

A review on recent advances in selective and sensitive detection of heavy toxic metal ions in water using g-C₃N₄-based heterostructured composites

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Supplementary information

Figures

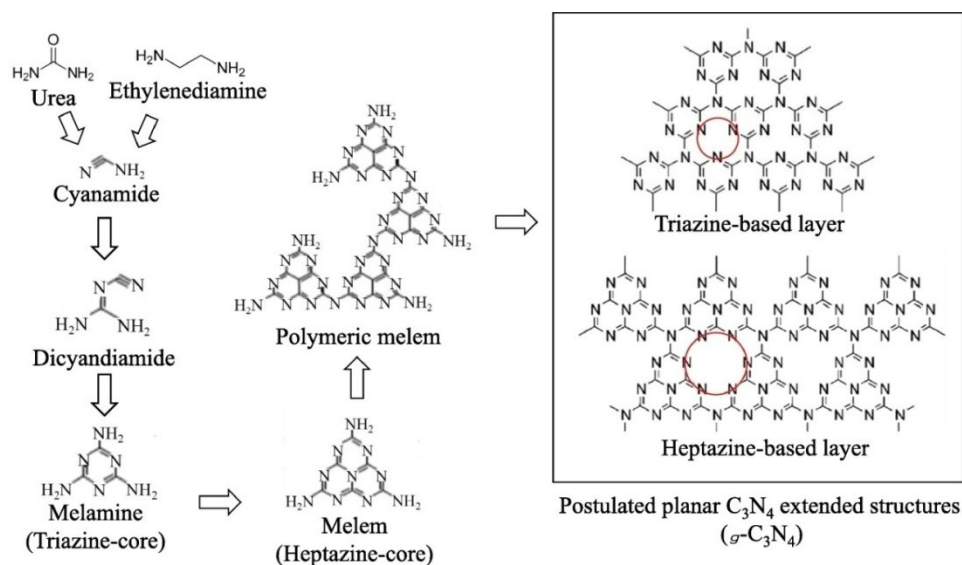


Fig. S1 Structural evolution from urea and ethylenediamine to $g\text{-C}_3\text{N}_4$, Characteristic intrinsic vacancies surrounded by nitrogen atoms are emphasized by red circles.⁴³

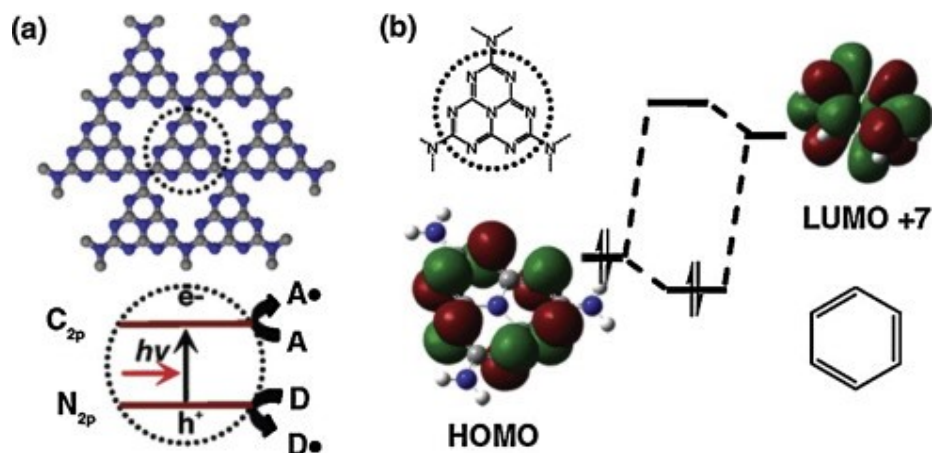


Fig. S2 (a) Stacked $g\text{-C}_3\text{N}_4$ sheets function as an all-organic solid-state photocatalyst promoting redox reactions with visible light; (b) chemical interaction of benzene and defective $g\text{-C}_3\text{N}_4$ via HOMO–LUMO hybridization of melem and benzene.²⁷

