

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/232608919>

# Efficient Fluorescence Quenching in Carbon Dots by Surface-Doped Metals – Disruption of Excited State Redox Processes and Mechanistic Implications

ARTICLE *in* LANGMUIR · OCTOBER 2012

Impact Factor: 4.46 · DOI: 10.1021/la302506e · Source: PubMed

---

CITATIONS

26

---

READS

101

12 AUTHORS, INCLUDING:



**Sushant Sahu**

Clemson University

16 PUBLICATIONS 734 CITATIONS

SEE PROFILE



**Yamin Liu**

Clemson University

8 PUBLICATIONS 124 CITATIONS

SEE PROFILE



**Haijun Qian**

Clemson University

20 PUBLICATIONS 330 CITATIONS

SEE PROFILE

# Efficient Fluorescence Quenching in Carbon Dots by Surface-Doped Metals - Disruption of Excited State Redox Processes and Mechanistic Implications

Juan Xu,<sup>†</sup> Sushant Sahu,<sup>†</sup> Li Cao,<sup>†,\*</sup> Christopher E. Bunker,<sup>‡,\*</sup> Ge Peng,<sup>†</sup> Yamin Liu,<sup>†</sup> K. A. Shiral Fernando,<sup>§</sup> Ping Wang,<sup>†</sup> Elena A. Guliants,<sup>§</sup> Mohammed J. Meziani,<sup>†</sup> Haijun Qian,<sup>†</sup> and Ya-Ping Sun<sup>†,\*</sup>

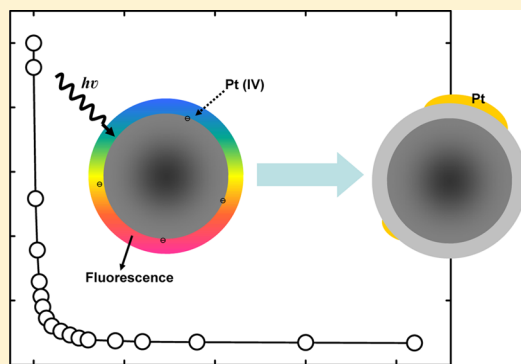
<sup>†</sup>Department of Chemistry and Laboratory for Emerging Materials and Technology, Clemson University, Clemson, South Carolina 29634, United States

<sup>‡</sup>Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, Dayton, Ohio 45433, United States

<sup>§</sup>University of Dayton Research Institute, Sensors Technology Office, Dayton, Ohio 45469, United States

## S Supporting Information

**ABSTRACT:** The carbon dots in this study were small carbon nanoparticles with the particle surface functionalized by oligomeric poly(ethylene glycol) diamine molecules. Upon photoexcitation, the brightly fluorescent carbon dots in aqueous solution served the function of excellent electron donors to reduce platinum(IV) and gold(III) compounds into their corresponding metals to be deposited on the dot surface. The deposited metals even in very small amounts were found to have dramatic quenching effects on the fluorescence emission intensities, but essentially no effects on the observed fluorescence decays. The obviously exclusive near-neighbor static quenching could be attributed to the disruption of electron–hole radiative recombinations (otherwise responsible for the fluorescence emissions in carbon dots). The results provide important evidence for the availability of photogenerated electrons that could be harvested for productive purposes, which in turn supports the current mechanistic framework on fluorescence emission and photoinduced redox properties of carbon dots.

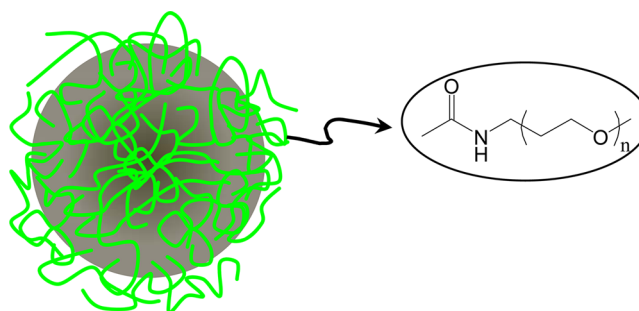


## INTRODUCTION

Small semiconductor nanoparticles and related core–shell nanostructures, generally referred to as quantum dots (QDs) due to the presence of quantum confinement effects, have attracted much attention for their excellent optical properties and a variety of potential applications.<sup>1</sup> Among well-established QDs are those based on insoluble cadmium salts, especially the popular and now commercially available CdSe/ZnS core–shell nanoparticles with various surface coatings.<sup>1–5</sup> However, there have also been some significant concerns on these presently dominating QDs, especially with respect to their toxicity associated with the heavy metal content.<sup>6,7</sup> Therefore, the search for alternative QD-like optical nanomaterials that are nontoxic yet still high performance has continued.<sup>8–11</sup>

Nanoscale carbon particles have recently emerged as a unique class of optical nanomaterials targeting both biomedical and energy conversion applications.<sup>11–30</sup> Small carbon nanoparticles upon surface functionalization by organic molecules were found to exhibit bright and colorful fluorescence emissions. These strongly fluorescent nanoparticles, dubbed “carbon dots” (Scheme 1),<sup>11</sup> have been demonstrated for their competitive optical performance to that of well-established

Scheme 1



semiconductor QDs.<sup>16,19,30</sup> Carbon dots have also been evaluated for their potential bioimaging applications in vitro and in vivo.<sup>15,21,30</sup> For energy conversion, carbon dots are apparently capable of harvesting visible photons to drive catalytic processes to reduce carbon dioxide into formic acid

Received: June 21, 2012

Revised: September 27, 2012

Published: October 22, 2012



and in a similarly photocatalytic process to split water for the generation of hydrogen molecules.<sup>29</sup>

