

Electronic Supplementary Information (ESI) for *RSC Advances*

This journal is © The Royal Society of Chemistry 2016

Facile Synthesis of Multi-Responsive Functional Graphene Quantum Dots for Sensing Metal Cations

Yan-Fu Chen^a, Chang-Long Kao^{a*}, Ping-Chih Huang^b, and Ching-Yun Hsu^b, Chun-Hsiung Kuei^{a*}

Experiment

Reagents

All chemicals are commercial available and analysis pure grade without further purification. Citric acid monohydrate was purchased from Sigma Chemicals (USA). All Metal cation standards, ethylene diamine tetraacetic acid (EDTA), ethylene diamine (EDA) and phosphorous acid (PA) were purchased from Merck (Germany).

Instrumentations

Ultraviolet-visible (UV-Vis) absorption spectra were recorded using a Hitachi UV-2550 UV-Vis spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) spectra were measured using Perkin-Elmer 560 FT-IR (USA) spectrometer. FT-IR spectra were measured on Spectrum with the KBr pellet method to characterize with the wave numbers from 400 to 4000 cm^{-1} . The fluorescence properties of all samples were recorded by using Hitachi F-4500 spectrofluorometer. The emission spectra were recorded in the wavelength range of 400-600 nm with an excitation at 345 nm. The slit widths for excitation and emission were 5 nm. XRD diffraction data were collected on a Siemens D-5005 X-ray diffractometer using Cu $K\alpha$ radiation. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were acquired using Hitachi H7500 transmission electron microscope operated at 80 kV and JEOL JEM-2100F transmission electron microscope operated at 200 kV, respectively. Dynamic light scattering (DLS) was used to determine the size distribution profile of materials using Nano BT-90. X-Ray photoelectron spectra were measured using Physical Electronics (USA) PHI 5000 VersaProbe scanning X-Ray Photoelectron Spectrometer (XPS). Raman spectrum were recorded by Horiba Jobin Yvon (Japan) LABRAM HR 800 UV Raman spectrometer with 325 nm He-Cd laser, 30 mW power and 20 sec scanning time.

One-pot Fabrication of functional GQDs modified with EDA and PA

We synthesized the functional GQDs from citric acid with one pot procedures.¹ GQDs were first obtained from citric acid (5 g in 150 mL flask) at 160°C for three hours then cool down to room temperature to further modification. NGQDs (GQD modified with ethylene diamine) were synthesized from mixed EDA (10 g, dropwise addition) with previous GQDs and reflux overnight, then the excess EDA were removed by oven or vacuum rotary evaporator. Finally, PiNGQDs (GQD modified with ethylene diamine and phosphate) were obtained from mixed NGQDs with PA (20 g, dropwise addition) and reflux for overnight. After simple purification by filtration and vacuum rotary evaporator, the obtained PiNGQDs were prepared as aqueous solutions (DI water), which further filtered twice (0.2 μm porous size filter paper) and diluted to 100 ppb before further analysis and characterized. PiNGQDs were identified by FTIR, UV-VIS and photoluminescence spectroscopy, X-ray diffraction, TEM and DLS. Ionic strength effect of PiNGQDs (10 ppm) was also investigated by different ionic strength of NaCl aqueous solutions (as shown in Fig. S4). The fluorescence quantum yield of the PiNGQDs was determined by comparing the integrated fluorescence intensities as shown in publications.²

Characterization of PiNGQDs

DLS (Fig. S1) showed that the average size of the as-prepared PiNGQDs are ~ 2.7 nm and ~ 2.85 nm. The lifetimes of GQDs samples could last at least 6 months (Fig. S2). Selective metal recognitions of PiNGQDs at different pH (5, 6, 8, and 9) were shown in Fig. S3-6. Ionic strength effect of PiNGQDs was shown in Fig. S7. LOD was calculated with Stern-Volmer equation and shown in Fig. S8. Fig. S9 and S10 showed the overlay PL spectra of PiNGQDs with different metal cations with or without adding EDTA (pH=7).

