Electronic Supplementary Information

Graphitic carbon nitride solid nanofilms for selective and recyclable sensing of Cu^{2+} and Ag^{+}

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Experimental section

Chemicals: Melamine was purchased from Sinopharm Chemical Reagent (Shanghai, China). Magnesium chloride hexahydrate, hydrogen peroxide (27.2% in H_2O), acetone, 2-propanol, methanol, ethanol, sulfuric acid (98% in H_2O) and toluene were obtained from the International Laboratory (USA). Iron (Ⅲ) chloride anhydrous and aluminium nitrate were ordered from Fisher (USA). Copper (Ⅱ) nitrate trihydrate, potassium nitrate, lithium nitrate, silver nitrate, (3-aminopropyl) triethoxysilane (APTES), aluminium chloride hexahydrate, acetonitrile and L-Glutathione reduced (GSH) were from Sigma-Aldrich (USA). Sodium hydroxide was obtained from VWR international (USA). Zinc nitrate hexahydrate was purchased from Unichem (USA). Fetal bovine serum (E.U.-approved, South America origin) was bought from Gibco (USA). All chemicals were used as received without further purification. The organic solutions were HPLC grade, and water utilized throughout all experiments was purified from Millipore system.

Preparation of g-C_3N_4 nanosheets: According to previous report,[1] bulk g-C_3N_4 was synthesized via the condensation of melamine. In a typical synthesis, melamine was heated to and maintained at 600 ℃ for 2 hours in ambient condition with heating and cooling rates of 3 ℃min^{-1}. Then the produced bulk g-C_3N_4 was grinded with agate mortar, and collected as yellow powder until use. The g-C_3N_4 nanosheets were prepared via a “green” liquid exfoliation method.[22] In detail, 40 mg of bulk g-C_3N_4 were dispersed in 40 ml of water, and the mixture was treated with sonication for 12 hours. The resulted solution was centrifuged (5000 rpm, 10 min) to remove unexfoliated g-C_3N_4, and the centrifugation process was repeated several times until no precipitation occurred.

Preparation of Mg_2Al-Cl-LDH nanoparticles: Mg_2Al-Cl-LDH nanoparticles were synthesized with Xu’s method.[2,3] In detail, 40 ml of NaOH solution (0.15 M in H_2O) was mixed with 10 ml of solution containing 2.0 mmol of $MgCl_2$ and 1 mmol of $AlCl_3$ under vigorous stirring. The obtained milky solution was sealed and stirred under nitrogen protection for 10 min. The as-resulted mixture was centrifuged (5000 rpm, 10 min) and washed with water for several times, and the resulted white slurry was dispersed into 40 ml water. Then, the hydrothermal exfoliated process was carried out in a sealed flask at 80 ℃ for 4 hours. The obtained solution was stored for future use.

Layer-by-layer self-assembly: Glass slides were thoroughly cleaned by sonication sequentially in methanol, acetone and methanol, each for 15 min, followed by rinsing with 2-propanol and water. Then the substrates were immersed in piranha solution (90 ℃, 3:1, v/v. 98% H_2SO_4: 27.2% H_2O_2) for 1 hour. Subsequently, the substrates were washed with a great amount of water, then rinsed in methanol, 1:1 methanol/toluene, toluene, and dried with nitrogen. After that, the substrates were rinsed in an APTES solution (10% in toluene) in nitrogen atmospheres overnight. Once the required deposition time elapsed, the substrates were washed via sonication within ethanol, 2-propanol and water, finally dried with nitrogen gas. The preparation of g-

C_3N_4/LDH films was achieved with a typical LBL self-assembly process. Firstly, the dried substrates were dipped into g-C_3N_4 nanosheets solution for 15 min, and rinsed in water for 5 min. After that, the g-C_3N_4 covered substrates were dipped into the LDH solution for 15 min, then washed with water for 5 min. These self-assembly processes were repeated for 5 times. The resulted films were dried with nitrogen gas.

Fluorescence sensing: The prepared films were dipped in metal ions solution for 15 min, and dried with N_2. For determining the ions concentration in serum, fetal bovine serum was mixed with metal ions solution to form samples with certain metal ion concentration, and the serum content of each sample was 10%. The fluorescence intensities of the treated films were recorded with a fluorescence spectrophotometer. The recovery of the fluorescence of the treated films and the reusability of the sensing device were also investigated. For reuse of the sensor, the used films were thoroughly washed with water for 48 h and dried with nitrogen to remove the absorbed metal ions. Furthermore, the washing agent can be replaced with chelate (e.g., 1:1 acetonitrile water solution or 0.5 mM glutathione solution). Next, the washed films were dipped in water for an extra of 5 min to remove residual washing agents. The detection of serum samples were achieved by dropping a 50 μl droplet on the top of g-C_3N_4/LDH films. When 15 min balance time elapsed, the films were washed with water, and then the emission of the treated area were recorded and compared with the initial fluorescent intensities.

Characterization: UV-Visible spectra were obtained with the Cary 50 series UV-Vis spectrophotometer (Varian, USA). Photoluminescence emission spectra were recorded with a Cary edipse fluorescence spectrofluorometer (Varian, USA). Transmission electron microscopy images and high resolution transmission electron microscopy images were taken with TEM CM200 FEG for investigation of Mg_2Al-Cl-LDH nanoparticles and g-C_3N_4 nanosheets (Philips, Netherland). The size and thickness of g-C_3N_4 nanosheets were investigated by Veeco Multimode-V atomic force microscope (Veeco, USA). X-ray photoelectron spectra of g-C_3N_4/LDH films were acquired on Scanning Auger XPS PHI Model 5802 (PHI, USA). The fitting of the XPS spectra was carried out with XPS Peak software and the Lorentzian-Gaussian ratio was locked at 80%. X-ray powder diffraction (XRD) was performed by D2 PHASER X-ray Diffraction Analyzer (Bruker, USA). Zeta potential and dynamic light scattering sizes of g-C_3N_4 nanosheets and LDH nanoparticles were collected with Dynamic Light Scattering Particle Size Analysis (Malvern, Britain).

