# Nitrogen-doped Carbon Nanoparticles Derived from Silkworm Excrement as On-off-on Fluorescent Sensors to Detect Fe(III) and Biothiols

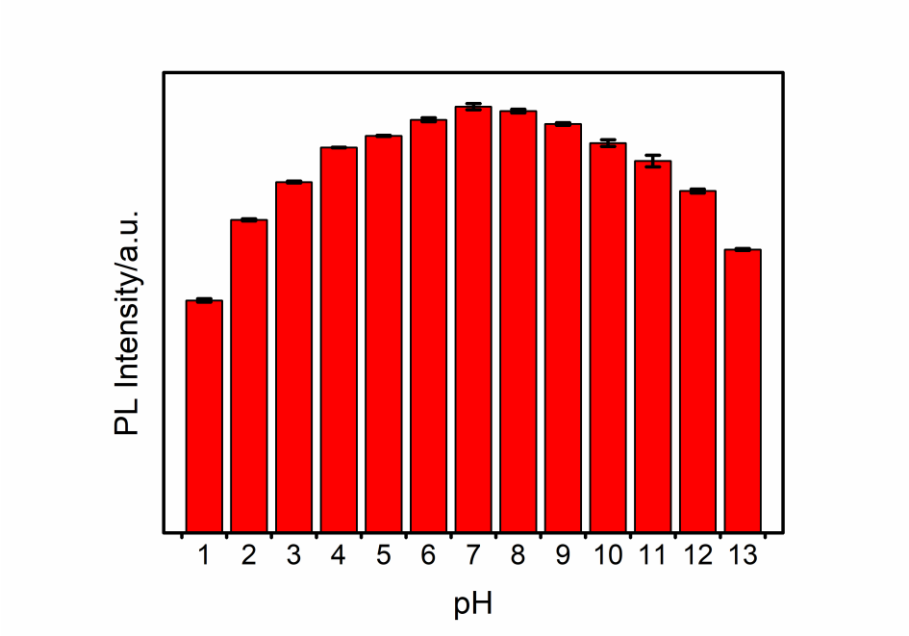


**Figure S1**. pH effect on PL intensity (424 nm) of N-CNPs under 340 nm excitation.

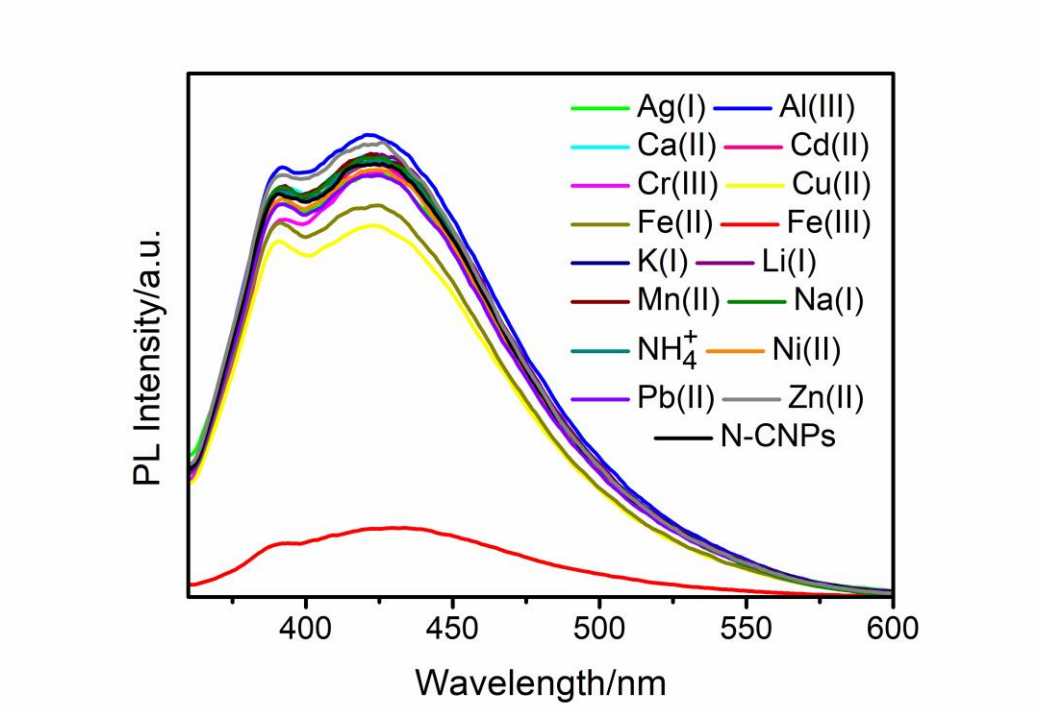


**Figure S2**. PL emission spectra of N-CNPs in absence and presence of various ions under 340 nm excitation.