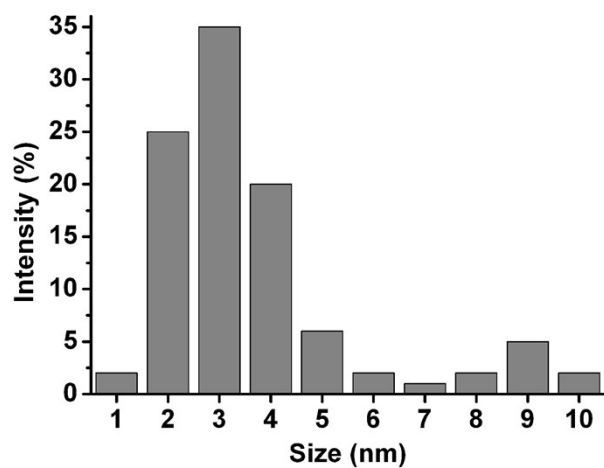


Fig. S1 DLS of PiNGQDs.

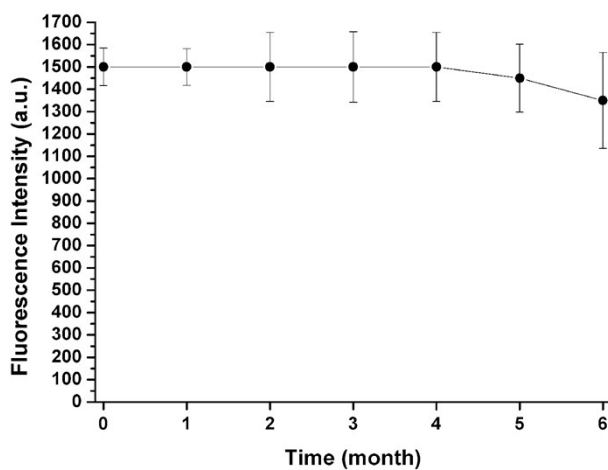


Fig. S2 Life time of PiNGQDs.