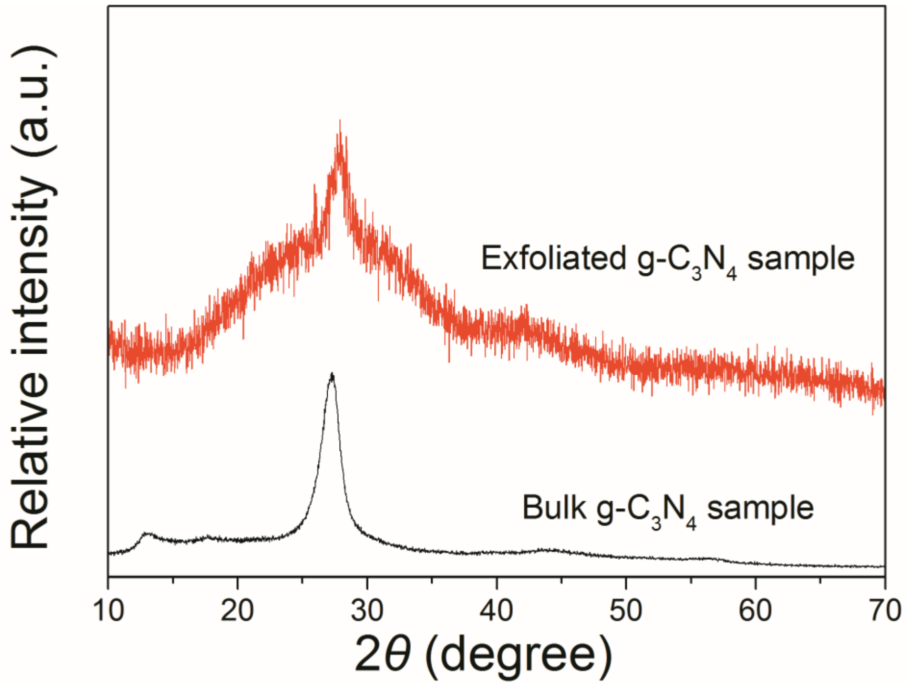

Figure S1. XRD patterns of g-C_3N_4 nanosheets and bulk g-C_3N_4

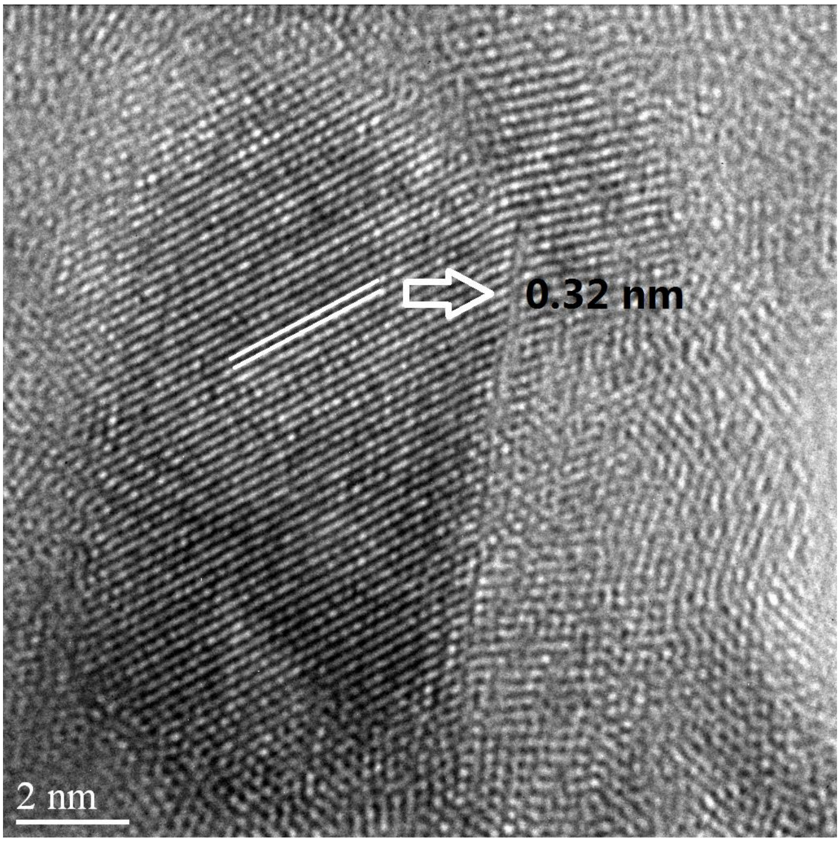

Figure S2. HRTEM image of an exfoliated g-C_3N_4 nanosheet

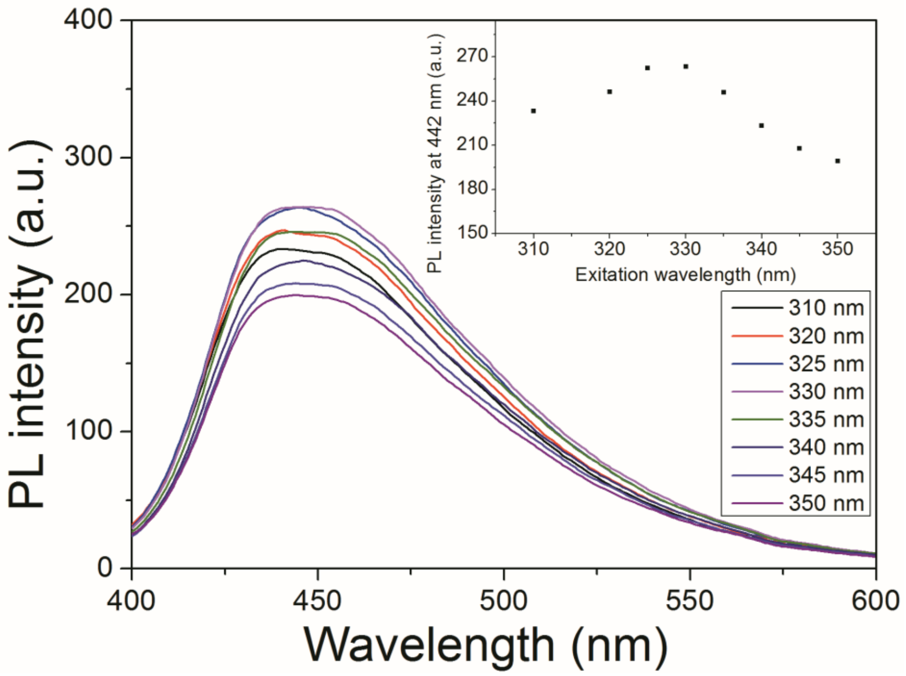

Figure S3. Photoluminescence (PL) spectra recorded with various excitation wavelengths (310 to 350 nm).

