

Cite this: *Chem. Commun.*, 2011, **47**, 5313–5315

www.rsc.org/chemcomm

## Metal-enhanced photoluminescence from carbon nanodots

Yongxia Zhang,<sup>a</sup> Helena Gonçalves,<sup>b</sup> Joaquim C. G. Esteves da Silva<sup>c</sup> and Chris D. Geddes<sup>\*d</sup>

Received 13th September 2010, Accepted 8th March 2011

DOI: 10.1039/c0cc03832f

In the last couple of years, carbon dots have emerged as a new novel luminescent particle for applications in fluorescence and microscopy in some ways analogous to quantum dots and silicon nanocrystals/particles. As with any fluorescent label or tag, absolute fluorescence intensity, brightness, and particle photostability are a primary concern. In this communication we subsequently show that similar to classical fluorophores, carbon dots located in the near-field, near to Plasmon supporting materials, show enhanced intensities and improved photostabilities.

In the last several years, there has been a growing literature on the synthesis and utility of carbon dots, also known as carbon nanoparticles.<sup>1–3</sup> Similar to the well-known and commercialized semiconductor quantum dots, the carbon nanoparticles display high quantum yields and photostability, but conversely have low cytotoxicity and excellent biocompatibility. Subsequently, these new fluorescent labels have found use in biological imaging applications.<sup>4</sup> As with all the new luminescent particle embodiments reported to date, absolute brightness, photostability as well as optical tunability remain primary concerns. In this communication we subsequently show that Plasmon supporting materials, such as silver island films,<sup>5</sup> can further enhance carbon nanodot brightness, photostability and thus potentially detectability in biological imaging applications.

Over the last 10 years, metal-enhanced fluorescence (MEF) has emerged as a technology which directly complements fluorescent labels. In the near-field, within the wavelength of light, luminescent species can interact with metallic surface plasmons in ways which ultimately enhance particle/fluorophore brightness and reduce the excited “system” decay times, which invariably leads to enhanced photostability.

For a fluorescent species in the far-field condition, *i.e.* more than 1 wavelength of light away from either a surface or particle, the quantum yield of a fluorophore is given by:<sup>6</sup>

$$Q_0 = \frac{\Gamma}{\Gamma + K_{nr}} \quad (1)$$

where  $\Gamma$  is the fluorophores’ radiative decay rate and  $K_{nr}$  are the nonradiative decay rates for excited state relaxation. In the presence of metal, *i.e.* near-field condition, Geddes and Lakowicz have shown that the *system quantum yield*,  $Q_m$ , can readily be defined by:<sup>6</sup>

$$Q_m = \frac{\Gamma + \Gamma_m}{\Gamma + \Gamma_m + K_{nr}} \quad (2)$$

where  $\Gamma_m$  is the system modified radiative rate. Similarly, both far- and near-field lifetimes are given by:

$$\tau = \frac{1}{\Gamma + K_{nr}} \quad (3)$$

$$\tau_m = \frac{1}{\Gamma + \Gamma_m + K_{nr}} \quad (4)$$

Interestingly, by increasing  $\Gamma_m$  in eqn (2) and (4), *i.e.* the near-field condition, MEF readily affords for increased *system quantum yields* and reduced decay times, *i.e.* enhanced photostabilities. This is in contrast to the far-field condition, where the lifetime and quantum yield change in unison. In these equations we do not account for metal-modified non-radiative rates, and while some authors have reported very-close proximity quenching, Geddes *et al.* have recently hypothesized that these reductions in close range luminescent intensities are in fact due to changes in the near-field electric field distributions, which are substrate specific.<sup>7</sup>

Polyethylene Glycol (PEG) terminated carbon dots were synthesized as previously reported.<sup>1</sup> Excitation of the carbon

<sup>a</sup> Institute of Fluorescence and Department of Chemistry and Biochemistry, University of Maryland Baltimore County, 701 East Pratt Street, Baltimore, MD 21202, USA

<sup>b</sup> Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal

<sup>c</sup> Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal

<sup>d</sup> Institute of Fluorescence and Department of Chemistry and Biochemistry, University of Maryland Baltimore County, 701 East Pratt Street, Baltimore, MD 21202, USA.  
E-mail: geddes@umbc.edu; Fax: +1 410-576-5722;  
Tel: +1 410-576-5720

