Supplementary Information

Photoluminescence enhancement of carbon dots by gold nanoparticles conjugated via PAMAM dendrimers

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TGA curves of Au-MPA, Au-PAMAM, and Au-PAMAM-CDs

![TGA curves of Au-MPA, Au-PAMAM, and Au-PAMAM-CDs](image)

**Fig. S1** TGA curves of (a) Au-MPA, (b) Au-PAMAM, and (c) Au-PAMAM-CDs conjugates.

**The Estimate of the Density of CDs**

We have confirmed from selected area electron diffraction (SAED) of CDs that the presence of diffraction rings due to d-spacing values of 2.28 and 1.41 Å, which correspond to (100) and (110) lattice spacing of carbon-based materials, respectively. 30 As we know, glassy carbon, graphite, and diamond are the most
common carbon-based materials. Compared with these materials, CDs are diamond-like in view of their d-spacing values.\textsuperscript{S1} In addition, among the amorphous carbon, glassy carbon has only sp\textsuperscript{2} bonds. Graphite consists purely of sp\textsuperscript{2} hybridized bonds, whereas diamond consists purely of sp\textsuperscript{3} hybridized bonds. Carbon-based materials which are high in sp\textsuperscript{3} hybridized bonds are referred to as tetrahedral amorphous carbon (owing to the tetrahedral shape formed by sp\textsuperscript{3} hybridized bonds) or as diamond-like carbon (owing to the similarity of many physical properties to those of diamond). It also suggests CDs are diamond-like as the max peak (285.0 eV) in the XPS spectrum of CDs (Fig. S2) is in line with sp\textsuperscript{3} bonding in the spectrum of tetrahedral amorphous carbon.\textsuperscript{S2}

\textbf{Fig. S2} C 1s XPS spectra of CDs.

Because the specimen for XPS is prepared by drop casting the sample dispersion onto a Teflon film, carbon film is considered to be formed. A series of studies have shown that the density of amorphous carbon increases with increasing contributions from sp\textsuperscript{3} bonding.\textsuperscript{S3-S4} It showed that amorphous carbon films have different densities ranging from 1.7 to 3.1 g/cm\textsuperscript{3}. And tetrahedral amorphous carbon film has a typical density in the range of 2.1 to 2.4 g/cm\textsuperscript{3}. Therefore, the density of CDs can be estimated to be 2.1 to 2.4 g/cm\textsuperscript{3}.

\textbf{Calculation of the Amount of Au, PAMAM, and CDs}

Attempts to obtain TEM images of Au-PAMAM-CDs conjugates were unsuccessful. So here we try to calculate the amount of Au, PAMAM, and CDs to fix their ratio.

\textbf{1. Calculation of the amount of CDs}
The calculation method is as follows:

The concentration of the solution of CDs is

$$\rho (\text{solution of CDs}) = 0.5 \text{ mg/mL}$$

If the volume of the solution of CDs is

$$V(\text{solution of CDs}) = 0.5 \text{ mL}$$

then

$$m(\text{CDs}) = \rho (\text{solution of CDs}) \times V(\text{solution of CDs}) = 0.25 \text{ mg} = 2.5 \times 10^{-7} \text{ kg}$$

The average diameter of CDs is $$d(\text{CDs}) = 2.1 \times 10^{-9} \text{ m}$$, thus the radius of CDs is

$$r(\text{CDs}) = \frac{d(\text{CDs})}{2} = \frac{2.1}{2} \times 10^{-9} \text{ m}$$

The volume of single carbon dot is

$$V(\text{CDs}) = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi 3.1415926 \times \left(\frac{2.1}{2} \times 10^{-9}\right)^3 \text{ m}^3$$

$$= \frac{116.3772}{24} \times 10^{-27} \text{ m}^3$$

A. If the density of solid CDs is $$\rho = 2.1 \times 10^3 \text{ kg/m}^3$$

The volume of 0.25 mg of solid CDs is

$$V_1 = \frac{m}{\rho} = \frac{2.5 \times 10^{-7}}{2.1 \times 10^3} \text{ m}^3$$

The number of CDs is

$$N_1 = \frac{V_1}{V} = \frac{2.5 \times 10^{-7}}{2.1 \times 10^3} \times \frac{24 \times 10^{27}}{116.3772} = \frac{6 \times 10^{16}}{2.4439212}$$

Thus, the amount of CDs is

$$n(\text{CDs}) = \frac{N_1}{N_A} = \frac{6 \times 10^{16}}{2.4439212 \times 6.022 \times 10^{23}} = 4.0768 \times 10^{-8} \text{ mol}$$

$$\approx 4 \times 10^{-8} \text{ mol}$$

B. If the density of solid CDs is $$\rho = 2.4 \times 10^3 \text{ kg/m}^3$$

The volume of 0.25 mg of solid CDs is

$$V_1 = \frac{m}{\rho} = \frac{2.5 \times 10^{-7}}{2.4 \times 10^3} \text{ m}^3$$
The number of CDs is

\[ N_1 = \frac{V_1}{V} = \frac{2.5 \times 10^{-7}}{2.4 \times 10^3} \times \frac{24 \times 10^{27}}{116.3772} = \frac{2.5 \times 10^{16}}{1.163772} \]

Thus, the amount of CDs is

\[ n(\text{CDs}) = \frac{N_1}{N_A} = \frac{2.5 \times 10^{16}}{1.163772 \times 6.022 \times 10^{23}} = 3.5672 \times 10^{-8} \text{ mol} \approx 4 \times 10^{-8} \text{ mol} \]

Therefore, the amount of CDs is estimated to be \( 4 \times 10^{-8} \text{ mol} \).

