Electronic Supplementary information

Influence of surface chemistry on optical, chemical and electronic properties of blue luminescent carbon dots

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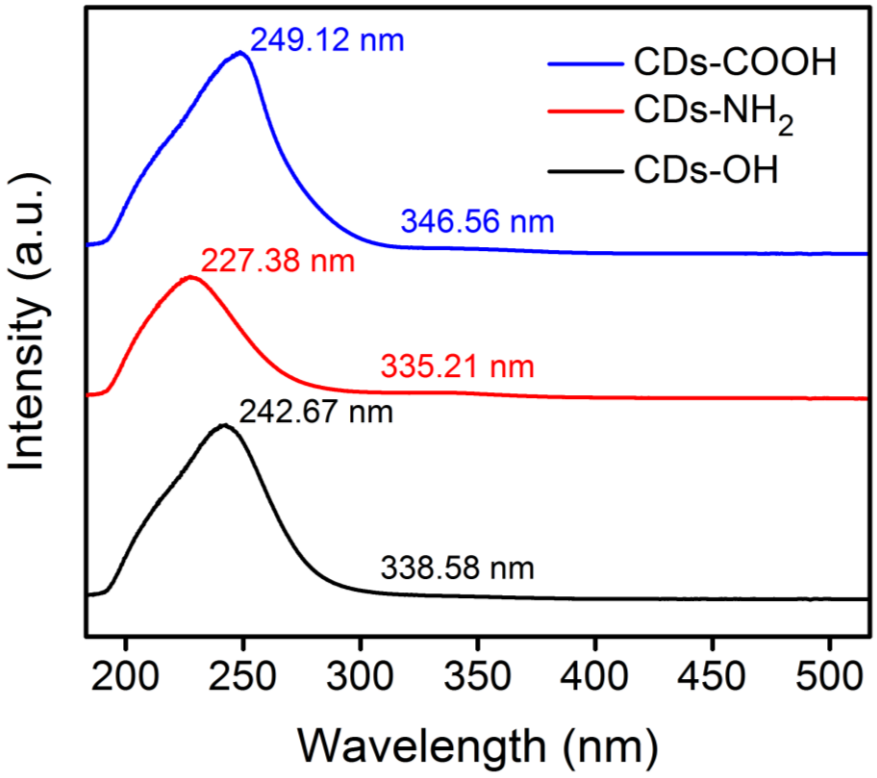

Fig. S1. UV−vis absorption spectra of the three carbon dots samples.

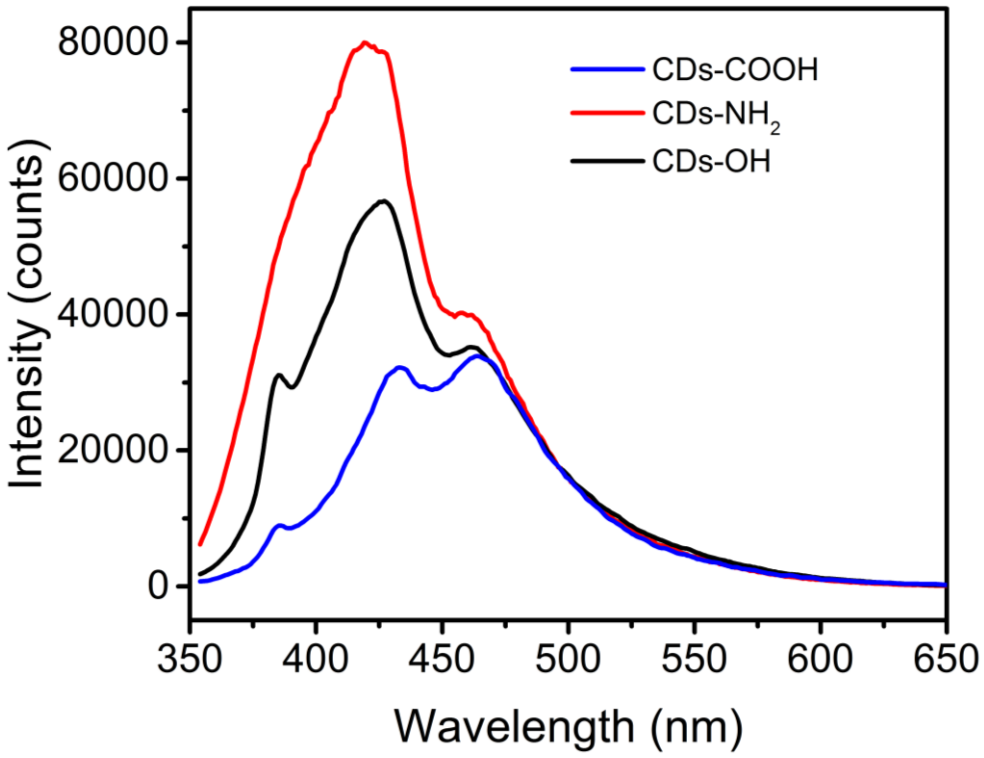

Fig. S2. Non-normalized photoluminescence spectra of the three carbon dots samples.