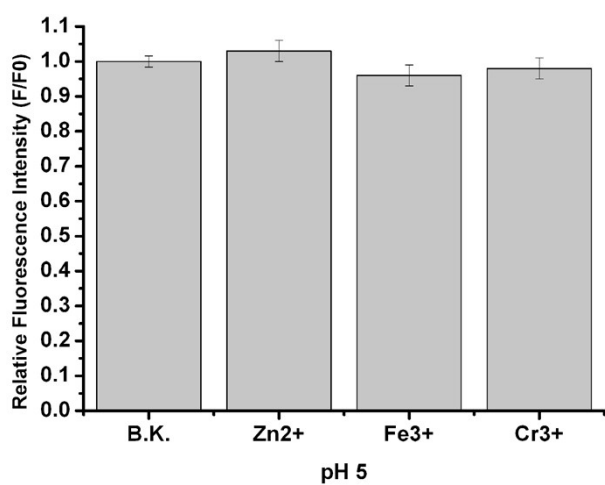


Fig. S3 Selective metal recognition of PiNGQDs at pH =5

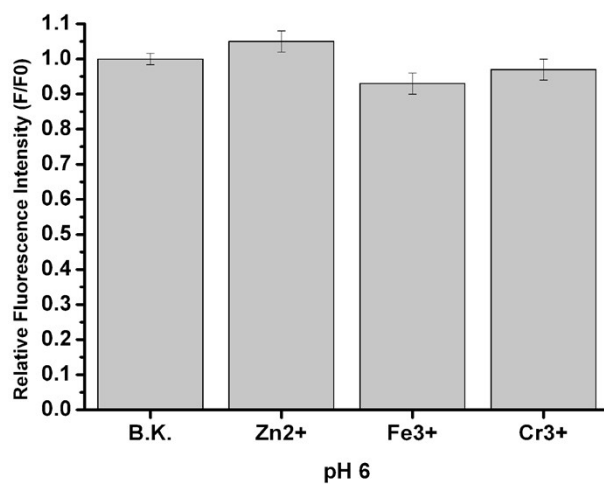


Fig. S4 Selective metal recognition of PiNGQDs at pH=6

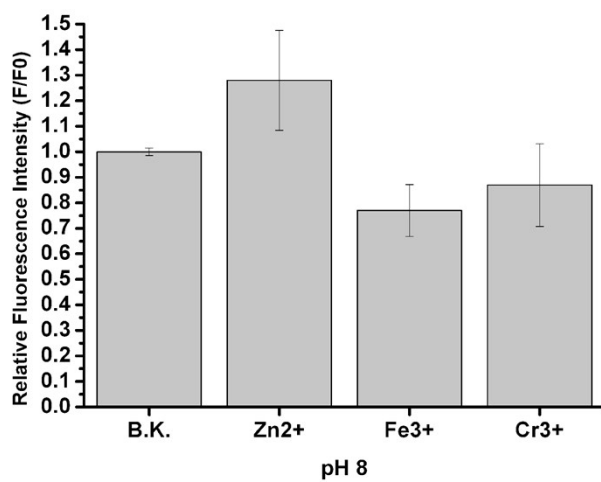


Fig. S5 Selective metal recognition of PiNGQDs at pH=8

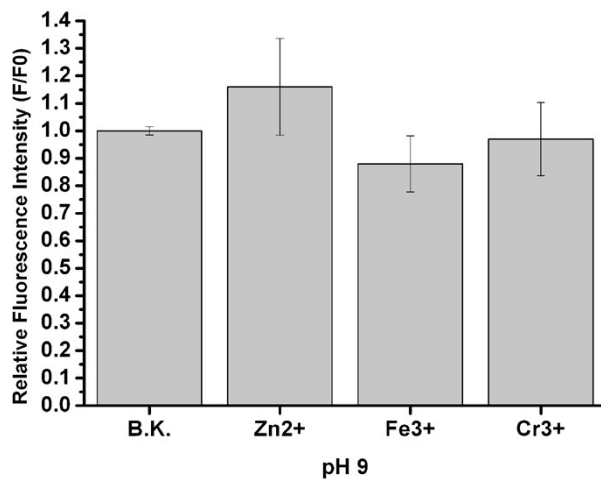


Fig. S6 Selective metal recognition of PiNGQDs at pH=9

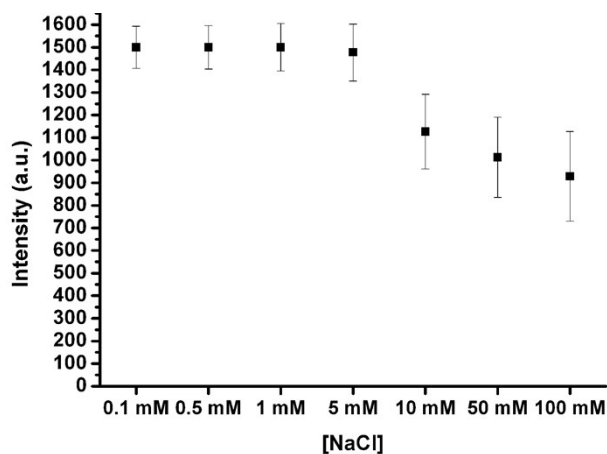


Fig. S7 Ionic strength effect of PiNGQDs

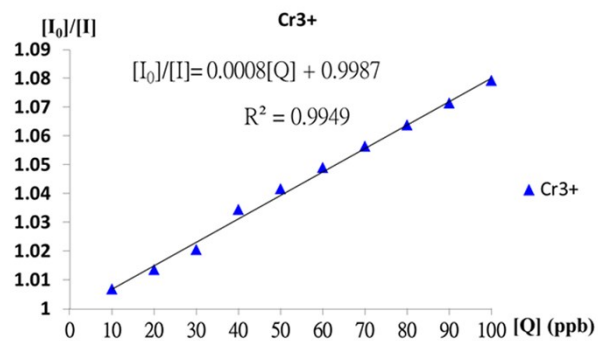
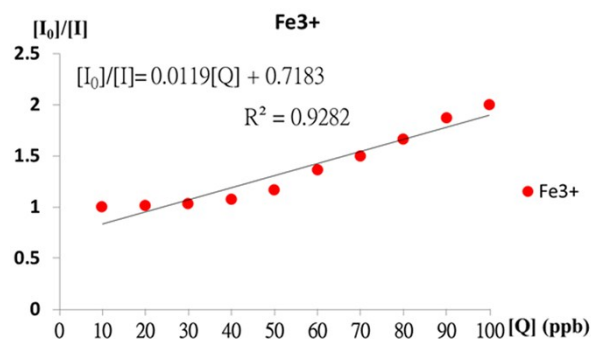
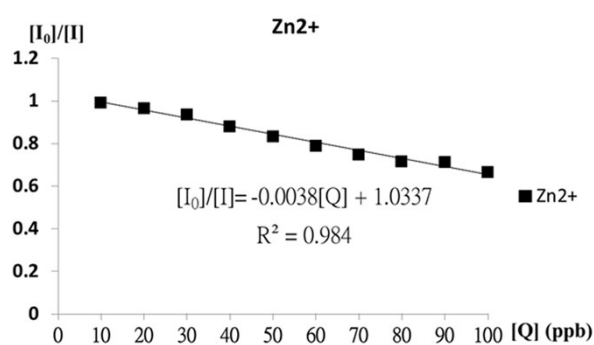


Fig. S8 LOD was calculated with Stern-Volmer equation.

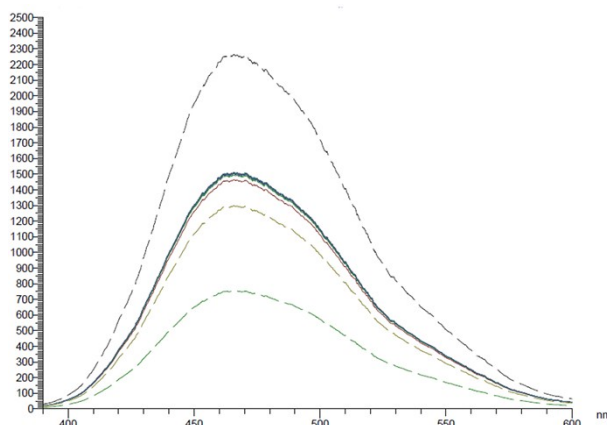