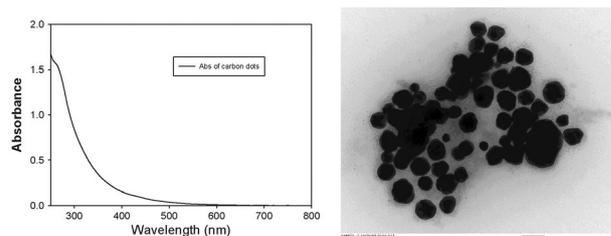
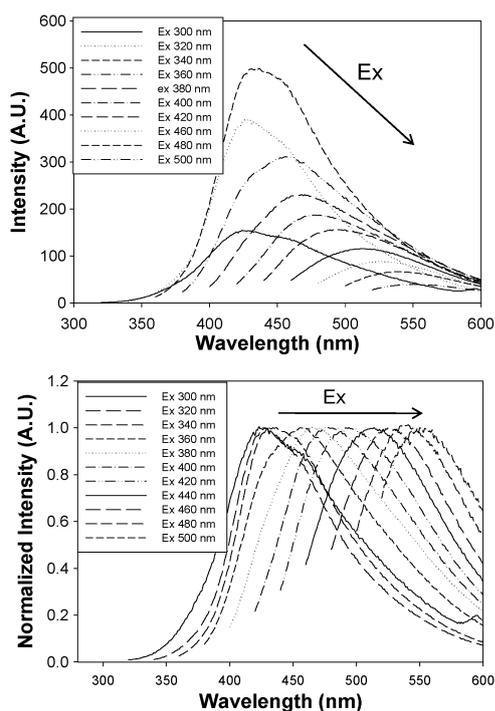
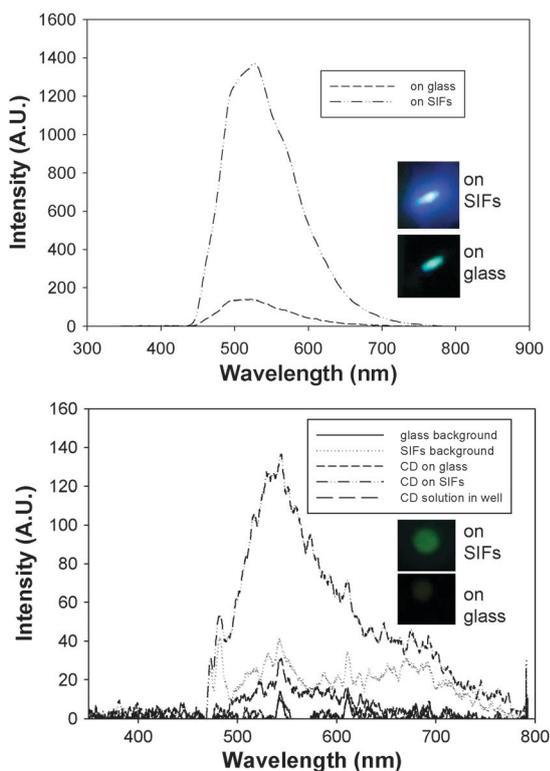


Fig. 1 TEM image (right) of carbon dots and absorbance spectrum (left).



**Fig. 2** Fluorescence emission spectra (top) and normalized emission spectra (bottom) of carbon dots for different excitation wavelengths.

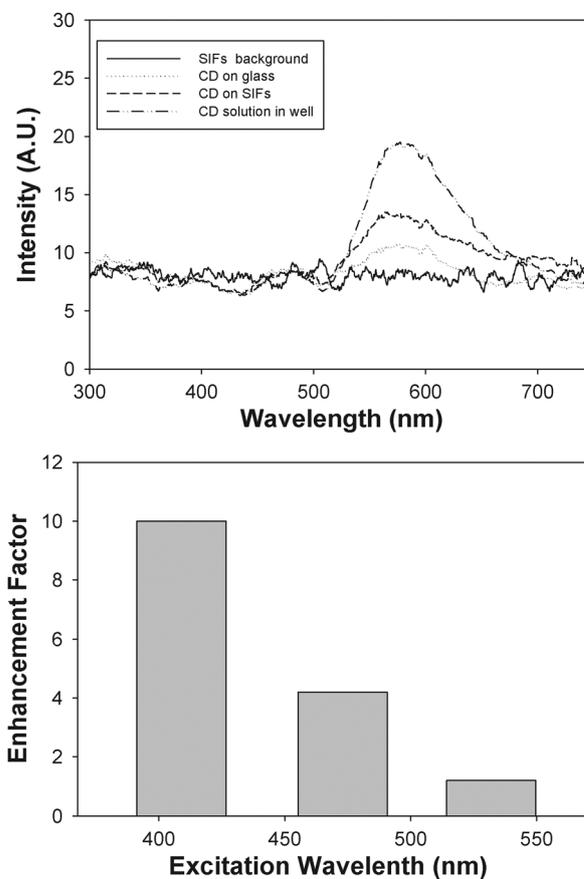
dots was undertaken using a Spectrofluorometer Fluoromax 4 for excitation dependence studies, and using 405, 473 and



**Fig. 3** (top) Fluorescence emission spectra of carbon dots with  $\lambda_{\text{Ex}} = 405$  nm CW laser from both a SiFs surface and also from a glass control sample. (bottom) Fluorescence emission spectra of carbon dots with  $\lambda_{\text{Ex}} = 473$  nm. Real color photographs were taken through a 473 nm razor edge filter.

