

## Supporting Information

### **Ion imprinted dual reference ratiometric fluorescence probe for respective and simultaneous detection of Fe<sup>3+</sup> and Cu<sup>2+</sup>**

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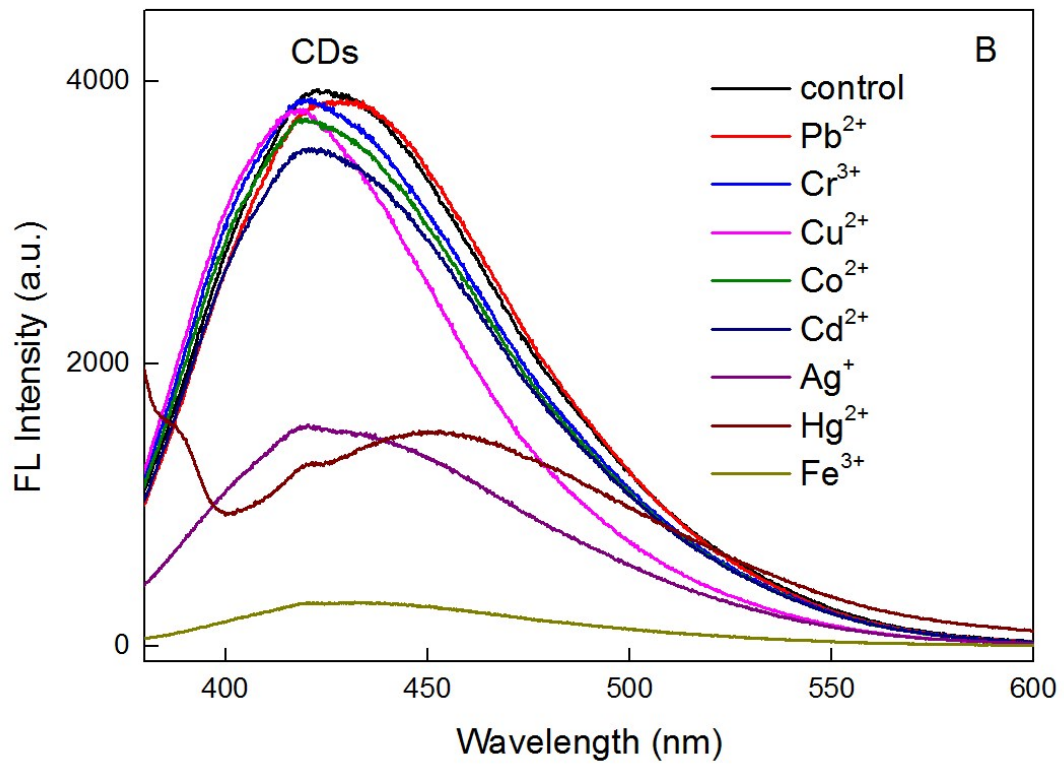
