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Photoluminescence Properties of Graphene versus Other Carbon Nanomaterials

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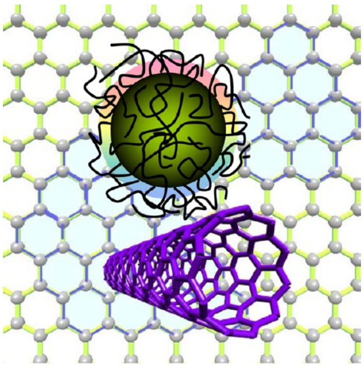
CONSPECTUS



Photoluminescent nanomaterials continue to garner research attention because of their many applications. For many years, researchers have focused on quantum dots (QDs) of semiconductor nanocrystals for their excellent performance and predictable fluorescence color variations that depend on the sizes of the nanocrystals. Even with these advantages, QDs can present some major limitations, such as the use of heavy metals in the high-performance semiconductor QDs. Therefore, researchers continue to be interested in developing new QDs or related nanomaterials. Recently, various nanoscale configurations of carbon have emerged as potential new platforms in the development of brightly photoluminescent materials.

As a perfect π-conjugated single sheet, graphene lacks electronic bandgaps and is not photoluminescent. Therefore, researchers have created energy bandgaps within graphene as a strategy to impart fluorescence emissions. Researchers have explored many experimental techniques to introduce bandgaps, such as cutting graphene sheets into small pieces or manipulating the π electronic network to form quantum-confined sp^2 "islands" in a graphene sheet, which apparently involve the formation or exploitation of structural defects. In fact, defects in graphene materials not only play a critical role in the creation of bandgaps for emissive electronic transitions, but also contribute directly to the bright photoluminescence emissions observed in these materials. Researchers have found similar defect-derived photoluminescence in carbon nanotubes and small carbon nanoparticles, dubbed carbon "quantum" dots or "carbon dots". However, they have not systematically examined the emissions properties of these different yet related carbon nanomaterials toward understanding their mechanistic origins.

In this Account, we examine the spectroscopic features of the observed photoluminescence emissions in graphene materials. We associate the structural characteristics in the underlying graphene materials with those emission properties as a way of classifying them into two primary categories: emissions that originate from created or induced energy bandgaps in a single graphene sheet and emissions that are associated with defects in single- and/or multiple-layer graphene. We highlight the similarities and differences between the observed photoluminescence properties of graphene materials and those found in other carbon nanomaterials including carbon dots and surface defect-passivated carbon nanotubes, and we discuss their mechanistic implications.

I. Introduction

Graphene and related materials have been studied extensively for their interesting and in many cases unique properties and application potentials.[1] While much effort has been focused on electronic characteristics in single- and few-layer graphene sheets, their optical properties including especially photoluminescence emissions have attracted growing recent attention. It is now widely acknowledged that graphene materials could be made photoluminescent over the visible spectral region, extending into the near-IR, though mechanistically various emissions observed experimentally might have different origins. A "perfect" (that found in computer simulations) or nearly perfect single-layer graphene sheet is not photoluminescent for a lack of electronic bandgaps. Therefore, the creation of energy bandgaps has been a popular strategy to impart fluorescence emissions in graphene.[2−7] There are obviously many different ways to create or induce the bandgaps, such as cutting graphene

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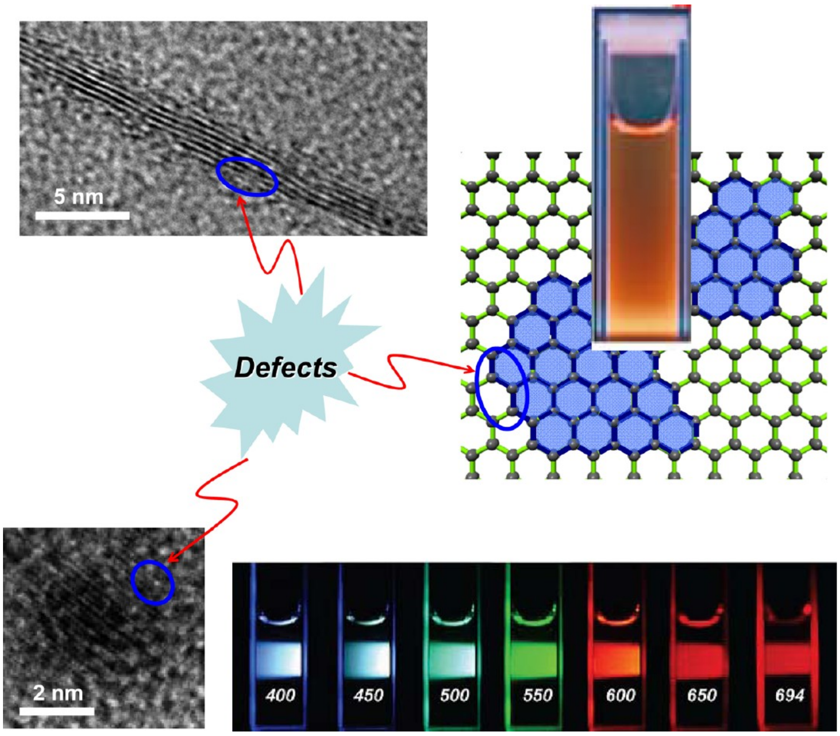

FIGURE 1. Upper: Isolated sp^2 islands in a graphene sheet and a photo showing bandgap fluorescence in solution (right, ref 7), and a multiple-layer graphene piece (left). Lower: a carbon nanoparticle with surface defects (left), and emission color variations in carbon dots (right, ref 9). Adapted from refs 7 and 9 with permission. Copyright 2011 American Chemical Society and Copyright 2006 American Chemical Society.

sheets into small pieces (or producing the pieces directly) or manipulating the π electronic network to form sp^2 "islands" in a graphene sheet (Figure 1), though most of these are associated with structural defects as well. In fact, one may argue that the formation of islands is in itself a result of specifically engineered defects in the graphene sheet (Figure 1).

Defects and their effects on electronic transitions are apparently at the center of both opportunities (for bright photoluminescence emissions) and complications relevant to the optical properties of graphene and related materials. Some in the carbon nanomaterials research communities have complained about confusions associated with how the observed photoluminescence is attributed or defined, such as how to differentiate fluorescence emissions found in specifically engineered graphene sheets and in "graphene quantum dots". Adding to the complications and confusions is the fact that similar (at least phenomenologically and likely also mechanistically) photoluminescence emissions have been found in carbon nanotubes[8] and small carbon nanoparticles (dubbed carbon "quantum" dots or "carbon dots", Figure 1).[9,10] In those carbon nanomaterials, bandgap transitions and especially the critical role of structural defects and their passivation by various means have been explored extensively. Thus, there is a need for a systematic examination on photoluminescence emissions in these different yet related carbon nanomaterials toward a global view on the shared or distinctive mechanistic origins.