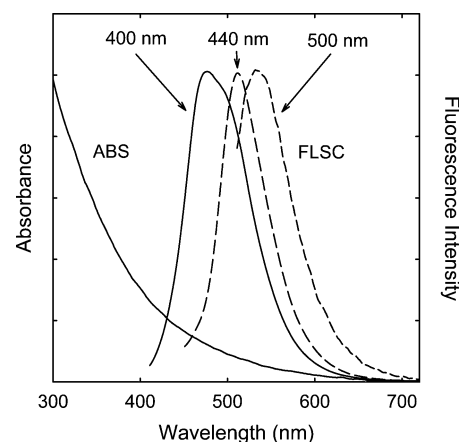
Mechanistically, the fluorescence emissions in carbon dots are attributed to radiative recombinations of the photoinduced electrons and holes that are confined to the carbon nanoparticle surface,<sup>11,19</sup> phenomenologically resembling those found in nanoscale semiconductors. In such a mechanistic framework, more favorable to stronger fluorescence emissions in carbon dots would be a larger ratio of the carbon particle surface to the particle volume, thus carbon nanoparticles of smaller sizes. Also favorable would be diverse energy trapping sites on the carbon nanoparticle surface stabilized more effectively by the passivation agents. The available experimental results are generally in support of the mechanistic framework, including especially those concerning the photoinduced redox properties of carbon dots.<sup>18,29</sup> As reported in the literature, carbon dots upon photoexcitation can serve as not only excellent electron acceptors,<sup>18</sup> but also electron donors to be responsible for the observed visible-light photocatalytic energy conversion.<sup>29</sup> In this regard, small carbon nanoparticles are dramatically different from fullerenes as size-wise comparable carbon clusters, since the latter are incapable of donating electrons even in the photoexcited states.<sup>31</sup> It is therefore interesting to examine more closely the somewhat unique photoinduced electron donating characteristics in carbon dots, which is particularly relevant to their photocatalytic and other applications.

Fluorescence quenching has been used extensively in the investigation of photoinduced redox processes in fullerenes and other carbon nanomaterials. In this study, we examined the efficient and effective quenching of fluorescence emissions in carbon dots by noble metals on the dot surface, for which the progressive metal coating was achieved in the photoreduction of the corresponding aqueous metal salts. The fluorescence quenching was determined to be exclusively static in nature, as one might predict, attributable to the metallic species deposited on the dot surface interrupting the radiative recombination processes. Thus, the results further support the existing mechanistic framework for the fluorescence emissions and the photoinduced redox properties in carbon dots.

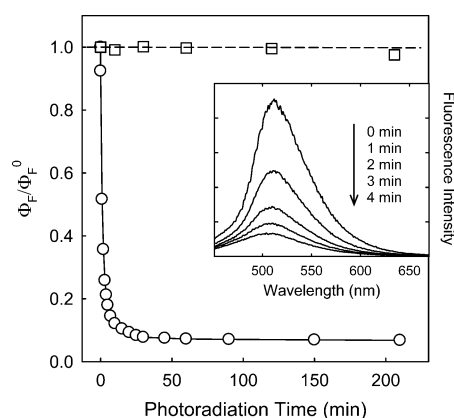
## RESULTS AND DISCUSSION

The carbon dots with oligomeric poly(ethylene glycol) diamine (PEG<sub>1500N</sub>, Scheme 1) as surface functionalization agent were synthesized as previously reported.<sup>19</sup> Aqueous solutions of the carbon dots were very stable, with solution colors from yellow at a low concentration to nearly black at a high concentration. The observed optical absorption spectrum was generally broad, so were fluorescence spectra at different excitation wavelengths (Figure 1). As known in the literature, the fluorescence quantum yields in carbon dots are generally dependent on excitation wavelengths, with the highest yield found in the green. For the sample of PEG<sub>1500N</sub>-functionalized carbon dots in this study, the observed fluorescence quantum yields were about 20% at 440 nm excitation and about 6% at 500 nm excitation (Figure 1).

Optical absorption and fluorescence spectra of the carbon dots in aqueous solution were both stable with respect to photoirradiation (450 W xenon source coupled with filters for the 425–720 nm spectral range and for up to 10 h), with the observed fluorescence spectral profiles and intensities essentially unchanged (within experimental uncertainties generally expected in the photophysics community on measurements of fluorescence quantum yields, Figure 2). The results suggested



**Figure 1.** UV-vis absorption (ABS) and fluorescence (FLSC, with the excitation wavelengths marked) spectra of the carbon dots in aqueous solution.

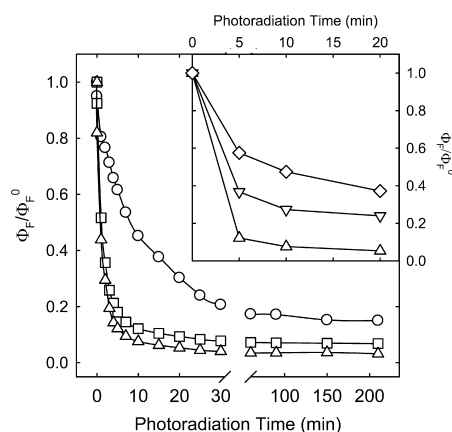


**Figure 2.** Observed fluorescence quantum yields ( $\Phi_F$ , 440 nm excitation, normalized against the value at time zero  $\Phi_F^0$ ) of the carbon dots in aqueous solution without ( $\square$ ) and with the Pt(IV) compound ( $\circ$ ) after visible light photoirradiation for various periods of time. The corresponding spectral intensity changes for the first few ( $\circ$ ) data points (with increasing photoirradiation times in the arrow direction) are shown in the inset.

that there were no meaningful photochemical reactions in the aqueous solution of carbon dots without any other substances. In the presence of a metal salt, however, specifically the platinum(IV) compound  $\text{H}_2\text{PtCl}_6$  or gold(III) compound  $\text{HAuCl}_4$  in the aqueous solution, the same photoirradiation resulted in dramatic decreases in observed fluorescence intensities (or relative quantum yields) over a relatively short period of time (Figure 2), namely substantial quenching of the fluorescence emissions (Figure 2 inset). The minor spectral shifts or changes with the quenching probably reflected the fact that the quenching efficiencies for the various emissions in the fluorescence spectrum of carbon dots were slightly different.