Table S1. Interpretation of C K edge XA spectra of carbon dots based on local time-dependent DFT calculations.

Feature	Energy (exp.) (eV)	Energy (theo.) (eV)	Group*	Assignment
A	285.2	285.5	C=C (all sp^2)	π*(C=C)
		285.3	**C**–COOH (edge)	π*(C=C)
		284.7 / 286.3	Epoxy (basal sp^2/ edge sp^2)	π*(C–C)
B	287.5	287.6 / 287.1 / 287.7	Epoxy (basal / bridge / edge)	π*(C–O–C)
		286.9 / 286.8 / 288.6	C–OH (basal / bridge / edge)	π*(C–COH)
C1	288.4	288.6	C=C (bridge), C–OH (edge)	π*(C=C)
		288.6	COOH	π*(C=O)
C	288.9	288.5	**C**–C=O (basal / edge)	π*(C=O) and π*(C–C)
		289.2 / 289.1 / 290.1	C–OH (basal / bridge / edge)	π*(C–COH) and σ*(O–H)
		289.7	**C**–COOH (edge)	π*(C=O) and π*(C=C)
		289.1 / 289.4 / 289.1	C–H (basal / edge)	σ*(C–H)
C2	290.6	290.7	COOH	σ*(O–H)
		289.7 / 291.3	**C**–COOH (edge)	π*(C=O) / σ*(C–O)
		291.2	Epoxy(edge)	σ*(C–C)
		291.5 / 291.2 / 291.1	C–OH (basal / bridge / edge)	σ*(C–O) / σ*(O–H) and σ*(C–C)
D	294-297	295.0 / 294.7	C–H (basal sp^3/ edge sp^3)	σ*(C–C)
		294.5 / 295.9	C–C (edge / bridge)	σ*(C–C)
		295.6 / 295.8 / 294.7	Epoxy (basal / bridge / edge)	σ*(C–C)
		293.0 / 294.0–296.0	C–OH (bridge / edge)	σ*(C–O) and σ*(C–C)
		292.8 / 293.5	**C**–COOH (edge)	σ*(C–C) / σ*(O–H)
		296.4	COOH	σ*(C–O)

*Group refers to the type of carbon atom that is excited in a localized, single-electron excitation calculation. When there are more than one carbon atoms in a group label, the one highlighted with bold font was excited