Here we begin with a classification of the widely reported photoluminescence emissions in graphene materials into two primary categories, followed by an examination on the phenomenological and/or mechanistic similarities and differences between the observed photoluminescence properties in graphene materials and those found in other carbon nanomaterials. The emphases will be on cross references to the emissions in carbon dots and surface defect-passivated carbon nanotubes.

II. A Classification of Observed Photoluminescence Emissions

There have been many literature reports on the observation of photoluminescence emissions in graphene materials, which have been assigned to various origins.[2−7,11−21] A closer examination on the spectroscopic features of the emissions and the associated structural characteristics in the underlying materials would suggest that most of the observed photoluminescence emissions could be divided roughly into two categories. One is due to bandgap transitions corresponding to conjugated π-domains, and the other with more complex origins that are more or less associated with defects in the graphene structures. The two categories may be interconnected in many cases, as the creation or induction of the π-domains is often based on the exploitation or manipulation of defects in graphene sheets.

Bandgap Fluorescence of Conjugated π-Domains. A graphene sheet is characterized by the extended π-network, which is structurally analogous to an infinitely large planar aromatic molecule, but fundamentally different in terms of electronic transitions. The lack of bandgaps in graphene is on one hand widely considered as being of unique advantages in applications such as nanoelectronics, but on the other hand presents challenges to the community that is more interested in the optical properties of graphene materials. Therefore, much effort has been devoted to making the π-network in graphene from infinite to finite for the creation of electronic bandgaps. In simplistic terms, this is essentially to isolate conjugated π-domains that are structurally the same as large aromatic molecules in the graphene sheet, regardless of whether the isolation is through creating sp^2 islands in a large sheet or cutting a graphene sheet into small pieces or through other fundamentally similar means or configurations. A popular approach for the creation of sp^2 islands has been the reduction of graphene oxides (GOs), which are typically obtained from exhaustively oxidizing graphite under harsh conditions (Hummers method), followed by exfoliation into predominantly single-layer sheets.[22] GOs have been used as precursors for the conversion to reduced GOs (rGOs), which possess some of the basic structures found in single-layer graphene sheets. Generally the conversion chemistry for the rGOs with fluorescent π-domains is controlled to such a degree that there are no π-connections between the sp^2 islands, as that would otherwise result in interisland quenching of the targeted fluorescence emissions.[2,16] Among more representative illustrations for such an approach is the one shown in Figure 2 due to Eda et al.[2] In that study, GOs were reduced via exposure to hydrazine to recover only partially the graphene π-network that was destroyed under the extreme oxidation conditions in the reaction for GOs, so that the isolated nanosized sp^2 islands were immersed in the sp^3 carbon$-$oxygen matrix (Figure 2), conceptually and phenomenologically equivalent to large aromatic molecules dispersed in nonconjugated carbon$-$oxygen polymers. These conjugated π-domains could localize electron$-$hole pairs, with the created energy bandgaps dependent on domain sizes (Figure 2), as expected.[2]

A critical requirement for the bandgap fluorescence is that the single-layer configuration must be preserved in the partial conversion to rGOs or in other strategies for creating or inducing isolated sp^2 islands in order to avoid any interlayer quenching effects. For example, in the work by Gokus et al., graphene sheets were treated with oxygen plasma etching to impart fluorescence emissions, which were found to be strong in the single-layer sheets but essentially none in the multiple-layer sheets due to significant interlayer quenching.[12]

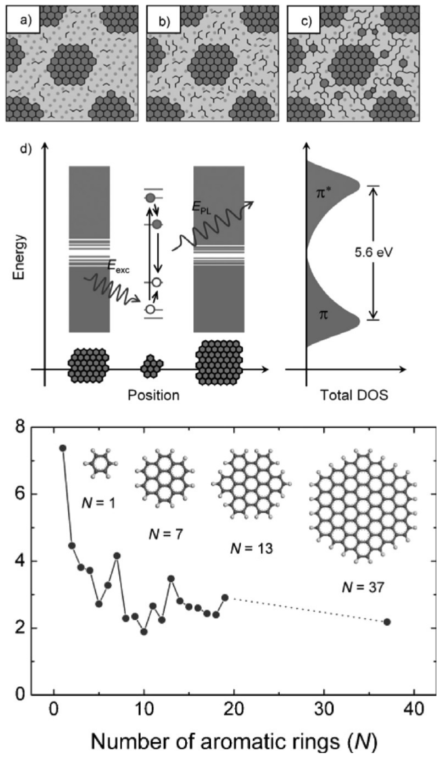

FIGURE 2. Structural models of GO at different stages of reduction (upper), and the energy gap of $\pi-\pi^*$ transitions calculated based on DFT as a function of the number of fused aromatic rings (lower). Adapted from ref 2 with permission. Copyright 2010 Wiley-VCH.

Several nomenclatures have been used to describe such an approach of making graphene materials fluorescent by creating or inducing electronic energy bandgaps, capturing various aspects or features of the observed fluorescence emissions. In essence, the approach may be considered as reflecting more of a molecular view on graphene, namely, that a single-layer graphene sheet is used as a precursor for being electronically sliced into isolated π-conjugated nanopieces, each of which resembles a large aromatic molecule of a distinctive energy bandgap for both optical absorption and fluorescence emission. Issues that may complicate such a molecular view include the role and consequence of π-plasmon absorption (common in carbon nanomaterials) into those percolated sp^2 islands that are nonemissive, and effects of defects in the graphene sheets, especially in the commonly used ones from partial conversion of GOs. Experimentally, the observed bandgap fluorescence has not

TABLE 1. Photoluminescence Parameters for Selected Graphene Materials

sample source	sample characteristics	excitation wavelength (nm)	emission quantum yield	ref	notes
from GOs	mostly single-layer sheets	325	negligible	2	sp^2 islands
		450	0.5%	7	
from polycyclic aromatic hydrocarbons	132 conjugated carbons	510	2%	18	sp^2 islands and edges
from GOs	small graphene pieces	420	7.5%	6	likely more defect-derived
		360	11.4%	19	
		350	12.8%	4	butylamine functionalization
from GO-like material		450	10%	20	PEG_{600N} functionalization
from GOs		360	28%	21b	PEG_{1500N} functionalization