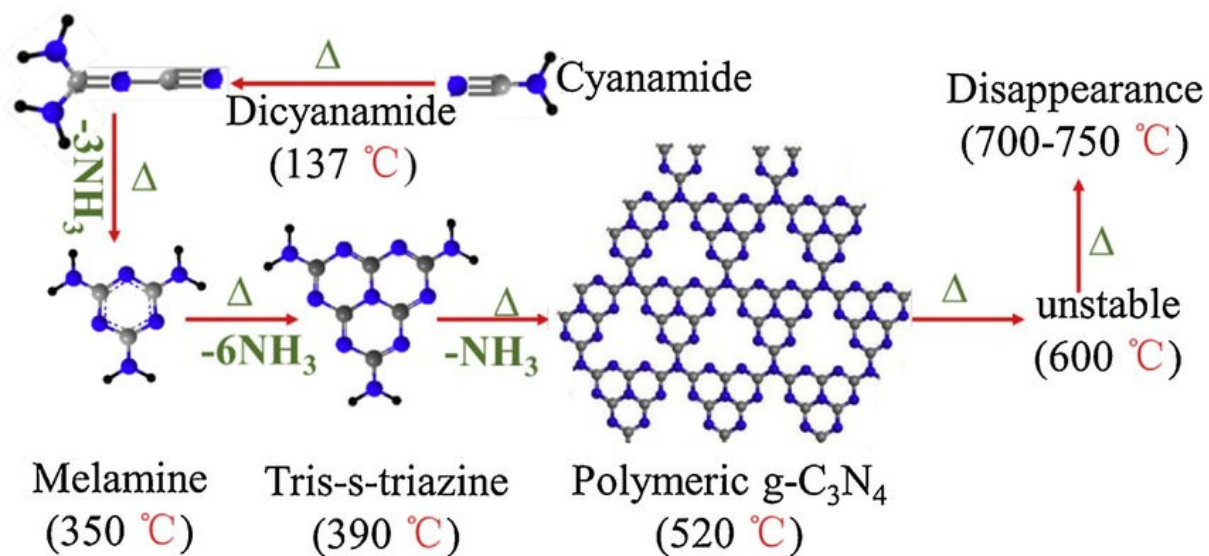


Fig. S3 Reaction path for the formation of g-C₃N₄ starting from cyanamide.⁵¹

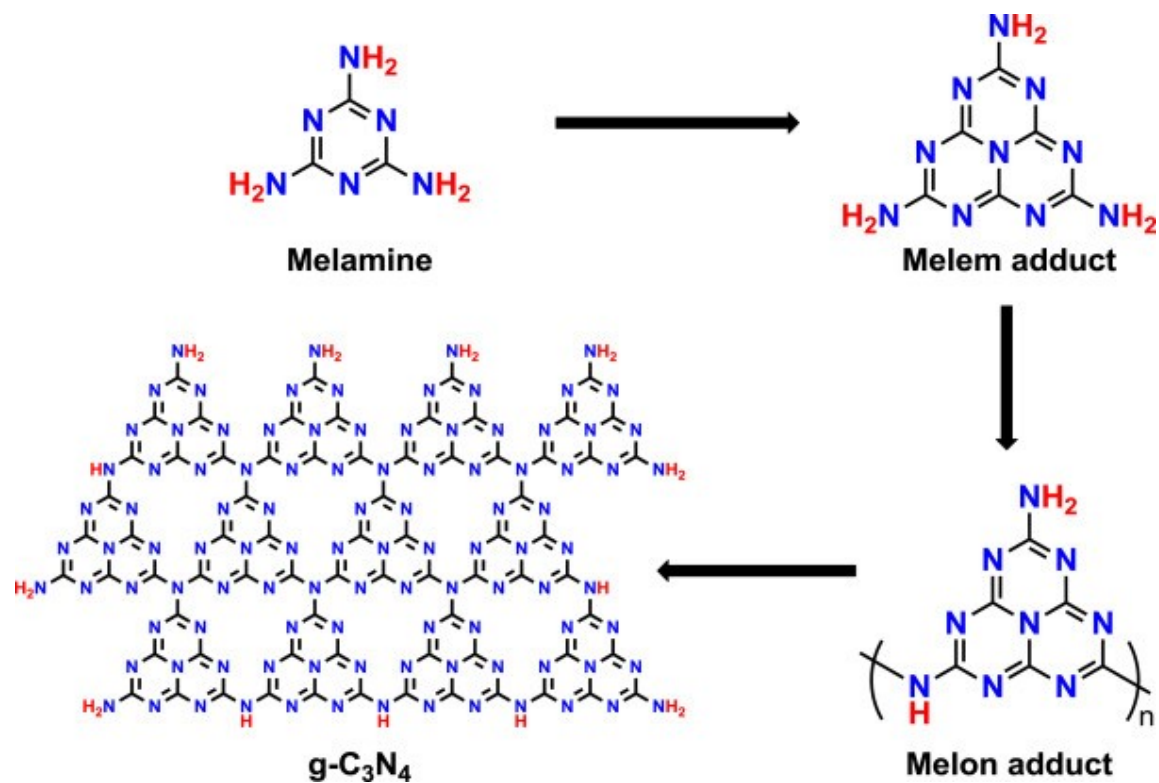


Fig. S4 Reaction pathway for the formation of g-C₃N₄ by polycondensation of Melamine.⁶⁴

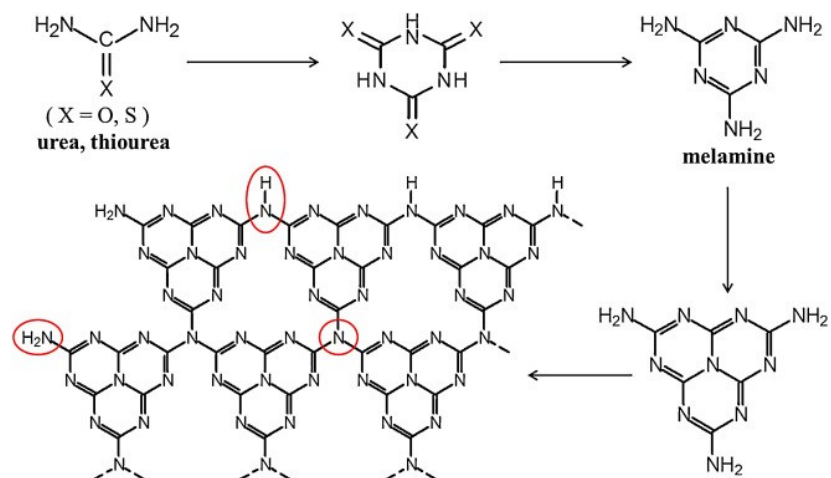


Fig. S5 Reaction paths for the formation of g-C₃N₄ from melamine, thiourea, and urea.⁶⁵

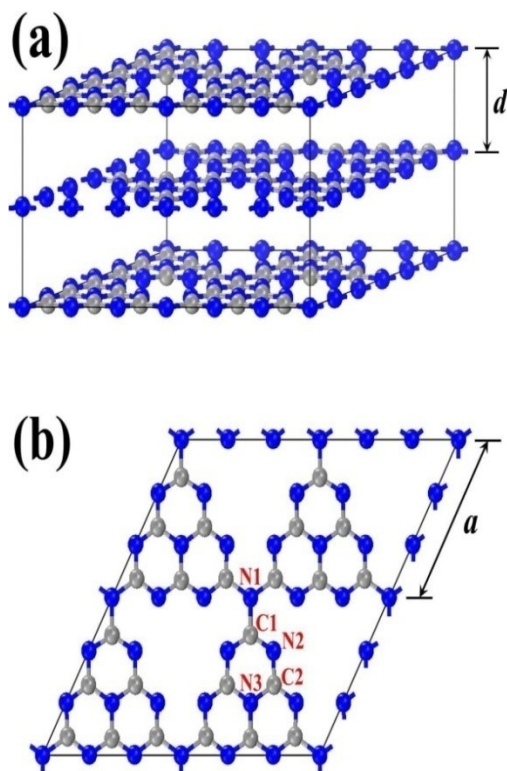


Fig. S6 Geometric structures of (a) bulk g-C₃N₄ and (b) single layer g-C₃N₄; the gray and blue balls are carbon and nitrogen atoms, respectively.⁶⁷

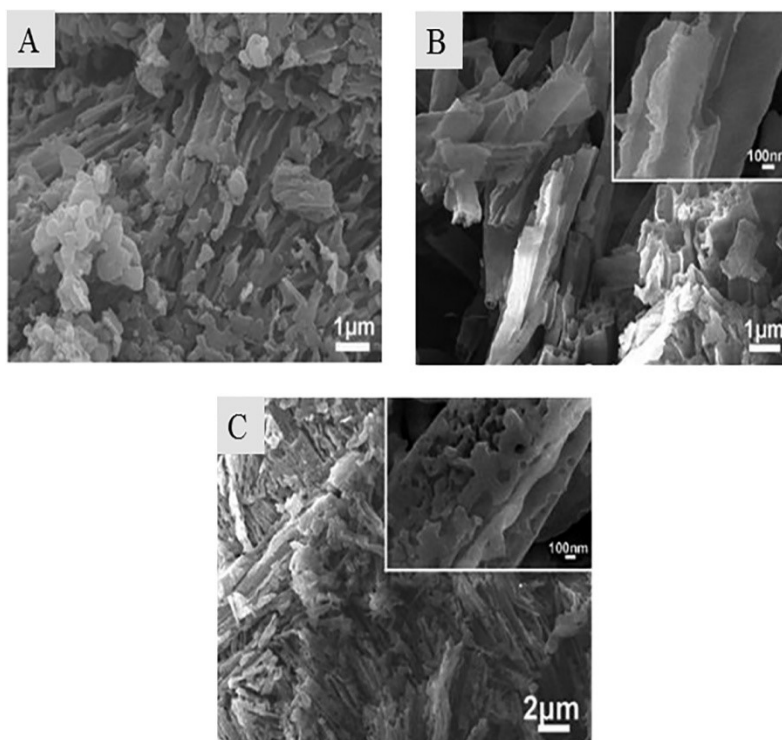


Fig. S7 SEM images of $g\text{-C}_3\text{N}_4$ with different morphology. (A) nanoflakes, (B) nanotubes, (C) rod-like structure.⁷⁴

