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Selective Gold Recovery by Carbon Nitride through Photoreduction

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Experimental Section

All chemicals used in this work were purchased from Sigma Aldrich (St. Louis, MO, USA).

1. The preparation of graphitic carbon nitride (g-C_3N_4)

g-C_3N_4 was prepared in the following way: 10 g melamine powder was put into an alumina crucible with a cover, which was further put into a muffle furnace and heated at 520℃ for two hours. Heating rate was 7℃/min.

2 The preparation of $HAuCl_4$, $Cr(NO_3)_3$, $CdCl_2$ and $CuSO_4$ solution.

82.3 mg $HAuCl_4 \cdot 4H_2O$ was put into a 500 ml volumetric flask to prepare $HAuCl_4$ solution with concentration of 0.4mmol/L. The pH of the $HAuCl_4$ solution is 3.4. Similar procedures have been done to prepare 0.4mmol/L solution of $Cr(NO_3)_3$, $CdCl_2$ and $CuSO_4$, respectively. Then, the pH of these solutions are adjusted to 3.4.

The mixture solution containing $HAuCl_4$, $Cr(NO_3)_3$, $CdCl_2$ and $CuSO_4$ was prepared, in which the concentration of $AuCl_4^-$, Cr^{3+}, Cd^{2+} and Cu^{2+} is 0.4mmol/L, respectively. Then, the pH of the mixture solutions is adjusted to 3.4.

3 Characterization

X-ray diffraction (XRD) patterns of samples were collected with the X-ray Diffractomer (Utilma III Tokyo, Japan) with Cu Kα (λ=1.540562 Å) radiation in the 2θ range from 0.7° to 5°or from 10° to 80°, in which the X-ray tube was operated at 40 kV and 40 mA. UV-Vis diffuse reflectance spectra (DRS) were obtained on a UV-visible (UV-vis) spectrophotometer (Shimadzu, UV 2550). XPS characterization was performed with PHI5000 VersaProbe X-ray photoelectron spectroscopy. Transmission electron microscopy (TEM) image was recorded on a JEM-2100 electron microscope. Inductively coupled plasma optical emission spectrometer (ICP-OES) results was obtained with Optima 5300DV.

4 photoreduction experiments

4.1 Photoreduction of $HAuCl_4$ with g-C_3N_4 as photocatalyst

20 ml $HAuCl_4$ solution was pour into the three light reaction tubes, respectively. Then, they were tabbed with “stable”, “light” and “dark” labels, and followed by the addition of 0.3g g-C_3N_4

into the tubes tabbed with “light” and “dark” labels. After that, the tubes tabbed with “stable” and “light” labels were put into the photocatalytic reactor and the photoreduction experiment was started under full-spectrum light irradiation and nitrogen atmosphere for four hours. The tube tabbed with “dark” label proceeded a similar process without the light irradiation.

The photoreduction results were characterized with Uv-vis, TEM and ICP methods.

4.2 Photoreduction of $Cr(NO_3)_3$ with g-C_3N_4 as photocatalyst

20 ml $Cr(NO_3)_3$ solution was pour into two light reaction tubes, respectively. Then, the two reaction tubes were tabbed with “light” and “stable” labels, and followed by the addition of 0.3g g-C_3N_4 into the tube tabbed with “light” label. After that, the tubes tabbed with “stable” and “light” labels were put into the photocatalytic reactor and the photoreduction experiment was started under full-spectrum light irradiation and nitrogen atmosphere for four hours.

The photoreduction results were characterized with Uv-vis, TEM and ICP methods.

4.3 Photoreduction of $CdCl_2$ with g-C_3N_4 as photocatalyst

20 ml $CdCl_2$ solution was pour into two light reaction tubes, respectively. Then, the two reaction tubes were tabbed with “light” and “stable” labels, and followed by the addition of 0.3g g-C_3N_4 into the tube tabbed with “light” label. After that, the tubes tabbed with “stable” and “light” labels were put into the photocatalytic reactor and the photoreduction experiment was started under full-spectrum light irradiation and nitrogen atmosphere for 4 h.

The photoreduction results were characterized with Uv-vis, TEM and ICP methods.

4.4 Photoreduction of $CuSO_4$ with g-C_3N_4 as photocatalyst

20 ml $CuSO_4$ solution was pour into two light reaction tubes, respectively. Then, the two reaction tubes were tabbed with “light” and “stable” labels, and followed by the addition of 0.3g g-C_3N_4 into the tube tabbed with “light” label. After that, the tubes tabbed with “stable” and “light” labels were put into the photocatalytic reactor and the photoreduction experiment was started under full-spectrum light irradiation and nitrogen atmosphere for 4 h.

