Potassium doping: Tuning the optical properties of graphene quantum dots

Cite as: AIP Advances 6, 075116 (2016); https://doi.org/10.1063/1.4959906
Submitted: 06 June 2016 . Accepted: 15 July 2016 . Published Online: 22 July 2016

Fuli Qian, Xueming Li, Libin Tang, Sin Ki Lai, Chaoyu Lu, and Shu Ping Lau

ARTICLES YOU MAY BE INTERESTED IN

Synthesis and upconversion luminescence of N-doped graphene quantum dots
Applied Physics Letters 101, 103107 (2012); https://doi.org/10.1063/1.4750065

Functionalization of graphene quantum dots by fluorine: Preparation, properties, application, and their mechanisms
Applied Physics Letters 110, 221901 (2017); https://doi.org/10.1063/1.4984238

Chlorine doped graphene quantum dots: Preparation, properties, and photovoltaic detectors
Applied Physics Letters 105, 111116 (2014); https://doi.org/10.1063/1.4896278
Potassium doping: Tuning the optical properties of graphene quantum dots

Fuli Qian,1 Xueming Li,1,a Libin Tang,2,b Sin Ki Lai,3 Chaoyu Lu,1 and Shu Ping Lau3
1Solar Energy Research Institute, Yunnan Normal University, Kunming, 650092, P. R. China
2Kunming Institute of Physics, Kunming 650223, P. R. China
3Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong SAR, P. R. China

(Received 6 June 2016; accepted 15 July 2016; published online 22 July 2016)

Doping with hetero-atoms is an effective way to tune the properties of graphene quantum dots (GQDs). Here, potassium-doped GQDs (K-GQDs) are synthesized by a one-pot hydrothermal treatment of sucrose and potassium hydroxide solution. Optical properties of the GQDs are altered as a result of K-doping. The absorption peaks exhibit a blue shift. Multiple photoluminescence (PL) peaks are observed as the excitation wavelength is varied from 380 nm to 620 nm. New energy levels are introduced into the K-GQDs and provide alternative electron transition pathways. The maximum PL intensity of the K-GQDs is obtained at an excitation wavelength of 480 nm which is distinct from the undoped GQDs (375 nm). The strong PL of the K-GQDs at the longer emission wavelengths is expected to make K-GQDs more suitable for bioimaging and optoelectronic applications.

I. INTRODUCTION

Graphene has numerous unique properties including high electrical conductivity1 and good chemical stability2 when compared with other two-dimensional (2D) materials like transition metal dichalcogenides (TMDs) and phosphorene. However, graphene has zero band gap and does not exhibit photoluminescence (PL), which makes it less outstanding in terms of optical properties. PL has extensive applications in bioimaging,3 anti-counterfeiting,4 and optoelectronics.5 This deficiency has been overcome by employing graphene quantum dots (GQDs), which is the nano-sized graphene with quantum confinements in all three dimensions and typically with diameters below 10 nm. Electron transition between discrete energy level in GQDs leads to PL.6 Previous studies have shown that doping of hetero-atoms into the GQDs is an effective way to alter the band gap or introduce new energy levels into the GQDs which can be used to tune the PL properties in order to make GQDs suitable for various applications.7

Up to date, research efforts have been mainly focused on doping non-metallic atoms like nitrogen,8 sulphur,7,9 chlorine,10 fluorine11 and selenium12 into GQDs. Some works have also been reported for co-doped GQDs like B, N-doped GQDs,13 N, S-doped GQDs,14 and N, P-doped GQDs.15 However, less studies have been carried out on metal-doping of GQDs. Habiba et al. reported the synthesis of Ag-GQDs nanocomposite using pulsed laser and demonstrated good biocompatibility and non-toxicity of the nanocomposite.16 Nonetheless, the effect of metallic atoms doping on the optical properties of GQDs has not been well-addressed. Non-metallic atoms doping has shown to vary the electronic structure of the GQDs, it is therefore of central importance to investigate the
change in electronic structure of GQDs with metallic atoms doping through probing its optical properties. In addition, the large surface-to-volume ratio also endows GQDs with rich surface chemistry. Doping of hetero-atoms in the GQDs has also been used to vary the functional groups or active sites on the surface of the GQDs, which leads to promising applications of GQDs in energy storage devices, bioanalysis and environmental analysis.\textsuperscript{17–19}