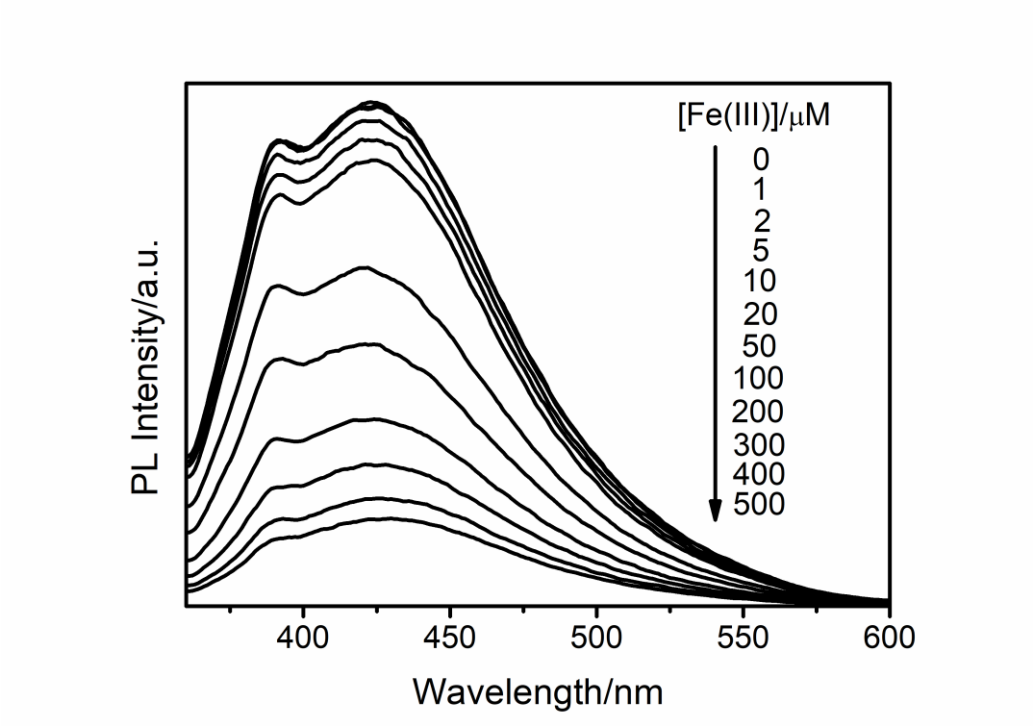


**Figure S3**. PL emission spectra of N-CNPs with different concentrations of Fe(III).

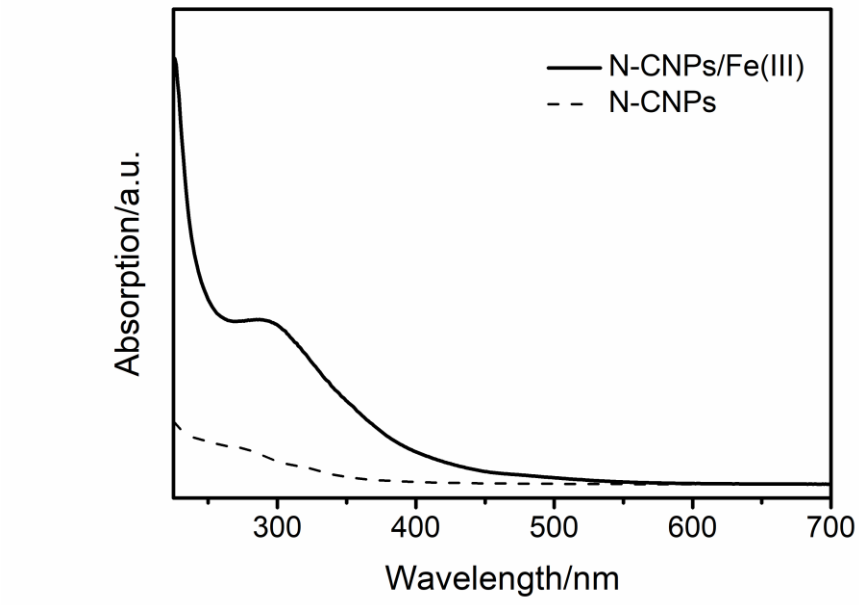


**Figure S4**. UV-vis absorption spectra of N-CNPs/Fe(III) and N-CNPs.

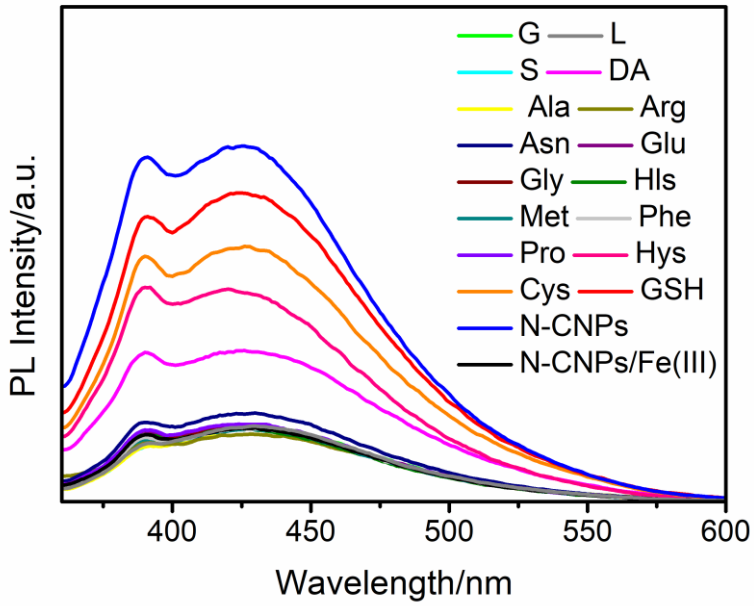


**Figure S5**. PL emission spectra of N-CNPs/Fe(III) in absence and