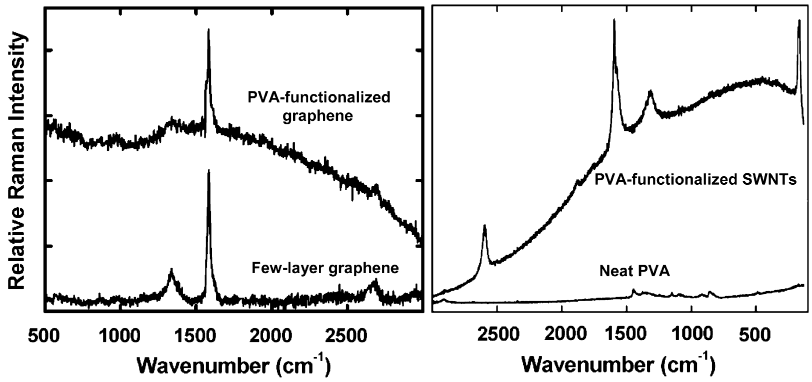

FIGURE 3. Raman results on poly(vinyl alcohol) (PVA) functionalization of few-layer graphene (left, ref 23) and SWNTs (right, ref 24). Adapted from refs 23 and 24 with permission. Copyright 2009 The Royal Society of Chemistry and Copyright 2003 American Chemical Society.

been so bright in terms of quantum yields (Table 1), generally lower than those of defect-derived photoluminescence emissions in graphene materials.

Photoluminescence of Defect-Derived Origins. The creation of electronic energy bandgaps in graphene has been a popular approach to impart fluorescence, but many other observed photoluminescence emissions can hardly be assigned to any bandgap origins. In the bandgap-based fluorescence discussed above, the single-layer configuration and nonpercolation between sp^2 islands are necessary in order to avoid any significant interlayer and interisland fluorescence quenching effects, respectively. Therefore, the photoluminescence emissions observed in multiple-layer graphene sheets could obviously not be originated from the same kind of conjugated π-domains. An early example for such photoluminescence was in the chemical functionalization of few-layer graphene sheets, where there was significant luminescence interference in Raman characterization of the functionalized samples (Figure 3),[23] similar to what were encountered in the chemical modification or functionalization of carbon nanotubes (Figure 3).[24] In a number of studies on small graphene pieces, including multiple-layer ones, similar photoluminescence emissions were observed (Table 1).[25]

Defects in graphene sheets are loosely defined, probably as a necessary due to a variety of possible structural details. There are sp^2 and sp^3 carbons in the sheets that are not perfect, so that defects are really any sites other than the perfect sp^2 domains. Many seemingly distinctive photoluminescence emissions in graphene materials have been found, which could not be explained in terms of fluorescent sp^2 islands or the like. Among representative examples were emissions proposed as being originated from functionalized surface defect sites,[21] those ascribed to CO-related localized electronic states at the oxidation sites after oxygen plasma treatment of graphene,[5,12] and "quasi-molecular fluorescence" in oxidized graphene arising from carboxylic acid groups electronically coupled with nearby atoms in polycylic aromatic compound-like moieties.[13] These nonbandgap emissions apparently share a common attribute for their relationships to or even dependence on defects in the graphene materials, though mechanistic details are probably more complex. A characteristic feature in many of the observed photoluminescence emissions was a lack of substantial interlayer quenching, contrary to the critical requirement for being single-layer only for the bandgap fluorescence discussed above. The defect-derived photoluminescence emissions are also generally much brighter, corresponding to higher observed quantum yields (Table 1). For at least those emissions that are sensitive to the passivation of defects in graphene materials, with those well-passivated ones exhibiting much enhanced emission intensities,[4,20,21] the observed photoluminescence properties are generally similar to those found in surface-passivated carbon nanoparticles and nanotubes,[8–10,26–28] thus likely for their sharing the same or similar mechanistic origins.

III. "Graphene Quantum Dots" versus Carbon "Quantum" Dots

Quantum dots (QDs) were originally referred to semiconductor nanoparticles of sizes in the quantum-confined regime (less than the exciton Bohr radius typically in a few nanometers), namely, that excitons in the small particles are confined in the spatial dimensions with quantized energy states. Typical semiconductor QDs are nanocrystals of inorganic compounds from the group II–VI elements in the periodic table. As a result of the quantum confinement, QDs often exhibit unique size- and composition-dependent optical and electrical properties. For example, semiconductor QDs such as CdS or CdSe are well-known for their predictable energy bandgaps at different nanocrystal sizes, corresponding to beautiful fluorescence color variations.[29]

Surface defects in conventional QDs of semiconductor nanocrystals are generally considered as being undesirable, causing energy "leaks" and other negative effects on the bandgap fluorescence emissions. Therefore, a number of strategies have been developed to minimize the defect-related effects, such as the capping of a semiconductor nanocrystal by another wider-bandgap semiconductor (the particularly famous CdSe/ZnS core–shell nanostructures, for example) to achieve much enhanced fluorescence properties.[29]

There are obvious similarities between electrons being confined in the conjugated π-domains in graphene and in nanoscale semiconductor particles, with similar size (dimension) dependent electronic energy bandgaps (Figure 2) and corresponding variations in fluorescence colors. Therefore, the former is conceptually similar to the latter, perhaps logical to be named as graphene quantum dots (GQDs), even though the isolated sp^2 islands are structurally not "dots" at all. As for the small graphene pieces, they appear closer to dots, but issues such as effects on or possible contributions to the observed fluorescence emissions by the edges and/or defects still need to be addressed. In fact, the fluorescence color variations with the π-domain sizes in graphene sheets are less pronounced in comparison with those found in classical semiconductor QDs due to the intrinsic properties of the created or induced energy bandgaps (Figure 2),[2] and also likely to the expected "contamination" by the defect-derived photoluminescence emissions.