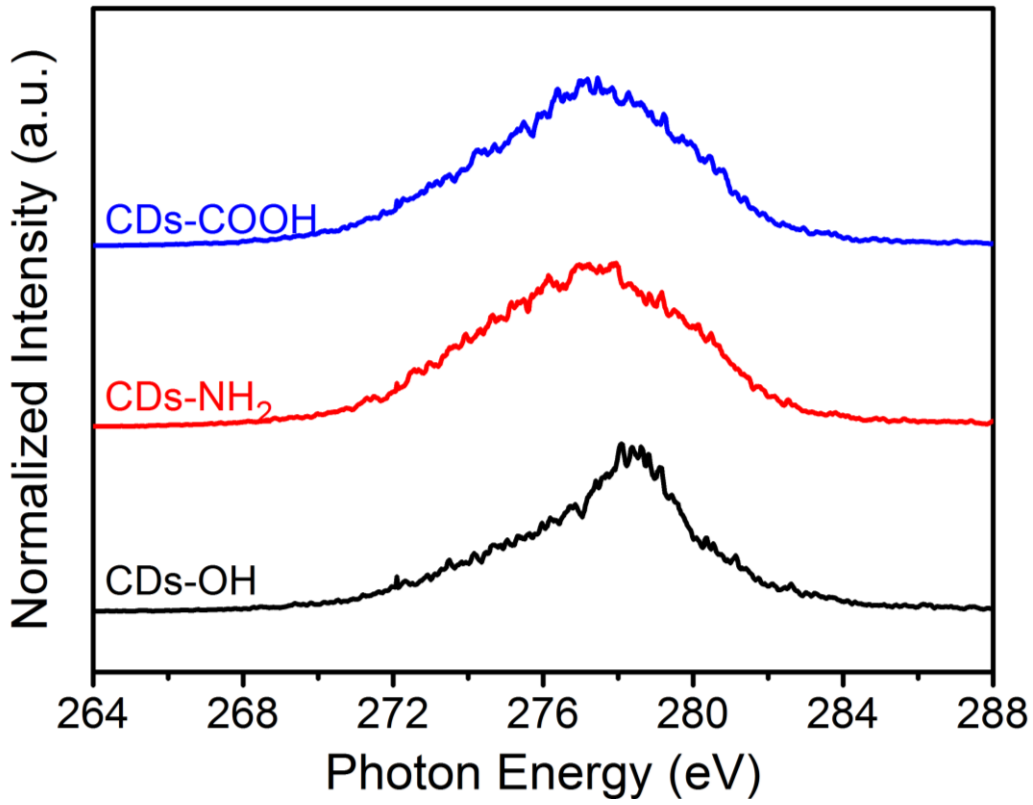

Fig. S3. C K-edge Kα XE spectra of the three carbon dots samples.

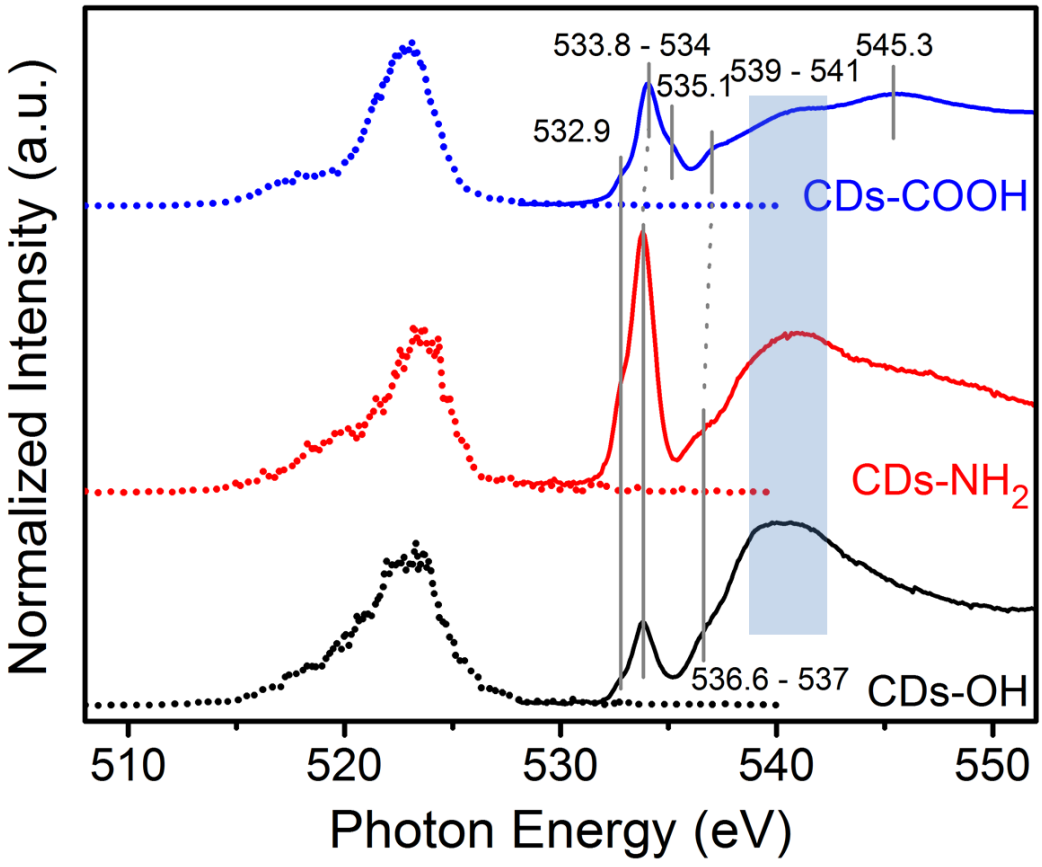

Fig. S4. O K-edge XA/XE spectra of the three carbon dots samples.

