A One-step Hydrothermal Method of Nitrogen-doped Graphene Quantum Dots Decorated Graphene for Fabrication of Paper-based Fluorescent Composite

Yu Bian,[a] Beihai He,[a,b] and Junrong Li [a,*]

A facile approach for producing fluorescent composite paper containing nitrogen-doped graphene quantum dots (N-GQDs) and graphene on the surface of the modified fibers was implemented from the exfoliation of graphite oxide (GO) using a one-step hydrothermal method. The properties of the composite paper were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet visible spectroscopy (UV), photoluminescence spectroscopy (PL), and confocal laser scanning microscopy (CLSM). The results indicated that the GO was reduced to graphene sheets, and the N-GQDs nanoparticles were deposited on the surface of these sheets. The composite paper remained undamaged, with a three-dimensional structure and smooth fibers during the hydrothermal process, and the average particle size of N-GQDs was less than 10 nm. Photoluminescence measurements showed that the composite paper had a strong ultraviolet absorption in the range of 200 to 340 nm, and the band edge emission occurred at 475 nm. The CLSM image of composite paper exhibited a well-defined excitonic emission feature with an excitation wavelength of 405 nm.

Keywords: Cellulose; Composite paper; Nitrogen-doped graphene quantum dots; Graphene; Fluorescence

*Contact information: a: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China; b: National Engineering Research Center of Papermaking and Pollution Control, Guangzhou, 510640, China; *Corresponding author: lljrr@scut.edu.cn*

INTRODUCTION

Cellulose is the most abundant carbohydrate polymer resource on earth, and it shows many great properties such as flexibility, mechanical strength, biocompatibility, biodegradability, and renewability. Cellulose has been widely used in papermaking, printing, packing products, food and medicine products, *etc*. Recently, cellulose has shown potential applications in the field of optoelectronic composite materials, such as new cellulosic photoluminescent nanocomposite films, flexible cellulose-based sheets of electrical transducers, and energy storage devices (Chen *et al*. 2013).

Luna-Martinez *et al*. (2011) embedded ZnS nanoparticles in carboxyl methyl cellulose to produce photoluminescent nanocomposite films. A type of flexible nanocomposite film of bacterial cellulose (BC) and graphene oxide (GO) with a layered structure prepared by a vacuum-assisted self-assembly technique displayed a notable improvement in electrical conductivity (Feng *et al*. 2012). A layer-by-layer assembled hybrid multilayer thin film using cellulose nanofibers (CNFs) as substrate was promising for flexible supercapacitors (Wang *et al*. 2014). A transparent and ultraviolet shielding composite film based on graphene oxide and cellulose acetate was fabricated *via* a solvent-casting method. This material could be potentially applied as transparent UV-protective

coatings for packing biomedical, pharmaceutical, and food products (de Moraes *et al.* 2015). Cellulose/graphene nanocomposites could be applied in multifunctional electronic and solvent sensor materials (Kafy *et al.* 2015).

Graphene quantum dots (GQDs) are a type of zero-dimensional graphene sheets with lateral sizes less than 100 nm, and they are superior to traditional semiconductor quantum dots (QDs) because of their outstanding photoluminescence (PL) properties, excellent stability, high resistance to photobleaching, low toxicity, and good biocompatibility. These outstanding properties make GQDs potentially applicable in fluorescent anti-counterfeiting materials, optoelectronic functional composites, bioanalysis, drug and gene delivery, chemosensors, and biosensors (Yuan *et al.* 2012; Liu *et al*. 2013; Tang *et al.* 2015).

Chemical heteroatom-doped GQDs, especially nitrogen-doped GQDs (N-GQDs), have a large surface area and more active sites to tune their intrinsic, carbon-based properties such as electronic characteristics, surface activity, and local chemical features (Xu *et al.* 2015; Zhao *et al.* 2015). For example, nitrogen-doped graphene quantum dots (N-GQDs) have an intrinsic peroxidase-like catalytic activity, which can be used to detect H_2O_2 and glucose over a wide range of pH and temperature (Lin *et al.* 2015). N-GQDs/BiOBr nanohybrids show optimal photoactivity and excellent performance in the photoelectrochemical detection of glutathione as well as the photocatalytic degradation of rhodamine B (Yin *et al.* 2016).