The photoreduction results were characterized with Uv-vis, TEM and ICP methods.

4.5 Photoreduction of mixture solution containing $HAuCl_4$, $Cr(NO_3)_3$, $CdCl_2$ and $CuSO_4$

20 ml mixture solution was added into a light reaction tube, in which the concentration of $HAuCl_4$, $Cr(NO_3)_3$, $CdCl_2$ and $CuSO_4$ were 0.4 mmol/L, respectively. Then, 0.3g g-C_3N_4 was added into the tube. The photoreduction reaction proceeded under full-spectrum light irradiation and nitrogen atmosphere for 4 h.

The photoreduction results were characterized with ICP methods.

5. Theoretical calculation

All calculations were performed with B3LYP methods[1] in Gaussian 03 program[2]. LanL2DZ basis set was used to for Au, Cr, Cd and Cu atoms. 3-21g basis set was applied to C, N, O, Cl and H atoms. Given that ions are involved, solvent effect has been considered in all optimizations by using PCM model [3] with water as solvent. All molecular structures were constructed with Gview program based the optimized results.

1 A. D. Becke, *J. Chem. Phys*. **1993**, 98, 5648.

2 G. W. T. M. J. Frisch, et al, Gaussian 03, Revision E.01, Wallingford, CT, 2004.

3 G. Scalmani and M. J. Frisch, *J. Chem. Phys*. **2010**, 132, 114110.

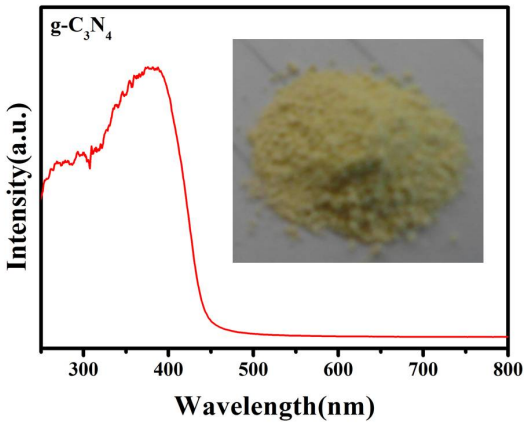


Fig.S1 UV-vis absorption spectrum of g-C_3N_4 sample.

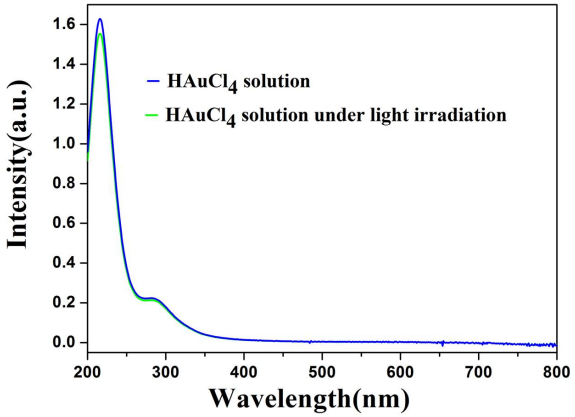


Fig.S2 UV-vis absorption spectra of $HAuCl_4$ and $HAuCl_4$ solution after full-spectrum light irradiation under nitrogen atmosphere.

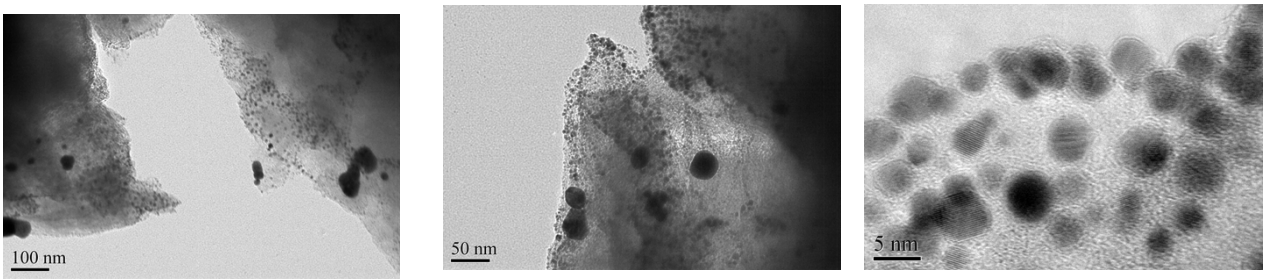


Fig.S3 TEM images of g-C_3N_4 sample after photo-reducing $HAuCl_4$ at 100nm, 50nm and 5nm scale, respectively.

