Supporting Information

Hydroxyl-rich C-dots Synthesized with One-pot Method and Its Application in the Preparation of Noble Metal Nanoparticles

Qiujun Lu, Jianhui Deng, Yuxin Hou, Haiyan Wang, Haitao Li, Youyu Zhang* and Shouzhuo Yao

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, PR China

*Corresponding author. Fax: +86 73188872531; Tel: +86 73188865515;
E-mail address: zhangyy@hunnu.edu.cn

1 Experimental

1.1 Materials

All chemicals were used as received without any further purification. Ultrapure water (18.2 mΩ; Millpore Co., USA) was used throughout the experiment.

1.2 Synthesis of C-dots

C-dots were electrochemically synthesized based on our previous work with a few modifications. Briefly, ethylene glycol and sodium hydroxide mix solution was used as the electrolytes, platinum sheets as the positive and the negative electrodes. The C-dots were synthesized by electrolyzing electrolyte solution under 30 V (DC) for 40 min. After electrolysis, the electrolyte solution was neutralized with hydrochloric acid and then dialyzed (Mw 1000) against water for over two days.

1.3 Synthesis of AuNPs, AgNPs and Au@AgNPs

The AuNPs were synthesized as follows. A certain amount of HAuCl₄ aqueous solution (0.1 mM) was added to 1 mL aqueous solution of as-synthesized C-dots (0.07 mg mL⁻¹) at room temperature for 20 min. Similarly, the syntheses of AgNPs were conducted in an aqueous solution consisting of C-dots (0.07 mg mL⁻¹), AgNO₃ (0.1
mM) and NaOH (0.01 M) at room temperature for 18 min. Au@AgNPs were synthesized using seed colloid technique. Using as-synthesized AuNPs as seeds, then different concentration of AgNO$_3$ and NaOH (0.01 M) solution were added to the seeds solution at room temperature for a certain time.

1.4 Detection of H$_2$O$_2$ and glucose
The detection of H$_2$O$_2$ is conducted by the following procedures: 100 μL of the as-synthesized metal nanoparticles solution (0.5 mg mL$^{-1}$) was added into 790 μL NaAc buffer solution (50 mM, pH 4.0), followed by adding 10 μL of TMB solution (50 mM in DMSO), then 100 μL of H$_2$O$_2$ solution with different concentrations was added, then kept in 37 °C bath for 30 min before absorbance measurement.

For the detection of glucose, 50 μL of GOx (2 mg mL$^{-1}$) and 50 μL glucose with different concentrations were first incubated at 37 °C for 30 min. Afterward, 10 μL of TMB, 100 μL of metal nanoparticles solution (0.5 mg mL$^{-1}$), and 790 μL of NaAc solution were added, and the mixture was further incubated at 37 °C for another 30 min before absorbance measurement.

1.5 Characterizations
Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern of C-dots were obtained using a JEOL-1230 transmission electron microscope (JEOL, Japan). The sample for TEM characterization was prepared by placing a drop of the colloidal solution on the carbon-coated copper grid and dried at room temperature. The Scanning transmission electron microscopy (STEM) image, elemental analysis mappings were taken by using a Tecnai G2 F20 S-T win HRTEM operated at 200 kV. Fourier transform infrared spectra (FT-IR) in the 4000 to 400 cm$^{-1}$ regions were recorded on a Nicolet Nexus 670 FT-IR spectroscope (Nicolet Instrument Co., USA). The UV-Vis spectra and the fluorescence spectra (FL) were obtained using a UV-2450 UV-Vis spectrophotometer (Shimadzu Co., Japan) and a F-4500 fluorescence spectrophotometer (Hitachi Ltd, Japan), respectively. X-ray photoelectron spectroscopy (XPS) analysis was done on an Thermo Fisher
Scientific K-Alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, Britain) using Al, K as the exciting source.
Fig. S1 FT-IR spectra of as-synthesized C-dots
Fig. S2 (A) UV-vis spectra and FL spectra of C-dots, inset: the color of C-dots solution under UV irradiation. (B) FL emission spectra of C-dots at different excitation wavelengths.
Fig. S3 Size distribution histograms of as-synthesized AuNPs.
Fig. S4 (A, B) Elemental maps of Au-L and C-K respectively. (C, D) Corresponding Cross-sectional compositional line profiles of (A) and (B).

The STEM measured was performed by placing a drop of as-synthesized nanoparticles colloidal solution on the carbon-coated copper grid. In the absence of nanoparticles, the carbon signal was little low which was obtained from the carbon-coated copper grid. On the contrary, the presence of nanoparticles brought a higher carbon signal in the experiments (both carbon of carbon-coated copper grid and carbon of C-dots can cause of carbon signal). Also the higher signal width in Fig. S4 was the same large as the size of C-dots. In addition, there are many hydroxyl groups on the surface of the C-dots, which can interact with gold nanoparticles to protect AuNPs from aggregating. Thus, the increased signal indicated the presence of carbon on AuNPs surface.
Fig. S5 (A) FT-IR spectra of C-dots before and after reduction. (B, C) C1s spectra of C-dots before (B) and after (C) reduction.
Fig. S6 Time-dependent absorbance changes of TMB at 652 nm in different assays. Inserts are the photograph of them: (from left to right) TMB-AuNPs, TMB-H$_2$O$_2$ and TMB-AuNPs-H$_2$O$_2$, respectively. The pH of NaAc buffer was 4.0; the concentration of AuNPs was 0.05 mg mL$^{-1}$. The concentration of TMB was 0.5 mM, and H$_2$O$_2$ was 0.5 mM. Before absorbance test, all the samples were kept in 37 °C.
Fig. S7 Temporal evolution UV-vis spectra of C-dots and C-dots mixed with AgNO$_3$ and NaOH (0.01 mM) under room temperature.
Fig. S8 Size distribution histograms of as-synthesized AgNPs.
Fig. S9 Size distribution histograms of as-synthesized Au@AgNPs.
Tab S1

The changes of binding energy area of C-dots before and after reduction

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>Area CPS.eV C-dots</th>
<th>Area CPS.eV AuNPs/C-dots</th>
<th>Area Ratio C-dots</th>
<th>Area Ratio AuNPs/C-dots</th>
</tr>
</thead>
<tbody>
<tr>
<td>284.7 (C-C)</td>
<td>32989.99</td>
<td>28442.73</td>
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<td>1.00</td>
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<td>286.1 (C-OH)</td>
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<td>287.8 (C=O)</td>
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<td>2719.44</td>
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<tr>
<td>289.0 (O=C-OH)</td>
<td>1713.95</td>
<td>2134.22</td>
<td>0.05</td>
<td>0.08</td>
</tr>
</tbody>
</table>