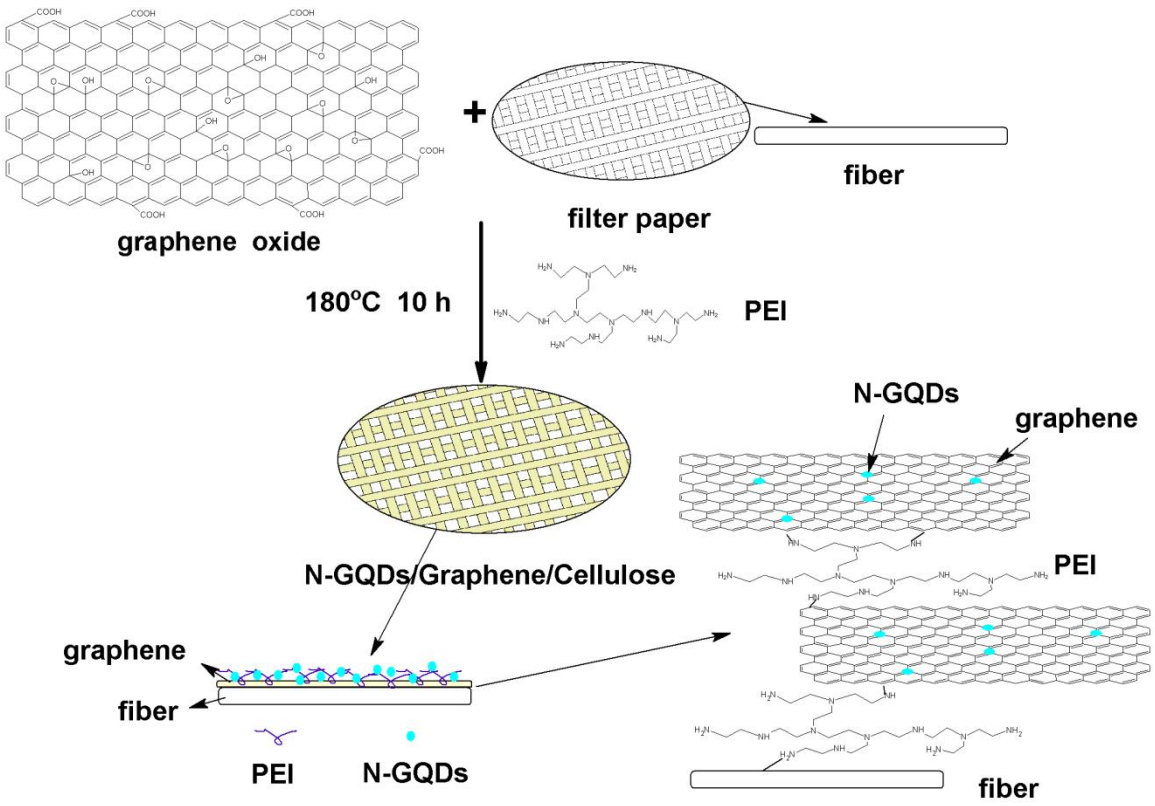

Fig. 1. Fabrication procedure of paper-based composite N-GQDs/graphene/cellulose

In this work, a one-step and facile method for preparing paper-based fluorescent materials on a large scale is presented. This method includes the assembly of zero-

dimensional N-GQDs and two-dimensional graphene sheets on the surface of three-dimensional paper fibers (Fig. 1). The resulting composite paper has potential applications in optoelectronic functional composites for bioanalysis, drug and gene delivery, chemosensors, and biosensors. Filter papers were selected as the template for the composites. Polyethyleneimine (PEI) played several important roles in the preparation of composite paper: a) forming of amine groups with the positive ionic charge to disperse the graphene sheets in the water suspension, b) modifying the charge of the fibers in filter paper to hold the graphene sheets onto the negatively charged fiber surfaces, and (c) maintaining a strong adhesion of graphene to the filter paper fibers even in the dry state (Guan *et al*. 2015). GO was exfoliated to fluorescent N-GQDs and large pieces of graphene sheets in the hydrothermal process. Meanwhile, N-GQDs were distributed on these graphene sheets to form N-GQDs/graphene (N-GQDs/G) composites. The N-GQDs/G coating on the surface of paper fibers created fluorescent properties in the paper-based composite.