presence of different biomolecules under 340 nm excitation.

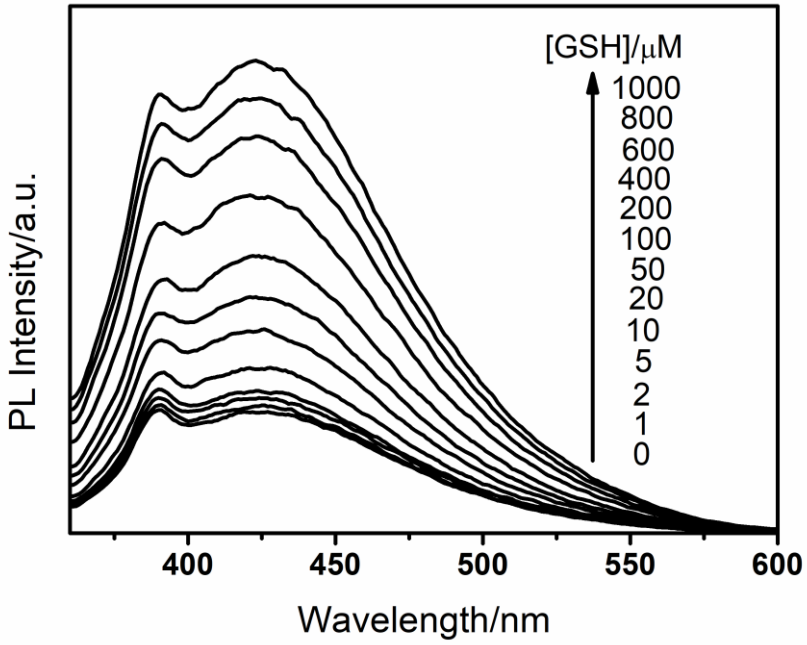


**Figure S6**. PL emission spectra of N-CNPs/Fe(III) with different concentrations of GSH.

**Table S1**. QY calculation of N-CNPs.

| Sample | I | A | η | QY |
|---|---|---|---|---|
| Quinine sulfate | 25533.83 | 0.015 | 1.333 | 0.54 |
| N-CNPs | 29656.837 | 0.072 | 1.333 | 0.131 |