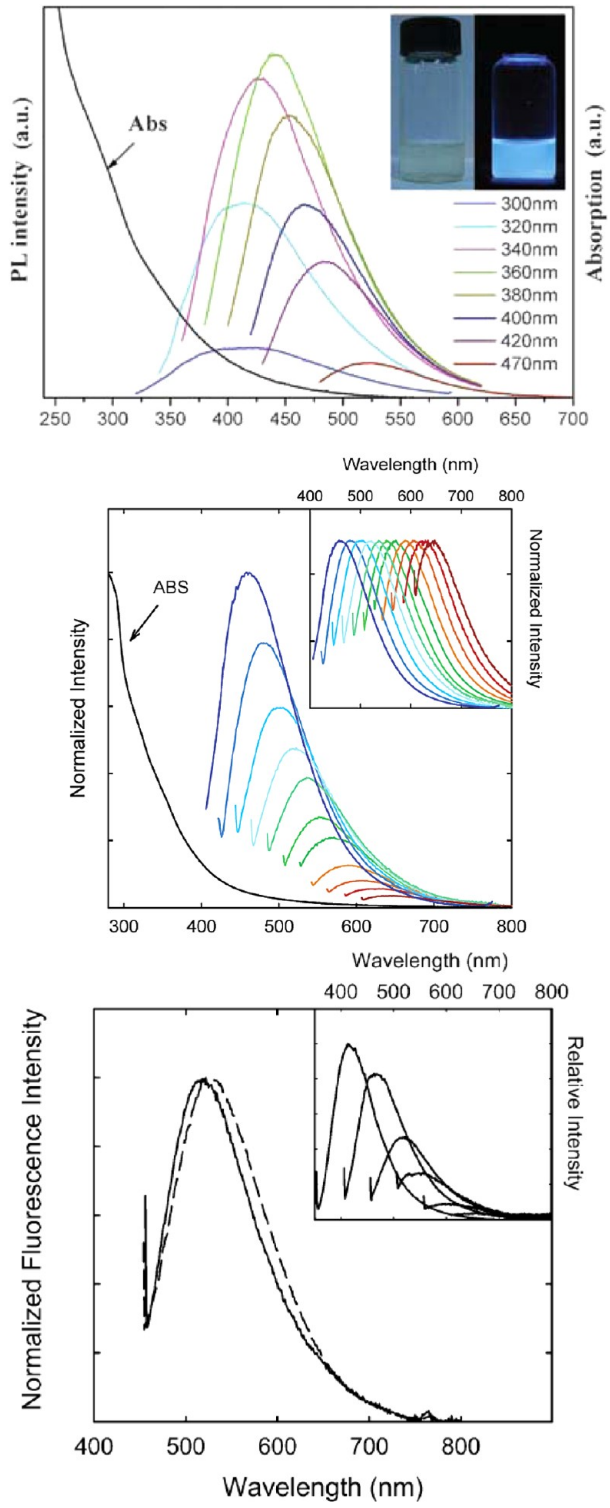

FIGURE 4. Comparison on the excitation wavelength dependencies of photoluminescence emissions in PEG-functionalized graphene pieces (upper, ref 21a), PPEI-EI polymer-passivated carbon dots (middle, ref 9, with the normalized spectra in the inset), and functionalized SWNTs (lower, ref 37, dashed line for PEG$_{1500N}$-SWNT and solid line for PPEI-EI-SWNT at 450 nm excitation, and other excitation wavelengths in the inset). Adapted from refs 21a, 9 and 37 with permission. Copyright 2011 The Royal Society of Chemistry, Copyright 2006 American Chemical Society and Copyright 2005 American Chemical Society.

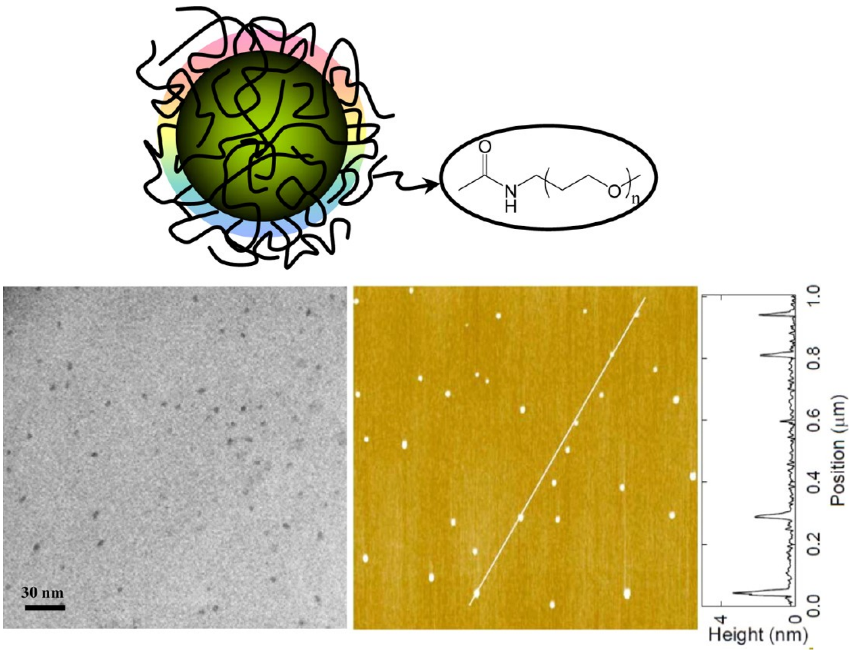

FIGURE 5. Cartoon illustration on a typical carbon dot (upper), and representative TEM and AFM images of the ultrabright PEGylated carbon dots (lower, ref 26). Adapted from ref 26 with permission. Copyright 2010 Wiley-VCH.

GQDs have also been used in many reports to refer to graphene materials of photoluminescence emissions that are not associated with isolated sp^2 islands and thus cannot be assigned to bandgap transitions, but with a somewhat different version of emission color variations (Figure 4). Many of the observed emission properties resemble those found in surface-passivated small carbon nanoparticles (Figure 4), dubbed carbon "quantum" dots or carbon dots (Figure 5),[9,10] where the word quantum is in quotation marks for the lack of the same kind of classical quantum confinement found in semiconductor QDs. The only quantum effect in carbon dots seems to be associated with the requirement for the carbon nanoparticles to be small enough to achieve an extremely large surface-to-volume ratio.[9]

Carbon dots have recently emerged as a new class of brightly photoluminescent (or fluorescent if the proposed electronic transition character is ultimately proven correct) nanomaterials,[9,10,26−28,30] with their photophysical properties resemble in many respects those commonly found in semiconductor QDs. A typical carbon dot is a small carbon nanoparticle with the particle surface functionalized by organic molecules or coated with polymers or other species (Figure 5). Spectroscopically, carbon nanoparticles are rather effective in photon-harvesting, with the optical absorptions covering a broad spectral region, which are primarily π-plasmon in nature.[31] Upon the near-UV or visible photoexcitation of even bare carbon nanoparticles without any surface functionalization, relatively weak emissions have been observed in aqueous and other suspensions (Figure 6, where the solvent molecules might have provided some relatively minor surface passivation effect).[32,33] With the surface passivation, carbon dots are strongly emissive in the visible, extending into the near-IR (Figure 6). So far the ultrabright carbon dots are those with emissions in the green, marching surprisingly well the spectral coverage of green fluorescence proteins, with experimentally determined emission quantum yields up to more than 75%.[27] The observed emission decays in carbon dots are generally not single-exponential, but on average not fast, with averaged lifetimes on the order of 4−5 ns.[26] Therefore, in another way to look at the strong optical transitions in carbon dots, the radiative rate constants for the emissions, which are known to reflect on the electronic transition probability, are around 10^8 s^{-1}, much larger than those found in any organic chromophores.