In this work, the synthesis of potassium-doped GQDs (K-GQDs) is reported for the first time. The K-GQDs form a stable dispersion in water with good crystallinity and uniform diameters. They show distinctive optical properties when compared with the undoped GQDs.\textsuperscript{20} The PL peaks of the K-GQDs are red-shifted from that of pristine GQDs under a series of excitation wavelengths ranging from 320 nm to 560 nm. In addition, the K-GQDs exhibit multicolor emissions with five different emission peaks observed in the above excitation range, which is also consistent with the photoluminescence excitation (PLE) results. It is proposed that new electron energy levels are introduced into the GQDs as a result of K-doping. Excited electrons are relaxed through additional pathways which endow the K-GQDs with multicolor emissions.

II. EXPERIMENTAL

A. Preparation of K-GQDs

Sucrose (0.5 g) and 0.15 g of potassium hydroxide were dissolved in 40 ml of deionized water with stirring. The solution was then transferred to a Teflon-lined autoclave. The hydrothermal reaction was carried out at 170 °C for 4 hrs. The autoclave was cooled naturally to room temperature. The product was transferred to a 1000 Da dialysis bag and dialyzed against DI water to remove any residue sucrose. K-GQDs were obtained for further analysis.

B. Characterizations of K-GQDs

The morphology and size distribution of the K-GQDs were investigated by transmission electron microscopy (TEM, Tecnai G2F30-TWIN) with an operating voltage of 300 kV. Atomic force microscopy (AFM) was performed on Seiko S-image/E-sweep to investigate the topography and height of the GQDs films. X-ray diffraction (XRD) was carried out with TTRIII X-ray diffractometer (\(\lambda = 1.5408 \, \text{Å}\)) operating at 40 kV and 200 mA, with a scan range of 2\(\theta = 5^\circ\)–90° to analyze the crystallinity of the GQDs. The elemental composition of K-GQDs was investigated by x-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe II). Functional groups on the GQDs were investigated by Fourier Transform infra-red spectroscopy (FTIR, UV-3600). Raman spectra were obtained by in via confocal Raman microscope using 514.5 nm laser. UV-Vis absorption spectra were measured by Specord200 spectrometer using deionized water as the reference with a scan range from 190 to 900 nm. PL and PLE spectra were acquired by F-7000 fluorescent spectrometer.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the TEM image of the K-GQDs. The K-GQDs are spherical in shape and have similar diameters. They dispersed randomly on the carbon grid with no sign of aggregation. The size analysis of the K-GQDs is shown in Figure 1(b). Majority of the K-GQDs have diameters of 3 to 4 nm. The sizes of K-GQDs follow a Gaussian distribution with an average diameter of 3.4 nm and the full-width-at-half-maximum (FWHM) is 1 nm. The good crystallinity of the K-GQDs can be clearly observed from the high resolution TEM (HR-TEM) image as shown in Figure 1(c) and 1(d). The \(d\)-spacing between the lattice planes is \(d = 0.246 \, \text{nm}\) which corresponds to the (100) planes of graphite\textsuperscript{21} and illustrates that the K-GQDs retains the same hexagonal crystal structure as the un-doped GQDs, which would be further discussed below. Figure 1(e) shows the line section of the K-GQD in Figure 1(d). The lattice planes have equal separation of 0.246 nm, meaning that the K-doping does not alter the internal crystal structure of GQDs. Fast Fourier Transform (FFT) was further performed on a randomly chosen K-GQD as indicated by the red box in
FIG. 1. Structural and morphological characterization of the K-GQDs. (a) TEM image of the K-GQDs. (b) The size distribution of the K-GQDs, the red line is the Gaussian fitting curve. (c) and (d) The HRTEM images of the K-GQD. (e) The line profile of the diffraction fringes shown in (d). (f) The fast Fourier transform (FFT) image (inset) of a selected area (red square). (g) The AFM image of the K-GQDs. (h) The height analysis of locations A, B, C and D indicated in (g).

