Electronic Supplementary Material (ESI) for Nanoscale

Supplementary Information

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

Jie Zong,[a, b, c] Xiaoling Yang,[a] Adrian Trinchi,[b] Simon Hardin,[b] Ivan Cole,[b] Yihua Zhu,[*a] Chunzhong Li,[a] Tim Muster[*b] and Gang Wei,[c]

[a] Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, P.R. China. Fax: +86 21 6425 0624; Tel.: +86 21 6425 2022; E-mail: yhzhu@ecust.edu.cn

[b] CSIRO Materials Science and Engineering (CMSE), Clayton, VIC 3168, Australia. Fax: +61 3 9544 1128; Tel. +61 3 9545 7964; E-mail: Tim.Muster@csiro.au

[c] CSIRO Materials Science and Engineering (CMSE), Lindfield, NSW 2070, Australia.

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

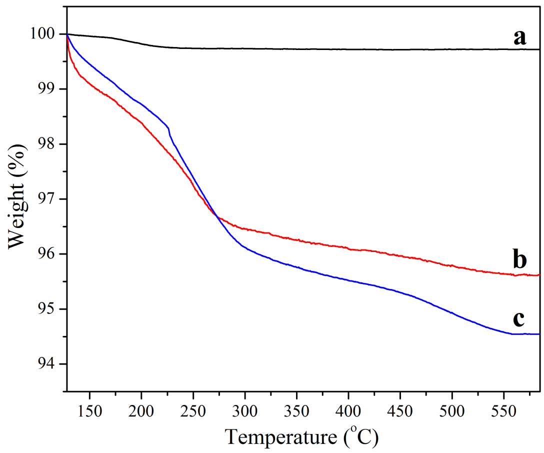

Fig. S1 TGA curves of (a) Au-MPA, (b) Au-PAMAM, and (c) Au-PAMAM-CDs conjugates.

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.[S1] In addition, among the amorphous carbon, glassy carbon has only sp^2 bonds. Graphite consists purely of sp^2 hybridized bonds, whereas diamond consists purely of sp^3 hybridized bonds. Carbon-based materials which are high in sp^3 hybridized bonds are referred to as tetrahedral amorphous carbon (owing to the tetrahedral shape formed by sp^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^3 bonding in the spectrum of tetrahedral amorphous carbon.[S2]

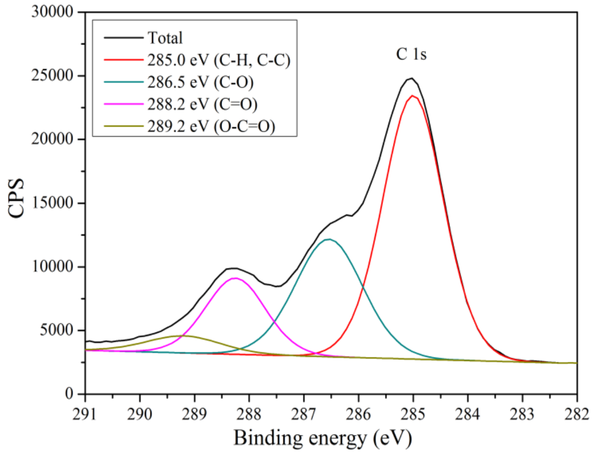

Fig. S2 C 1s XPS spectra of CDs.

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^3 bonding.[S3-S4] It showed that amorphous carbon films have different densities ranging from 1.7 to 3.1 g/cm^3. And tetrahedral amorphous carbon film has a typical density in the range of 2.1 to 2.4 g/cm^3. Therefore, the density of CDs can be estimated to be 2.1 to 2.4 g/cm^3.

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.

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

$$V(\text{CDs}) = \frac{4}{3} \times \pi r^3 = \frac{4}{3} \times 3.1415926 \times \left(\frac{2.1}{2} \times 10^{-9}\right)^3 \text{m}^3$$
$$= \frac{116.3772}{24} \times 10^{-27}\text{m}^3$$

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 4×10^{-8} 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

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

Sample	V (Au NPs)/ μL	V (PAMAM)/ mL	V (CDs)/ mL	Molar ratio (Au:PAMAM:CDs)	Enhancement factor
a	0	6	0.5	0:1:0.67	8
b	100	6	0.5	0.5:1: 0.67	47
c	400	6	0.5	2:1: 0.67	62
d	800	6	0.5	4:1: 0.67	16

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.

Sample	V (Au NPs)/ μL	V (PAMAM)/ mL	V (CDs)/ mL	Molar ratio (Au:PAMAM:CDs)	Enhancement factor
d	400	6	0.5	2:1:0.67	62
e	400	6	1	2:1:1.33	10
f	400	6	1.5	2:1:2	6

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[30].

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.[S5]

The quantum yield of Au-PAMAM-CDs conjugates in ethanol-water solution was calculated according to:

$$\phi = \phi_r \times \frac{A_r}{I_r} \times \frac{I}{A} \times \frac{n^2}{n_r^2}$$

Where Φ 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.[S6] 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.

Sample	Integrated emission intensity (I)	Abs. at 340 nm (A)	Refractive index of solvent (n)
Rhodamine B	1561.36	0.053	1.33
Au-PAMAM-CDs	13148.61	0.039	1.34

References

[S1] A. H. C. Sirk and D. R. Sadoway, *J. Electrochem. Soc.*, 2008, **155 (5)**, E49.

[S2] M. Iwasaki and A. Hirata, *New Diam. Front. C. Tec.*, 2005, **15**, 139.

[S3] P. K. Chu and L. H. Li, *Mater. Chem. Phys.*, 2006, **96**, 253.

[S4] S. R. P. Silva. *INSPEC*, *The Institution of Electrical Engineers*, 2003, pp 81.

[S5] D. Magde, G. E. Rojas and P. G. Seybold, *Photochem. Photobiol.*, 1999, **70**, 737.

[S6] M. S. Santosh, D. K. Bhat and A. S. Bhatt, *J. Chem. Eng. Data*, 2011, **56**, 768.