As alluded to above, many of the observed photoluminescence emissions in graphene materials are similar to those in carbon dots in almost all aspects of the spectroscopic properties, including especially the passivation effect for significantly enhanced emission quantum yields (Table 1) and characteristic spectral changes with excitation wavelengths (Figure 4). For example, Shen and co-workers used a mixture of different sized graphene pieces for surface-passivation by polyethylene glycol (PEG). The resulting materials exhibited excitation wavelength dependent photoluminescence

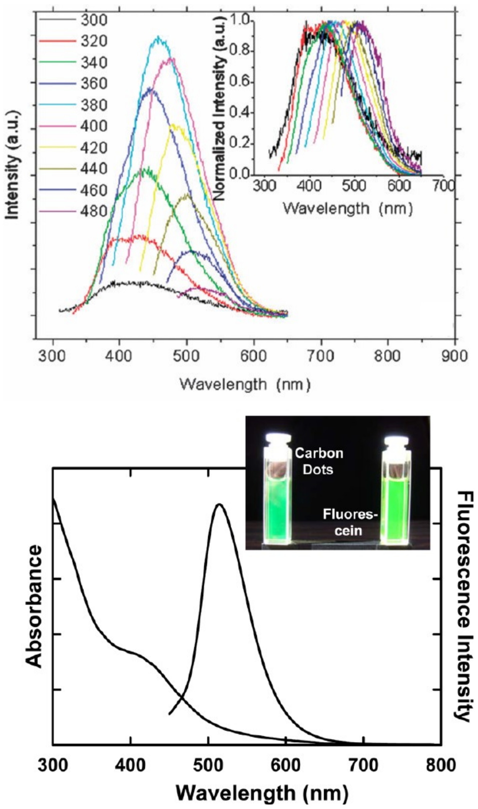

FIGURE 6. Upper (adapted from ref 32): Photoluminescence spectra of suspended carbon nanoparticles (excitation from 300 to 480 nm). Lower (adapted from ref 26): Absorption and photoluminescence (440 nm excitation) spectra of the ultrabright PEGylated carbon dots, with the photo in the inset comparing an aqueous solution of the carbon dots and an ethanol solution of fluorescein with matching optical density at 440 and 490 nm, respectively, under sunlight. Adapted from refs 32 and 26 with permission. Copyright 2011 The Royal Society of Chemistry and Copyright 2010 Wiley-VCH.

emissions that are comparable with those found in carbon dots (Figure 4).[21]

Structurally, defects in graphene sheets involving sp^3 carbons are really no difference in any fundamental fashion from what are on the surface of a small carbon nanoparticle with an extremely large surface-to-volume ratio (Figure 1). It is therefore logical to expect their sharing the same photoluminescence mechanism. For the emission mechanism in carbon dots, it was proposed[9,10] and is now increasingly adopted in the relevant research community that radiative recombinations of the carbon nanoparticle surface-confined electrons and holes (Figure 7) are responsible for the observed bright photoluminescence (or simply called fluorescence in such a mechanistic framework). The electrons and holes are generated likely by efficient photoinduced charge separations in the carbon nanoparticles, and the role of surface passivation by the organic or other functionalization is probably to make the surface sites more stable to facilitate more effective radiative recombinations. Experimental evidence in support of the mechanistic framework includes the photoluminescence quenching results with both electron donors and acceptors, which could apparently scavenge the surface-confined holes and electrons in carbon dots, respectively (Figure 7), to result in efficient and effective quenching of the emissions (diffusion-controlled with additional static contributions).[34] Recently, it was also demonstrated that the photogenerated electrons in carbon dots could be used for reduction purposes,[31,35] and more importantly the electrons could be concentrated into the gold or platinum metal doped on the carbon particle surface (Figure 7) for the photocatalytic conversion of carbon dioxide and also the photocatalytic splitting of water for hydrogen generation.[35] These results have reinforced the view that carbon dots essentially resemble nanoscale semiconductors in terms of photoinduced redox processes, in which the radiative recombinations in the absence of quenchers result in bright photoluminescence. For the defect-derived photoluminescence emissions in graphene materials, similar redox-driven quenching processes with both electron donors and acceptors have been reported.[14,21] The results are further evidence for the obvious similarities between defect-derived photoluminescence emissions in the different carbon nanomaterials.

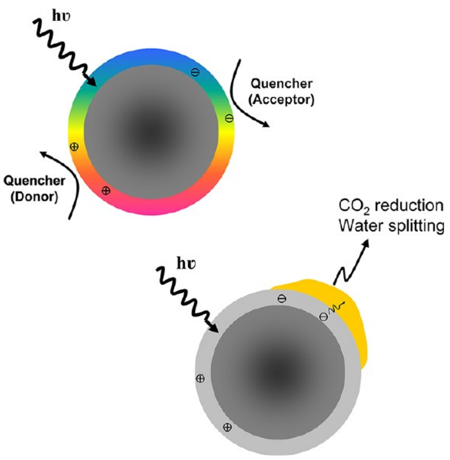

FIGURE 7. Cartoon illustrations on structural features and related mechanistic implications in carbon dots (upper) and those with the dot surface doped with gold or platinum metal (lower). Adapted from ref 35 with permission. Copyright 2011 American Chemical Society.

In the final analysis of GQDs versus carbon dots, the former has essentially been used loosely in the literature to refer to two rather different categories of photoluminescent graphene materials, those fluorescent due to created or induced electronic energy bandgaps and others that are associated with defects. The defect-derived photoluminescence emissions in graphene materials are phenomenologically and likely also mechanistically no different from those in carbon dots. Since the emissions due to defects are generally much brighter, with significantly higher quantum yields (Table 1), there is thus the question on how much they contaminate the relatively weaker bandgap emissions in quantized sp^2 islands (probably more legitimate mechanistically for their being designated as GQDs), as defects obviously play a significant role in the creation or induction of conjugated π-domains in graphene. One might even argue that some of the reported bandgap fluorescence emissions in graphene were actually combinations with defect-derived photoluminescence emissions.