Figure 1(f). The FFT image as shown in the inset of Figure 1(f) provides evidence on the hexagonal crystal structure of the K-GQDs. Based on the above analyses, it can be concluded that potassium doping does not alter the graphitic crystal structure of the K-GQDs.

AFM measurement of the K-GQDs which is drop-casted on silicon substrate as shown in Figure 1(g). Height analysis was performed on four locations labelled as A, B, C and D in the figure. Their heights are 3.82 nm, 3.58 nm, 3.19 nm and 3.54 nm respectively, with an average height of 3.53 nm, which is consistent with the TEM size analysis (with an average diameter of 3.4 nm), and again verified the spherical shape of the K-GQDs.

XPS measurements were used to investigate the elemental composition and chemical bondings in the K-GQDs. Figure 2(a) shows the XPS full-scan of K-GQDs. The C-1s, O-1s, K-2p$_{3/2}$ and K-2s peaks are located at 285 eV, 532.2 eV, 292.2 eV and 377 eV respectively. Figure 2(b) shows the enlarged C-1s spectrum. Five peaks obtained from the deconvolution of the C-1s peak are centered at 284.7 eV (C=C), 285.3 eV (C-C, C-H), 286.4 eV (C-OH), 287.3 eV (C-O-C) and 288.3 eV (C=O). The numerous functional groups enable K-GQDs to have good solubility in water. The intensity of the peaks at 284.7 eV and 285.3 eV are stronger, meaning that C=C, C-C and C-H are the major chemical configuration in K-GQDs, in particular, C=C is related to sp$^2$ hybridization while C-C and C-H are related to the sp$^3$ hybridization. Figure 2(c) shows the K-2p XPS spectrum,
The K-2p\textsubscript{3/2} orbitals are present at 294.2 eV and 294.5 eV. The K-2s spectrum was also observed at the binding energy of 377.2 eV as shown in Figure 2(d),\textsuperscript{23} which demonstrates that potassium has been effectively doped into the GQDs.

FTIR was further utilized to probe the functional groups in the K-GQDs. As shown in Figure 3(a), a large number of vibrational peaks are resulted from the K-GQDs, with the strongest peak located at 1589 cm\textsuperscript{-1} which corresponds to the C=\text{C} stretching mode. Both XPS and FTIR results indicate that potassium hetero-atoms are doped into GQDs through interaction with the C=\text{C} bonds are also the basic constitutional structures of the GQDs. Other vibrational peaks are related to the CH\textsubscript{2} vibrational mode (852 cm\textsuperscript{-1}), C-O (1124 cm\textsuperscript{-1}), C-C (1413 cm\textsuperscript{-1}), C-H (1413 cm\textsuperscript{-1} and 2976 cm\textsuperscript{-1}) and O-H (3319 cm\textsuperscript{-1}). Comparing with the pristine GQDs reported by Tang \textit{et al.},\textsuperscript{20} an additional peak appeared at 1770.3 cm\textsuperscript{-1} (indicated by a red dashed box in figure 3(a)) for the K-GQDs, which is probably resulted from potassium-related bonding. The K-GQDs are rich in functional groups. Under the interaction of π-π conjugated bonds, the K-GQDs have more dangling bonds and a large surface area, which would be useful in bioimaging for K-GQDs to effectively graft into biomaterials.