In the experiment for a more systematic examination, an aqueous solution of carbon dots with 0.3 mM of  $\text{H}_2\text{PtCl}_6$  was irradiated with visible light (425–720 nm) for various time intervals, and effects of the photoirradiation were monitored by optical absorption and fluorescence measurements on the solution immediately after the photoirradiation. While the absorption of the carbon dots was insensitive to the photoirradiation, the observed fluorescence intensities (thus fluorescence quantum yields) were highly sensitive at all

excitation wavelengths (Figure 3). At 440 or 500 nm excitation of the solution that was photoirradiated with the visible light for

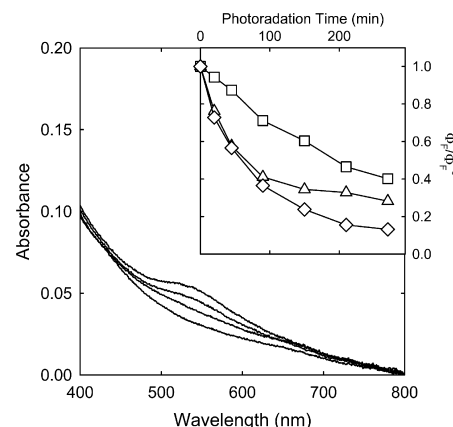


**Figure 3.** The normalized fluorescence quantum yields ( $\Phi_F/\Phi_F^0$  with excitation at 400 nm:  $\circ$ , 440 nm:  $\square$ , and 500 nm:  $\triangle$ ) of the carbon dots in aqueous solution with 0.3 mM of the Pt(IV) compound after visible light photoirradiation for various periods of time. Shown in the inset are the results ( $\Phi_F/\Phi_F^0$  with 500 nm excitation) for different concentrations of the Pt(IV) salt used in the photoirradiation (0.3 mM:  $\triangle$ , 0.06 mM:  $\nabla$ , and 0.012 mM:  $\diamond$ ).

only about 10 min, the decrease in fluorescence quantum yields was around 90% (Figure 3), and somewhat less dramatic decrease at 400 nm excitation but still more than 50% (Figure 3). The relationship between the decrease in fluorescence intensities in the photoirradiated solution and the duration of the photoirradiation was apparently dependent on the initial  $\text{H}_2\text{PtCl}_6$  concentration in the solution. When a lower  $\text{H}_2\text{PtCl}_6$  concentration of 0.012 mM was used, for example, the fluorescence quenching as a function of the photoirradiation time was less dramatic, although still highly efficient (Figure 3).

The replacement of the platinum(IV) compound by  $\text{HAuCl}_4$  in the aqueous solution of carbon dots for the same photoirradiation resulted in similar but somewhat less efficient fluorescence quenching after the photoirradiation. As shown in Figure 4, the decrease in fluorescence quantum yield in the photoirradiated solution was again more significant at 440 or 500 nm excitation than that at 400 nm excitation. Interestingly, however, at 550 nm excitation, the fluorescence quenching as a result of the photoirradiation was overall obviously less significant (Figure 4).

The observed dramatic quenching of fluorescence emissions in carbon dots could not be due to the presence of  $\text{H}_2\text{PtCl}_6$  or  $\text{HAuCl}_4$  in the aqueous solution. In control experiments, the observed fluorescence quantum yields of carbon dots in aqueous solution were found to be little changed without and with the presence of the metal salts, namely that the platinum(IV) and gold(III) compounds at the concentrations used in the aqueous solution of carbon dots were hardly fluorescence quenchers. The dramatic decreases of fluorescence quantum yields shown in Figures 3 and 4 must be due to the photoreductive deposition of platinum or gold metal on the carbon dot surface, which could effectively quench or nearly diminish the fluorescence emissions in carbon dots. As originally proposed,<sup>11</sup> mechanistically the fluorescence emissions in carbon dots may generally be attributed to radiative recombinations of the electrons and holes from the photo-induced charge separation, which are likely confined/trapped at

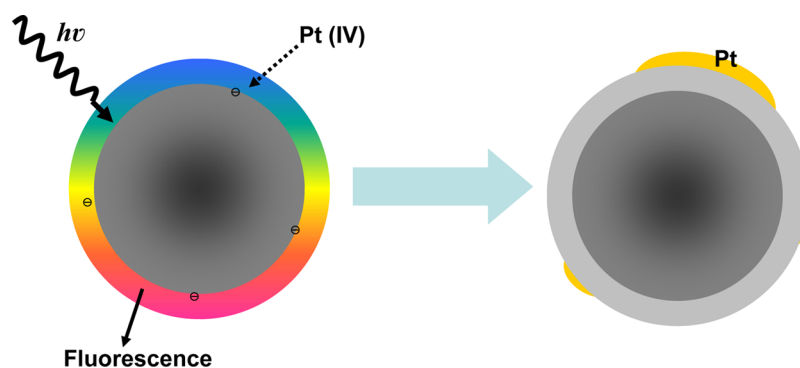


**Figure 4.** The emergence and increases of the gold plasmon absorption band (around 550 nm) after aqueous solution of the carbon dots with the Au(III) compound was photoirradiated for 15, 270, 330, and 390 min. Shown in the inset are the normalized fluorescence quantum yields ( $\Phi_F/\Phi_F^0$  with excitation at 400 nm:  $\square$ , 440 nm:  $\diamond$ , and 500 nm:  $\triangle$ ) of the same solution after visible light photoirradiation for various periods of time.