Fig. S9 Overlay PL spectra of PiNGQDs with different metal cations before adding EDTA. Dash line represented Zn^{2+} , Cr^{3+} , and Fe^{3+} from top towards bottom.

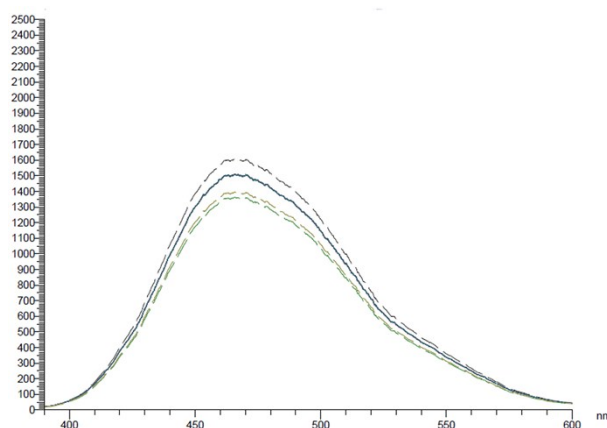


Fig. S10 Overlay PL spectra of PiNGQDs with obvious response metal cations after adding EDTA. Dash line represented Zn^{2+} , Cr^{3+} , and Fe^{3+} from top towards bottom.

References

1. (a) Yongqiang Dong, Jingwei Shao, Congqiang Chen, Hao Li, Ruixue Wang, Yuwu Chi, , Xiaomei Lin, and Guonan Chen, *Carbon*, 2012, **50**, 4738-4743. (b) Dan Qu, Min Zheng, Ligong Zhang, Haifeng Zhao, Zhigang Xie, Xiabin Jing, Raid E. Haddad, Hongyou Fan and Zaicheng Sun, *Scientific Reports*, 2014, **4**, 5249, 1-9.
2. Shuhua Li, Yunchao Li, Jun Cao, Jia Zhu, Louzhen Fan, and Xiaohong Li, *Anal. Chem.*, 2014, **86**, 10201-10207.