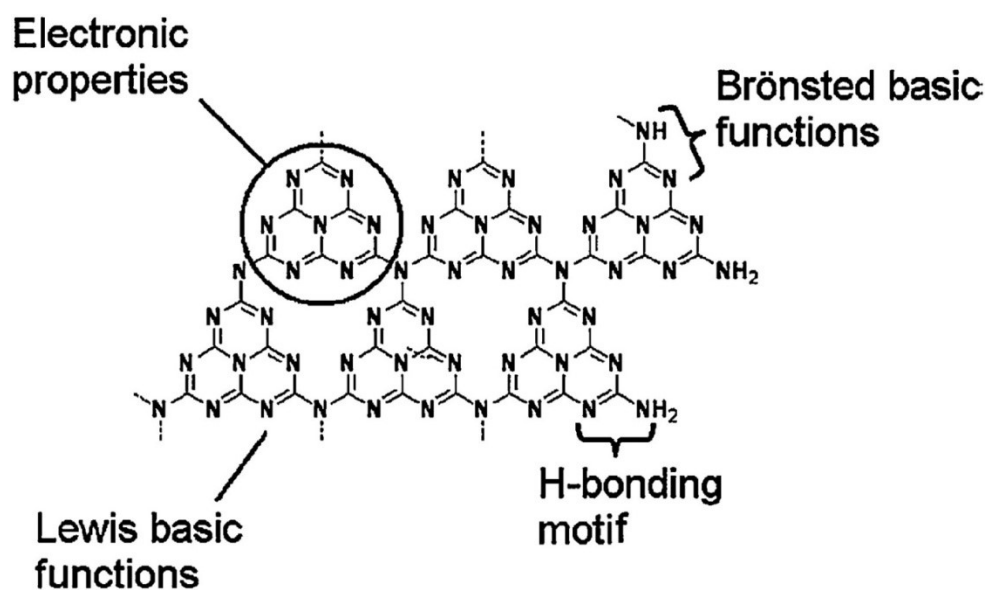


Fig. S8 Multiple functional surface properties of polymeric $g\text{-C}_3\text{N}_4$ material with defects.³⁷

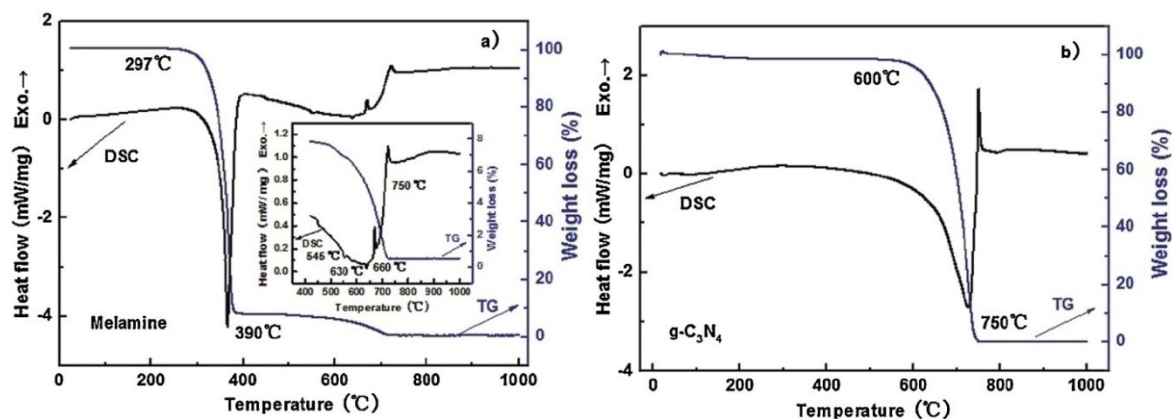


Fig. S9 The TG-DSC analysis for heating the melamine (a) and the g-C₃N₄ (b) obtained by heat polymerization of melamine at 520 °C.⁸²

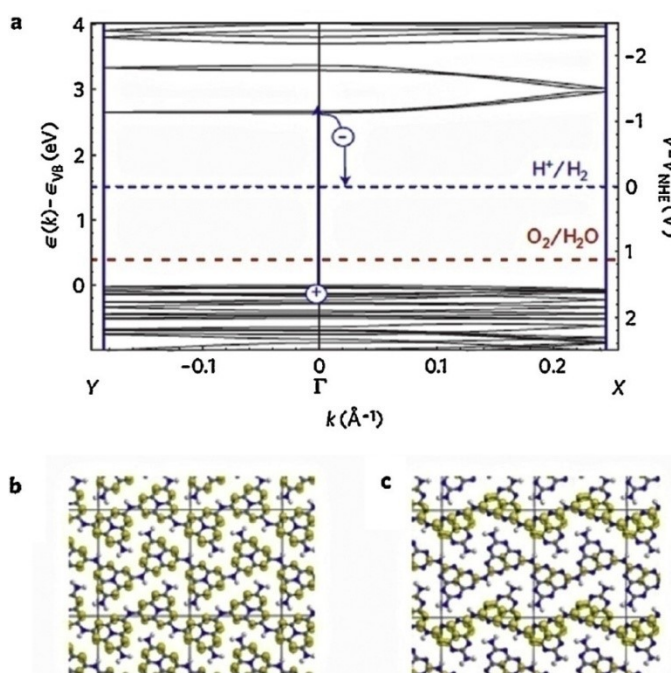


Fig. S10 Electronic structure of g-C₃N₄, (a) DFT band structure for g-C₃N₄ calculated along the Γ -X and Y- Γ directions. The potentials for H⁺ to H₂ and H₂O to O₂ are displayed by the blue and red dashed lines, respectively; the Kohn-Sham orbitals for the valence band (b) and conduction band (c) of g-C₃N₄. The C, N and H atoms are gray, blue and white, respectively. The isodensity surfaces are drawn for a charge density of 0.01 qe⁰Å⁻³.²²