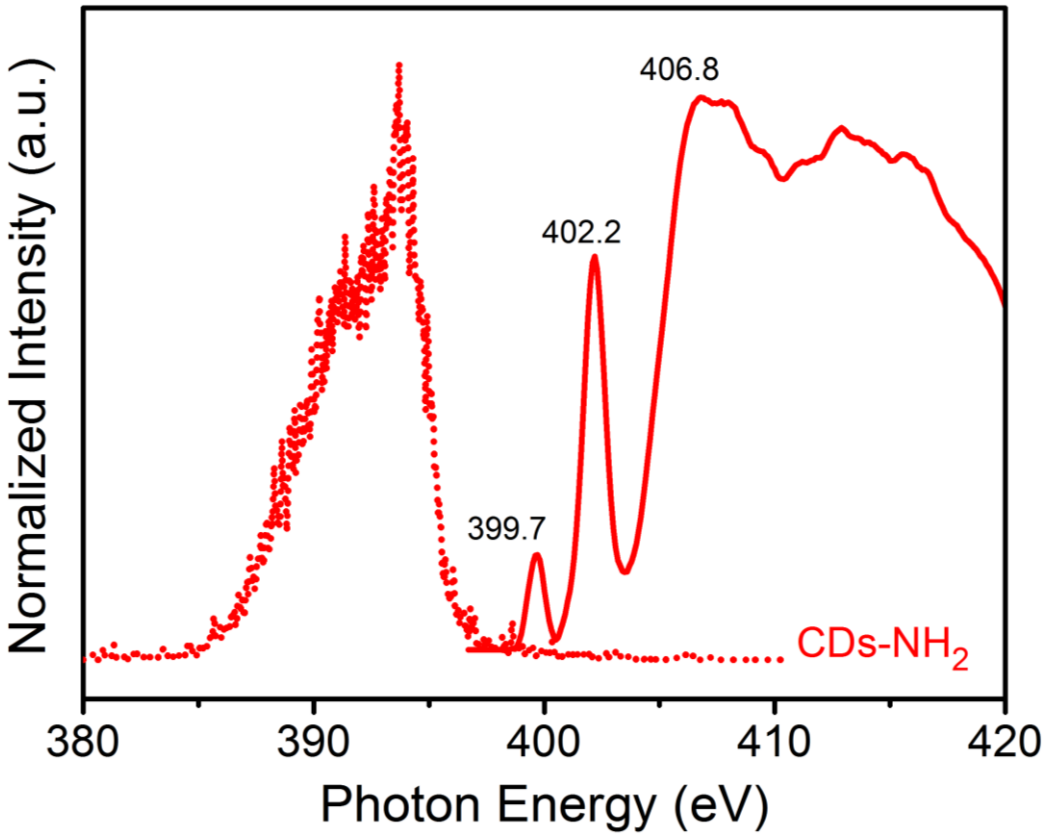

Fig. S5. N K-edge XA/XE spectra of the aminated carbon dots (CDs-NH_2).