EXPERIMENTAL

Materials

Sulfuric acid (99%) was purchased from Yongda Chemical Reagents Co., Ltd. (Foshan, China). Potassium permanganate ($KMnO_4$) was supplied by Tianjin Fengchuan Chemicals Reagents Co., Ltd. (Tianjin, China). Peroxide (H_2O_2) was provided from Tianjin Damao Chemical Reagents factory (Tianjin, China). Polyethyleneimine (PEI) was provided by Aladdin (Shanghai, China).

Methods

Synthesis of graphene oxide (GO)

GO was obtained from graphite powder by the modified Hummers method (William *et al.* 1958).

Preparation of N-GQDs/G/C composite paper

Approximately 10 mg of GO was exfoliated in 30 mL of ultrapure water by sonication for 30 min. Next, 10 mL of PEI aqueous solution was added to the GO solution drop-wise under ultrasonication for 15 min and 50 mL of ultrapure water was also added for diluting to form a 90 mL stable GO-PEI suspension. The GO-PEI suspension and a filter paper were placed in a Teflon-lined stainless steel autoclave (100 mL) and heated to 180 °C. After 10 h, the prepared N-GQDs/G/C composite paper was washed several times with water and absolute ethanol and dried in a vacuum oven at 60 °C for 24 h.

Analytical methods

The crystallinities of the samples were examined by X-ray diffraction (D8 Advance, Bruker, Karlsruhe, Germany) with Cu-Kα radiation from 5° to 60°. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ulra DLD X-ray photoelectron spectrometer (Manchester, United Kingdom).

Scanning electron microscopy (SEM) images were recorded with Shimadzu SS-550 instrument (Shimadzu Corp., Kyoto, Japan). Transmission electron microscopy (TEM) images were obtained from a JEM-2100 electron microscope (Kyoto, Japan).

The UV-Vis absorbance spectra were collected on a Jasco V-570 spectrometer (Kyoto, Japan).

The photoluminescence (PL) spectra were acquired with a PerkinElmer L55 fluorescence spectrometer (Fremont, USA) under excitations from 300 nm to 375 nm with a 7.3 W Xe lamp.

Confocal laser scanning microscopy (CLSM) was obtained with Leica TCS-SP5 (Solms, Germany) to observe the photoluminescence phenomenon of paper-based composites.

RESULTS AND DISCUSSION

In the XRD pattern of graphite powder (Fig. 2a), a strong diffraction peak at 26.2° represented the hexagonal structure lattices of the (002) plane. The peak shifted to 10.2° in Fig. 2b as a result of the presence of carbonyl and oxygen functional groups in the graphitic structure of GO (Rajendran Ramachandran *et al.* 2015). The sharp peak at approximately 10.2° disappeared in the crystalline patterns of N-GQDs/G and N-GQDs/G/C, which was attributed to the exfoliation of graphene oxide to reduce to N-GQDs and graphene sheets during the hydrothermal process because of the removal of oxygen-containing functional groups.

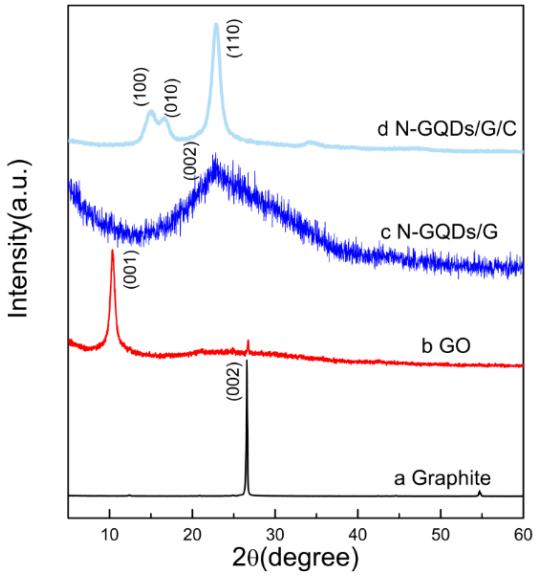

Fig. 2. XRD patterns of (a) graphite, (b) GO, (c) N-GQDs/graphene, and (d) N-GQDs/G/C composite paper

And a new broad diffraction peak (2θ) centered at approximately 22.5° in the N-GQDs/G spectrum (Fig. 2c) was the characteristic diffraction peak of N-GQDs and graphene, which corresponded with the XRD patterns of nitrogen-doped carbon quantum dots (N-CQDs) and graphene reported in the literature (Xue *et al.* 2011; Han *et al.* 2015; Hu *et al.* 2015). The XRD peak corresponded to the (002) crystal plane of N-GQDs and graphene with turbostratic disorder.