532 nm laser lines for the MEF studies, where an ocean optics HD 2000 + Spectrometer with a 600  $\mu\text{m}$  fiber bundle was used for the collection of fluorescence emission. The preparation of SiFs has been reported previously.<sup>8</sup> Fluorescence lifetimes of the carbon dots from both SiFs surfaces and glass substrates (a control sample containing no silver) were undertaken using the Time-Correlated Single Photon Counting Technique (TCSPC) with a 400 nm laser for excitation and a TBX-4 module for detection. Deconvolution analysis of the respective luminescence decays was performed using DAS 6.0 software. The calculation of the mean  $\tau$  and amplitude weighted lifetimes  $\langle\tau\rangle$  has been reported previously.<sup>8</sup>

Fig. 1 (right) shows a typical TEM image of the carbon dots, where the size of the dots appears to be in the range of 60–80 nm. The optical absorption of the carbon nanodots is primarily in the UV and tails out beyond 500 nm, Fig. 1—left. Interestingly, the dots show an excitation wavelength and quantum yield dependence, Fig. 2, with the luminescence quite weak when excited beyond 500 nm. The spectral width of the emission is also very similar when normalized, Fig. 2 (bottom). The mechanism of photoluminescence from carbon dots was attributed to the presence of surface energy traps that become emissive upon stabilization as a result of the surface



**Fig. 4** (top) Fluorescence emission spectra of carbon dots with  $\lambda_{\text{Ex}} = 532$  nm laser from both SiFs and a glass control sample. (bottom) Enhancement factor vs. excitation wavelength: 405 nm, 473 nm and 532 nm. Enhancement factor was calculated as the ratio between the emission from the SiFs substrate divided by that observed from an otherwise identical control sample (glass), containing no metal.

**Table 1** Fluorescence intensity decay analysis.  $\bar{\tau}$ —mean lifetime,  $\langle\tau\rangle$ —amplitude-weighted lifetime. CD—carbon dots. Ex: 400 nm

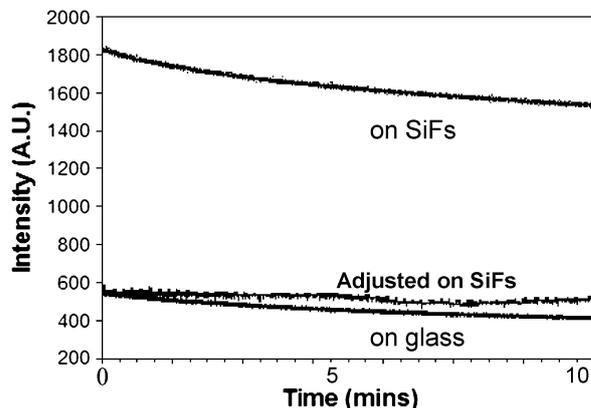
|                | $\tau_1$ /ns | $\alpha_1$ (%) | $\tau_2$ /ns | $\alpha_2$ (%) | $\tau_3$ /ns | $\alpha_3$ (%) | $\langle\tau\rangle$ /ns | $\bar{\tau}$ /ns | $\chi^2$ |
|----------------|--------------|----------------|--------------|----------------|--------------|----------------|--------------------------|------------------|----------|
| CD in cuvette  | 1.23         | 23.49          | 0.19         | 50.94          | 6.67         | 25.57          | 5.65                     | 2.09             | 1.24     |
| CD glass/glass | 0.12         | 76.64          | 0.55         | 21.32          | 5.14         | 2.04           | 0.31                     | 1.94             | 1.17     |
| CD glass/SiFs  | 0.14         | 81.83          | 0.56         | 16.81          | 5.81         | 1.36           | 0.26                     | 1.53             | 1.30     |

passivation. These findings suggest that the spectral properties are dependent on not only the particle size but also a distribute of different emissive sites on each passivated carbon dots.<sup>9</sup>