**Table S2**. The comparison between various CNPs and CDs toward Fe(III).

| Material | LOD (μM) | Linear range (μM) | Response towards metal ions | Reference |
|---|---|---|---|---|
| N-CDs | 0.5 | 0–150 | Fe(III), Cr(VI) | [S1] |
| CDs | 0.239 | 0–80 | Fe(III) | [S2] |
| N-CDs | 74 | 200-5000 | Fe(III) | [S3] |
| FNCDs | 0.9 | 2–25 | Fe(III) | [S4] |
| N/P-CDs | 0.33 | 1−150 | Fe(III) | [S5] |
| B/N−CDs | 1.62 | 0-200 | Fe(III) | [S6] |
| N-CDs | 0.52 | 1-250 | Fe(III) | [S7] |
| N-CDs | 10.8 | 50-300 | Fe(III) | [S8] |
| N-CDs | 0.38 | 0.5–4 | Fe(III) | [S9] |
| N-GQDs | 0.09 | 1–1945 | Fe(III), Hg(II) | [S10] |
| N-GQD | 0.08 | 1-70 | Fe(III) | [S11] |
| S-GQDs | 0.0042 | 0-0.7 | Fe(III) | [S12] |
| N-CNPs | 0.20 | 1-500 | Fe(III) | This work |

N-CDs: nitrogen-doped carbon dots, FNCDs: fluorescent nitrogen-doped carbon dots, N/P-CDs: N, P codoped carbon dots, B/N−CDs: B,N codoped carbon dots, N-GQDs: nitrogen-doped graphene quantum dots, S-GQDs: sulfur-doped graphene quantum dots.

**Table S3**. The comparison between various fluorescent sensors based on CNPs or CDs toward GSH.

| System | LOD (μM) | Linear range (μM) | Reference |
|---|---|---|---|
| Au(III)/CDC | 2.02 | 0-150 | [S13] |
| N,S-CQDs | 6.7 | 0-50 | [S14] |
| CQDs | 0.943 | 1-50 | [S15] |
| CDs-Br | 0.14 | 0-34 | [S16] |
| CDs–MnO2 | 0.6 | 1-200 | [S17] |
| N-CNPs/Fe(III) | 0.13 | 1~1000 | This work |

Au(III)/CDC: Au(III) decorated carbon dot cluster; N, S-CQDs: N, S co-doped carbon quantum dots; CQDs: carbon quantum dots; CDs-Br: bromoacetyl bromide functionalized CDs.

**References**


S1. Wang, C.; Hu, T.; Wen, Z.; Zhou, J.; Wang, X.; Wu, Q.; Wang, C. Concentration-dependent color tunability of nitrogen-doped carbon dots and their application for iron(III) detection and multicolor bioimaging. *J. Colloid. Interf. Sci.* **2018**, *521*, 33–41.

S2. Rao, L.; Tang, Y.; Li, Z.; Ding, X.; Liang, G.; Lu, H.; Yan, C.; Tang, K.; Yu, B. Efficient synthesis of highly fluorescent carbon dots by microreactor method and their application in $Fe^{3+}$ ion detection.

*Mater. Sci. Eng. C* **2017**, *81*, 213–223.

S3. Chin, S.-F.; Tan, S.-C.; Pang, S.-C.; Ng, S.-M. Nitrogen doped carbon nanodots as fluorescent probes for selective detection and quantification of Ferric(III) ions. *Opt. Mater.* **2017**, *73*, 77-82.