Interestingly, there were no diffraction peaks originating from N-GQDs or graphene in the paper-based N-GQDs/G/C composite. The XRD pattern of N-GQDs/G/C (Fig. 2d) presented peaks around 2θ values of 14.93°, 16.60°, and 22.83°, which were attributed to the 100, 010, and 110 planes, respectively, of the cellulose *Iβ* crystalline structure (French 2014). The typical cellulose crystalline structure of N-GQDs/G/C indicated that the structure of cellulose in the filter paper was not destroyed under the high temperature and high pressure of the hydrothermal reaction system. The disappearance of the peak at 22.5° in Fig. 2c might be due to the uniform dispersion of N-GQDs and graphene on the surface of filter paper fibers, which matched with the XRD results reported previously (Feng *et al.* 2012; Kafy *et al.* 2015; Ramachandran *et al.* 2015).

The XPS spectrum of N-GQDs/graphene/cellulose showed its surface functional groups and elemental states, including C, O, and N peaks (Fig. 3). The N 1s peak indicated the presence of PEI in the reaction system. The peak at 284.6 eV (C-C) in the C1s region suggested the graphitic sp^2 carbon atoms in the graphene sheets. The cellulose and oxygen functional groups in N-GQDs and graphene sheets gave rise to the O 1s peak.

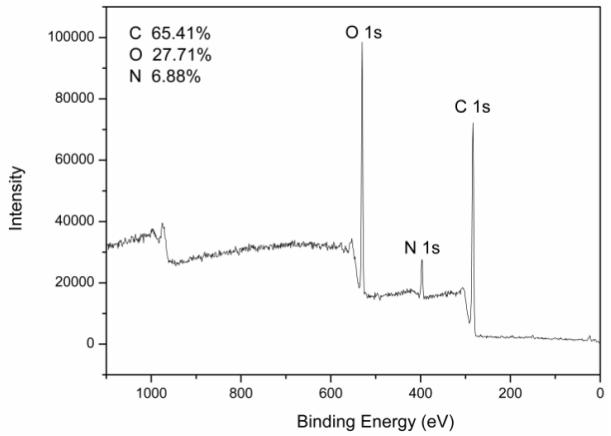

Fig. 3. XPS spectrum of N-GQDs/graphene/cellulose

The morphology of the N-GQDs/G/C composite paper was characterized by SEM (Fig. 4a, b, and c) and TEM (Fig. 4d through h). In the SEM images of N-GQDs/G composites, graphene sheets appeared as thin layers that covered the paper fibers, and the N-GQDs nanoparticles were deposited on the graphene sheets.

TEM images of graphene sheets demonstrated an amorphous lamellar structure (Fig. 4d). N-GQDs nanoparticles were dispersed well on the surface of graphene sheets, and they were quasi-spheres with an average size of less than 10 nm (Fig. 4f and 4g). The N-GQDs loaded on the graphene sheets might reduce the formation of a multilayer structure of the majority of graphene sheets like undoped graphene (Fig. 4e). The typical HRTEM image of N-GQDs indicated clearly that the lattice spacing of crystallinity was about 0.2 nm (Fig. 4h). This result agreed with previous reports (Dey *et al*. 2014; Yin *et al.* 2016).

To explore the optical properties of N-GQDs/G/C composite paper, the ultraviolet absorption spectrum was obtained with a UV spectrophotometry. As shown in Fig. 5a, there were two absorption regions in the ranges of 200 nm to 300 nm and 350 nm to 400 nm. Absorption bands from 200 nm to 300 nm were due to the n-π* and π-π* transitions of C¼C and C¼O bonds. The absorption band at approximately 360 nm indicated the formation of excited defect surface states, which was induced by the N heteroatoms from composite paper. These results were consistent with the literature (Gong *et al.* 2015; Han

et al. 2015). Moreover, the absorption bond of composite paper at 360 nm had a red shifter from that of 340 nm in N-GQDs solution reported by other researchers (Lin *et al.* 2015; Yin *et al.* 2016).