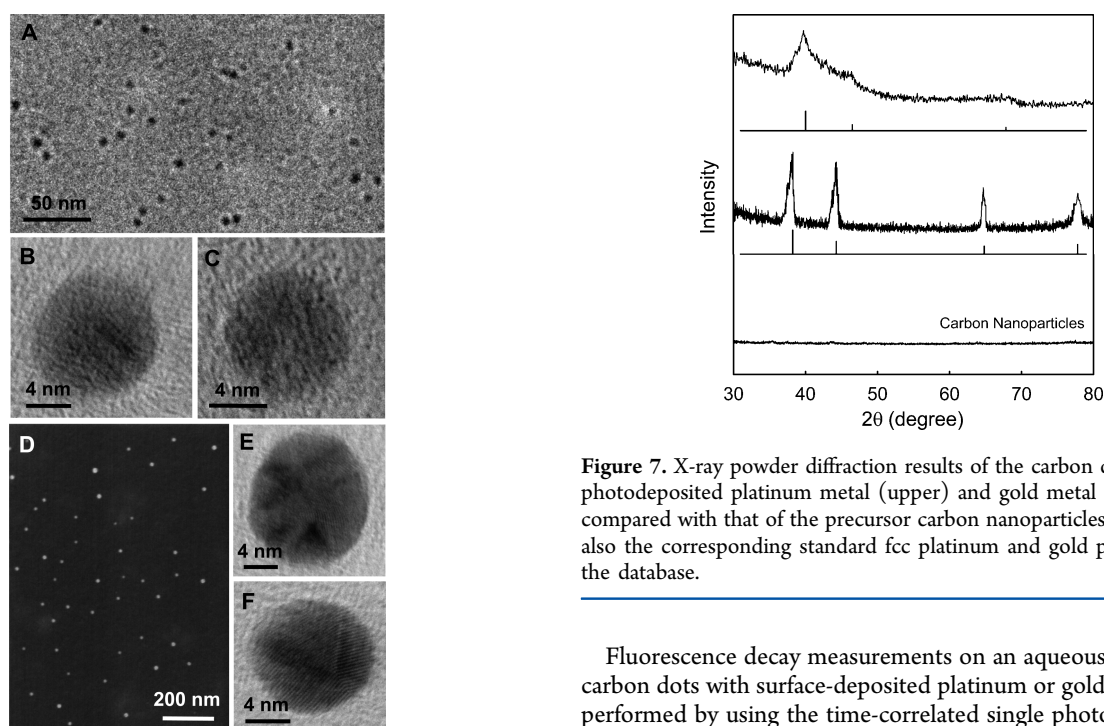
the surface sites of the core carbon nanoparticles and stabilized by the surface passivation in carbon dots (Figure 5). Experimental evidence in support of such a mechanistic framework included the demonstration that photoexcited carbon dots could serve as both excellent electron donors and acceptors.<sup>18</sup> The electron donating ability of carbon dots was also shown in the photoreduction of noble metal salts into their respective metals (silver, gold, or platinum).<sup>29,32</sup> The same photoreduction reactions must have resulted in the deposition of platinum or gold metal at the electron rich surface sites on the carbon dots (Figure 5), which subsequently acted as highly effective near-neighbor fluorescence quenchers. The deposition of gold metal was confirmed experimentally at longer photoirradiation times, with the emergence and gradual increases of the gold plasmon absorption (Figure 4).

The deposition of platinum or gold metal on the carbon dot surface due to the dot-catalyzed photoreduction of the corresponding metal salt was confirmed in transmission electron microscopy (TEM) imaging experiments, especially in terms of the Z-contrast mode to take advantage of the significant difference in electron density between carbon and platinum or gold metal (Figure 6). Electron dispersive X-ray spectroscopy (EDX) analyses performed on individual particles in randomly selected regions of the TEM specimen also confirmed the platinum or gold coating, with the observed EDX spectra exhibiting platinum or gold peaks, respectively, in addition to those of carbon, silicon (due to the holder), and copper (from the TEM grid). For even longer photoirradiation times, the amount of deposited metal on carbon dots became sufficient for the resulting samples to be characterized by using X-ray diffraction (Figure 7). The broadness in the diffraction peaks signified the nanoscale nature of the deposited metals on the carbon dot surface.

All of the results described above are consistent with the mechanistic framework of several key features: (1) There is photoinduced charge separation in the small core carbon nanoparticles in carbon dots; (2) The electrons and holes are confined to the surface sites in the dots; (3) The radiative recombinations of the electrons and holes are responsible for the observed fluorescence emissions in carbon dots; (4) The



**Figure 5.** A schematic illustration on the photoreductive deposition of Pt metal onto the carbon dot surface and the subsequent fluorescence quenching. The rainbow “shell” is to indicate that the fluorescence is likely from the passivated carbon particle surface.



**Figure 7.** X-ray powder diffraction results of the carbon dots with the photodeposited platinum metal (upper) and gold metal (middle) are compared with that of the precursor carbon nanoparticles (lower) and also the corresponding standard fcc platinum and gold patterns from the database.