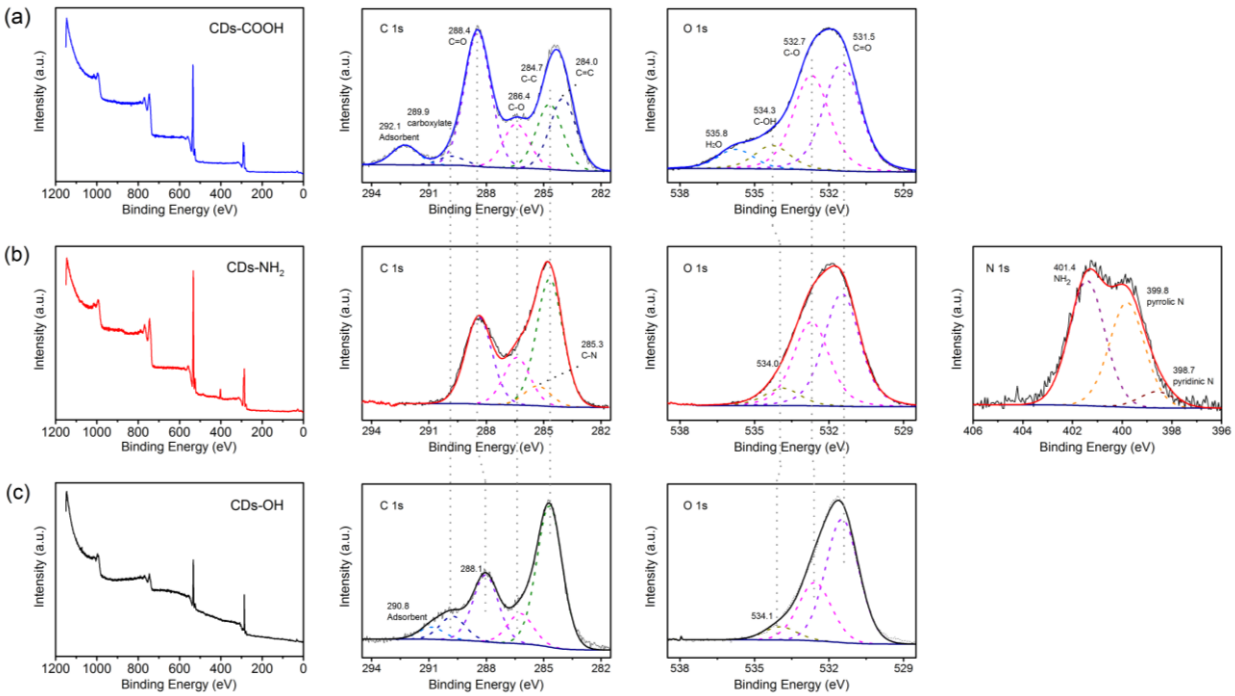

Fig. S6. XPS results of the three carbon dots samples: (a) CDs-COOH, (b) CDs-NH_2 and (c) CDs-OH.

Fig. S5 shows the XPS results measured for three CDs samples. In C 1s XPS, three peaks at 284.7, 286.4, and 288.4 eV can be assigned to C–C, C–O and C=O respectively.[1] C=C component can be remarkably distinguished at 284 eV in CDs-COOH sample, suggesting that CDs-COOH consist of large π-conjugated domains in the carbogenic cores.[2] The peak at 289.9 eV shown in CDs-OH corresponds to carboxylate-like structure[3] formed with the C=O in the core. The presence of C–N bonds was also confirmed in the C 1 s spectra of CDs-NH_2 with the peak at 285.3 eV. Another contribution is observed at 292.1 eV (290.8 eV) on CDs-COOH (CDs-OH), which could potentially be related to adsorbed CO_2 or carbonate-like species. O 1s spectra can be deconvoluted into three peaks of C–O at 531.5 eV, C=O at 532.7 eV, and C–OH around 534.2 eV.[1] There is one more constituent peak at higher binding energy (535.8 eV) in CDs-COOH sample, which can be attributed to adsorbed H_2O molecules.[4,5] The N 1s spectrum of CDs-NH_2 (Figure S5b) contains three peaks at 398.6, 399.8, and 401.4 eV, for pyridinic C–N–C, pyrrolic C2–N–H, and NH_2, respectively.[6] The atomic percentage of each element was estimated by comparing the relative area of each core levels (Table S2).

Table S2. Atomic percentage of each element in three samples, calculated from XPS.

Sample	Element	Atomic percentage (%)
CDs-COOH	carbon	49.3
	oxygen	50.7
CDs-NH_2	carbon	50.9
	oxygen	41.5
	nitrogen	7.6
CDs-OH	carbon	58.7
	oxygen	41.3

