**Supporting Information**

Mn, B, N co-doped graphene quantum dots for fluorescence sensing and biological imaging

*Bingyang Li,1,§ Xiao Xiao2,§ Menglei Hu,3§ Yanxin Wang,1\* Yiheng Wang, 1 Xianhang Yan,1 Zhenzhen Huang,1Peyman Servati, 3\* Linjun Huang, 1\*Jianguo Tang 1\**

1Institute of Hybrid Materials, National Center of International Research for Hybrid Materials Technology, National Base of International Science & Technology Cooperation, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, P. R. China.

2Shenzhen Geim Graphene Center, Tsinghua-Berkeley Shenzhen Institute & Tsinghua Shenzhen International Graduate School, Shenzhen, 518055 P. R. China.

3Department of Electrical and Computer Engineering University of British Columbia, Vancouver British Columbia, V6T 1Z4, Canada.

§These authors contributed equally to this work.

\*E-mail: wangyanxin@qdu.edu.cn (Y.W.), peymans@ece.ubc.ca(P.S.), huanglinjun@qdu.edu.cn (L.H.), tang@qdu.edu.cn (J.T.),

**Table of Contents**

**Supporting Figures………………...……………………………………3**

**Figure S1:** Fluorescence intensity of manganese chloride tetrahydrate doped with different concentrations.

**Figure S2:** Molecular formulas for a. citric acid, b. urea, c. borax, d. BN-GQDs and e. Mn-BN-GQDs.

**Figure S3:** The size distribution of Mn-BN-GQDs.

**Figure S4:** The XRD of citric acid, urea and borax.

**Figure S5:** Comparison of N 1s spectra of Mn-BN-GQDs and BN-GQDs.

**Figure S6:** Luminance spectrum of the Mn-BN-GQDs.

**Figure S7:** Fitting curves of time-resolved fluorescence decay curve of BN-GQDs.

**Figure S8:** Fitting curves oftime-resolved fluorescence decay curve of the Mn-BN-GQDs for the 100 μM Fe3+ analysis.

**Figure S9:** The Electron Transfer Process from Mn-BN-GQDs to Fe3+.

**Figure S10:** The FTIR of Mn-BN-GQDs in the presence and absence of Fe3+.

**Figure S11:** The fluorescence intensity of 1 mM-1 M EDTA was added into the Mn-BN-GQDs solution of Fe3+.

**Figure S12:** CIE chromaticity coordinates corresponding to color-filtered PL spectra.

**Supporting Tables………………...………………………………………15**

Table S1: The peaks table of Mn-BN-GQDs and BN-GQDs.

Table S2: Comparison of Different Fluorescent Probes for Fe3+ Detection.

Table S3: Fluorescence decay time (τave) and pre-exponential factor (B) of Mn-BN-GQDs and BN-GQDs.

**Supporting References………………...…………………………………18**

****

**Figure S1** Fluorescence intensity of manganese chloride tetrahydrate doped with different concentrations.



**Figure S2** Molecular formulas for a. citric acid, b. urea, c. borax, d. BN-GQDs and e. Mn-BN-GQDs.



**Figure S3** The size distribution of Mn-BN-GQDs.



**Figure S4** The XRD of citric acid, urea and borax.



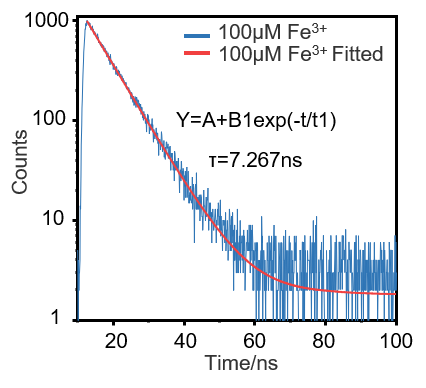
**Figure S5** Comparison of N 1s spectra of Mn-BN-GQDs and BN-GQDs.