Figure 3(b) shows the XRD spectrum of the K-GQDs. A broad diffraction peak appears at 2\textdegree = 15\degree to 45\degree, which corresponds to the c-axis lattice parameter of graphitic materials.\textsuperscript{20} The large FWHM of the diffraction peak can be correlated to the small size of the K-GQDs. Figure 3(c) shows the Raman spectrum of the K-GQDs. The G peak at 1567.7 cm\textsuperscript{-1} corresponds to the sp\textsuperscript{2} in-plane vibration of carbon.\textsuperscript{24} The outstanding G peak indicates that the K-GQDs have good crystallinity. The D peak at 1278.9 cm\textsuperscript{-1} is attributed to the large number of edge states in K-GQDs and the defect states in the K-GQDs.\textsuperscript{25} The GQDs prepared by hydrothermal method are rich in surface functional groups, which give a higher probability for the formation of surface defects. The intensity of D peak is much weaker than the G peak, the D/G ratio is \textasciitilde0.115, which illustrates that the K-GQDs prepared by hydrothermal methods are not dominated by internal defects and have a low degree of disorder.
Figure 3(d) shows the UV-Vis absorption spectrum of a 36-fold diluted K-GQDs solution, while the inset in Figure 3(d) shows the optical image of the K-GQDs solution under 365 nm UV illumination. The K-GQDs solution shows intensive blue PL under UV light, and its absorption extends to the visible light region. Two absorption peaks are found at 222 nm and 274 nm, which corresponds to the $\pi \rightarrow \pi^*$ transition of $\text{C}=\text{C}$ and $n \rightarrow \pi^*$ transition of $\text{C}=\text{O}$ respectively. Comparing with the undoped GQDs, the absorption peaks shows a blue shift (228 nm and 282 nm for un-doped GQDs) after K-doping. This is explained by the introduction of K-related energy band into the GQDs which shift the energy levels of the above two transitions. Upon light excitation, the K-GQDs absorb light and bring about the transition from $\text{C} \pi$ orbital to $\text{C} \pi^*$ orbital, the potassium doping introduce additional orbital into GQDs, and results in a change in electron transition pathways.

The PL spectra of the K-GQDs are shown in Figure 4(a). The excitation wavelength was varied from 320 nm to 560 nm, with 20 nm interval. Out of the many emission peaks observed in Figure 4(a) with some of them overlapping with each other. Five emission peaks located at 513 nm, 527 nm, 544 nm, 551 nm and 600 nm can be clearly identified, which positions are fixed with respect to the changing excitation wavelength as indicated by blue arrows in the figure. This corresponds to five different electron transitions under different energies of photons absorbed. The K-GQDs also exhibit excitation wavelength dependent PL similar to the undoped GQDs with the major emission peak shift with the excitation wavelength. We proposed that except for the O, H functional groups that form surface states and introduce electronic orbital as in the case of pristine GQDs, the K-doping has also introduced orbital between the $\pi$ and $\pi^*$ orbital of the GQDs. The change in energy structure leads to the change in light absorption and PL properties mentioned above. The maximum PL intensity was obtained at an excitation wavelength of 480 nm and an emission wavelength of 544 nm, which is red-shifted as compared to undoped GQDs with maximum PL.
FIG. 4. (a) The PL emission spectra of the K-GQD solution excited by wavelengths ranging from 320 to 560 nm. (b) The PLE spectra of the K-GQDs recorded as a function of $\lambda_{\text{Em}}$ ranging from 380 to 620 nm (* interference peak (half $\lambda_{\text{Em}}$) from the instrument).

The stronger PL of the K-GQDs at longer wavelength is beneficial for bioimaging applications\textsuperscript{27–31} where the usage of UV light on biomaterials is not preferred due to the damage caused by higher energy (UV) radiation.