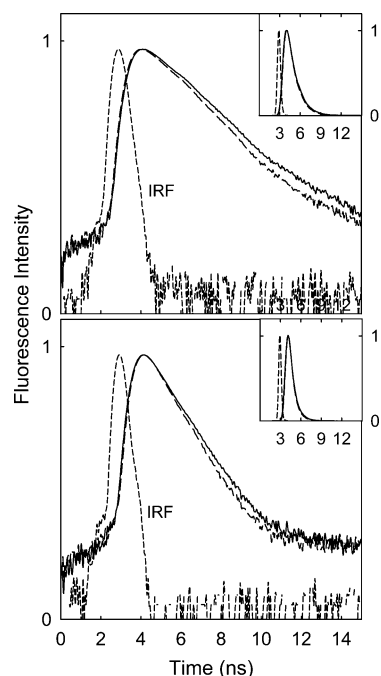
**Figure 6.** TEM results on the carbon dots with the photodeposited platinum metal (A, and B, and C at high resolution) or gold metal (D in the Z-contrast mode, and E and F at high resolution). In F, the spacing in the crystal lattice fringes of 0.29 nm is consistent with fcc gold (110). Except for D (a dark-field image), all others are bright-field images.

electrons are capable of reducing platinum or gold salt into the corresponding metal, resulting in the deposition of the metal on the dot surface; and (5) The surface-deposited metal even in small amounts (far below the threshold for the observation of plasmon absorption in case of gold) can effectively quench or almost diminish the fluorescence emissions in the dots. This is probably understandable because the metal deposition is expected to be primarily or at least to initiate at the surface sites that host the electrons, thus particularly effective in interrupting the subsequent photoinduced charge separation and/or radiative recombinations. In such a mechanistic framework, the fluorescence quenching must be static in nature, as confirmed experimentally in terms of the complete decoupling between quencherings in fluorescence quantum yields and lifetimes.

Fluorescence decay measurements on an aqueous solution of carbon dots with surface-deposited platinum or gold metal were performed by using the time-correlated single photon counting (TCSPC) technique. Shown in Figure 8 are the observed fluorescence decays compared with those of neat carbon dots (without any photoirradiation and thus no metal deposition) in aqueous solutions. While the decay curves could not be deconvoluted from the corresponding instrumental response functions by using a monoexponential decay function, the direct comparison between the curves obviously suggests no meaningful quenching effects on the fluorescence decays of carbon dots by the surface-deposited metal. However, the corresponding observed fluorescence quantum yields were reduced dramatically (Figures 3 and 4). The complete decoupling between the effects on fluorescence intensities and decays is classical for pure static quenching, namely that the quencher is near-neighbors to the emissive species.<sup>33</sup> In this case, the near-neighbor configuration must be absolute with the platinum or gold metal (the quencher) right at the emissive sites on the carbon dot surface, thus the observation of exclusively static fluorescence quenching.

The fluorescence emissions in carbon dots are generally dependent on excitation wavelengths. The different excitation wavelengths might affect the subsequent excited state energy distribution, the charge separation, and/or the confinement of electrons and holes on the dot surface and their radiative





**Figure 8.** Observed fluorescence decays (log scale for the fluorescence intensities, excited at 407 nm, and monitored with 470 nm narrow bandpass filter) of the carbon dots in aqueous solution without (—) and with (---) the photodeposited platinum metal (upper) or gold metal (lower). The same data are plotted on linear scale in the insets.

recombinations. The observed fluorescence quenching results at various wavelengths (Figures 3 and 4) suggested that the emissions corresponding to excitation wavelengths around the green were more vulnerable to the quenching, generally consistent with the observed higher fluorescence quantum yields at those excitation wavelengths.<sup>19</sup>

For the comparison between platinum and gold, the extremely effective fluorescence quenching upon photoirradiation of the carbon dots in the presence of  $\text{H}_2\text{PtCl}_6$  for only a few minutes might be due to contributions beyond the photogenerated platinum metal deposited on the dot surface, as the photoreduction might be insufficient for any significant platinum deposition within such a short period of photoirradiation time (5 min or less). According to what has already been reported in the literature, the photoreduction of platinum(IV) to platinum(II) ( $\text{PtCl}_6^{2-} \rightarrow \text{PtCl}_4^{2-}$ , for example) is highly efficient.<sup>34,35</sup> The platinum(II) species as initial photoreduction products accumulated on the surface of carbon dots might have contributed to the observed unusually efficient fluorescence quenching. Such an explanation was supported by experimental results. The aqueous solution of carbon dots with  $\text{H}_2\text{PtCl}_6$  was first photoirradiated for 5 min to have the fluorescence intensities quenched by almost 90%, as described above (Figure 3). The solution was then sonicated mildly for the purpose of dispersing the platinum(II) species accumulated on the dot surface, which did result in a significant rebound in the observed fluorescence intensities. The same argument for the metal salt contributing to the obviously efficient fluorescence quenching might go beyond just the contribution of the platinum(II) species. It is also possible that the photoirradiation and the associated photoinduced charge separation processes in carbon dots made the dot surface more susceptible to the accumulation of the metal salt species, contributing to the subsequent fluorescence quenching. The

photoirradiation-induced accumulation of the metal salt species around the carbon dots might have also contributed to the initial photoreduction of the salts into their corresponding metals to be deposited on the dot surface.