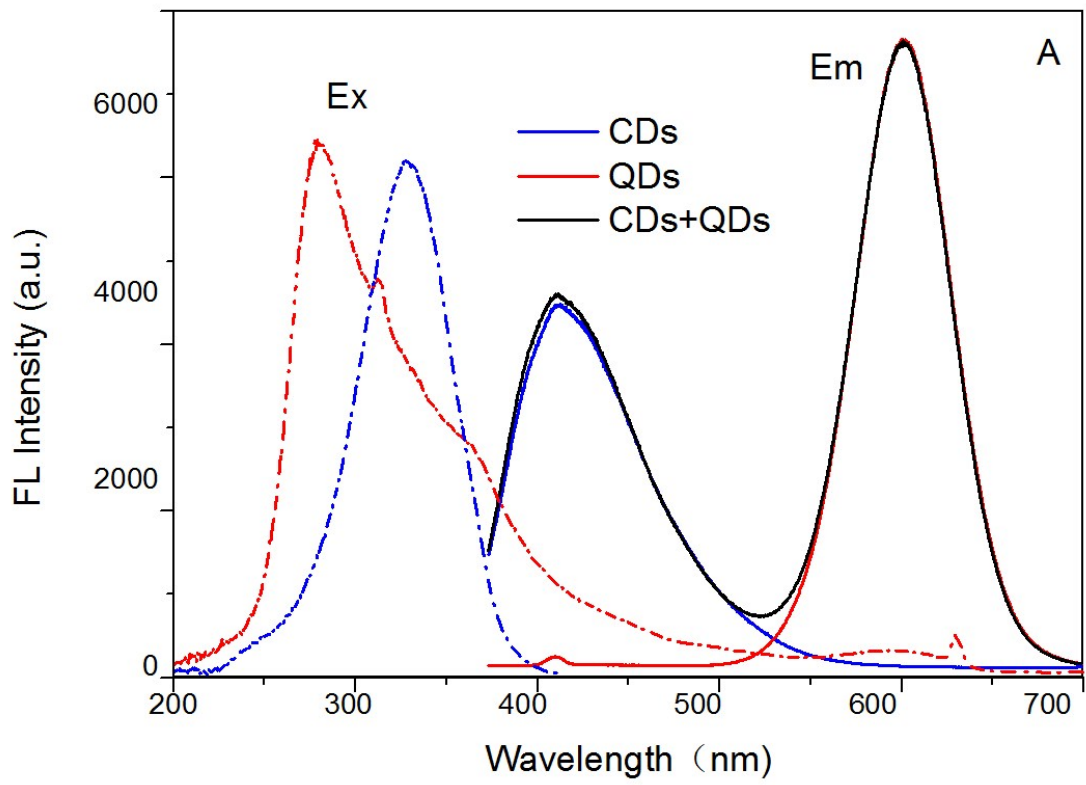
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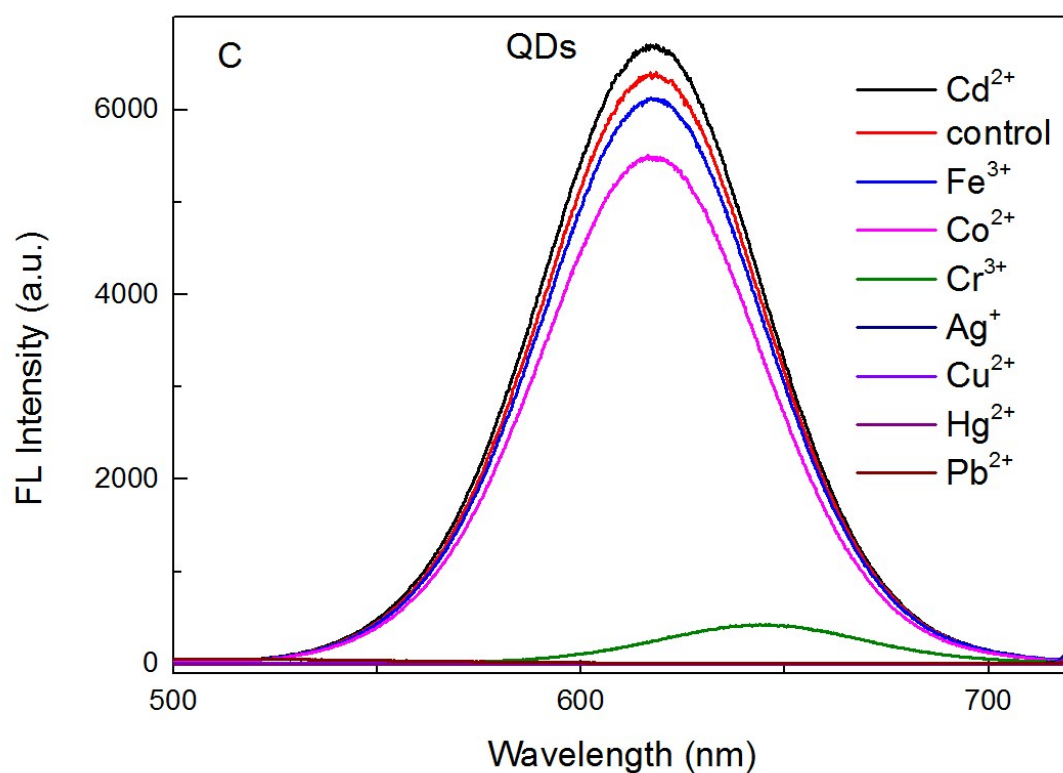
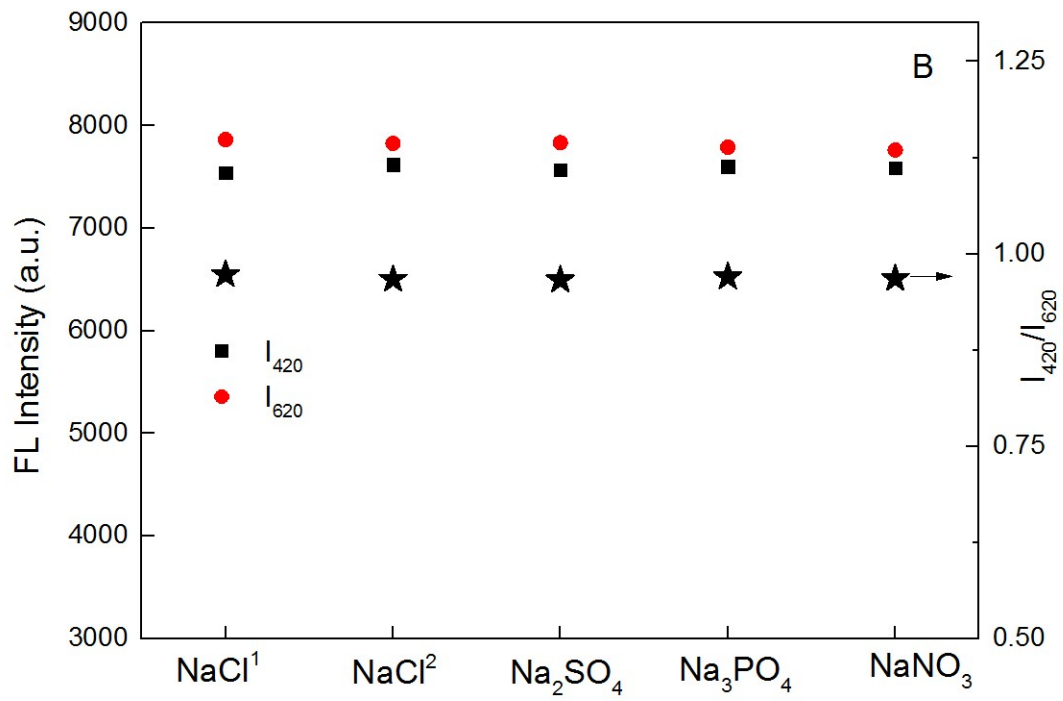