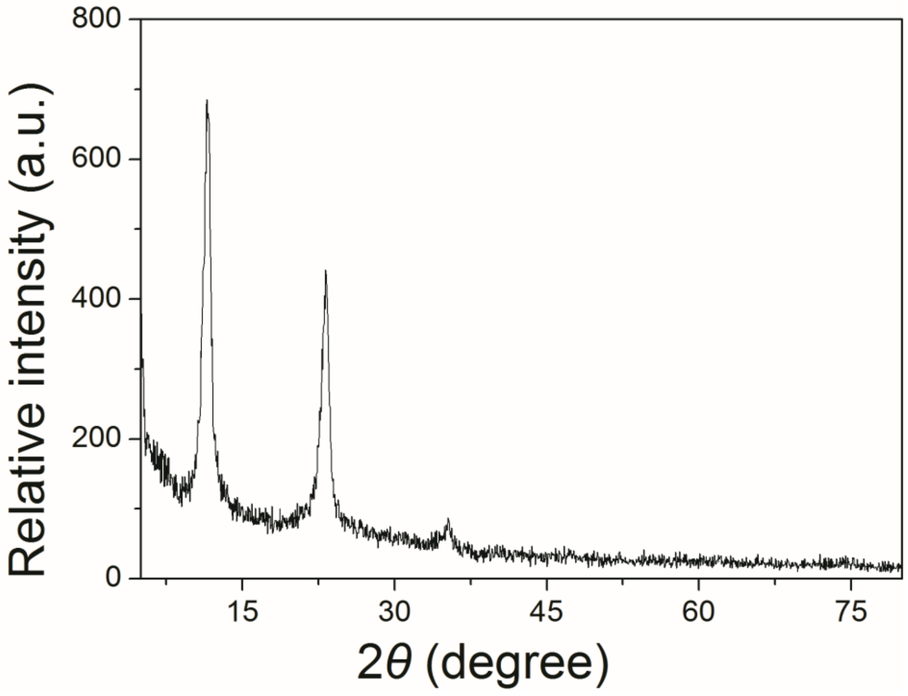

Figure S4. X-ray diffraction pattern of pristine LDH nanoparticles.

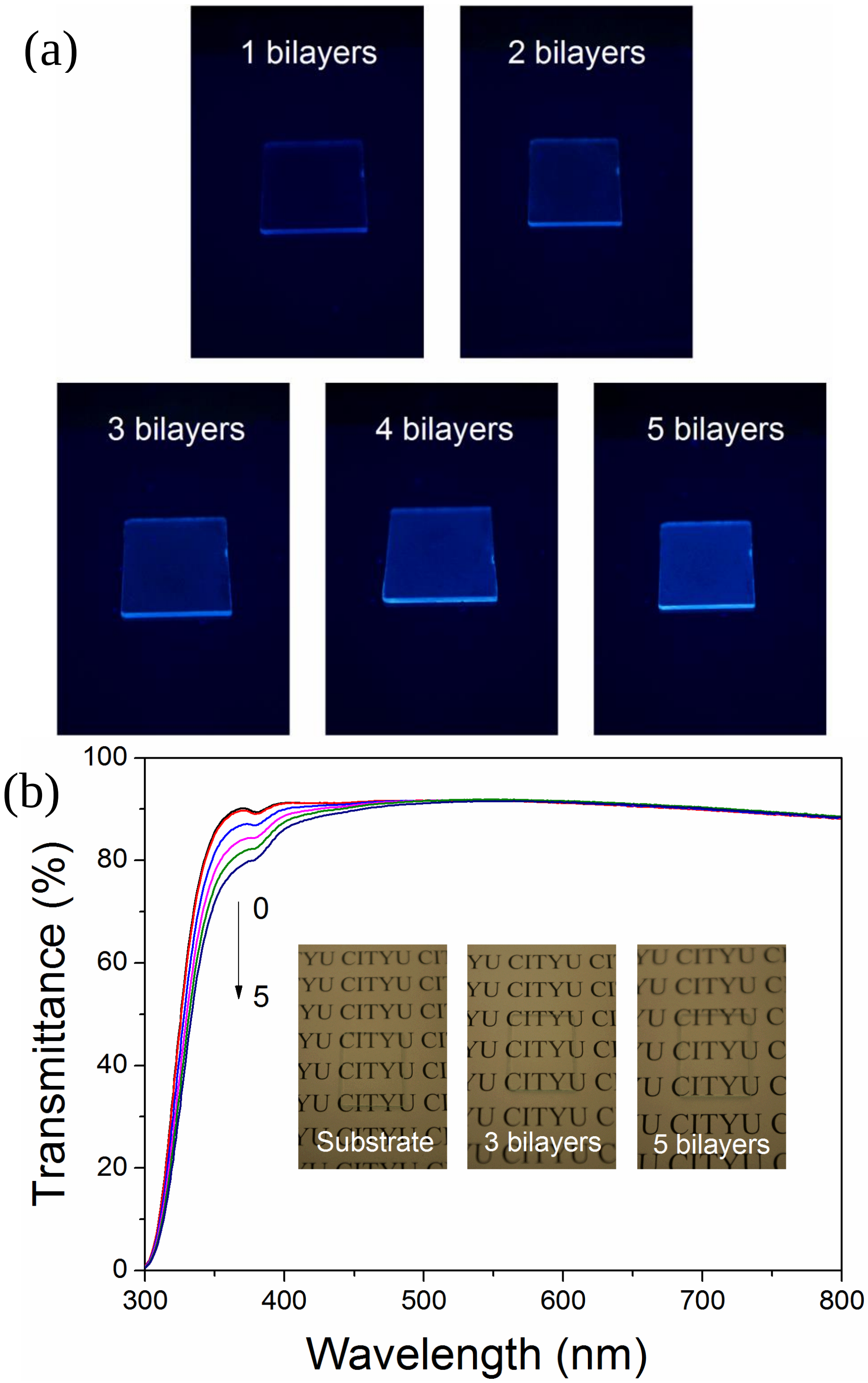

Figure S5. (a) Photographs of the g-C_3N_4/LDH films under 365 nm UV light (n=1-5); (b) the transparency of g-C_3N_4/LDH films (n=0, 3, 5) and photographs under visible light.