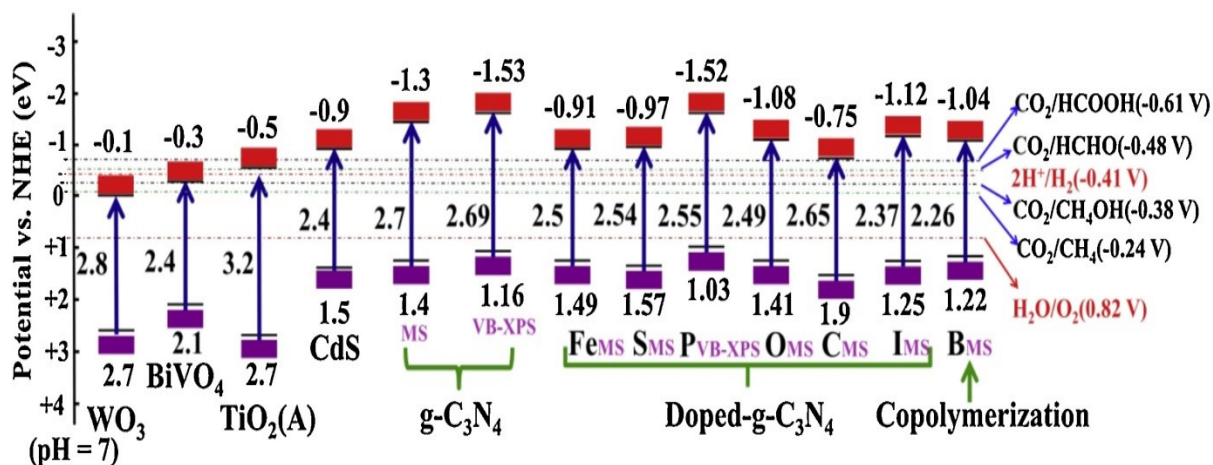


Fig. S11 Schematic illustration of the band structures of different types of $g\text{-C}_3\text{N}_4$ samples and other samples (VB-XPS: valence band X-ray photoelectron spectroscopy; MS: electrochemical analysis by Mott–Schottky plots).⁵⁴

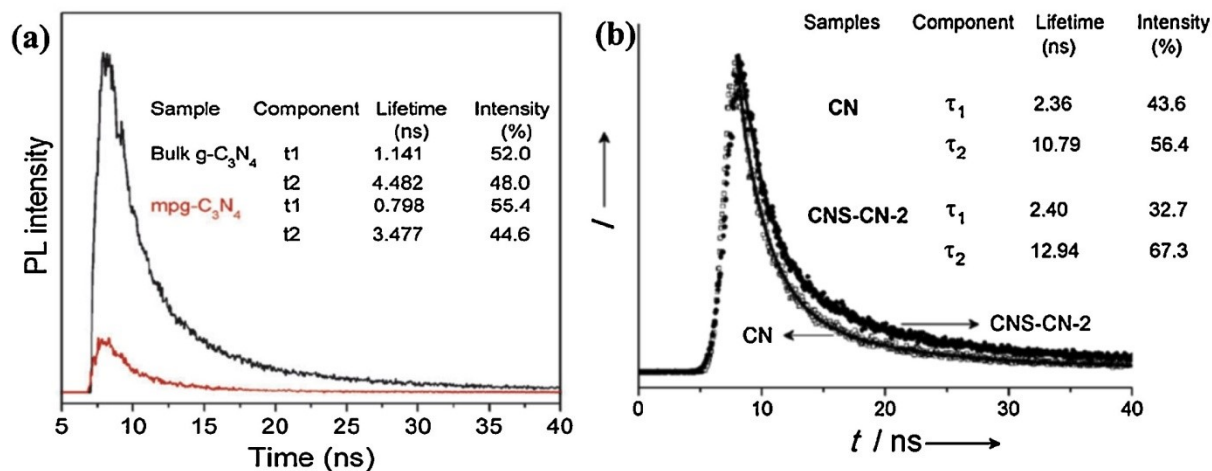


Fig. S12 (a) time-resolved PL spectrum monitored at 525 nm under 420 nm excitation at 298 K for bulk $g\text{-C}_3\text{N}_4$ (black) and $mpg\text{-C}_3\text{N}_4$ (red);³¹ (b) time-resolved PL spectra monitored at 480 nm under 420 nm excitation at 77 K for CN and CNS-CN.¹¹¹

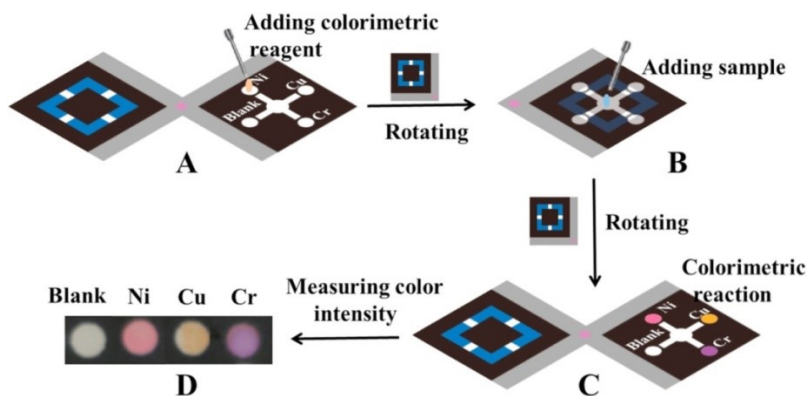


Fig. S13 Analytical procedure for the multiplexed colorimetric detection of heavy metals on the rotational paper-based device; (A) Dropping the colorimetric reagent and detection reagent into each detection zone as rotational valves were closed, (B) rotating the auxiliary layer to open valves, and adding the sample solution to the sample reservoir, (C) rotating the auxiliary layer to disconnect the detection zones with the sample reservoir, and allowing colorimetric reaction for ten minutes, (D) colorimetric detection of Ni(II), Cu(II) and Cr(VI).¹³⁹