In summary, the carbon dots in aqueous solution upon photoexcitation were excellent electron donors for the reduction of platinum(IV) and gold(III) compounds into their corresponding metals to be deposited on the dot surface, probably more so at the surface defect-derived energy trapping sites. Consequently, the deposited metals even in very low quantity could effectively quench to the degree of almost eliminated the fluorescence emissions in carbon dots. The observed dramatic quenching effects must be due to the disruption of electron–hole recombination processes (otherwise responsible for the emissions) by the photodeposited metals on the carbon dot surface. The expected static nature of the quenching was confirmed experimentally by the observation of the absolute decoupling between responses of fluorescence quantum yields and decays toward the presence of the quenchers. The results add more and important support to the current mechanistic framework for fluorescence emissions and their associated photoinduced charge separation and recombination processes in carbon dots.

## EXPERIMENTAL SECTION

**Materials.** Carbon nanopowder (>99%) was purchased from Sigma-Aldrich, and gold chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) from Alfa Aesar. The oligomeric poly(ethylene glycol) diamine ( $\text{PEG}_{1500\text{N}}$ ) was supplied by Anvia Chemicals, and thionyl chloride ( $\text{SOCl}_2$ ) by Alfa Aesar. Dialysis membrane tubing was acquired from Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterProS water purification system.

**Measurements.** Baxter Megafuge (model 2630) and Beckman-Coulter ultracentrifuge (Optima L-90K with a type 90 Ti fixed-angle rotor) were used in the synthesis of carbon dots. UV–vis absorption spectra were recorded on a Shimadzu UV2501-PC spectrophotometer. Fluorescence spectra were acquired on a Jobin-Yvon emission spectrometer equipped with a 450 W xenon source, Gemini-180 excitation and Tirax-550 emission monochromators, and a photon counting detector (Hamamatsu R928P PMT at 950 V). 9,10-Bis(phenylethynyl)-anthracene in cyclohexane and quinine sulfate in 0.1 M  $\text{H}_2\text{SO}_4$  were used as standards in the determination of fluorescence quantum yields by the relative method (matching the absorbance at the excitation wavelength between the sample and standard solutions and comparing their corresponding integrated total fluorescence intensities). Fluorescence decays were measured on a time-correlated single photon counting (TCSPC) setup with a Hamamatsu stabilized picosecond light pulser (PLP-02) for 407 nm excitation (<100 ps pulses at 1 MHz repetition rate), coupled with a Phillips XP2254/B PMT in a thermoelectrically cooled housing as detector for an overall instrument time resolution better than 500 ps. Transmission electron microscopy (TEM) analyses were performed on Hitachi 9500 TEM and Hitachi HD-2000 S-TEM systems in both transmission and Z-contrast modes. The energy dispersive X-ray spectroscopy (EDX) analyses were also performed in the Z-contrast mode. X-ray diffraction measurements were carried out on a Scintag XDS-2000 powder diffraction system. The photolysis setup consisted of a 450 W xenon arc source, coupled with a “hot” filter (405–720 nm transmission) to eliminate any infrared heating effect.

**Carbon Dots.** The  $\text{PEG}_{1500\text{N}}$ -functionalized carbon dots were synthesized according to previously reported procedures,<sup>19</sup> with slight modifications and more rigorous controls of the experimental conditions for improved fluorescence properties. Briefly, a carbon nanopowder sample (3 g) was refluxed in an aqueous nitric acid solution (2.6 M, 240 mL) for 24 h. The reaction mixture back at room temperature was dialyzed against fresh water, and then centrifuged at

1 000 g to retain the supernatant. The recovered surface-oxidized small carbon nanoparticles were refluxed in neat thionyl chloride for 6 h, followed by the removal of excess thionyl chloride under nitrogen. The treated carbon particle sample (300 mg) was mixed well with carefully dried PEG<sub>1500N</sub> (3 g) in a flask, heated to 180 °C and stirred under nitrogen for 76 h. The reaction mixture was cooled to room temperature, dispersed in water, and then centrifuged at 25 000 g to retain the dark supernatant as an aqueous solution of the as-prepared carbon dots.

**Photolysis and Fluorescence Quenching.** An aqueous solution of the PEG<sub>1500N</sub>-functionalized carbon dots (observed fluorescence quantum yield about 20% at 440 nm excitation) with targeted optical density was prepared, and to the solution was added H<sub>2</sub>PtCl<sub>6</sub> to the desired final molar concentration. The optically transparent mixture in a cylindrical optical cell with flat front and back windows was photoirradiated in the photolysis setup through a 425 nm cutoff filter coupled with a hot filter (405–720 nm transmission) for a varying period of time, followed immediately by absorption and fluorescence measurements of the solution for the monitoring of spectral changes and the determination of fluorescence intensity (quantum yield) quenchings. The same photolysis procedure and conditions were applied to an aqueous solution of the carbon dots with H<sub>2</sub>AuCl<sub>4</sub> of the targeted concentration for a varying period of time, followed by the same absorption and fluorescence measurements of the solution for the evaluation on the effect of photolysis. Aqueous solutions of the carbon dots without and with H<sub>2</sub>PtCl<sub>6</sub> or H<sub>2</sub>AuCl<sub>4</sub> but no photoirradiation were used as controls or references.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

EDX results of Pt- and Au-coated carbon dot specimens on silicon-based grids, with their corresponding imaged areas (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [lcao@clemson.edu](mailto:lcao@clemson.edu) (L.C.), [christopher.bunker@wpafb.af.mil](mailto:christopher.bunker@wpafb.af.mil) (C.E.B.), [syaping@clemson.edu](mailto:syaping@clemson.edu) (Y.-P.S.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was made possible by financial support from Air Force Research Laboratory through the nanoenergetics program. Additional support from NSF (Y.-P.S.) and South Carolina Space Grant Consortium (Y.-P.S.) is also acknowledged. J.X. was on leave from Changzhou University in Changzhou, P.R. China (with a visiting scholarship jointly funded by NSF-China and Jiangsu Province), G.P. on leave from Ningbo University of Technology in Ningbo, P.R. China (with a visiting scholarship jointly funded by CSC-China and Zhejiang Province), and M.J.M. on leave from the Department of Chemistry and Physics at Northwest Missouri State University. L.C. was supported by a *Susan G. Komen for the Cure* Postdoctoral Fellowship. H.Q. was affiliated with and supported by Clemson University Electron Microscopy Facility.