2. Calculation of the amount of PAMAM

\[ c(\text{PAMAM}) = 10^{-5} \text{ mol/L} \]

\[ V(\text{PAMAM}) = 6 \text{ mL} = 6 \times 10^{-3} \text{ L} \]

The amount of PAMAM is

\[ n(\text{PAMAM}) = c(\text{PAMAM}) \times V(\text{PAMAM}) = 10^{-5} \times 6 \times 10^{-3} = 6 \times 10^{-8} \text{ mol} \]

3. Calculation of the amount of Au NPs

\[ c(\text{Au}) = 3 \times 10^{-4} \text{ mol/L} \]

If the volume of Au colloids is

\[ V(\text{Au}) = 400 \mu\text{L} = 4 \times 10^{-4} \text{ L} \]

The amount of Au is

\[ n(\text{Au}) = c(\text{Au}) \times V(\text{Au}) = 3 \times 10^{-4} \times 4 \times 10^{-4} = 12 \times 10^{-8} \text{ mol} \]

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>V (Au NPs)/(\mu\text{L})</th>
<th>V (PAMAM)/mL</th>
<th>V (CDs)/mL</th>
<th>Molar ratio (Au:PAMAM:CDs)</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>6</td>
<td>0.5</td>
<td>0:1:0.67</td>
<td>8</td>
</tr>
<tr>
<td>b</td>
<td>100</td>
<td>6</td>
<td>0.5</td>
<td>0.5:1:0.67</td>
<td>47</td>
</tr>
<tr>
<td>c</td>
<td>400</td>
<td>6</td>
<td>0.5</td>
<td>2:1:0.67</td>
<td>62</td>
</tr>
<tr>
<td>d</td>
<td>800</td>
<td>6</td>
<td>0.5</td>
<td>4:1:0.67</td>
<td>16</td>
</tr>
</tbody>
</table>

The enhancement factor was calculated as the ratio of the maximum peak intensity of
Au-PAMAM-CDs conjugates to CDs.

**Table 2**

Effects of different amounts of CDs on the PL intensity of Au-PAMAM-CDs conjugates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V (Au NPs)/μL</th>
<th>V (PAMAM)/mL</th>
<th>V (CDs)/mL</th>
<th>Molar ratio (Au:PAMAM:CDs)</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>400</td>
<td>6</td>
<td>0.5</td>
<td>2:1:0.67</td>
<td>62</td>
</tr>
<tr>
<td>e</td>
<td>400</td>
<td>6</td>
<td>1</td>
<td>2:1:1.33</td>
<td>10</td>
</tr>
<tr>
<td>f</td>
<td>400</td>
<td>6</td>
<td>1.5</td>
<td>2:1:2</td>
<td>6</td>
</tr>
</tbody>
</table>

The enhancement factor was calculated as the ratio of the maximum peak intensity of Au-PAMAM-CDs conjugates to CDs.

**Quantum yields of CDs and Au-PAMAM-CDs conjugates**

The quantum yield of CDs is 0.23, which was demonstrated in our previous work. The quantum yield of Au-PAMAM-CDs conjugates was determined using rhodamine B as a reference, respectively. The details were as follows.

The quantum yield of rhodamine B in water is 0.31. The quantum yield of Au-PAMAM-CDs conjugates in ethanol-water solution was calculated according to:

\[
\Phi = \phi_r \times \frac{A}{I_r} \times \frac{1}{A} \times \frac{n^2}{n_r^2}
\]

Where \( \Phi \) is the quantum yield, \( I \) is the measured integrated emission intensity, \( n \) is the refractive index, and \( A \) is the optical density. The refractive index of water and aqueous ethanol mixture (60% ethanol) is 1.33 and 1.34, respectively. The subscript “r” refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects, absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength of 340 nm. The resulting quantum yield of Au-PAMAM-CDs conjugates is 3.60.

**Table 3**

Quantum yield of Au-PAMAM-CDs conjugates.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Integrated emission intensity (I)</th>
<th>Abs. at 340 nm (A)</th>
<th>Refractive index of solvent (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine B</td>
<td>1561.36</td>
<td>0.053</td>
<td>1.33</td>
</tr>
<tr>
<td>Au-PAMAM-CDs</td>
<td>13148.61</td>
<td>0.039</td>
<td>1.34</td>
</tr>
</tbody>
</table>

References