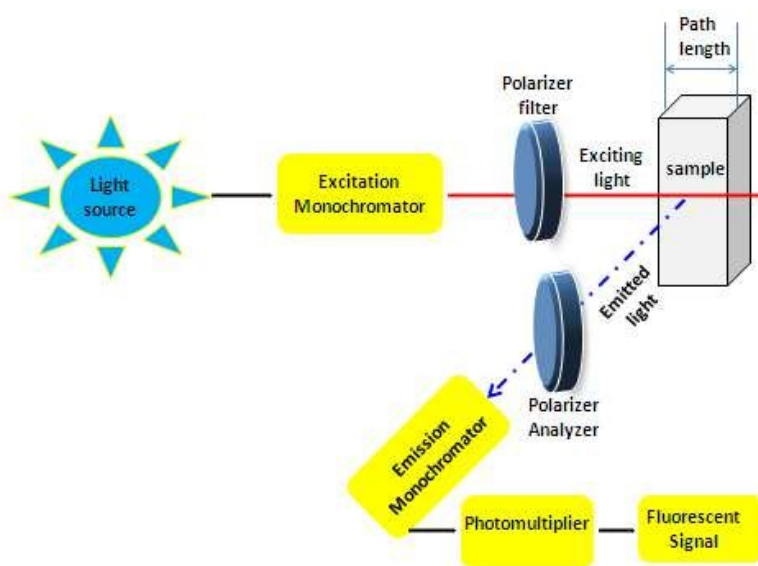


Fig. S14 Schematic representation of a fluorescence spectrophotometer.¹⁴⁰

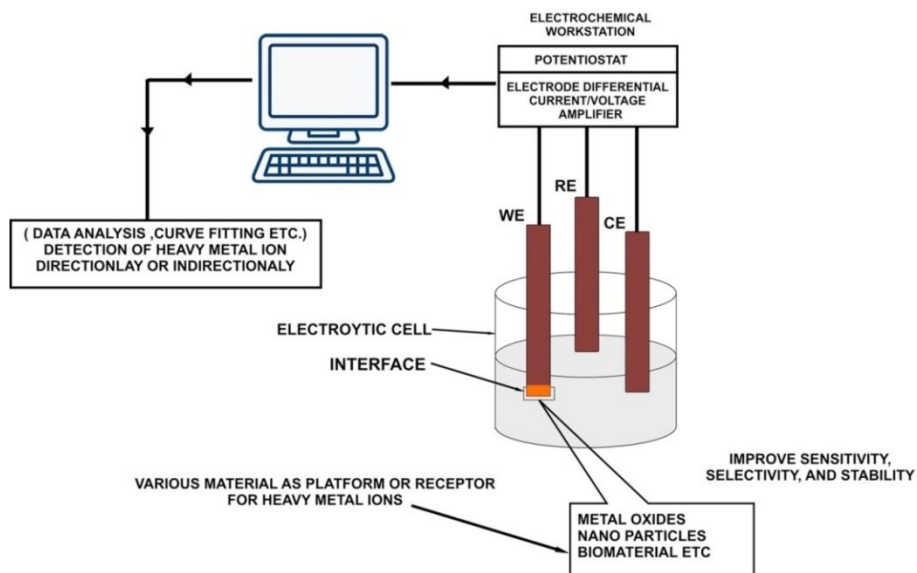


Fig. S15 General setup for electrochemical detection of heavy metal ions.¹⁴⁵

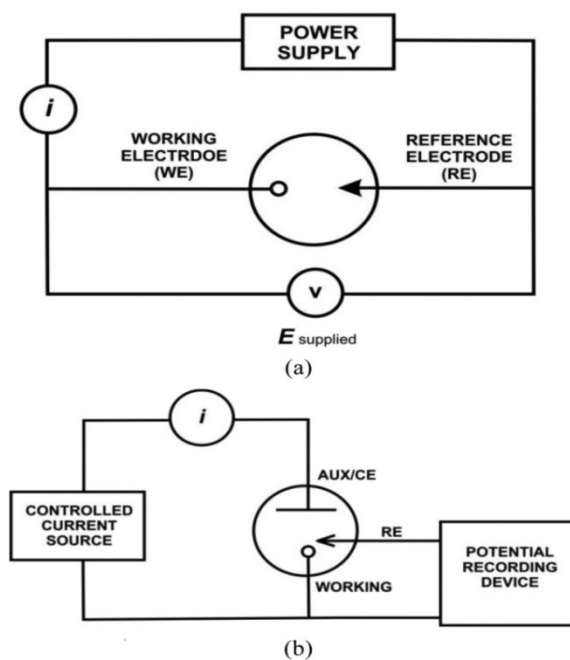


Fig. S16 (a) Two electrode cell setup and (b) three electrode cell setup.¹⁴⁸

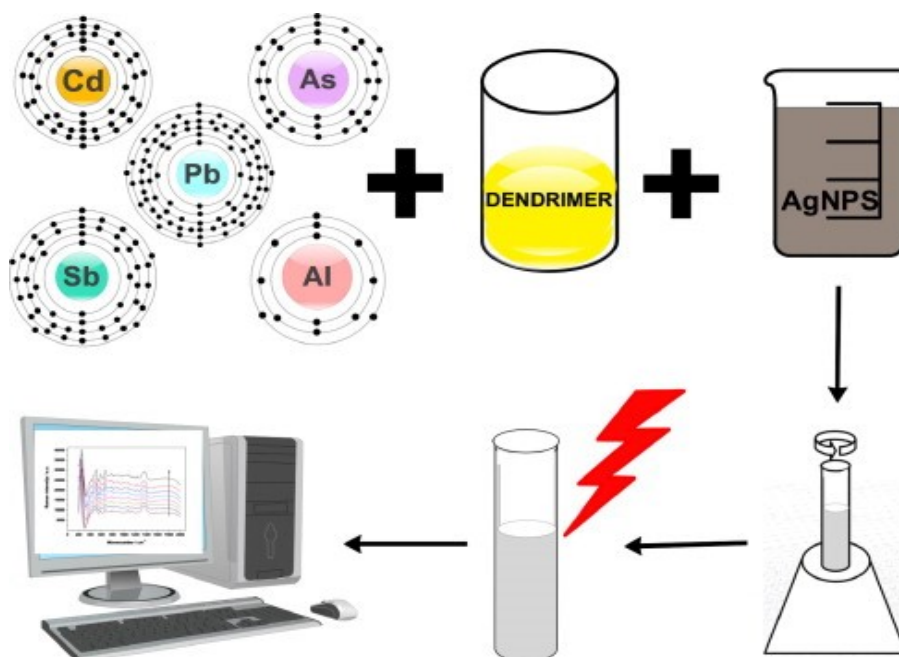


Fig. S17 Schematic illustration of experimental design.¹⁴⁹

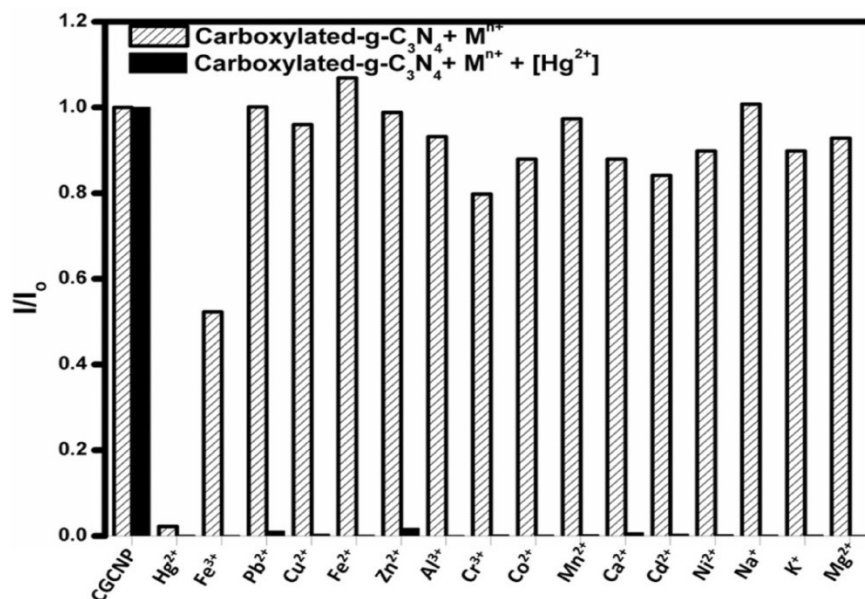


Fig. S18 Selective relative PL intensities of carboxylated-g-C₃N₄ (0.03 g L⁻¹) after treatment with 50 μM metal ion solutions (white bar), and interference of 50 μM of other metal ions with 15 μM Hg²⁺ (black bar), λ_{ex} = 250 nm.¹⁶⁰

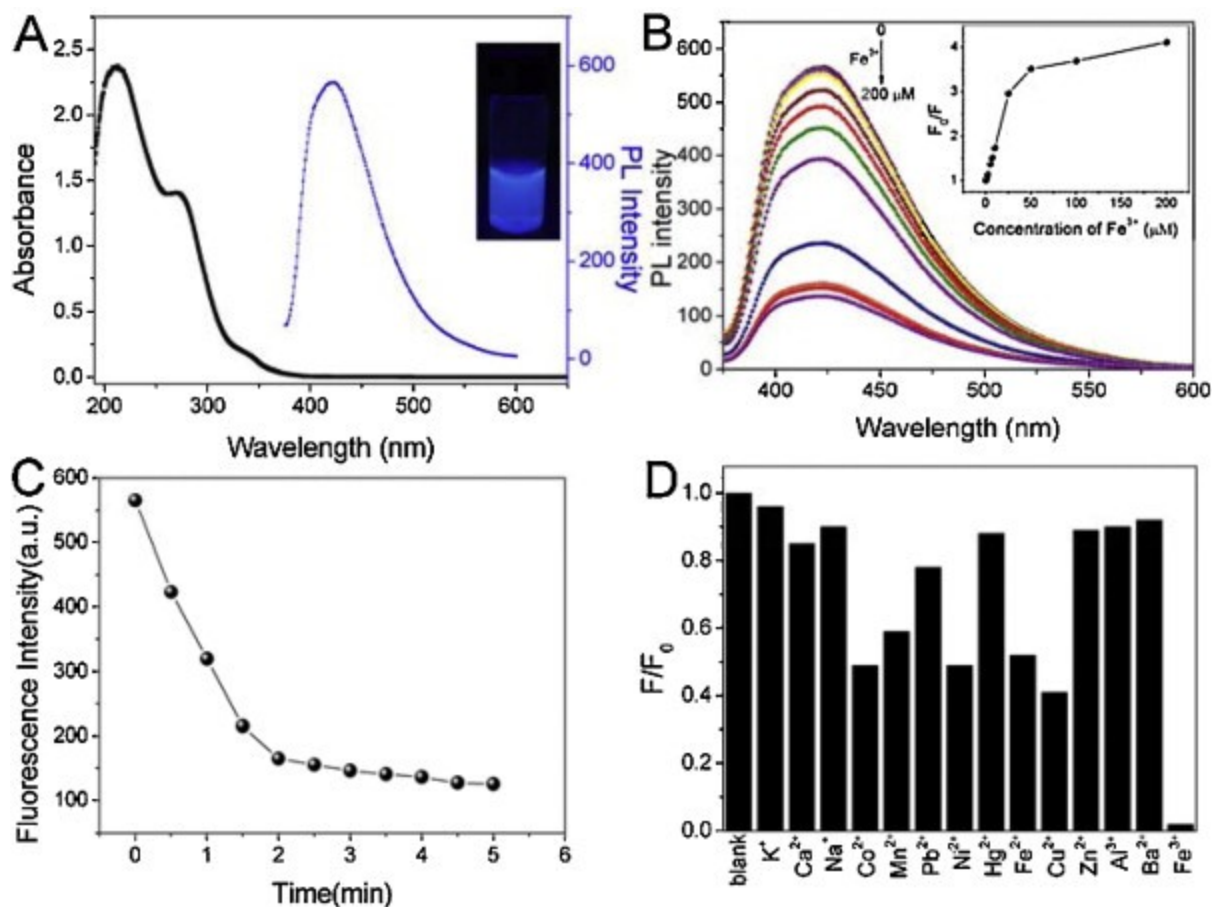


Fig. S19 (A) UV–vis absorption (black line) and PL emission (blue line) spectra of the g-C₃N₄ nanofibers thus obtained. Inset: the photograph of g-C₃N₄ nanofibers suspension under UV light (365 nm). (B) PL spectra of g-C₃N₄ nanofibers dispersion in the presence of different Fe³⁺ concentrations (from top to bottom: 0, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 7, 10, 25, 50, 100 and 200 μM). Inset: The dependent of F₀/F on the concentrations of Fe³⁺ ions within the range of 0–200 μM (excitation at 365 nm; F₀ and F are g-C₃N₄nanofibers fluorescence intensities at 425 nm in the absence and presence of Fe³⁺ ions, respectively). (C) Fluorescence quenching of g-C₃N₄ nanofibers by 200 μM Fe³⁺ in tris-HCl buffer (pH 7.4) as a function of time (λ_{ex} = 365 nm). (D) Selective PL response of g-C₃N₄ nanofibers after treatment with 1.0 mM metal ion solutions.²⁰³