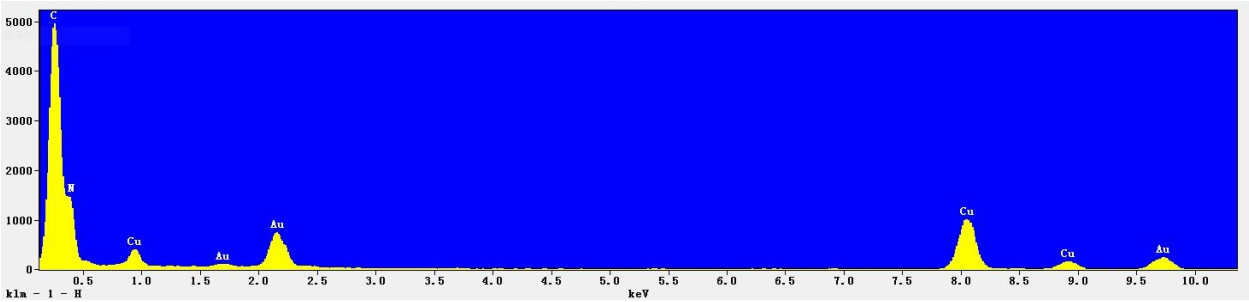


Fig.S4 EDX result for g-C_3N_4 sample after photo-reducing $HAuCl_4$.

	$HAuCl_4$ original solution (20 ml)	The solution (50 ml) acquired by heating the used g-C_3N_4 sample at 1000 °C and subsequent treatment with nitrohydrochloric acid
Au amount	79.0 ppm	25.8 ppm

Table S1 ICP results of $HAuCl_4$ original solution and the solution (50 ml) acquired by heating the used g-C_3N_4 sample at 1000 °C and succedent treatment with nitrohydrochloric acid. The heating time is two hours and nitrohydrochloric acid is produced by mixing nitric acid and hydrochloric acid with volume ratio ratio (1:3).

	Original solution (20 ml)	The solution (50 ml) acquired by heating the used g-C_3N_4 sample at 1000 °C and subsequent treatment with nitrohydrochloric acid
Cu amount	26.9 ppm	0.018 ppm
Cr amount	21.0 ppm	0.031ppm
Cd amount	45.0 ppm	0.005ppm

Table S2. ICP results of $CuSO_4$, $CdCl_2$ and $Cd(NO_3)_2$ original solutions and the solutions (50 ml) acquired by heating the used g-C_3N_4 samples at 1000 °C and succedent treatment with nitrohydrochloric acid. The heating time is two hours and nitrohydrochloric acid is produced by mixing nitric acid and hydrochloric acid with volume ratio ratio (1:3).

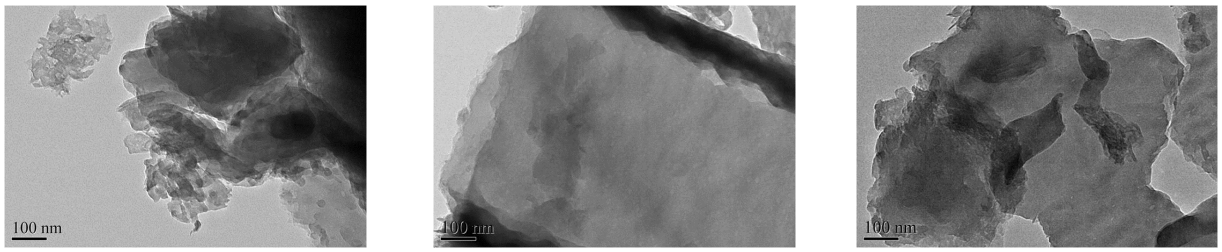


Fig.S5 TEM images of g-C_3N_4 after photoreduction of $Cd(NO_3)_2$ (left), $CrCl_3$ (middle) and $CuSO_4$(right), respectively.

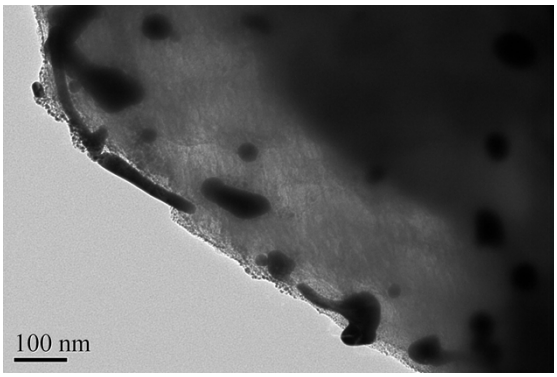


Fig.S6 TEM images of g-C_3N_4 after photo-reducing mixture solution of $HAuCl_4$, $CdCl_2$, $Cr(NO_3)_3$ and CuS