IV. Relevance to Photoluminescence Emissions in Carbon Nanotubes

Carbon nanotubes are a related class of carbon nanomaterials in which both bandgap fluorescence and defect-derived photoluminescence emissions have been found and studied in detail, and thus may serve as references in the understanding of similar emissions in graphene materials. Unlike the created or induced bandgaps in graphene, there are intrinsic energy bandgaps in semiconducting single-walled carbon nanotubes (SWNTs) due to the van Hove singularity in the electronic density of states. The bandgap energies are dependent on nanotube diameters, but generally well into the near-IR spectral region. The mapping of SWNTs with various diameters by using fluorescence spectroscopy has been accomplished.[36]

For both SWNTs and their multiple-walled counterparts (MWNTs), the as-produced sootlike samples often contain carbon and other impurities such as residual catalysts, which thus require purification by using oxidative acids or the like. The purification process exaggerates the existing defects and induces new defects in the nanotube structure. These defects become brightly emissive under some specific conditions, especially when functionalized for the purpose of dispersion at the individual nanotube level without bundling or aggregation.[8,37−40] For example, Sun and co-workers found strong photoluminescence emissions in carbon nanotubes purified by nitric acid treatment and then functionalized with amino or other polymers or oligomers (Figures 4 and 8), where the functionalization targeted and passivated defects on the nanotube surface.[8,28,37] This is both conceptually and practically similar to the passivation effect used in the preparation of carbon dots and also found in graphene materials of enhanced defect-derived photoluminescence emissions (Table 1).

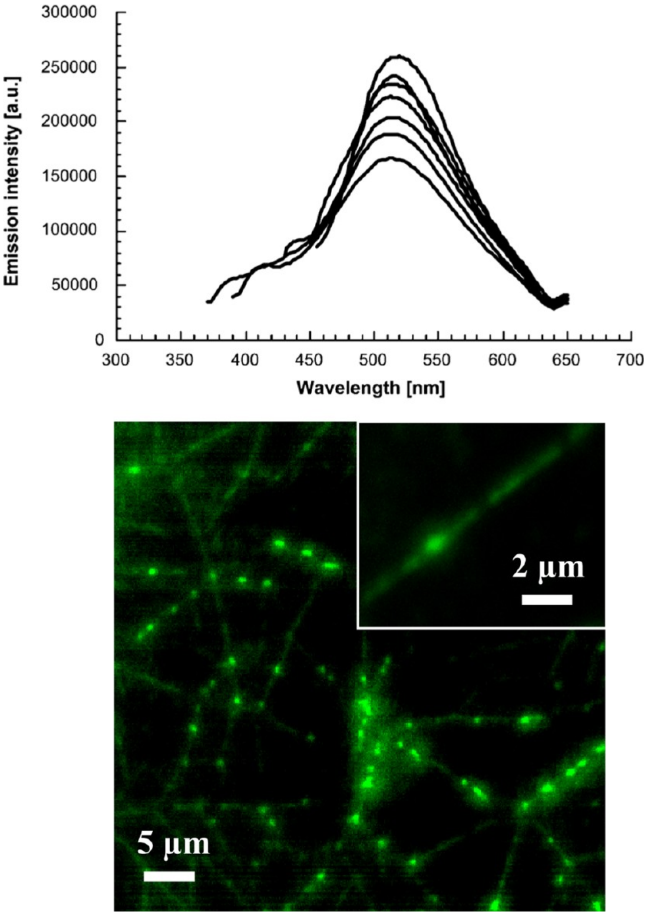

FIGURE 8. Upper (adapted from ref 38): Emission spectra of aqueous suspended SWNTs with excitation wavelengths of 340, 360, 380, 400, 420, 440, and 460 nm (bottom to top). Lower (adapted from ref 28): Fluorescence images (at 458 nm excitation) of PEG-functionalized MWNT/ZnS (referring to MWNTs of defect sites doped with ZnS) on cover glass, and the inset for corresponding selected species at a higher resolution. Adapted from refs 38 and 28 with permission. Copyright 2003 The Royal Society of Chemistry and Copyright 2010 American Chemical Society.

The passivated defects-based photoluminescence emissions in graphene materials, carbon dots, and carbon nanotubes likely share the same mechanistic framework, namely, that the emissions are due to radiative recombinations of trapped electrons and holes. In fact, the photoluminescence emissions in carbon nanotubes are indiscriminative between SWNTs and MWNTs, similar to the same indiscrimination between single- and few-layer graphene sheets for the defect-derived emissions. Unique to SWNTs, however, is the observed strong intertube quenching in nanotube bundles that effectively diminishes both bandgap and defect-derived emissions. This is interesting because MWNTs are essentially tubes that are coaxially stacked, but no "intertube" quenching effects on the defect-derived photoluminescence. It seems that the presence and absence of quenching effects may be understood in terms of the emissive entities in these carbon nanomaterials. The bandgap fluorescence in graphene is associated with the sp^2 island (the emissive entity) on a single sheet (Figures 1 and 2), which is quenched by π-domains in neighboring sheets in a few-layer configuration, whereas the defect-derived emissions are associated with the defect site (the emissive entity) across several sheets in a similar few-layer configuration (Figure 1), and thus little affected by the interlayer interactions. The same is true in carbon nanotubes, with SWNTs and MWNTs corresponding to single- and few-layer graphene sheets, respectively, except for no bandgap fluorescence in MWNTs. The photoluminescence emissions from defects (the emissive entity) in both SWNTs and MWNTs are similarly little affected by the rest of the nanotube electronic structures. As for the observed intertube quenching in nanotube bundles, it is mechanistically different, due to the close association of at least two nanotubes, equivalent to interactions between two separate pieces of graphene (either single- or few-layer). Therefore, the quenching behavior in these photoluminescent carbon nanomaterials may be valuable to mechanistic understanding or classification of the observed emissions.

There have been no reports in the literature on interactions between two or more graphene species that result in significant quenching of either bandgap fluorescence or defect-derived photoluminescence emissions. However, the quenching of this kind has been used successfully in probing the debundling of carbon nanotubes, including especially their dispersion in polymeric and other nanocomposite materials.[39,40] Obviously, the better the dispersion, the stronger the observed emissions due to the reduction or elimination of any intertube quenching effects. Similar applications for the photoluminescence properties of graphene materials may be expected.

V. Summary

The widely observed photoluminescence emissions in graphene materials may roughly be classified into two primary categories, those originated from created or induced energy bandgaps in a single graphene sheet and others that are one way or another associated with defects in single- and/or multiple-layer graphene. The former conceptually resembles conventional semiconductor QDs, and thus is more appropriately designated as GQDs. However, there seems to be a fundamental difference between these GQDs and conventional semiconductor QDs with respect to effects of structural (surface and/or edge) defects. The defects in QDs of semiconductor nanocrystal particles often act essentially as fluorescence quenchers, so that the passivation in terms of capping the particle surface with another wider-bandgap semiconductor greatly enhances the intrinsic fluorescence emissions in the semiconductor QDs. In GQDs referring to isolated sp^2 islands in a single graphene sheet, the edge or other defects are photoluminescent themselves, with high sensitivity to passivation. In fact, the same defect passivation strategy as used successfully for conventional semiconductor QDs may actually substantially enhance the defect-derived photoluminescence emissions to the extent that would overwhelm the desired bandgap fluorescence in the GQDs. Therefore, because the defect-derived photoluminescence emissions are relatively brighter, there may be a general risk for their contaminating the observed bandgap fluorescence in the GQDs, though a more precise differentiation between the bandgap and defect-derived emission contributions in the GQDs is hardly a trivial task spectroscopically.