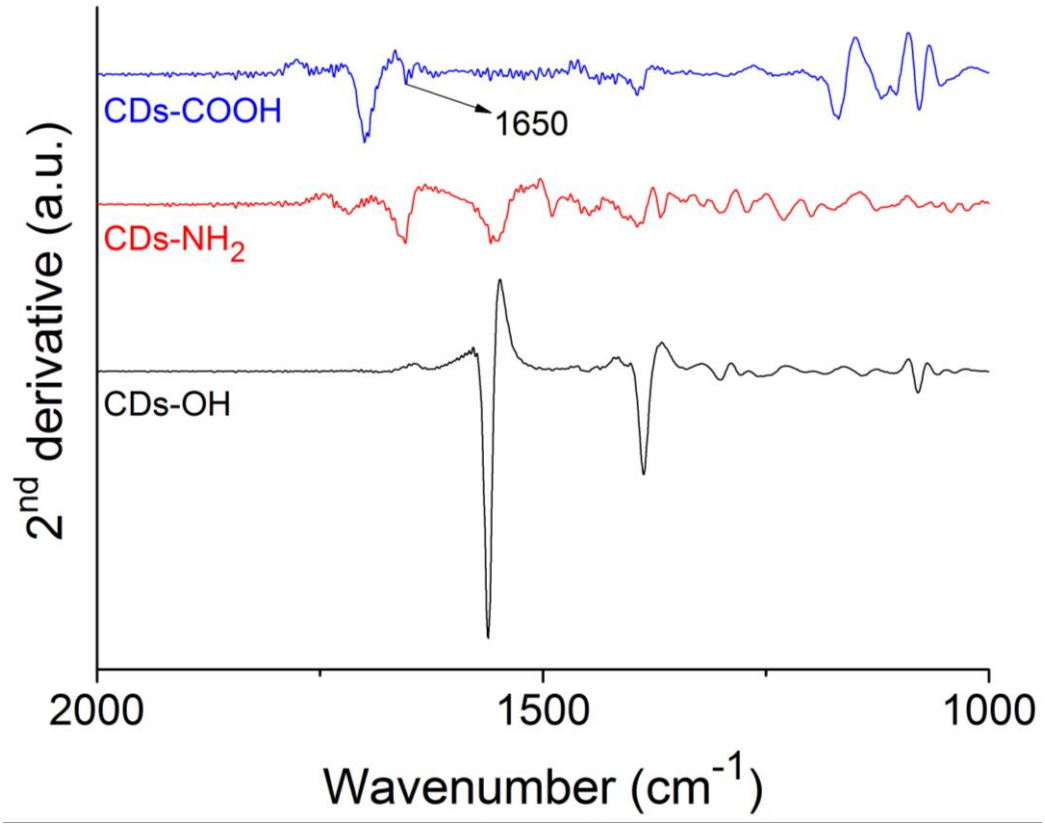

Fig. S7. Second derivative of FTIR spectra of three samples under dry air flow. Contribution from strongly adsorbed water molecules at 1650 cm^{-1} is observed on CDs-COOH.

Table S3. Technical data of three carbon dots

Sample	Product	Synthesis	Concentration	Size
CDs-COOH	GNQD0301 Carboxylated GQDs	Precursor pyrolysis[a]	5 mg/mL	＜ 10 nm[b]
CDs-NH_2	GNQD0201 Aminated GQDs	Hydrothermal method[a]	5 mg/mL	＜ 5 nm[b]
CDs-OH	GNQD0101 Blue Luminescent GQDs	polymerization of organic small molecule[a]	5 mg/mL	＜ 15 nm[b]

[a] as stated by ACS Materials.

[b] as estimated from Transmission Electron Microscopy images by ACS Materials.

Reference

(1) Ding, H.; Wei, J.-S.; Zhong, N.; Gao, Q.-Y.; Xiong, H.-M. Highly Efficient Red-Emitting Carbon Dots with Gram-Scale Yield for Bioimaging. *Langmuir* **2017**, *33*, 12635–12642.

(2) Huang, Y.-L.; Tien, H.-W.; Ma, C.-C. M.; Yang, S.-Y.; Wu, S.-Y.; Liu, H.-Y.; Mai, Y.-W. Effect of Extended Polymer Chains on Properties of Transparent Graphene Nanosheets Conductive Film. *J. Mater. Chem.* **2011**, *21*, 18236–18241.

(3) Yang, D.; Velamakanni, A.; Bozoklu, G.; Park, S.; Stoller, M.; Piner, R. D.; Stankovich, S.; Jung, I.; Field, D. A.; Ventrice, C. A.; *et al.* Chemical Analysis of Graphene Oxide Films after Heat and Chemical Treatments by X-Ray Photoelectron and Micro-Raman Spectroscopy. *Carbon N. Y.* **2009**, *47*, 145–152.

(4) Desimoni, E.; Casella, G. I.; Morone, A.; Salvi, A. M. XPS Determination of Oxygen-Containing Functional Groups on Carbon-Fibre Surfaces and the Cleaning of These Surfaces. *Surf. Interface Anal.* **1990**, *15*, 627–634.

(5) Gardner, S. D.; Singamsetty, C. S. K.; Booth, G. L.; He, G.-R.; Pittman, C. U. Surface Characterization of Carbon Fibers Using Angle-Resolved XPS and ISS. *Carbon N. Y.* **1995**, *33*, 587–595.

(6) Ding, H.; Wei, J.-S.; Xiong, H.-M. Nitrogen and Sulfur Co-Doped Carbon Dots with Strong Blue Luminescence. *Nanoscale* **2014**, *6*, 13817–13823.