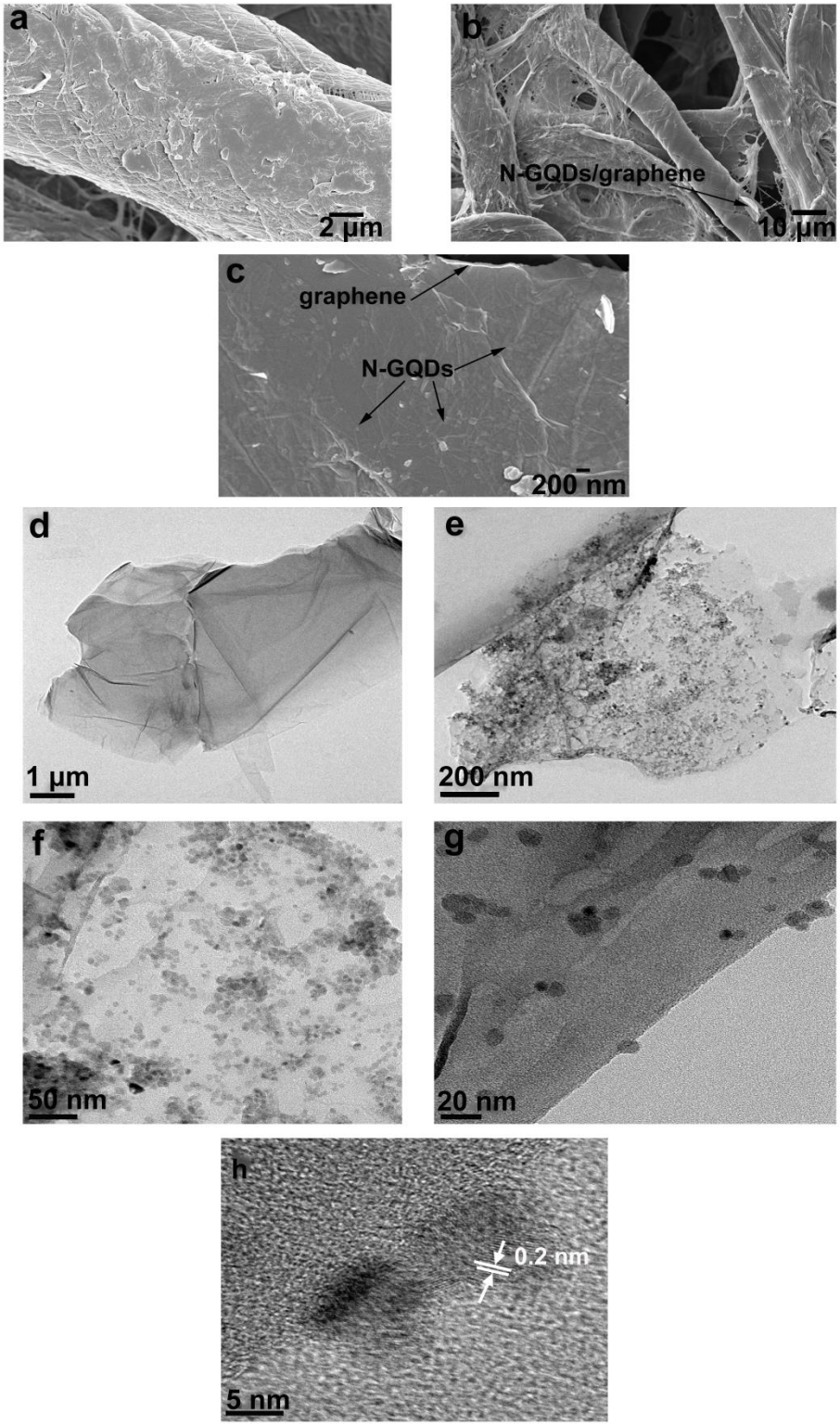

Fig. 4. (a through c) SEM images of N-GQDs/graphene/cellulose; (d through h) TEM images of N-GQDs/graphene