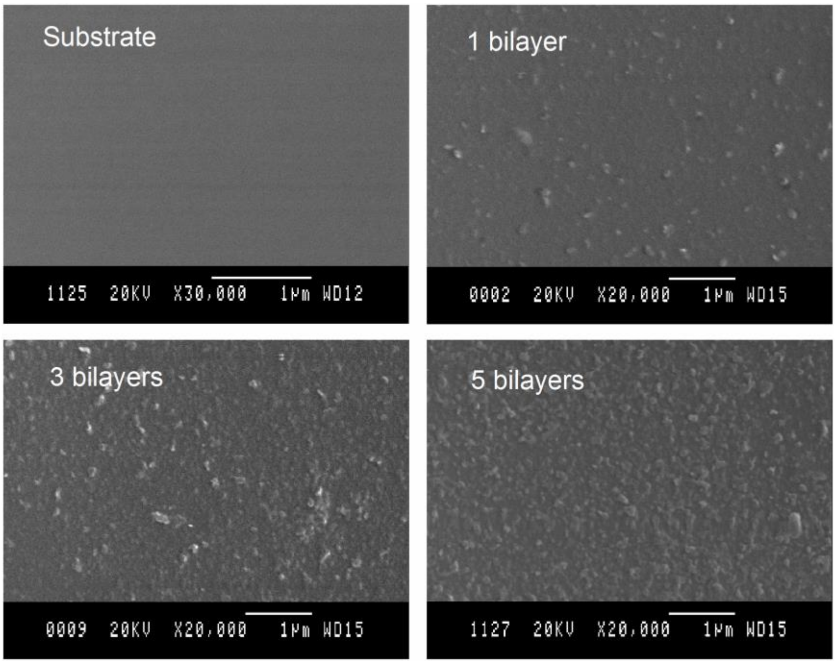

Figure S6. Top-view SEM image of g-C_3N_4/LDH films.

The surface morphology of g-C_3N_4/LDH films was observed by scanning electron microscope (Figure S6). Along with the layer-by-layer self-assembly, surface roughness is slightly affected by surface coverage and the microstructure of building blocks. In general, the surface of as-prepared films were microscopically continuous and uniform.

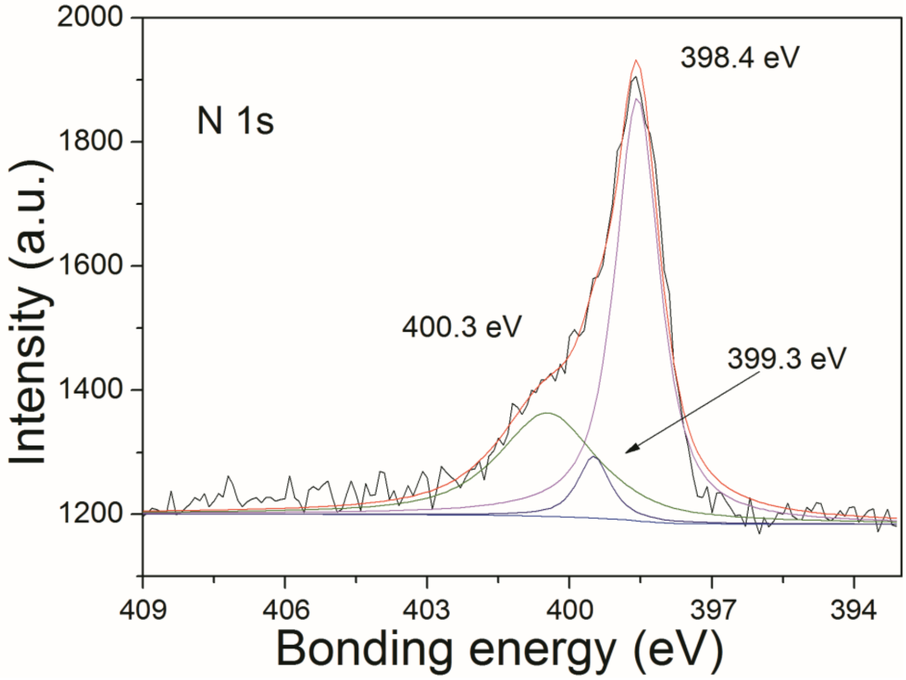

Figure S7. N 1s XPS spectrum of g-C_3N_4/LDH film.