## ■ REFERENCES

(1) Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem. Rev.* **2010**, *110*, 6873–6890.

(2) Hines, M. A.; Guyot-Sionnest, P. Synthesis and Characterization of Strongly Luminescing ZnS-Capped CdSe Nanocrystals. *J. Phys. Chem.* **1996**, *100*, 468–471.

(3) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility. *J. Am. Chem. Soc.* **1997**, *119*, 7019–7029.

(4) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weiss, S.; Alivisatos, A. P. Synthesis and Properties of Biocompatible Water-Soluble Silica-Coated CdSe/ZnS Semiconductor Quantum Dots. *J. Phys. Chem. B* **2001**, *105*, 8861–8871.

(5) Kim, S.; Fisher, B.; Eisler, H.-J.; Bawendi, M. Type-II Quantum Dots: CdTe/CdSe (Core/Shell) and CdSe/ZnTe (Core/Shell) Heterostructures. *J. Am. Chem. Soc.* **2003**, *125*, 11466–11467.

(6) Derfus, A. M.; Chan, W. C. W.; Bhatia, S. N. Probing the Cytotoxicity of Semiconductor Quantum Dots. *Nano Lett.* **2004**, *4*, 11–18.

(7) Kirchner, C.; Liedl, T.; Kudera, S.; Pellegrino, T.; Javier, A. M.; Gaub, H. E.; Stolzle, S.; Fertig, N.; Parak, W. J. Cytotoxicity of Colloidal CdSe and CdSe/ZnS Nanoparticles. *Nano Lett.* **2005**, *5*, 331–338.

(8) Holmes, J. D.; Ziegler, K. J.; Doty, R. C.; Pell, L. E.; Johnston, K. P.; Korgel, B. A. Highly Luminescent Silicon Nanocrystals with Discrete Optical Transitions. *J. Am. Chem. Soc.* **2001**, *123*, 3743–3748.

(9) Kang, Z.; Liu, Y.; Lee, S.-T. Small-Sized Silicon Nanoparticles: New Nanolights and Nanocatalysts. *Nanoscale* **2011**, *3*, 777–791.

(10) Yu, S.-J.; Kang, M.-W.; Chang, H.-C.; Chen, K.-M.; Yu, Y.-C. Bright Fluorescent Nanodiamonds: No Photobleaching and Low Cytotoxicity. *J. Am. Chem. Soc.* **2005**, *127*, 17604–17605.

(11) Sun, Y.-P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K. A. S.; Pathak, P.; Mezziani, M. J.; Harruff, B. A.; Wang, X.; Wang, H.; Luo, P. G.; Yang, H.; Kose, M. E.; Chen, B.; Veca, L. M.; Xie, S.-Y. Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. *J. Am. Chem. Soc.* **2006**, *128*, 7756–7757.

(12) Cao, L.; Wang, X.; Mezziani, M. J.; Lu, F.; Wang, H.; Luo, P. G.; Lin, Y.; Harruff, B. A.; Veca, L. M.; Murray, D.; Xie, S.-Y.; Sun, Y.-P. Carbon Dots for Multiphoton Bioimaging. *J. Am. Chem. Soc.* **2007**, *129*, 11318–11319.

(13) (a) Bourlino, A. B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Karakassides, M.; Giannelis, E. P. Surface Functionalized Carbogenic Quantum Dots. *Small* **2008**, *4*, 455–458. (b) Bourlino, A. B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Georgakilas, V.; Giannelis, E. P. Photoluminescent Carbogenic Dots. *Chem. Mater.* **2008**, *20*, 4539–4541.

(14) Peng, H.; Trivas-Sejdic, J. Simple Aqueous Solution Route to Luminescent Carbogenic Dots from Carbohydrates. *Chem. Mater.* **2009**, *21*, 5563–5565.

(15) Yang, S.-T.; Cao, L.; Luo, P. G.; Lu, F.; Wang, X.; Wang, H.; Mezziani, M. J.; Liu, Y.; Qi, G.; Sun, Y.-P. Carbon Dots for Optical Imaging in Vivo. *J. Am. Chem. Soc.* **2009**, *131*, 11308–11309.

(16) Yang, S.-T.; Wang, X.; Wang, H.; Lu, F.; Luo, P. G.; Cao, L.; Mezziani, M. J.; Liu, J.-H.; Liu, Y.; Chen, M.; Huang, Y.; Sun, Y.-P. Carbon Dots as Nontoxic and High-Performance Fluorescence Imaging Agents. *J. Phys. Chem. C* **2009**, *113*, 18110–18114.

(17) Ray, S. C.; Saha, A.; Jana, N. R.; Sarkar, R. Fluorescent Carbon Nanoparticles: Synthesis, Characterization, and Bioimaging Application. *J. Phys. Chem. C* **2009**, *113*, 18546–18551.