The defect-derived photoluminescence emissions in graphene materials, generally bright and enhanced significantly when the defects are effectively passivated, are similar to those found in carbon dots and functionalized carbon nanotubes, and they likely share mechanistic details. The bright emissions in these carbon nanomaterials are valuable to a number of potential technological applications, especially those in biology and medicine. Unlike some presently dominating semiconductor QDs that contain heavy metals such as cadmium, the carbon nanomaterials are generally nontoxic or less toxic, though further evaluations are still needed.

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BIOGRAPHICAL INFORMATION

Li Cao earned his Ph.D. at the Institute of Physics, Chinese Academy of Sciences in 2005. Since 2006, he has been a postdoctoral scientist in Prof. Ya-Ping Sun's group at Clemson focusing on nanotechnology research. His general research interest is in the field of optical, electronic, and thermal properties of nanostructured materials and their various applications.

Mohammed J. Meziani received his Ph.D. in chemistry from the University of Montpellier II (France) in 1999. He did postdoctoral research in Prof. Ya-Ping Sun's group at Clemson, and then headed a nanotech company. Since 2010, he has been an assistant professor of organic chemistry and nanoscale science in the Department of Chemistry and Physics at Northwest Missouri State University. His research is in the development of nanostructures and nanomaterials for optical, electronic, and biomedical applications.

Sushant Sahu received his B.Sc. degree in chemistry from the University of Mumbai, India in 2003 and obtained his M.Sc. degree in chemistry from the Indian Institute of Technology, Guwahati, India in 2006. He is presently a candidate for Ph.D. at Clemson, under the supervision of Prof. Ya-Ping Sun. His research involves the development of carbon dots for energy conversion applications.

Ya-Ping Sun earned his Ph.D. at Florida State University in 1989. After postdoctoral training at University of Texas at Austin, he joined the Clemson faculty in 1992. He has been the Frank Henry Leslie Chair Professor of Natural & Physical Sciences since 2003. His research interests are primarily in carbon-based nanomaterials.

FOOTNOTES

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The authors declare no competing financial interest.

REFERENCES

1 Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-based Composite Materials. *Nature* **2006**, *442*, 282–286.

2 Eda, G.; Lin, Y.-Y.; Mattevi, C.; Yamaguchi, H.; Chen, H.-A.; Chen, I.-S.; Chen, C.-W.; Chhowalla, M. Blue Photoluminescence from Chemically Derived Graphene Oxide. *Adv. Mater.* **2010**, *22*, 505–509.

3 Loh, K. P.; Bao, Q.; Eda, G.; Chhowalla, M. Graphene Oxide as a Chemically Tunable Platform for Optical Applications. *Nat. Chem.* **2010**, *2*, 1015–1024.

4 Mei, Q.; Zhang, K.; Guan, G.; Liu, B.; Wang, S.; Zhang, Z. Highly Efficient Photoluminescent Graphene Oxide with Tunable Surface Properties. *Chem. Commun.* **2010**, *46*, 7319–7321.

5 Nourbakhsh, A.; Cantoro, M.; Vosch, T.; Pourtois, G.; Clemente, F.; van der Veen, M. H.; Hofkens, J.; Heyns, M. M.; De Gendt, S.; Sels, B. F. Bandgap Opening in Oxygen Plasma-treated Graphene. *Nanotechnology* **2010**, *21*, 435203.

6 Pan, D.; Guo, L.; Zhang, J.; Xi, C.; Xue, Q.; Huang, H.; Li, J.; Zhang, Z.; Yu, W.; Chen, Z.; Li, Z.; Wu, M. Cutting sp^2 Clusters in Graphene Sheets into Colloidal Graphene Quantum Dots with Strong Green Fluorescence. *J. Mater. Chem.* **2012**, *22*, 3314–3318.

7 Chen, J.-L.; Yan, X.-P.; Meng, K.; Wang, S.-F. Graphene Oxide Based Photoinduced Charge Transfer Label-free Near-infrared Fluorescent Biosensor for Dopamine. *Anal. Chem.* **2011**, *83*, 8787–8793.

8 Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. Strong Luminescence of Solubilized Carbon Nanotubes. *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.

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

10 Cao, L.; Wang, X.; Meziani, 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.

11 Sun, X.; Liu, Z.; Welsher, K.; Robinson, J. T.; Goodwin, A.; Zaric, S.; Dai, H. Nano- Graphene Oxide for Cellular Imaging and Drug Delivery. *Nano Res.* **2008**, *1*, 203–212.

12 Gokus, T.; Nair, R. R.; Bonetti, A.; Böhmler, M.; Lombardo, A.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C.; Hartschuh, A. Making Graphene Luminescent by Oxygen Plasma Treatment. *ACS Nano* **2009**, *3*, 3963–3968.

13 Galande, C.; Mohite, A. D.; Naumov, A. V.; Gao, W.; Ci, L.; Ajayan, A.; Gao, H.; Srivastava, A.; Weisman, R. B.; Ajayan, P. M. Quasi-Molecular Fluorescence from Graphene Oxide. *Sci. Rep.* **2011**, *1*, 85.

14 Gupta, V.; Chaudhary, N.; Srivastava, R.; Sharma, G. D.; Bhardwaj, R.; Chand, S. Luminescent Graphene Quantum Dots for Organic Photovoltaic Devices. *J. Am. Chem. Soc.* **2011**, *133*, 9960–9963.

15 Li, J.-L.; Bao, H.-C.; Hou, X.-L.; Sun, L.; Wang, X.-G.; Gu, M. Graphene Oxide Nanoparticles as a Nonbleaching Optical Probe for Two-Photon Luminescence Imaging and Cell Therapy. *Angew. Chem., Int. Ed.* **2012**, *51*, 1830–1834.

16 Krishnamoorthy, K.; Veerapandian, M.; Mohan, R.; Kim, S.-J. Investigation of Raman and Photoluminescence Studies of Reduced Graphene Oxide Sheets. *Appl. Phys. A: Mater. Sci. Process.* **2012**, *106*, 501–506.

17 Peng, J.; Gao, W.; Gupta, B. K.; Liu, Z.; Romero-Aburto, R.; Ge, L.; Song, L.; Alemany, L. B.; Zhan, X.; Gao, G.; Vithayathil, S. A.; Kaipparettu, B. A.; Marti, A. A.; Hayashi, T.; Zhu, J.-J.; Ajayan, P. M. Graphene Quantum Dots Derived from Carbon Fibers. *Nano Lett.* **2012**, *12*, 844–849.