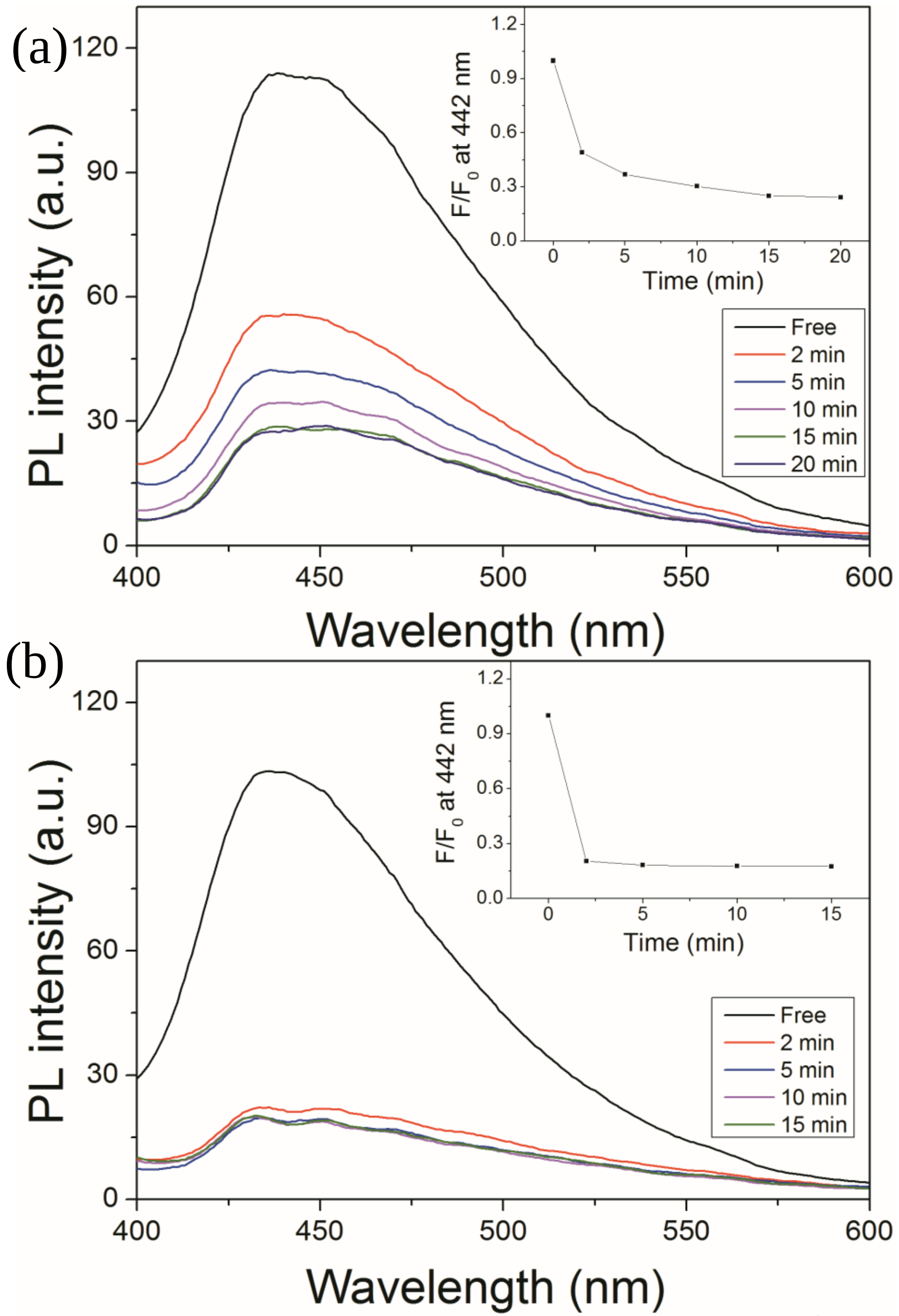

Figure S8. Fluorescence quenching of g-C_3N_4/LDH films by (a) 5 mM Cu^{2+} and (b) 500 μM Ag^+ solution. The insets display the remaining fluorescence intensity ratio as a function of time.

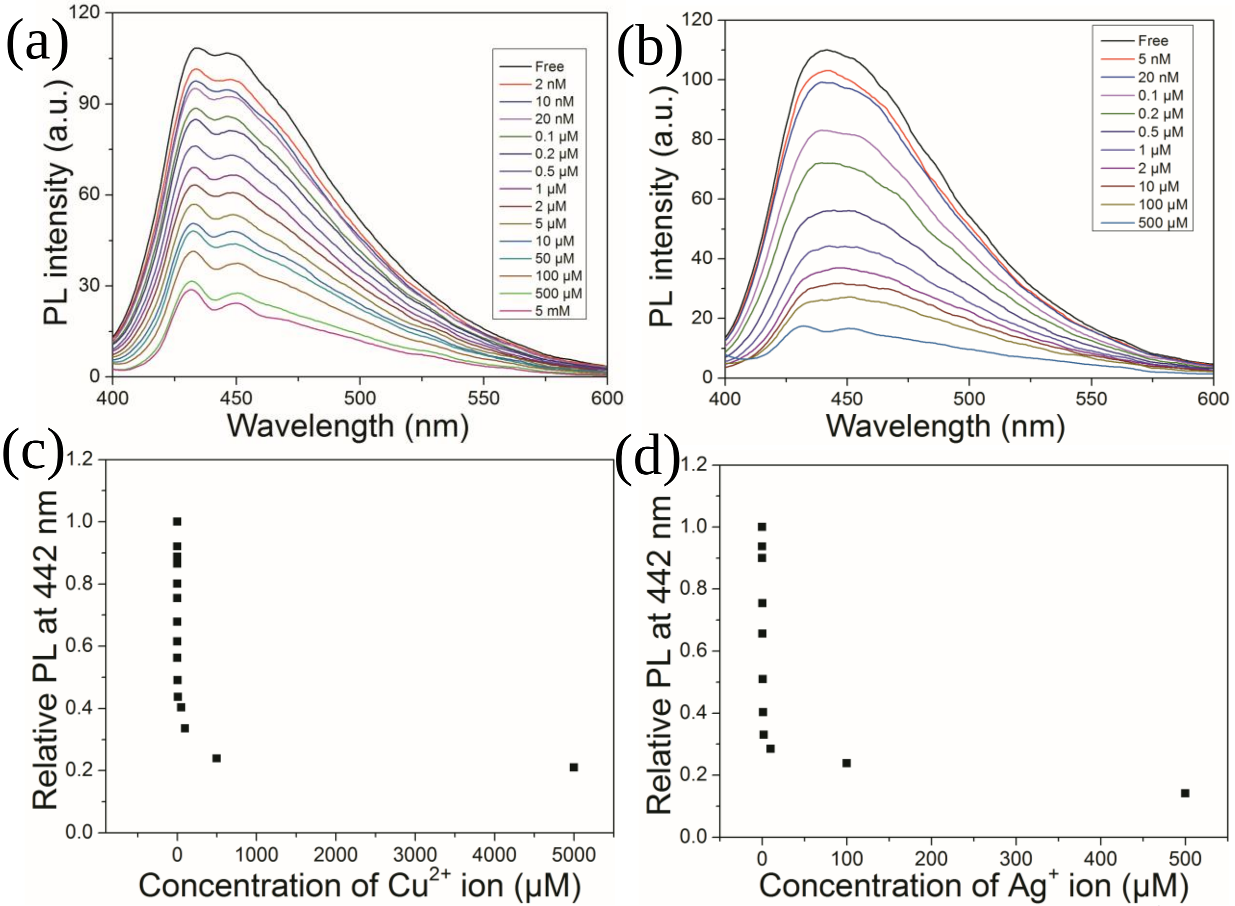

Figure S9. PL spectra of g-C_3N_4 nanosheets solution in the presence of different (a) Cu^{2+} and (b) Ag^+ concentrations; (c) and (d) display the relation between F/F_0 and the concentration of Cu^{2+} and Ag^+ ions. (F_0 and F are respectively the fluorescence intensities at 442 nm in the absence and presence of metal ions).