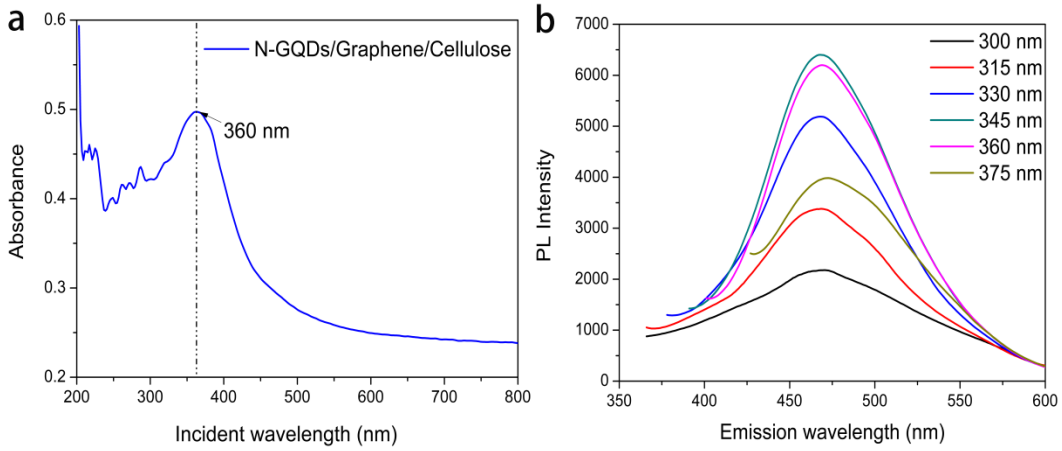

Fig. 5. (a) DRS UV-visible spectrum and (b) PL spectra of N-GQDs/graphene/cellulose

The photoluminescence (PL) properties of the N-GQDs/G/C composite paper were investigated with excitation in the range of 300 nm to 375 nm. As shown in Fig. 5b, there was a strong fluorescence emission peak at approximately 475 nm. This PL behavior might represent the distribution of fluorescent N-GQDs/G on the surface of paper fibers. The fluorescence emission band had a barely noticeable shift when the excitation wavelength changed from 300 nm to 375 nm. The emission spectra of fluorescent carbon quantum dots is usually affected by the CQDs size and surface states (Han *et al.* 2015; Hu *et al.* 2015), which demonstrated that N-GQDs in the composite paper had both uniform size and surface activity.

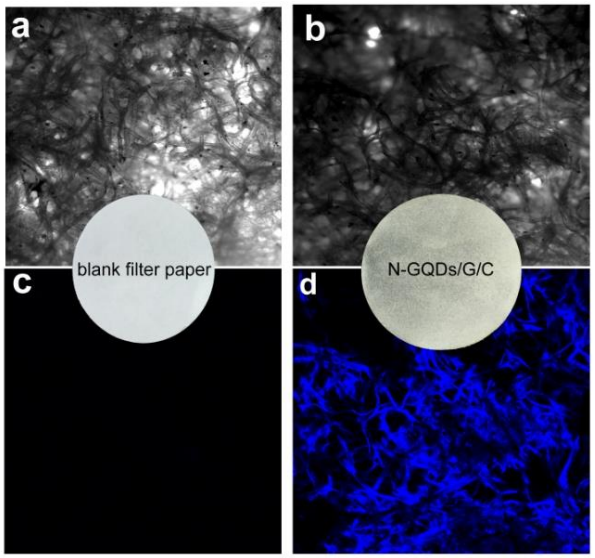

Fig. 6. CLSM images of blank filter paper in (a) bright field and(c) dark field; composite N-GQDs/graphene/cellulose in (b) bright field and(d) dark field

Moreover, the PL intensity of N-GQDs/G/C at 345 nm was much higher than that of the N-GQDs solution in previous reports (Dey *et al.* 2014; Shi *et al.* 2015). There are several possible reasons for this result. First, the N-GQDs have a high crystallinity, which reduces the non-radiative electron-hole recombination centers to give rise to the strongly

fluorescent C-dots. Secondly, energy transduction from graphene sheet to N-GQDs significantly enhances the PL intensity. Finally, the three-dimensional structure of filter paper fibers is an excellent substrate for the assembly N-GQDs and graphene, which creates the N-GQDs/G/C composite with a higher PL intensity.

The CLSM images of blank filter paper and composite paper N-GQDs/G/C from the bright filed are shown in Fig. 6a and b. Three-dimensional net structure of the filter papers fibers was observed evidently. The N-GQDs/G/C composite paper exhibited intense blue fluorescence under dark field with an excitation wavelength of 405 nm (Fig. 6b), but the blank filter paper did not produce any fluorescence (Fig. 6d). This result indicated that the composite paper has potential applications in optoelectronic materials, fluorescent materials, *etc*.