18 Mueller, M. L.; Yan, X.; McGuire, J. A.; Li, L. S. Triplet States and Electronic Relaxation in Photoexcited Graphene Quantum Dots. *Nano Lett.* **2010**, *10*, 2679–2682.

19 Zhu, S.; Zhang, J.; Liu, X.; Li, B.; Wang, X.; Tang, S.; Meng, Q.; Li, Y. F.; Shi, C.; Hu, R.; Yang, B. Graphene Quantum Dots with Controllable Surface Oxidation, Tunable Fluorescence and Up-conversion Emission. *RSC Adv.* **2012**, *2*, 2717–2720.

20 Liu, Y.; Liu, C.-Y.; Zhang, Z.-Y. Synthesis and Surface Photochemistry of Graphitized Carbon Quantum Dots. *J. Colloid Interface Sci.* **2011**, *356*, 416–421.

21 (a) Shen, J.; Zhu, Y.; Chen., C.; Yang, X.; Li, C. Facile Preparation and Upconversion Luminescence of Graphene Quantum Dots. *Chem. Commun.* **2011**, *47*, 2580–2582. (b) Shen, J.; Zhu, Y.; Yang, X.; Zong, J.; Zhang, J.; Li, C. One-pot Hydrothermal Synthesis of Graphene Quantum Dots Surface-passivated by Polyethylene Glycol and Their Photoelectric Conversion under Near-infrared Light. *New J. Chem.* **2012**, *36*, 97–101.

22 Park, S.; Ruoff, R. S. Chemical Methods for the Production of Graphenes. *Nat. Nanotechnol.* **2009**, *4*, 217–224.

23 Veca, L. M.; Lu, F.; Meziani, M. J.; Cao, L.; Zhang, P.; Qi, G.; Qu, L.; Shrestha, M.; Sun, Y.-P. Polymer Functionalization and Solubilization of Carbon Nanosheets. *Chem. Commun.* **2009**, 2565–2567.

24 Lin, Y.; Zhou, B.; Fernando, K. A. S.; Liu, P.; Allard, L. F.; Sun, Y.-P. Polymeric Carbon Nanocomposites from Carbon Nanotubes Functionalized with Matrix Polymer. *Macromolecules* **2003**, *36*, 7199–7204.

25 Li, Y.; Hu, Y.; Zhao, Y.; Shi, G.; Deng, L.; Hou, Y.; Qu, L. An Electrochemical Avenue to Green-Luminescent Graphene Quantum Dots as Potential Electron-Acceptors for Photovoltaics. *Adv. Mater.* **2011**, *23*, 776–780.

26 Wang, X.; Cao, L.; Yang, S. T.; Lu, F. S.; Meziani, M. J.; Tian, L. 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.

27 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.

28 Wang, X.; Cao, L.; Bunker, C. E.; Meziani, M. J.; Lu, F. S.; Guliants, E. A.; Sun, Y.-P. Fluorescence Decoration of Defects in Carbon Nanotubes. *J. Phys. Chem. C* **2010**, *114*, 20941–20946.

29 Dabbousi, B. O.; RodriguezViejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. (CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *J. Phys. Chem. B* **1997**, *101*, 9463–9475.

30 (a) Bourlinos, A. B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Karakassides, M.; Giannelis, E. P. Surface Functionalized Carbogenic Quantum Dots. *Small* **2008**, *4*, 455–458. (b) Peng, H.; Travas-Sejdic, J. Simple Aqueous Solution Route to Luminescent Carbogenic Dots From Carbohydrates. *Chem. Mater.* **2009**, *21*, 5563–5565.

31 Xu, J.; Sahu, S.; Cao, L.; Anilkumar, P.; Tackett, K. N., II; Qian, H. J.; Bunker, C. E.; Guliants, E. A.; Parenzan, A.; Sun, Y.-P. Carbon Nanoparticles as Chromophores for Photon Harvesting and Photoconversion. *ChemPhysChem* **2011**, *12*, 3604–3608.

32 Li, X. Y.; Wang, H. Q.; 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.

33 Cao, L.; Anilkumar, P; Wang, X.; Liu, J. H.; Sahu, S.; Meziani, M. J.; Myers, E.; Sun, Y.-P. Reverse Stern-Volmer Behavior for Luminescence Quenching in Carbon Nanoparticles. *Can. J. Chem.* **2011**, *89*, 104–109.

34 Wang, X.; Cao, L.; Lu, F. S.; Meziani, 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.

35 Cao, L.; Sahu, S.; Anilkumar, P.; Bunker, C. E.; Xu, J. A.; Fernando, K. A. S.; Wang, P.; Guliants, E. A.; Tackett, K. N., II; Sun, Y.-P. Carbon Nanoparticles as Visible-Light Photocatalysts for Efficient CO$_2$ Conversion and Beyond. *J. Am. Chem. Soc.* **2011**, *133*, 4754–4757.

36 Ghosh, S.; Bachilo, S. M.; Weisman, R. B. Advanced Sorting of Single-walled Carbon Nanotubes by Nonlinear Density-gradient Ultracentrifugation. *Nat. Nanotechnol.* **2010**, *5*, 443–450.

37 Lin, Y.; Zhou, B.; Martin, R. B.; Henbest, K. B.; Harruff, B. A.; Riggs, J. E.; Guo, Z. X.; Allard, L. F.; Sun, Y.-P. Visible Luminescence of Carbon Nanotubes and Dependence on Functionalization. *J. Phys. Chem. B* **2005**, *109*, 14779–14782.

38 Guldi, D. M.; Holzinger, M.; Hirsch, A.; Georgakilas, V.; Prato, M. First Comparative Emission Assay of Single-wall Carbon Nanotubes-solutions and Dispersions. *Chem. Commun.* **2003**, *10*, 1130–1131.

39 Lacerda, L.; Pastorin, G.; Wu, W.; Prato, M.; Bianco, A.; Kostarelos, K. Luminescence of Functionalized Carbon Nanotubes as a Tool to Monitor Bundle Formation and Dissociation in Water: The Effect of Plasmid-DNA Complexation. *Adv. Funct. Mater.* **2006**, *16*, 1839–1846.

40 Zhou, B.; Lin, Y.; Hill, D. E.; Wang, W.; Veca, L. M.; Qu, L.; Pathak, P.; Meziani, M. J.; Diaz, J.; Connell, J. W.; Watson, K. A.; Allard, L. F.; Sun, Y.-P. Polymeric Nanocomposite Films from Functionalized vs Suspended Single-walled Carbon Nanotubes. *Polymer* **2006**, *47*, 5323–5329.