S4. Atchudan, R.; Edison, T.N.J.I.; Aseer, K.R.; Perumal, S.; Karthik, N.; Lee, Y. R. Highly fluorescent nitrogen-doped carbon dots derived from *Phyllanthus acidus* utilized as a fluorescent probe for label-free selective detection of $Fe^{3+}$ ions, live cell imaging and fluorescent ink. *Biosens. Bioelectron.* **2018**, *99*, 303–311.

S5. Shangguan, J.; Huang, J.; He, D.; He, X.; Wang, K.; Ye, R.; Yang, X.; Qing, T.; Tang, J. Highly $Fe^{3+}$-Selective Fluorescent Nanoprobe Based on Ultrabright N/P Codoped Carbon Dots and Its Application in Biological Samples. *Anal. Chem.* **2017**, *89*, 7477−7484.

S6. Liu, J.; Li, J.; Xu, L.; Qiao, Y.; Chen, J. Facile Synthesis of N, B-Doped Carbon Dots and Their Application for Multisensor and Cellular Imaging. *Ind. Eng. Chem. Res.* **2017**, *56*, 3905−3912.

S7. Song, Y.; Zhu, C.; Song, J.; Li, H.; Du, D.; Lin, Y. Drug-Derived Bright and Color-Tunable N-Doped Carbon Dots for Cell Imaging and Sensitive Detection of $Fe^{3+}$ in Living Cells. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7399−7405.

S8. Li, G.; Lv, N.; Bi, W.; Zhang, J.; Ni, J. Nitrogen-doped carbon dots as a fluorescence probe suitable for sensing $Fe^{3+}$ under acidic conditions. *New J. Chem.* **2016**, *40*, 10213—10218.

S9. Liu, H.; Zhang, Y.; Liu, J.H.; Hou, P.; Zhou, J.; Huang, C.Z. Preparation of nitrogen-doped carbon dots with high quantum yield from Bombyx mori silk for Fe(III) ions detection. *RSC Adv*. **2017**, *7*, 50584–50590.

S10. Ju, J.; Chen, W. Synthesis of highly fluorescent nitrogen-doped graphene quantum dots for sensitive, label-free detection of Fe(III) in aqueous media. *Biosens. Bioelectron.* 2014, 58, 219–225.

S11. Xu, H.; Zhou, S.; Xiao, L.; Wang, H.; Lia, S.; Yuan, Q. Fabrication of a nitrogen-doped graphene quantum dot from MOF-derived porous carbon and its application for highly selective fluorescence detection of $Fe^{3+}$. *J. Mater. Chem. C* **2015**, *3*, 291–297.

S12. Li, S.; Li, Y.; Cao, J.; Zhu, J.; Fan, L.; Li, X. Sulfur-doped graphene quantum dots as a novel fluorescent probe for highly selective and sensitive detection of $Fe^{3+}$. *Anal. Chem.* **2014**, *86*, 10201−10207.

S13. Gu, J.; Hu, D.; Wang, W.; Zhang, Q.; Meng, Z.; Jia, X.; Xi, K. Carbon dot cluster as an efficient "off–on" fluorescent probe to detect Au(III) and glutathione. *Biosens. Bioelectron.* **2015**, *68*, 27–33.

S14. Song, Z.; Quan, F.; Xu, Y.; Liu, M.; Cui, L.; Liu, J. Multifunctional N,S co-doped carbon quantum dots with pH- and thermo-dependent switchable fluorescent properties and highly selective detection of glutathione. *Carbon* **2016**, 104, 169-178.

S15. Pan, J.; Zheng, Z.; Yang, J.; Wu, Y.; Lu, F.; Chen, Y.; Gao, W. A novel and sensitive fluorescence sensor for glutathione detection by controlling the surface passivation degree of carbon quantum dots. *Talanta* **2017**, *166*, 1–7.

S16. Yan, F.; Ye, Q.; Xu, J.; He, J.; Chen, L.; Zhou, X. Carbon dots-bromoacetyl bromide conjugates as fluorescence probe for the detection of glutathione over cysteine and homocysteine. *Sens. Actuators B Chem.* **2017**, *251*, 753–762.

S17. Xu, Y.; Chen, X.; Chai, R.; Xing, C.; Li, H.; Yin, X.-B. *Nanoscale* **2016**, *8*, 13414–13421.