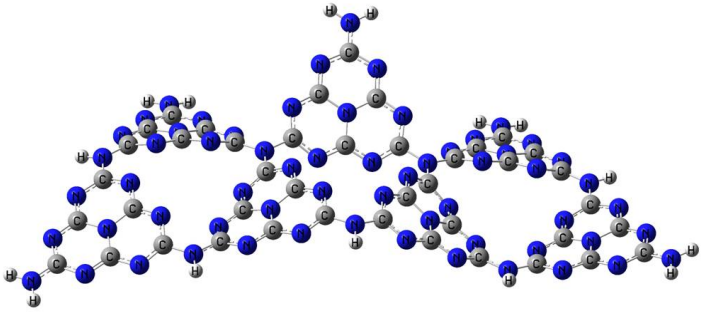
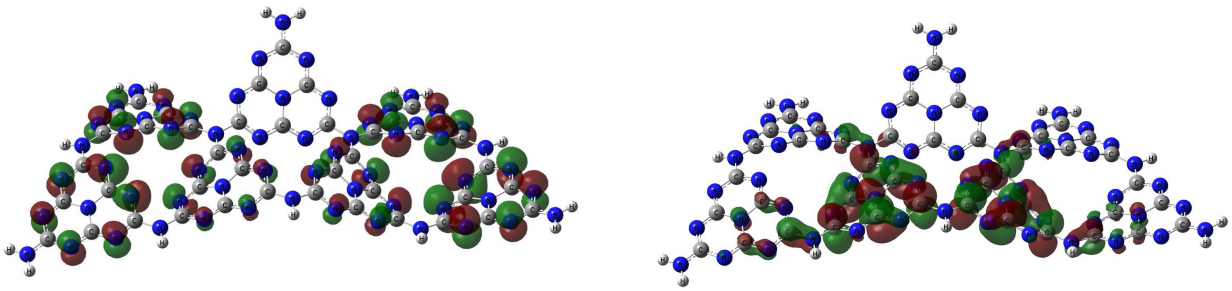


Fig.S7 The optimized structure of g-C_3N_4 model.



HOMO LUMO

Fig.S8 HOMO and LUMO orbital of the optimized structure of g-C_3N_4 model.

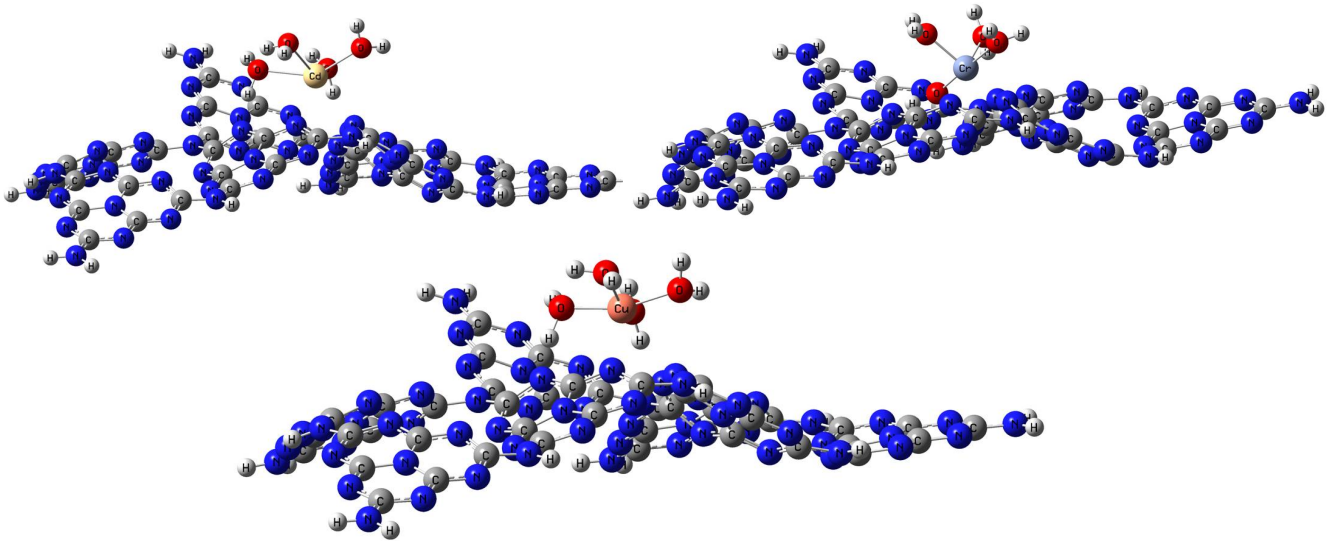


Fig.S9 The optimized structures of g-C_3N_4…$Cr(H_2O)_4^{3+}$, g-C_3N_4…$Cd(H_2O)_4^{2+}$ and g-C_3N_4…$Cu(H_2O)_4^{2+}$ complexes.

