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$_3$N$_4$)

g-C$_3$N$_4$ 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°C for two hours. Heating rate was 7°C/min.

2 The preparation of HAuCl$_4$, Cr(NO$_3$)$_3$, CdCl$_2$ and CuSO$_4$ solution.

82.3 mg HAuCl$_4$∙4H$_2$O 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$_3$N$_4$ 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$_3$N$_4$
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$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ 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\textsuperscript{1} in Gaussian 03 program\textsuperscript{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 \textsuperscript{3} with water as solvent. All molecular structures were constructed with Gview program based the optimized results.

\begin{itemize}
\end{itemize}
Fig. S1 UV-vis absorption spectrum of g-C\textsubscript{3}N\textsubscript{4} sample.

Fig. S2 UV-vis absorption spectra of HAuCl\textsubscript{4} and HAuCl\textsubscript{4} solution after full-spectrum light irradiation under nitrogen atmosphere.

Fig. S3 TEM images of g-C\textsubscript{3}N\textsubscript{4} sample after photo-reducing HAuCl\textsubscript{4} at 100nm, 50nm and 5nm scale, respectively.
Fig. S4 EDX result for g-C₃N₄ sample after photo-reducing HAuCl₄.

Table S1 ICP results of H AuCl₄ original solution and the solution (50 ml) acquired by heating the used g-C₃N₄ sample at 1000 °C and subsequent 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).

<table>
<thead>
<tr>
<th></th>
<th>H AuCl₄ original solution (20 ml)</th>
<th>The solution (50 ml) acquired by heating the used g-C₃N₄ sample at 1000 °C and subsequent treatment with nitrohydrochloric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au amount</td>
<td>79.0 ppm</td>
<td>25.8 ppm</td>
</tr>
</tbody>
</table>

Table S2. ICP results of CuSO₄, CdCl₂ and Cd(NO₃)₂ original solutions and the solutions (50 ml) acquired by heating the used g-C₃N₄ 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).

<table>
<thead>
<tr>
<th></th>
<th>Original solution (20 ml)</th>
<th>The solution (50 ml) acquired by heating the used g-C₃N₄ sample at 1000 °C and subsequent treatment with nitrohydrochloric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu amount</td>
<td>26.9 ppm</td>
<td>0.018 ppm</td>
</tr>
<tr>
<td>Cr amount</td>
<td>21.0 ppm</td>
<td>0.031 ppm</td>
</tr>
<tr>
<td>Cd amount</td>
<td>45.0 ppm</td>
<td>0.005 ppm</td>
</tr>
</tbody>
</table>
Fig. S5 TEM images of g-C₃N₄ after photoreduction of Cd(NO₃)₂ (left), CrCl₃ (middle) and CuSO₄ (right), respectively.

Fig. S6 TEM images of g-C₃N₄ after photo-reducing mixture solution of HAuCl₄, CdCl₂, Cr(NO₃)₃ and CuS.

Fig. S7 The optimized structure of g-C₃N₄ model.

Fig. S8 HOMO and LUMO orbital of the optimized structure of g-C₃N₄ 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 HAuCl₄ at different pH values.

Fig. S13 UV-vis absorption spectra of HAuCl₄ at different pH values before and after photoreduction.

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