(18) Wang, X.; Cao, L.; Lu, F.; Mezziani, M. J.; Li, H.; Qi, G.; Zhou, B.; Harruff, B. A.; Kermarrec, F.; Sun, Y.-P. Photoinduced Electron Transfers with Carbon Dots. *Chem. Commun.* **2009**, *25*, 3774–3776.

(19) Wang, X.; Cao, L.; Yang, S.-T.; Lu, F.; Mezziani, M. J.; Tian, L.; Sun, K. W.; Bloodgood, M. A.; Sun, Y.-P. Bandgap-Like Strong Fluorescence in Functionalized Carbon Nanoparticles. *Angew. Chem. Int. Ed.* **2010**, *49*, 5310–5314.

(20) Li, H.; He, X.; Kang, Z.; Huang, H.; Liu, Y.; Liu, J.; Lian, S.; Tsang, C. H. A.; Yang, X.; Lee, S.-T. Water-Soluble Fluorescent Carbon Quantum Dots and Photocatalyst Design. *Angew. Chem. Int. Ed.* **2010**, *49*, 4430–4434.

- (21) Li, Q.; Ohulchanskyy, T. Y.; Liu, R.; Koynov, K.; Wu, D.; Best, A.; Kumar, R.; Bonoiu, A.; Prasad, P. N. Photoluminescent Carbon Dots as Biocompatible Nanoprobes for Targeting Cancer Cells in Vitro. *J. Phys. Chem. C* **2010**, *114*, 12062–12068.
- (22) Li, X.; Wang, H.; Shimizu, Y.; Pyatenko, A.; Kawaguchi, K.; Koshizaki, N. Preparation of Carbon Quantum Dots with Tunable Photoluminescence by Rapid Laser Passivation in Ordinary Organic Solvents. *Chem. Commun.* **2011**, *47*, 932–934.
- (23) Wang, X.; Qu, K.; Xu, B.; Rena, J.; Qu, X. Microwave Assisted One-Step Green Synthesis of Cell-Permeable Multicolor Photoluminescent Carbon Dots without Surface Passivation Reagents. *J. Mater. Chem.* **2011**, *21*, 2445–2450.
- (24) Wang, F.; Chen, Y.-H.; Liu, C.-Y.; Ma, D.-G. White Light-Emitting Devices Based on Carbon Dots Electroluminescence. *Chem. Commun.* **2011**, *47*, 3502–3504.
- (25) Chandra, S.; Das, P.; Bag, S.; Laha, D.; Pramanik, P. Synthesis, Functionalization and Bioimaging Applications of Highly Fluorescent Carbon Nanoparticles. *Nanoscale* **2011**, *3*, 1533–1540.
- (26) Cao, L.; Anilkumar, P.; Wang, X.; Liu, J.-H.; Sahu, S.; Mezzani, M. J.; Myers, E.; Sun, Y.-P. Reverse Stern–Volmer Behavior for Luminescence Quenching in Carbon Nanoparticles. *Can. J. Chem.* **2011**, *89*, 104–109.
- (27) Zhu, S.; Zhang, J.; Qiao, C.; Tang, S.; Li, Y.; Yuan, W.; Li, B.; Tian, L.; Liu, F.; Hu, R.; Gao, H.; Wei, H.; Zhang, H.; Sun, H.; Yang, B. Strongly Green-Photoluminescent Graphene Quantum Dots for Bioimaging Applications. *Chem. Commun.* **2011**, *47*, 6858–6860.
- (28) Anilkumar, P.; Wang, X.; Cao, L.; Sahu, S.; Liu, J.-H.; Wang, P.; Korch, K.; Tackett, K. N., II; Parenzan, A.; Sun, Y.-P. Toward Quantitatively Fluorescent Carbon-Based “Quantum” Dots. *Nanoscale* **2011**, *3*, 2023–2027.
- (29) Cao, L.; Sahu, S.; Anilkumar, P.; Bunker, C. E.; Xu, J.; Fernando, K. A. S.; Wang, P.; Gulians, E. A.; Tackett, K. N., II; Sun, Y.-P. Carbon Nanoparticles as Visible-Light Photocatalysts for Efficient CO<sub>2</sub> Conversion and Beyond. *J. Am. Chem. Soc.* **2011**, *133*, 4754–4757.
- (30) Cao, L.; Yang, S.-T.; Wang, X.; Luo, P. G.; Liu, J.-H.; Sahu, S.; Liu, Y.; Sun, Y.-P. Competitive Performance of Carbon “Quantum” Dots in Optical Bioimaging. *Theranostics* **2012**, *2*, 295–301.
- (31) Wrobel, D.; Graja, A. Photoinduced Electron Transfer Processes in Fullerene-Organic Chromophore Systems. *Coord. Chem. Rev.* **2011**, *255*, 2555–2577.
- (32) Xu, J.; Sahu, S.; Cao, L.; Anilkumar, P.; Tackett, K. N. II; Qian, H.; Bunker, C. E.; Gulians, E. A.; Parenzan, A.; Sun, Y.-P. Carbon Nanoparticles as Chromophores for Photon Harvesting and Photoconversion. *ChemPhysChem* **2011**, *12*, 3604–3608.
- (33) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970. (b) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.
- (34) Cameron, R. E.; Bocarsly, A. B. Multielectron-Photoinduced Reduction of Chloroplatinum Complexes: Visible Light Deposition of Platinum Metal. *Inorg. Chem.* **1986**, *25*, 2910–2913.
- (35) Einaga, H.; Harada, M. Photochemical Preparation of Poly(*N*-vinyl-2-pyrrolidone)-Stabilized Platinum Colloids and Their Deposition on Titanium Dioxide. *Langmuir* **2005**, *21*, 2578–2584.