To provide more insights, the PLE spectra of the K-GQDs with different emission wavelengths are also acquired as shown in Figure 4(b). For emission wavelengths varying from 380 nm to 620 nm, five PLE peaks were observed at 216 nm, 248 nm, 374 nm, 445 nm and 489 nm, which are illustrated with blue arrows in the figure. These wavelengths are successively shorter than the five emissive wavelengths discussed above thus is consistent with the result obtained from PL emission. This indicates that the K-GQDs have five electron transition modes, which absorb at 216 nm (5.74 eV), 248 nm (5.00 eV), 374 nm (3.32 eV), 445 nm (2.79 eV) and 489 nm (2.54 eV) with the corresponding relaxation by emitting photons of 513 nm (2.42 eV), 527 nm (2.35 eV), 544 nm (2.28 eV), 551 nm (2.25 eV) and 600 nm (2.07 eV) respectively. Under the emission wavelength of 473 nm, PLE spectrum exhibits two peaks at 263 nm and 329 nm with different intensities, which are observed in undoped GQDs,\textsuperscript{20} except that the peak locations are shifted. For K-GQDs prepared by hydrothermal method, introduction of K hetero-atoms can create surface functional groups on the GQDs as in the case of O and H atoms in pristine GQDs. These hetero-atoms can thereby alter the energy level and structure of the GQDs. Based on the PL and PLE experimental results, an energy band diagram for K-GQDs is proposed (Figure 5) to illustrate the electron transitions in the process of excitation and emission. Electron transitions may take place when high energy photons is absorbed, followed by emitting a number of low energy photons after undergoing interband crossing\textsuperscript{7} and vibration relaxation. The introduction of new energy levels is the key for the fine-tuning of the optoelectronic properties of GQDs, which is important to make GQDs suitable for different applications.
IV. CONCLUSION

Metallic hetero-atoms doping of GQDs with potassium is reported. The K-GQDs synthesized by the highly effective and economical hydrothermal method exhibits good crystallinity, excellent water dispersability and uniform diameters. The hexagonal honeycomb crystal structure of the K-GQDs is not altered by the potassium doping. Blue PL was observed under 365 nm excitation. The K-GQDs absorb in the visible light region in addition to the UV region, which leads to an enhanced PL in the visible light region. Potassium-related energy levels are introduced into the GQDs to realize multicolor emission which corresponds to five electron transition modes. The study enriches the metallic hetero-atom doping studies of GQDs and realizes the energy level tuning in GQDs by K-doping. The K-GQDs opens the platform for multi-functional applications of GQDs.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (No. 61106098 and No. 51462037), and the Key Project of Applied Basic Research of Yunnan Province, China (No. 2012FA003).