**Figure S6** Luminance spectrum of the Mn-BN-GQDs.



**Figure S7** Fitting curves of time-resolved fluorescence decay curve of BN-GQDs.



**Figure S8** Fitting curves oftime-resolved fluorescence decay curve of the Mn-BN-GQDs for the 100 μM Fe3+ analysis.



**Figure S9** The Electron Transfer Process from Mn-BN-GQDs to Fe3+



**Figure S10** The FTIR of Mn-BN-GQDs in the presence and absence of Fe3+.



**Figure S11** The fluorescence intensity of 1 mM-1 M EDTA was added into the Mn-BN-GQDs solution of Fe3+.



**Figure S12** CIE chromaticity coordinates corresponding to color-filtered PL spectra.

Table S1 The peaks table of Mn-BN-GQDs and BN-GQDs.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Elements  Sample | C 1s  atomic% | N 1s  atomic% | O 1s  atomic% | B 1s  atomic% | Mn 2p atomic% |
| BN-GQDs | 37.73 | 9.63 | 46.62 | 6.03 | 0.00 |
| Mn-BN-GQDs | 48.75 | 7.64 | 39.28 | 3.87 | 0.47 |

Table S2 Comparison of Different Fluorescent Probes for Fe3+ Detection.

|  |  |  |  |
| --- | --- | --- | --- |
| Fluorescent probe | Detection limit (μM) | Linear range (μM) | Ref. |
| GQDs | 7.22 | 0-80 | (Ananthanarayanan et al., 2014) |
| MOF particles | 0.9 | 3-200 | (Yang et al., 2013) |
| Au nanoclusters | 3.5 | 5-1280 | (Ho et al., 2012) |
| 1,8-naphthalimide-based  fluorescence chemosensory | 2 | 5-50 | (Jia et al., 2015) |
| Pyrazoline derivative | 1.73 | 0-11 | (Ganesan et al., 2020) |
| N, S-GQDs | 0.8 | 6.0-200 | (Lu et al., 2015) |
| DPA-GQDs | 1.2 | 4-1800 | (Xuan et al., 2017) |
| Mn-BN-GQDs | 0.78 | 10-100 | This work |
| 9.08 | 100-800 |

Table S3 Fluorescence decay time (τave) and pre-exponential factor (B) of Mn-BN-GQDs and BN-GQDs.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| sample | τ1(ns) | B1 | χ2 | τave(ns) |
| BN-GQDs | 7.005 | 919.27 | 1.22 | 7.005 |
| Mn-BN-GQDs | 7.444 | 1008.52 | 1.11 | 7.444 |
| Mn-BN-GQDs+10 μM Fe3+ | 7.355 | 970.31 | 1.08 | 7.355 |
| Mn-BN-GQDs+100 μM Fe3+ | 7.267 | 991.85 | 1.09 | 7.267 |

References

Ananthanarayanan, A., X. Wang, P. Routh, et al., 2014. Facile synthesis of graphene quantum dots from 3D graphene and their application for Fe3+ sensing. Advanced Functional Materials. 24, 3021-3026.

Ganesan, J. S., M. Sepperumal, A. Balasubramaniem, et al., 2020. A novel pyrazole bearing imidazole frame as ratiometric fluorescent chemosensor for Al3+/Fe3+ ions and its application in HeLa cell imaging. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 230, 117993.

Ho, J. A., H. C. Chang and W. T. Su, 2012. DOPA-mediated reduction allows the facile synthesis of fluorescent gold nanoclusters for use as sensing probes for ferric ions. Analytical Chemistry. 84, 3246.

Jia, H., X. Gao, Y. Shi, et al., 2015. Fluorescence detection of Fe3+ ions in aqueous solution and living cells based on a high selectivity and sensitivity chemosensor. Spectrochimica Acta Part A Molecular & Biomolecular Spectroscopy. 149, 674-681.

Lu, W., X. Gong, M. Nan, et al., 2015. Comparative study for N and S doped carbon dots: synthesis, characterization and applications for Fe3+ probe and cellular imaging. Analytica chimica acta. 898, 116-127.

Xuan, W., L. Ruiyi, F. Saiying, et al., 2017. D-penicillamine-functionalized graphene quantum dots for fluorescent detection of Fe3+ in iron supplement oral liquids. Sensors and Actuators B: Chemical. 243, 211-220.

Yang, C. X., H. B. Ren and X. P. Yan, 2013. Fluorescent Metal–Organic Framework MIL-53(Al) for Highly Selective and Sensitive Detection of Fe 3+ in Aqueous Solution. Analytical Chemistry. 85, 7441-7446.