The detections of Cu^{2+} and Ag^+ ions with g-C_3N_4 nanosheets in solution were conducted in the Tris-HCI (10 mM, pH 7.4) buffer. Briefly, 300 μL g-C_3N_4 nanosheets solution, and 200 μL Cu^{2+} or Ag^+ ions solution were mixed with 1500 μL Tris-HCI buffer to achieve the calculated metal ion concentrations. The PL spectra were recorded after 10 min balance time at room temperature.

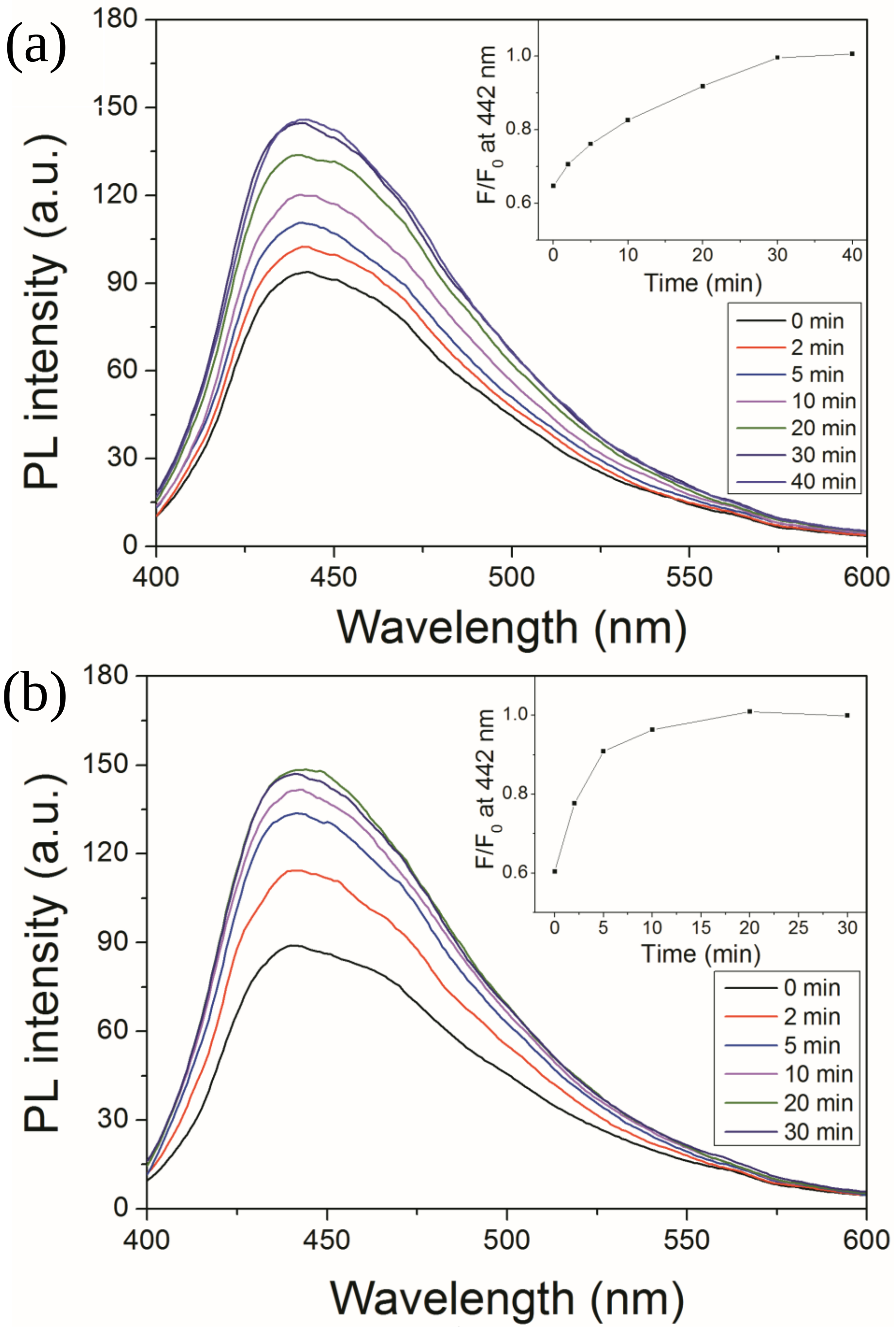

Figure S10. The fluorescence spectra of (a) Cu^{2+} (10 μM), and (b) Ag^{+} (1 μM) quenched g-C_3N_4/LDH films at different times after washing with 1:1 acetonitrile/water solution. (The insets display the recovery ratio at different washing times)