When solutions of the nanodots were excited on SiFs (silver island films), significantly enhanced luminescence could be seen, Fig. 3—top, and photograph insets. At an excitation wavelength of 405 nm, over a 10-fold increase in luminescence could be observed as compared to an otherwise identical control sample, but which contained no silver. Fig. 3 (bottom) shows the emission from carbon dots on SiFs and control glass substrate (containing no silver nanoparticles) at the excitation wavelength of 473 nm. Over 4-fold increase in luminescence could be observed. Furthermore, Fig. 4 (top) shows a 1.5-fold enhancement factor of carbon dots on SiFs with excitation wavelength 532 nm. Similar to the free space condition, the emission intensity is reduced with increasing wavelength, with very little enhanced luminescence observed when excited at 532 nm, Fig. 4—bottom. Interestingly, in the MEF literature, some authors have suggested that the enhancement factors near to metals are proportional to the reciprocal of the free space quantum yield, *i.e.*  $E.F \propto 1/Q_0$ , where Dragan and Geddes conversely suggest that the MEF enhancement factor is underpinned by an excitation volumetric effect (EVE).<sup>10</sup> Given that we in fact do not see greater enhancements for longer wavelengths of excitation, then this enhancement trend follows the MEF EVE hypothesis postulated by Dragan and Geddes, where modulation in MEF efficiency is by far-field excitation power volume dependence. The near-field volume changes non-linearly with far-field power, in Fig. 4—bottom.

The time-resolved decay times for carbon dots in both the far and near-field conditions were measured as shown in Table 1. The lifetime of the dots is multiexponential in solution with mean and amplitude weighted lifetimes of 2.09 and 5.65 ns respectively. In the near field, *i.e.* on SiFs, these values significantly decrease to 1.53 and 0.26 ns, respectively, which is consistent with current MEF thinking and eqn (2) and (4). Subsequently, we have studied the photostability of carbon dots from both the control sample and the SiFs surface. On the SiFs surface one readily sees more emission *vs.* time, *i.e.* photon flux, which is proportional to the integrated area under the curve, Fig. 5. From the glass substrate we readily see significantly less luminescence, which photobleaches more rapidly than the adjusted SiFs substrate, Fig. 5. This increase in photostability from SiFs is consistent with the reduced lifetime on SiFs, Table 1 and eqn (4), where luminescent species in an excited state are less prone to excited state photophysics if the decay time is shorter.

In this communication we have shown that similar to regular organic fluorophores, carbon dots can also show enhanced emission intensities and photostabilities from Plasmon supporting substrates. Given the need for highly luminescent and photostable particles, which are both

**Fig. 5** Emission intensity *vs.* time, photostability of carbon dots on SiFs and glass and with the laser power adjusted to give the same initial steady-state fluorescence intensity as observed on glass (bottom traces). SiFs—silver island films.

non-toxic and biocompatible, we foresee several approaches for carbon dots and MEF in imaging and multiplexed immunoassays. Work is currently underway in this regard and will be reported in due course.

The authors would like to thank the Mid Atlantic Regional Center of Excellent (MARCE), NAID, NIH, 2 U54 AIO57168-07, the Institute of Fluorescence, the Department of Chemistry and Biochemistry at the University of Maryland Baltimore County for financial support. Financial support from Fundação para a Ciência e Tecnologia (Lisboa, Portugal) (FSE-FEDER) (Project PTDC/QUI/71001/2006) and (Project PTDC/QUI/71336/2006) is acknowledged. A PhD grant to Helena Gonçalves SFRH/BD/46406/2008 is acknowledged to Fundação para a Ciência e Tecnologia (Lisboa).

## References

- 1 Y. Sun, B. Zhou, Y. Lin and A. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756–7757.
- 2 X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker and W. A. Scrivens, *J. Am. Chem. Soc.*, 2004, **126**, 12736–12737.
- 3 Q. Li, T. Y. Ohulchansky, R. Liu, K. Koynov, D. Wu, A. Best, R. Kumar, A. Bonoiu and P. N. Prasad, *J. Phys. Chem. C*, 2010, **114**, 12062–12068.
- 4 S. K. Nune, P. Gunda, P. K. Thallapally, Y. Y. Lin, M. L. Forrester and C. J. Berkland, *Expert Opin. Drug Delivery*, 2009, **6**, 1175–1194.
- 5 R. Pribik, A. I. Dragan, Y. Zhang, C. Gaydos and C. D. Geddes, *Chem. Phys. Lett.*, 2009, **478**, 70–74.
- 6 C. D. Geddes and J. R. Lakowicz, *J. Fluoresc.*, 2002, **12**, 121–129.
- 7 K. Aslan, Z. Leonenko, J. R. Lakowicz and C. D. Geddes, *J. Fluoresc.*, 2005, **15**, 643–654.
- 8 Y. Zhang, A. Dragan and C. D. Geddes, *J. Phys. Chem. C*, 2009, **113**, 12095–12100.
- 9 H. Gonçalves and J. C. G. Esteves da Silva, *J. Fluoresc.*, 2010, **20**, 1023–1028.
- 10 A. Dragan and C. D. Geddes, *Phys. Chem. Chem. Phys.*, 2010, **13**, 3831–3838.