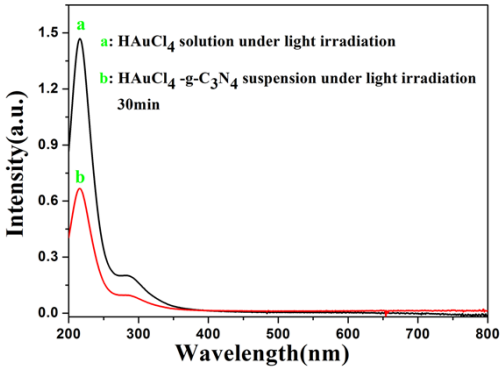


Fig. S10 UV-vis absorption spectra of $HAuCl_4$ solution at the initial time and 30 min after photoreduction.

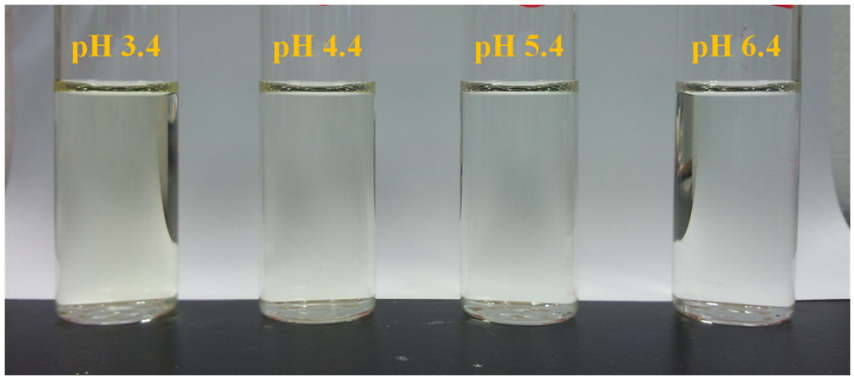


Fig.S11 $HAuCl_4$ solution at different pH values.

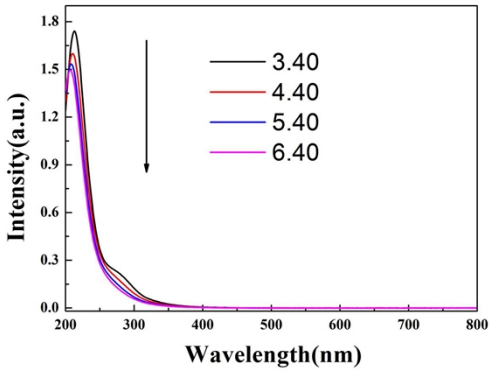


Fig.S12 UV-vis absorption spectra of $HAuCl_4$ at different pH values.

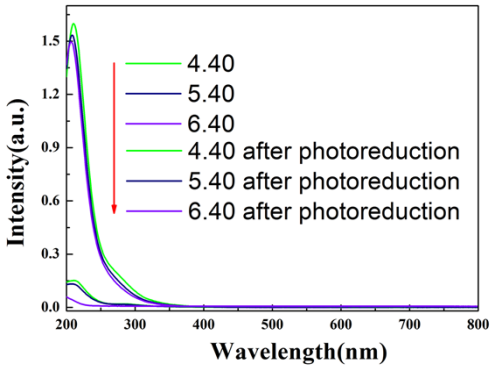


Fig. S13 UV-vis absorption spectra of $HAuCl_4$ at different pH values before and after photoreduction.

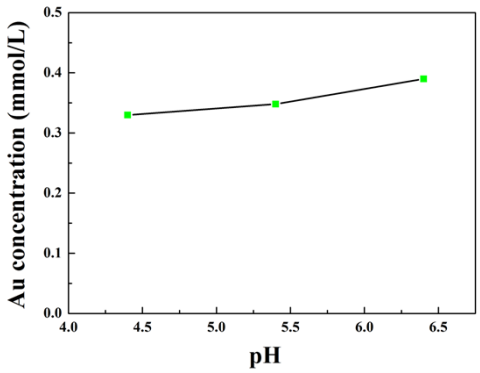


Fig.S14 The concentration of the recovered gold at different pH values.