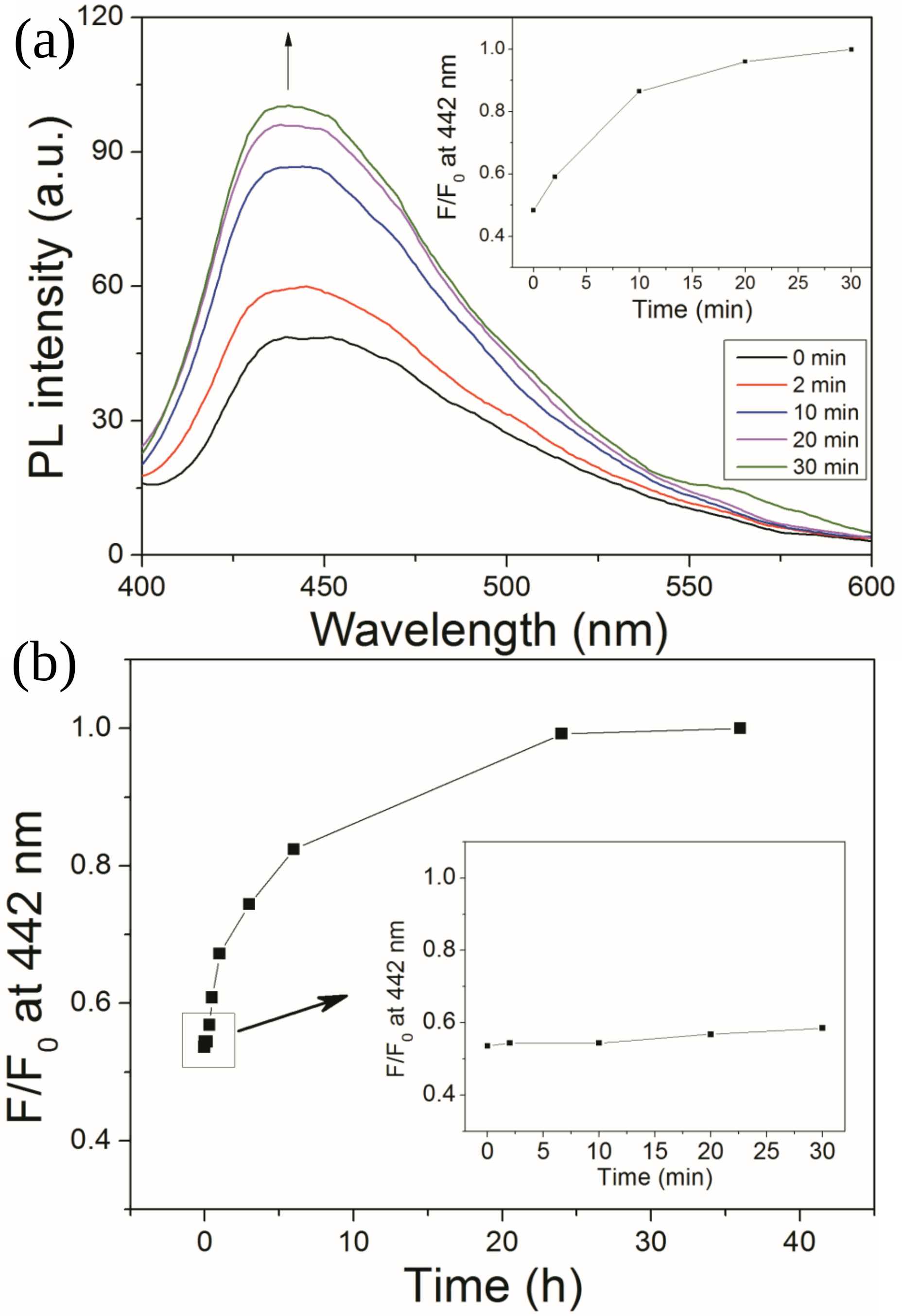

Figure S11. The fluorescence spectra of g-C_3N_4/LDH films treated by (a) 1 μM Ag^+ after washing with GSH solution. (insets display the relative fluorescent intensities with different washing times); (b) The relative fluorescence intensities of 10 μM Cu^{2+} quenched g-C_3N_4/LDH films at different times after washing with glutathione solution. (The inset displays the relative fluorescent intensities change in the first 30 min)

Computational section

Spin polarized density-functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE) functional[4] was applied to Ag and Cu ions adsorbed on a g-C_3N_4 monolayer. The Kohn-Sham equations were solved using the projected augmented wave (PAW) method, as coded in the Vienna Ab-initio Simulation Package (VASP 5.3.3).[5,6] For C, N, Cu and Ag atoms, the (2s, 2p), (2s, 2p), (3d, 4p) and (4d, 5s) states, respectively, were treated as valence with an energy cutoff of 400 eV. To model a C_3N_4 monolayer, a vacuum of 20 Å has been introduced, with 9 × 9 × 1 Monkhorst-Pack grid centered at the gamma point. The charge was set to be 1 and 2 for Ag (or Ag/g-C_3N_4) and Cu (or Cu/g-C_3N_4) model system, respectively. Structures are allowed to relax until the forces are below 0.01 eV/Å. The unit cell of g-C_3N_4 studied here is composed of 14 atoms, 6 of which are carbon atoms and 8 of which are nitrogen atoms. The relaxed constant of g-C_3N_4 is 7.11 Å, which is well consistent with previous experimental result by X-ray diffraction (7.3 Å)[7] and DFT calculation (7.1 Å).[8]

The adsorption of Ag (Cu) ions was analyzed on a single layer of g-C_3N_4 at 11 possible sites (Figure S12), where sites 1 and 2 are in the middle of a ring, sites 3 to 5 are on top of atom N, sites 6 and 7 are on top of atom C, sites 8 to 11 are on top of N-C bonds. The initial position h_0 of Ag (or Cu) above the substrate before optimization was 3 Å. The adsorption energy was calculated by subtracting the sum of the energy of an isolated ion (E_i) and the energy of the substrate ($E_\mathrm{g\text{-}C3N4}$) from the total energy of the system (E_tot), $E_\mathrm{ad} = E_\mathrm{tot} - (E_\mathrm{i}+E_\mathrm{g\text{-}C3N4})$. Negative adsorption energy indicates the adsorption is an energetic favorable (exothermic) reaction.

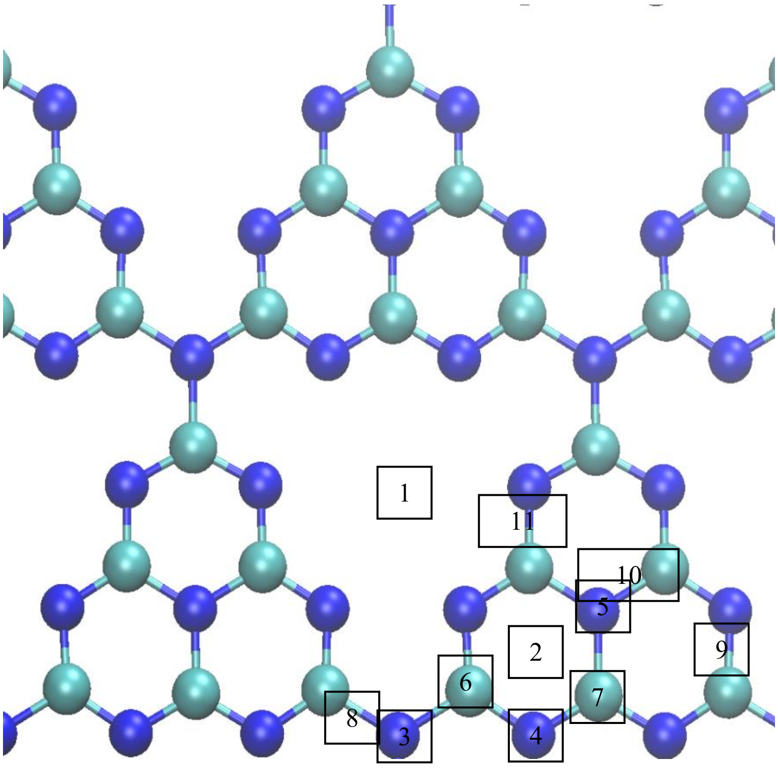

Figure S12. 11 possible surface adsorption sites of g-C_3N_4 (N atom in blue and C atom in cyan). Sites 1 and 2 are above rings, Sites 3 to 7 are above N or C atoms, and Sites 8-11 are above N-C bonds.