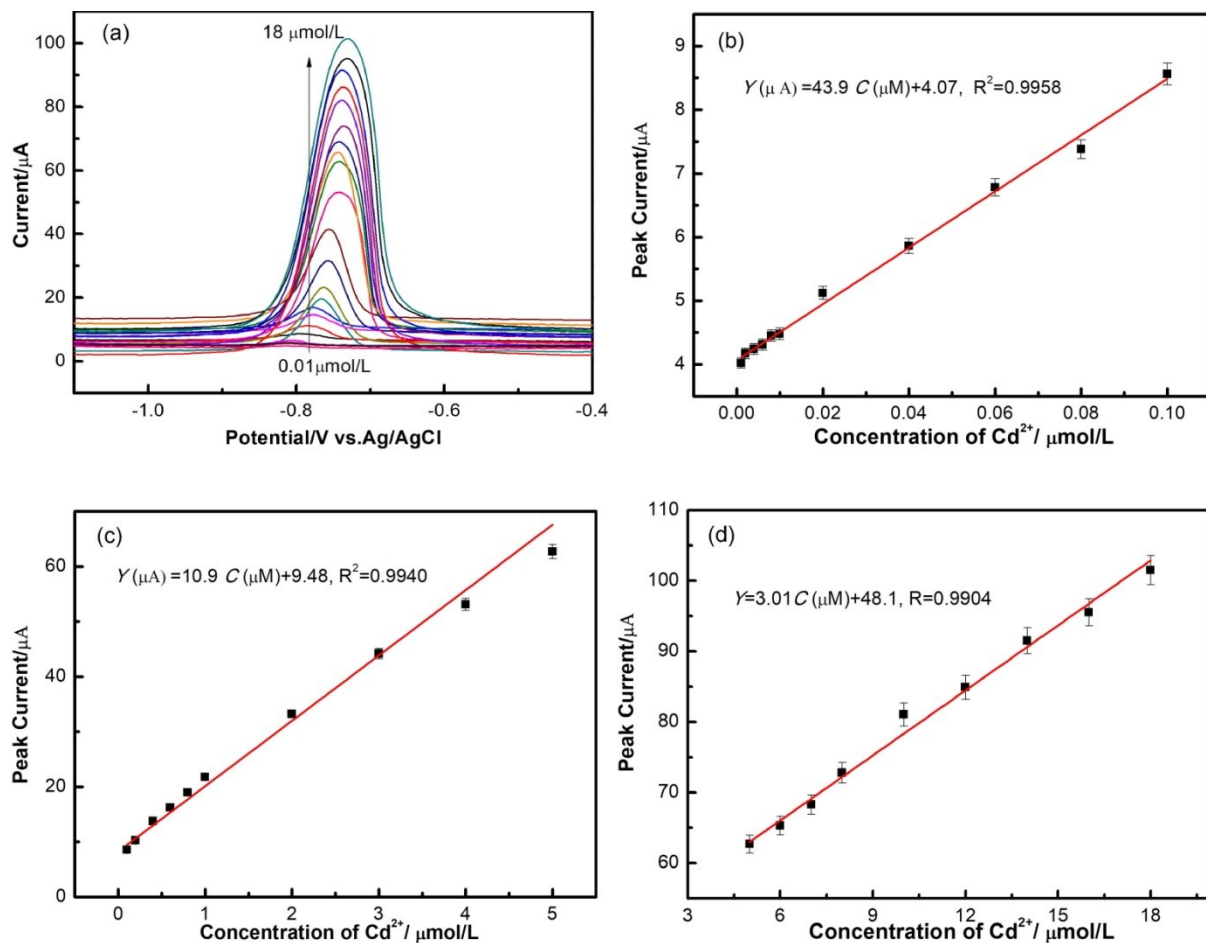


Fig. S20 (a) SWASV curves on NSCN-GC electrode in a 0.1 M HAc-NaAc buffer solution at concentrations ranging from 0.001 μM to 18 μM of Cd²⁺, and the fitting curves of the stripping peak areas versus the concentration range of 0.001–0.1 μM (b), 0.1–5 μM (c) and 5–18 μM (d).²⁴¹

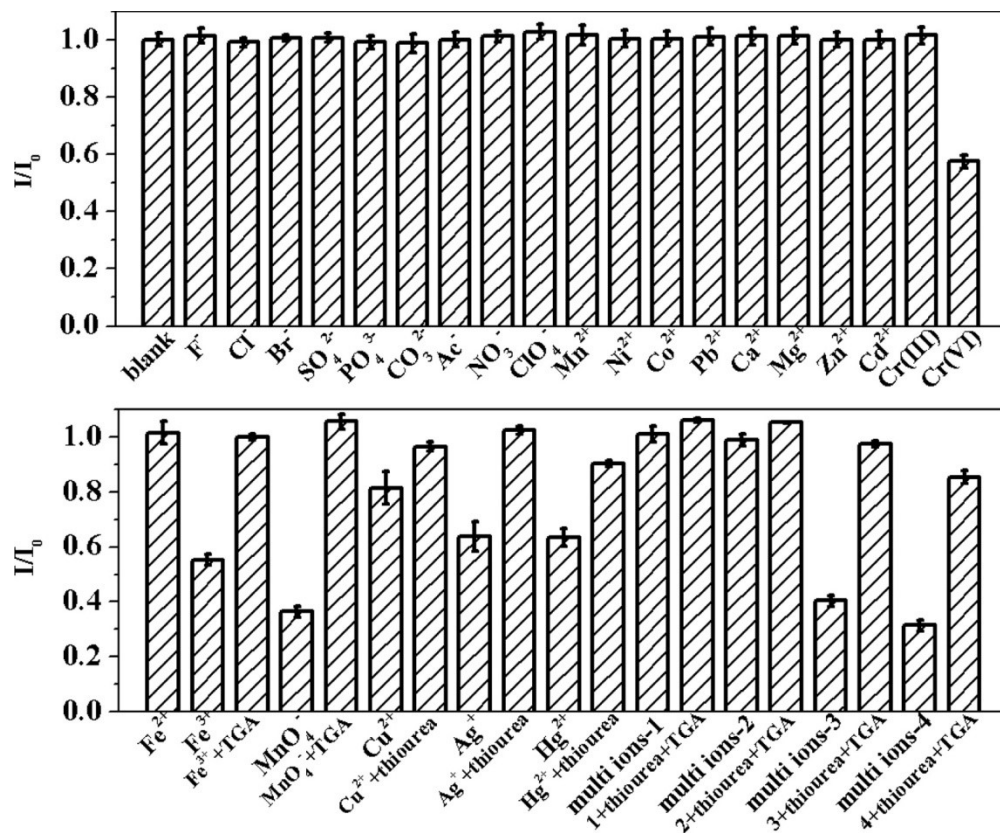


Fig. S21 Fluorescence responses of the g-C₃N₄ nanosheets in the presence of 200 μ M solution of various ion, The blank represents the fluorescence responses of the solution of g-C₃N₄ nanosheets without any ion, The multi-ions-1 contains Ca²⁺, Mg²⁺, K⁺, Na⁺; multi-ions-2 contains F⁻, Cl⁻, Br⁻, SO₄²⁻, PO₄³⁻, CO₃²⁻, Ac⁻, NO₃⁻; multi-ions-3 contains Mn²⁺, Cu²⁺, Ni²⁺, Fe³⁺, Zn²⁺, Co²⁺; multi-ions-4 contains Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, the concentration of each ion in the multi-ions groups was 200 μ M.²⁴⁷