1 K. S. Kim, Y. Zhao, H. Jang, Y. L. Sang, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, and B. H. Hong, Nature 457, 706 (2009).
2 K. Novoselov, A. K. Geim, S. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
3 S. J. Zhu, J. H. Zhang, S. J. Tang, C. Y. Qian, L. Wang, and H. H. Wang, Chem. Commun. 47, 6858 (2012).
4 Isnaeni, N. Yulianto, and M. M. Suliyanti, AIP Conf. Proc. 1719, 407 (2016).
5 K. Liu, Z. H. Zhu, X. J. Li, J. F. Zhang, X. D. Yuan, C. C. Guo, W. Xu, and S.Q. Qin, ACS Photonics 2, 797 (2015).
6 M. M. Xie, Y. J. Su, X. N. Lu, Y. Z. Zhang, Z. Yang, and Y. F. Zhang, Mater. Lett. 93, 161 (2013).
7 X. M. Li, S. P. Lau, L. B. Tang, R. B. Ji, and F. Z. Yang, Nanoscale 6, 5323 (2014).
8 L. B. Tang, R. B. Ji, X. M. Li, K. S. Teng, and S. P. Lau, J. Mater. Chem. C 1, 4908 (2013).
9 S. H. Li, Y. C. Li, J. Cao, J. Zhu, L. Z. Fan, and X. H. Li, Anal. Chem. 86, 10201 (2014).
10 X. M. Li, S. P. Lau, L. B. Tang, R. B. Ji, and P. Z. Yang, J. Mater. Chem. C 1, 7308 (2013).
11 Q. Feng, Q. Q. Cao, M. Li, F. C. Liu, N. J. Tang, and Y. W. Du, Appl. Phys. Lett. 102, 013111 (2013).
12 S. W. Yang, J. Sun, P. He, X. X. Deng, Z. Y. Wang, C. Y. Hu, G. Q. Ding, and X. M. Xie, Chem. Mater. 27, 954 (2015).
13 H. L. Fei, R. Q. Ye, G. L. Ye, Y. J. Gong, Z. W. Peng, X. J. Fan, E. L. G. Samuel, P. M. Ajayan, and J. M. Tour, ACS Nano 8, 10837 (2014).
14 A. Ananthanarayanan, Y. Wang, P. Routh, M. A. Sk, T. Aung, M. Lin, J. Zhang, J. Chen, H. D. Sun, and P. Chen, Nanoscale 7, 8159 (2015).
15 D. Qu, M. Zheng, P. Du, Y. Zhou, L. G. Zhang, D. Li, H. Q. Tan, Z. Zhao, Z. G. Xie, and Z. C. Sun, Nanoscale 5, 12272 (2013).
16 K. Habiba, J. Encarnacion-Rosado, K. Garcia-Pabon, J. C. Villalobos-Santos, V. I. Makarov, J. A. Avalos, B. R. Weiner, and G. Morell, Int. J. Nanomed. 11, 107 (2016).
17 X. W. Wang, G. Z. Sun, P. Routh, D. H. Kim, W. Huang, and P. Chen, Chem. Soc. Rev. 43, 7067 (2014).
18 Y. Q. Dai, H. Long, X. T. Wang, Y. M. Wang, Q. Gu, W. Jiang, Y. C. Wang, C. C. Li, T. H. Zeng, Y. M. Sun, and J. Zeng, Part. Part. Syst. Charact. 31, 597 (2014).
19 M. Seredych, K. Singh, and T. J. Bandosz, Electroanalysis 26, 109 (2014).
20 L. B. Tang, R. B. Ji, X. K. Cao, J. Y. Lin, H. X. Jiang, X. M. Li, K. S. Teng, C. M. Luk, S. J. Zeng, J. H. Hao, and S. P. Lau, ACS Nano 6, 5102 (2012).
21 S. K. Lai, C. M. Luk, L. Tang, K. S. Teng, and S. P. Lau, Nanoscale 7, 5338 (2015).
22 D. Gao, Q. Xu, J. Zhang, Z. Yang, M. Si, Z. Yan, and D. Xue, Nanoscale 6, 2577 (2014).
23 S. Li, E. T. Kang, K. G. Neoh, Z. H. Ma, K. L. Tan, and W. Huang, Appl. Surf. Sci. 181, 201 (2001).
24 S. K. Lai, C. Xie, K. S. Teng, Y. Li, F. Tan, F. Yan, and S. P. Lau, Adv. Optical Mater. 4, 555 (2016).
25 S. K. Lai, L. Tang, Y. Y. Hui, C. M. Luk, and S. P. Lau, J. Mater. Chem. C 2, 6971 (2014).
26 D. Pan, J. Zhang, Z. Li, and M. Wu, Adv. Mater. 22, 734 (2010).
27 K. Welsher, Z. Liu, S. P. Sherlock, J. T. Robinson, Z. Chen, D. Daranciang, and H. J. Dai, Nat Nanotechnol. 4, 773 (2009).
28 S. J. Zhu, N. Zhou, Z. Y. Hao, S. Maharjan, X. H. Zhao, Y. B. Song, B. Sun, K. Zhang, H. C. Sun, L. J. Lu, and B. Yang, Rsc Adv. 5, 39399 (2015).
29 A. Ananthanarayanan, Y. Wang, P. Routh, M. A. Sk, A. Than, M. Lin, J. Zhang, J. Chen, H. D. Sun, and P. Chen, Nanoscale 7, 8159 (2015).
30 Y. He, Y. Zhong, Y. L. Su, Y. Y. Lu, Z. Y. Jiang, F. Peng, T. T. Xu, S. Su, Q. Huang, C. H. Fan, and S. T. Lee, Angew. Chem., Int. Ed. 50, 5695 (2011).
31 X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir, and S. Weiss, Science 307, 538 (2005).