CONCLUSIONS

1. An effective method was adopted for the preparation of N-GQDs/graphene/cellulose composite paper. Its structure and fluorescence properties were analyzed by XRD, XPS, SEM, TEM, UV, PL, and CLSM.
2. The XRD and XPS results indicated the GO was reduced to N-GQDs and graphene sheets, and N-GQDs were deposited on these sheets.
3. SEM and TEM revealed that N-GQDs were distributed uniformly on the graphene sheets, and the average diameter of N-GQDs was 10 nm. The three-dimensional structure of the composite paper was not damaged during processing.
4. The optical properties of N-GQDs/G/C composite paper were measured by DRS UV, PL, and CLSM. The composite had strong absorption from 200 to 340 nm. Smooth PL spectra of composite paper showed fewer defects and higher fluorescence intensity. The paper-based composite exhibited intense blue fluorescence under dark field with an excitation wavelength of 405 nm.

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REFERENCES CITED

Chen, Q., Chen, F., and Yan, Y. (2013). "Fluorescent semiconductor nanocrystals, a promising fluorescent anti-counterfeiting material for specialty paper," *BioResources* 8(1), 6-7. DOI:10.15376/biores.8.1.6-7

de Moraes, A. C. M., Andrade, P. F., de Faria, A. F., Simões, M. B., Salomão, F. C. C. S., Barros, E. B., Goncalves, M. do C., and Alves, O. L. (2015). "Fabrication of transparent and ultraviolet shielding composite films based on graphene oxide and

cellulose acetate," *Carbohydrate Polymers* 123(2015), 217-227. DOI: 10.1016/j.carbpol.2015.01.034

Dey, S., Govindaraj, A., Biswas, K., and Rao, C. N. R. (2014). "Luminescence properties of boron and nitrogen doped graphene quantum dots prepared from arc-discharge-generated doped graphene samples," *Chemical Physics Letters* 595-596(2014), 203-208. DOI:10.1016/j.cplett.2014.02.012

Feng, Y., Zhang, X., Shen, Y., Yoshino, K., and Feng, W. (2012). "A mechanically strong, flexible and conductive film based on bacterial cellulose/graphene nanocomposite," *Carbohydrate Polymers* 87(2012), 644-649. DOI: 10.1016/j.carbpol.2011.08.039

French, A. D. (2014). "Idealized powder diffraction patterns for cellulose polymorphs," *Cellulose* 21(2), 885-896. DOI: 10.1007/s10570-013-0030-4

Gong, X., Lu, W., Paau, M. C., Hu, Q., Wu, X., Shuang, S., Dong, C., and Choi, M. M. F. (2015). "Facile synthesis of nitrogen-doped carbon dots for Fe^{3+} sensing and cellular imaging," *Analytica Chimica Acta* 861(2015), 74-84. DOI:10.1016/j.aca.2014.12.045

Guan, L., Tian, J., Cao, R., Li, M., Wu, Z., Nilghaz, A., and Shen, W. (2015). "Surface modification of cellulose paper for quantum dot-based sensing application," *BioResources* 10(1), 1587-1598. DOI:10.15376/biores.10.1.1587-1598

Han, T., Yan, T., Li, Y., Cao, W., Pang, X., Huang, Q., and Wei, Q. (2015). "Eco-friendly synthesis of electrochemiluminescent nitrogen-doped carbon quantum dots from diethylene triamine pentacetate and their application for protein detection," *Science Direct* 91(2015), 144-152. DOI:10.1016/j.carbon.2015.04.053

Hu, Y., Yang, J., Jia, L., and Yu, J. (2015). "Ethanol in aqueous hydrogen peroxide solution: Hydrothermal synthesis of highlyphoto luminescent carbon dots as multifunctional nanosensors," *Science Direct* 93(2015), 999-1007. DOI: 10.1016/j.carbon.2015.06.018

Kafy, A., Sadasivuni, K. K., Akther, A., Min, S.-K., and Kim, J. (2015). "Cellulose/graphene nanocomposite as multifunctional electronic and solvent sensor material," *Materials Letters* 159(2015), 20-23. DOI: 10.1016/j.matlet.2015.05.102