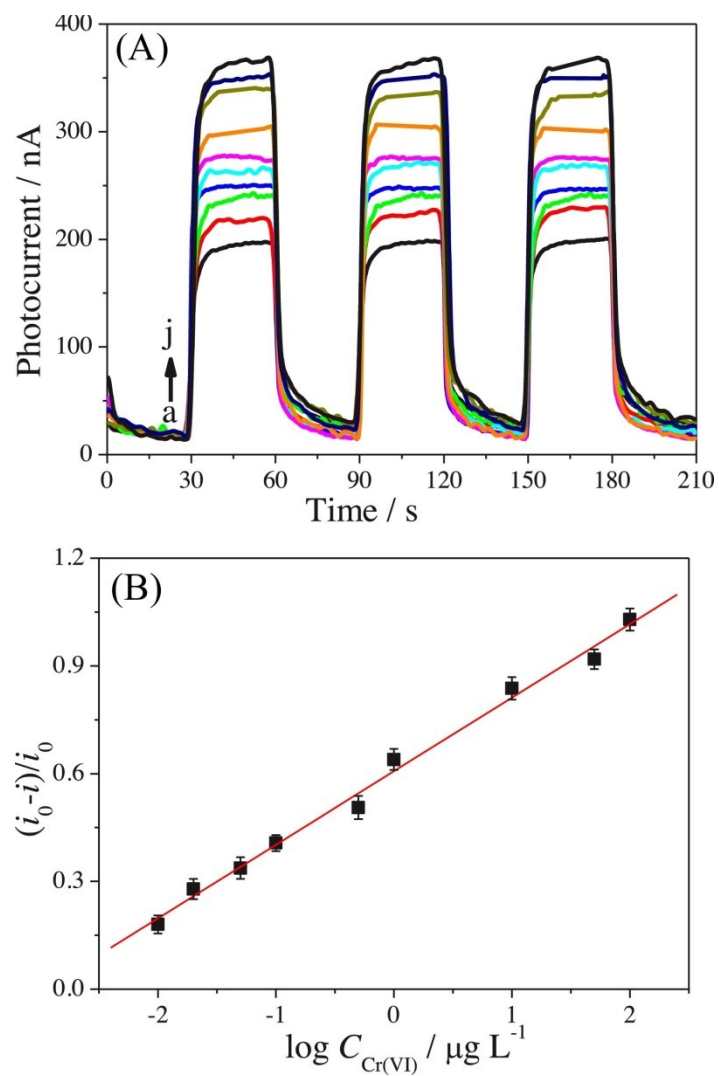


Fig. S22 (A) Photocurrent responses of IIP@F-g-C₃N₄/FTO toward Cr(VI) at increasing concentrations (from bottom to top, 0, 0.01, 0.05, 0.1, 0.5, 1.0, 10, 50 and 100 $\mu\text{g L}^{-1}$) in a supporting electrolyte of 0.1 M pH 6.0 tris-HCl, (B) Linear calibration curve.²⁴⁹

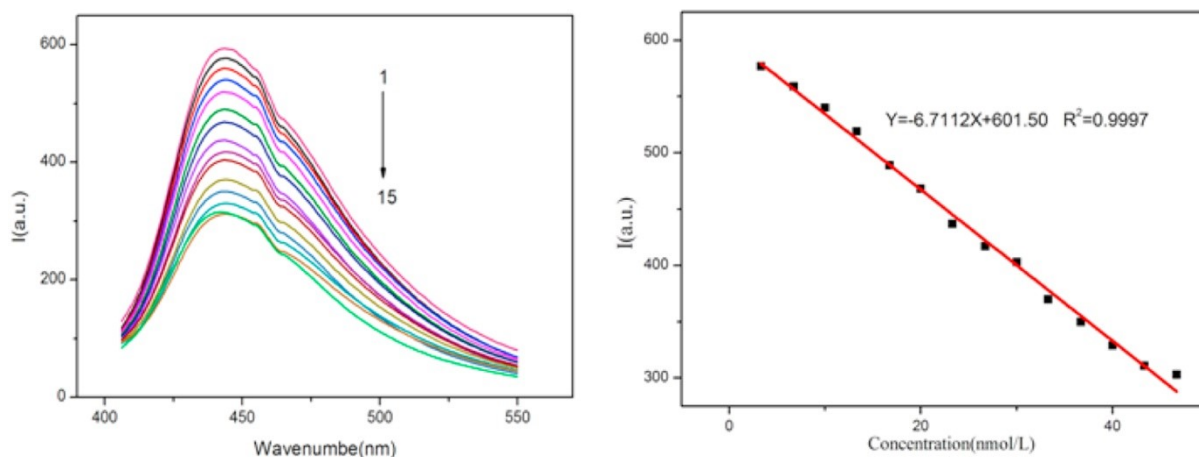


Fig. S23 Emission spectra of Ag^+ (0, 3.3., 6.7, 10, 13.3, 16.7, 20, 23.3, 26.7, 30, 33.3, 36.7, 40, 43.3, and 46.7 nM) with excitation at 310 nm (left) and the linearity of peak intensity with respect to Ag^+ concentrations (right).²⁶⁵

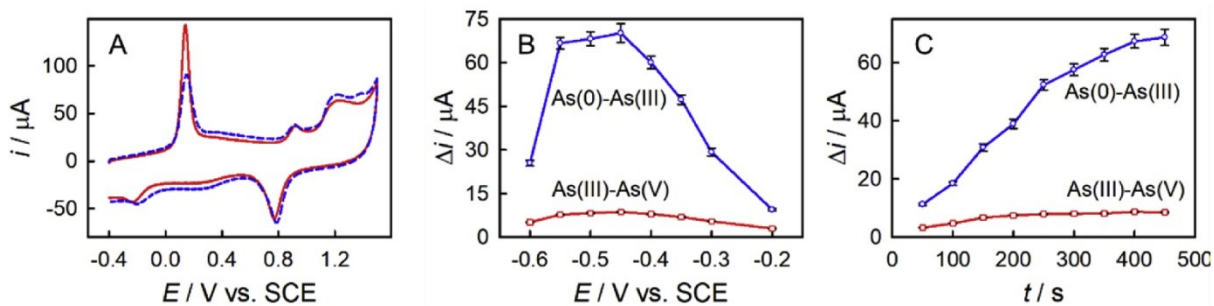


Fig. S24 (A) Cyclic voltammograms on AuNPs/GCE (dashed curve), AuNPs/g- C_3N_4 /GCE (solid curve) in 0.5 M aqueous H_2SO_4 containing 2.00 μM As(III) at 1 V s^{-1} . E_{cp} : 0.4 V; t_{cp} : 400 s, (B) Effect of E_{cp} and (C) effect of t_{cp} on LSASV (1 V s^{-1}) peak currents of 1.00 μM As(III) in 0.5 M aqueous H_2SO_4 at AuNPs/g- C_3N_4 /GCE, The LSASV experiments were conducted after preconcentration at -0.45 V for 400 s, except for the examined parameter.²⁸¹