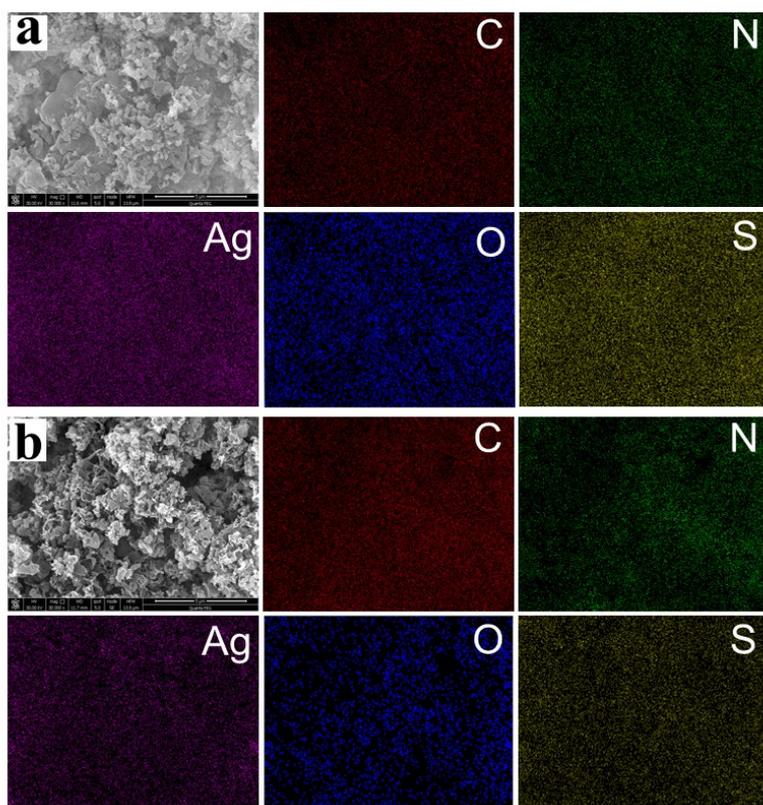


Figure S7. SEM mapping of (a) Ag₉NCs/g-CN and (b) Ag₃₂NCs/g-CN

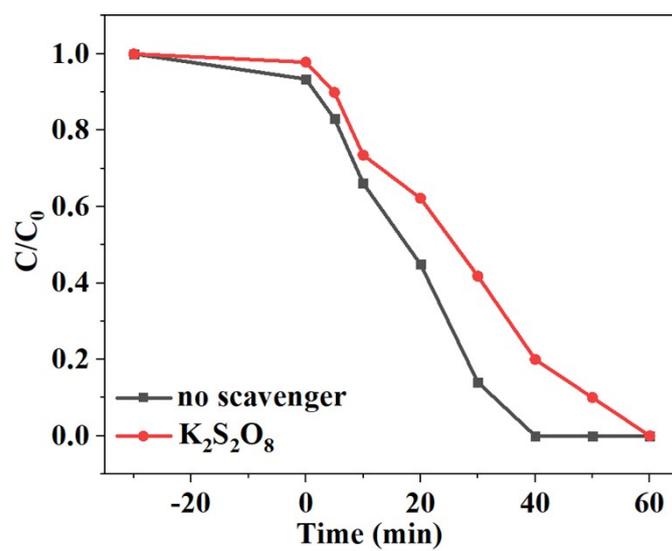


Figure S8. Effects of K₂S₂O₈ scavengers on Cr(VI) reduction in the presence of Ag₉NCs/g-CN.