Lin, L., Song, X., Chen, Y., Rong, M., Zhao, T., Wang, Y., Jiang, Y., and Chen, X. (2015). "Intrinsic peroxidase-like catalytic activity of nitrogen-doped graphene quantum dots and their application in the colorimetric detection of H_2O_2 and glucose," *Analytica Chimica Acta* 869(2015), 89-95. DOI:10.1016/j.aca.2015.02.024

Liu, X., Guo, M., Huang, J., and Yin, X. (2013). "Improved fluorescence of carbon dots prepared from bagasse under alkaline hydrothermal conditions," *BioResources* 8(2), 2537-2346. DOI:10.15376/biores.8.2.2537-2546

Luna-Martínez, J.F., Hernández-Uresti, D.B., Reyes-Melo, M.E., Guerrero-Salazar, C.A., González-González, V.A., and Sepúlveda-Guzmán, S. (2011). "Synthesis and optical characterization of ZnS–sodium carboxymethyl cellulose nanocomposite films," *Carbohydrate Polymers* 84, 566-570. DOI:10.1016/j.carbpol.2010.12.021

Ramachandran, R., Saranya, M., Kollu, P., Raghupathy, B. P. C, Jeong, S. K., and Grace, A. N. (2015). "Solvothermal synthesis of zinc sulfide decorated graphene (ZnS/G) nanocomposites for novel supercapacitor electrodes," *Electrochimica Acta* 178, 647-657. DOI:10.1016/j.electacta.2015.08.010

Shi, B., Zhang, L., Lan, C., Zhao, J., Su, Y., and Zhao, S. (2015). "One-pot green synthesis of oxygen-rich nitrogen-doped graphene quantum dots and their potential

application in pH-sensitive photoluminescence and detection of mercury (II) ions," *Talanta* 142, 131-139. DOI:10.1016/j.talanta.2015.04.059

Tang, J., Lv, H., Gong, Y., and Huang, Y. (2015). "Preparation and characterization of a novel graphene/biochar composite for aqueous phenanthrene and mercury removal," *Bioresource Technology* 196(2015), 355-363. DOI:10.1016/j.biortech.2015.07.047

Xu, C., Wang, G., Xing, C., M. Matuana, L., and Zhou, H. (2015). "Effect of graphene oxide treatment on the properties of cellulose nanofibril films made of banana petiole fibers," *BioResources* 10(2), 2809-2822. DOI:10.15376/biores.10.2.2809-2822

Xue, L., Shen, C., Zheng, M., Lu, H., Li, N., Ji, G., Pan, L., and Cao, J. (2011). "Hydrothermal synthesis of graphene–ZnS quantum dot nanocomposites," *Materials Letters* 65(2011), 198-200. DOI:10.1016/j.matlet.2010.09.087

Wang, X., Gao, K., Shao, Z., Peng, X., Wu, X., and Wang, F. (2014). "Layer-by-Layer assembled hybrid multilayer thin film electrodes based on transparent cellulose nanofibers paper for flexible supercapacitors applications," *Journal of Power Sources* 245(2014), 148-155. DOI:10.1016/j.jpowsour.2013.09.130

William, S., Hummers, Jr., and Richard E. Offeman. (1958). "Preparation of graphitic oxide," *Journal of the American Chemical Society* 80(1958), 1339. DOI:10.1021/ja01539a017

Yin, Y., Liu, Q., Jiang, D., Du, X., Qian, J., Mao, H., and Wang, K. (2016). "Atmospheric pressure synthesis of nitrogen doped graphene quantum dots for fabrication of BiOBr nanohybrids with enhanced visible-light photoactivity and photostability," *Carbon* 96(2016), 1157-1165. DOI: 10.1016/j.carbon.2015.10.068

Yuan, Y., Zhou, S., Zhao, B., Zhuang, L., and Wang, Y. (2012). "Microbially-reduced graphene scaffolds to facilitate extracellular electron transfer in microbial fuel cells," *Bioresource Technology* 116(2012), 453-458. DOI: 10.1016/j.biortech.2012.03.118

Zhao, H., Wang, W., Lü, Q., Lin, T., Lin, Q., and Yang, H. (2015). "Preparation and application of porous nitrogen-doped graphene obtained by co-pyrolysis of lignosulfonate and graphene oxide," *Bioresource Technology* 176(2015), 106-111. DOI:10.1016/j.biortech.2014.11.035

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