Geometry optimization results suggest that Site 1, a hollow site surrounded by N atoms (Figure S12), is the most possible adsorption site for both Ag and Cu ions. In Ag ion/g-C_3N_4 systems, initially placed at Site 1, Ag ion would relax to the g-C_3N_4 surface, and E_{ad} at this site is -3.87 eV, energetically the most favorable adsorption site. When Ag ion was initially placed at Sites 4, 7, 8 and 10, Ag ion would also relax to Site 1; while for other sites, Ag ion would relax to the middle of the vacuum. In Cu ion/g-C_3N_4 systems, the Cu ion would relax to the middle of the vacuum for all sites. More interestingly, when h_0 was set to 2.0 Å on Site 1, the Cu ion would also relax to the g-C_3N_4 surface. The adsorption energy E_{ad} is -5.13 eV. These observations suggest both Ag and Cu ion can be adsorbed to g-C_3N_4 surface and there is a transition state during the adsorption process to Site 1.

Furthermore, to explore the minimum energy pathway (MEP) of ions onto Site 1 in the H_2O solvent environment, the transition state was located by the complete linear synchronous transit and quadratic synchronous transit (LST/QST) method[9] and the nudged elastic band (NEB) method[10,11] in the program package DMol^3[12,13] in the Materials Studio 5.0 of Accelrys, Inc. Calculations were carried out within the generalized gradient approximation (GGA) of PBE[4]. The maximum iterations were set as 400 with the maximum step size of 0.1 Å so that all results could be converged. The localized double-numerical basis set with a polarization d-function on all non-hydrogen atoms was employed. The tolerances of energy, gradient and displacement convergence were 2×10^{-5} Ha (1 Ha = 27.21 eV), 4×10^{-3} Ha/Å, and 0.005 Å, respectively. The self-consistent field (SCF) calculations were carried out with the spin-polarization Kohn-Sham equation, in which DIIS was used to accelerate convergence. The maximum SCF cycles were 400 with tolerance of 10^{-5} Ha and the reciprocal space is sampled using a ($3\times3\times1$) k-point grid generated automatically using the Monkhorst-Pack method centered at the gamma (Γ) point. The orbital cutoff of was set as 4.0 Å. COSMO, i.e., conductor-like screening model,[14] was applied to simulate the H_2O solvent environment with a dielectric constant of 78.54.

In the reactant configuration, or the initial state (IS) the ion was far above from Site 1 after fully relaxation. In the product configuration, or the final state (FS), the ion was close to Site 1 after geometry optimization.

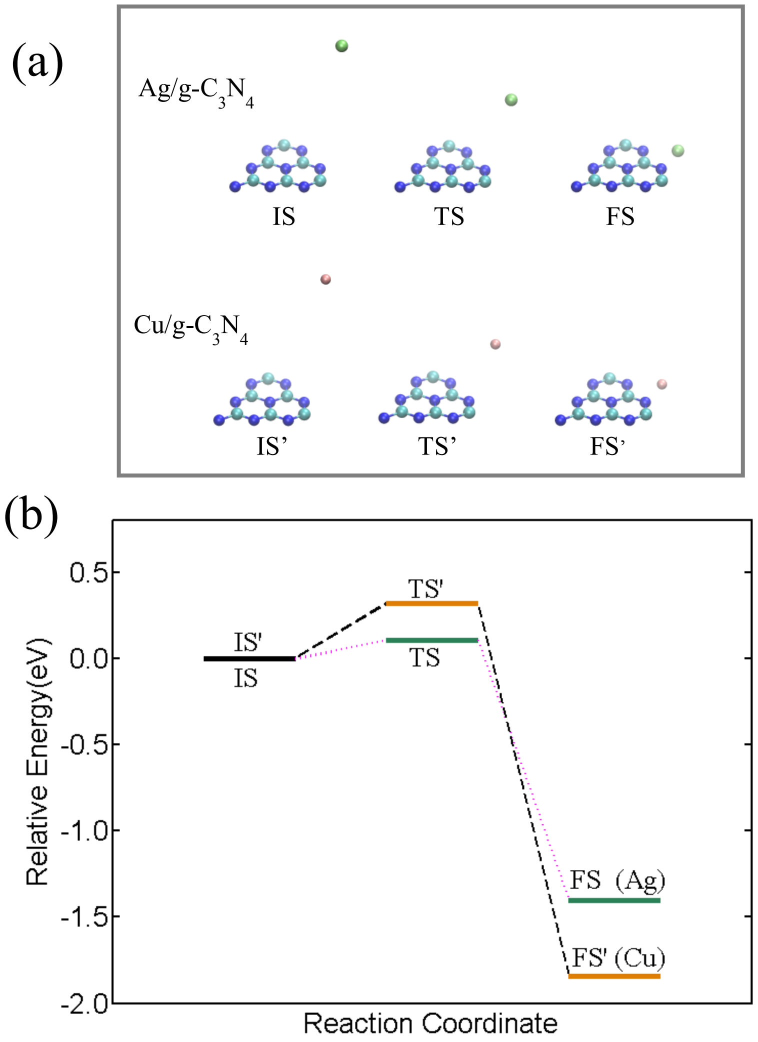

Figure S13. (a) Initial state (IS), transition state (TS) and final state (FS) of the adsorption process of Ag (top panel in (a)) and Cu (bottom panel in (a)) ions to g-C_3N_4 (N atom in blue and C atom in cyan). In IS, Ag (green) and Cu (light red) are far away from g-C_3N_4 surface. In FS, Ag and Cu are close to g-C_3N_4 surface. Panel (b) summarizes the relative energy of different states with respect to the initial state. Both the adsorption energy barrier and the dissociation energy barrier of the Ag/g-C_3N_4 system are smaller than those of the Cu/g-C_3N_4 system.

References

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