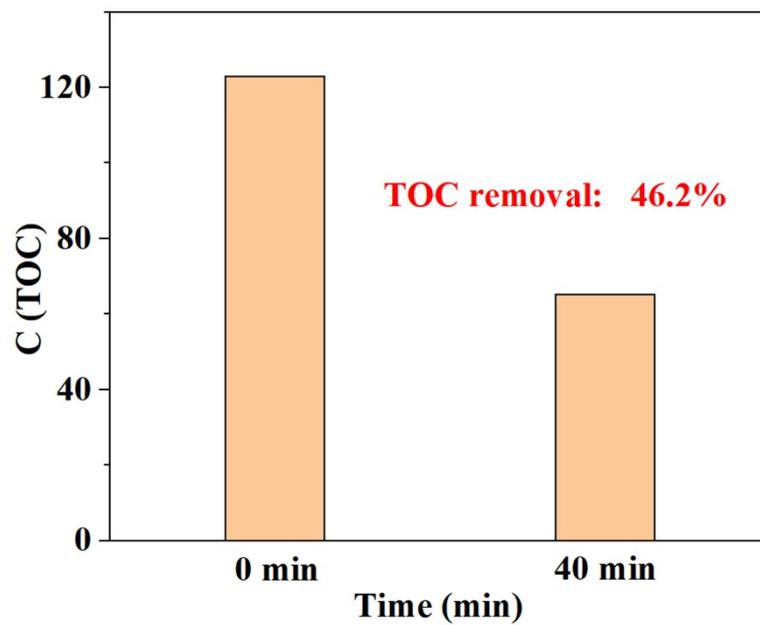


Figure S9. TOC removal of Ag₉NCs/g-CN.

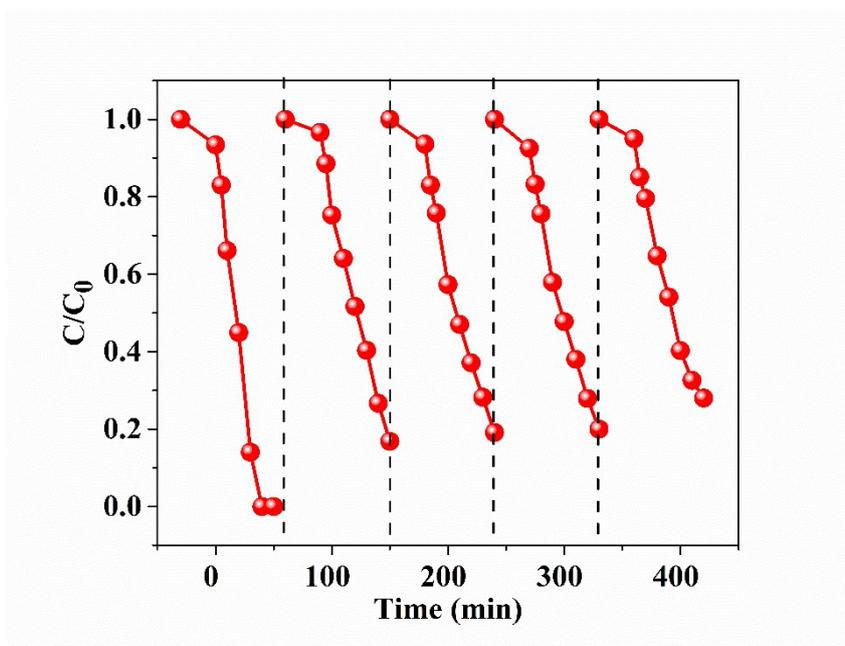


Figure S10. The reusability of Ag₉NCs/g-CN toward Cr(VI) reduction under visible light.

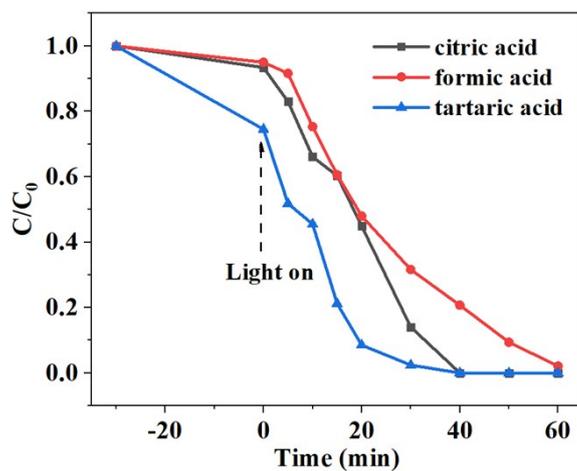


Figure S11. Photocatalytic reduction of Cr(VI) with different hole scavenger for the Ag₉NCs/g-CN photocatalysts.

Table S3. Comparisons between E_{HOMO} and AIP of citric acid, tartaric acid and formic acid.

Name	E _{HOMO} (a.u.)	AIP (a.u.)
tartaric acid	-0.2368	0.3247
citric acid	-0.2441	0.3318
formic acid	-0.2562	0.4082

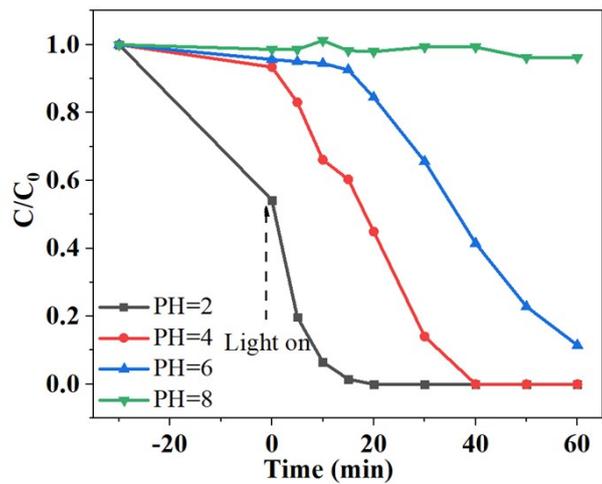


Figure S12. The effect of initial pH on Cr(VI) reduction for the Ag₉NCs/g-CN photocatalysts.

The optical band gap energy (E_g) of g-C₃N₄ can be calculated by the following formula:

$$\alpha h\nu = A(h-E_g)^{1/2} \quad (1)$$

Where α , $h\nu$, A and E_g represent the absorption coefficient, Planck constant, light frequency, proportionality and band gap energy, respectively. Thus, the band gap energy of the g-C₃N₄ was calculated via a plot of the $(\alpha h\nu)^{1/2}$ versus $h\nu$. As shown in Figure S13, the band gaps of the g-C₃N₄ was estimated to be 2.7 eV.

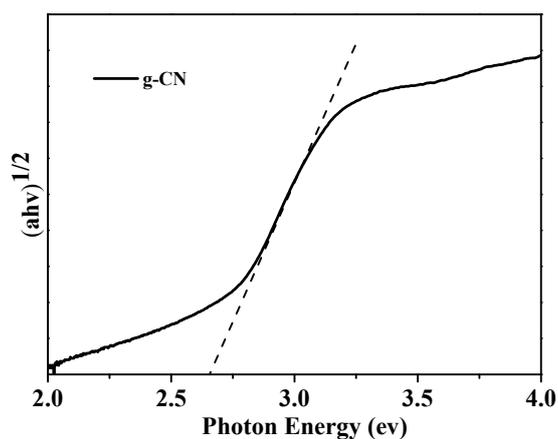


Figure S13. Plot of the $(\alpha h\nu)^{1/2}$ versus $h\nu$ for g-CN.

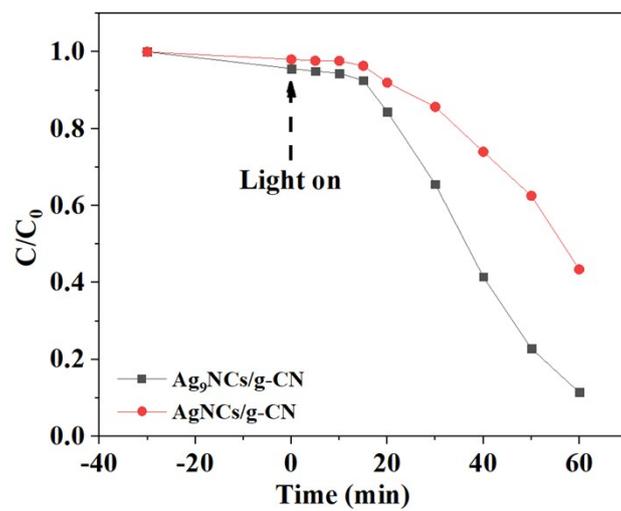


Figure S14. Photocatalytic activities of the $AgNCs/g-CN$ and $Ag_9NCs/g-CN$ composites for the photocatalytic reduction of $Cr(VI)$ solution under visible-light irradiation.

References

1. Z. D. Lei, Y. C. Xue, W. Q. Chen, L. Li, W. H. Qiu, Y. Zhang and L. Tang, The Influence of Carbon Nitride Nanosheets Doping on the Crystalline Formation of MIL-88B(Fe) and the Photocatalytic Activities, *Small*, 2018, **14**, e1802045.
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