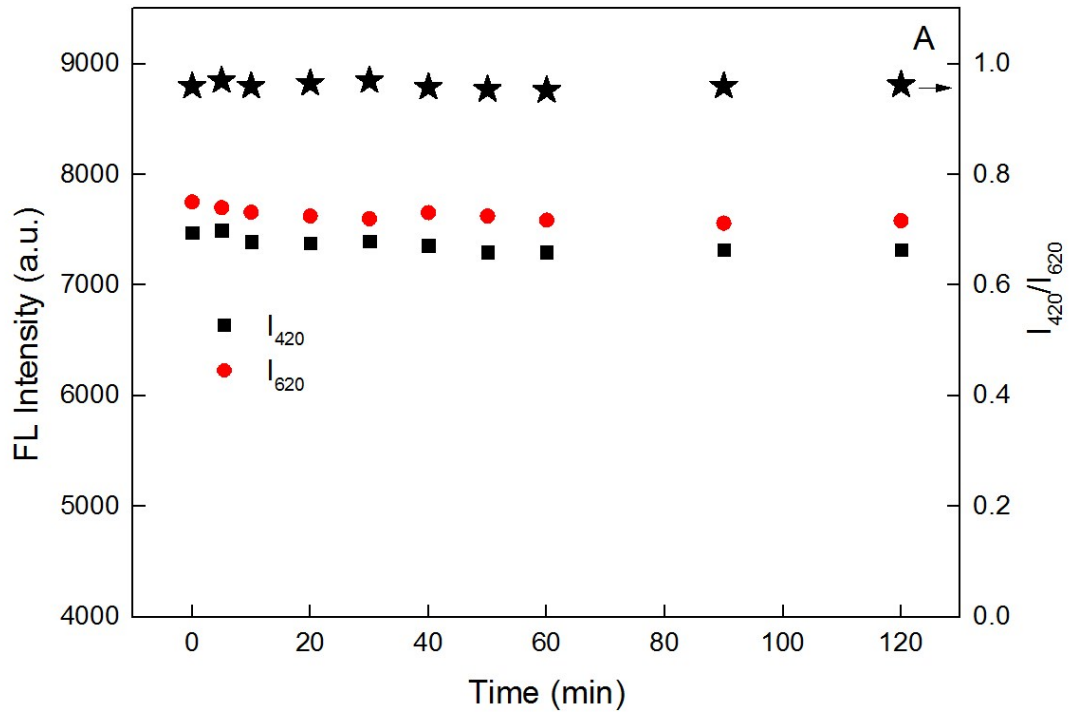
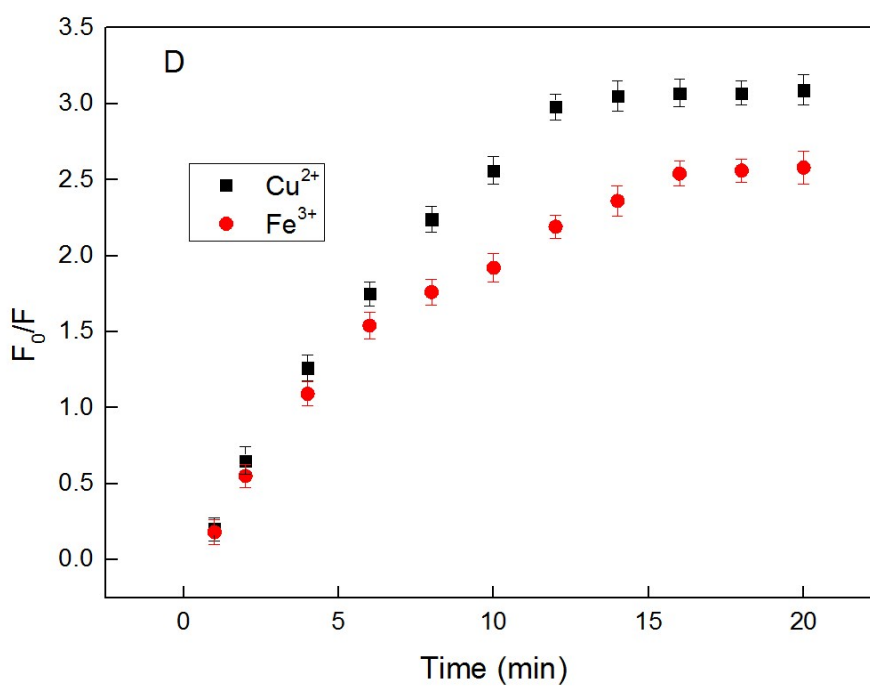
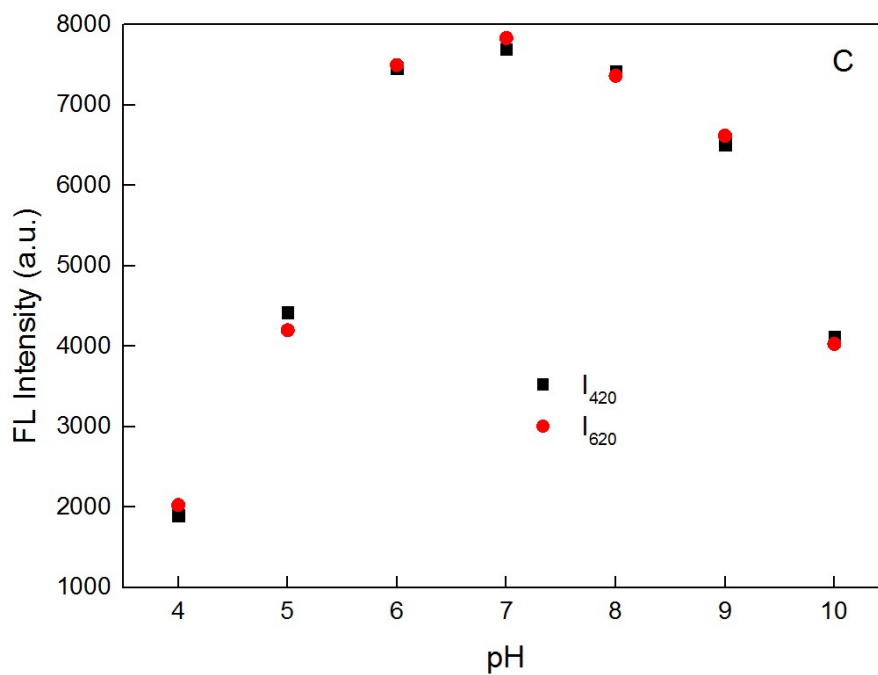
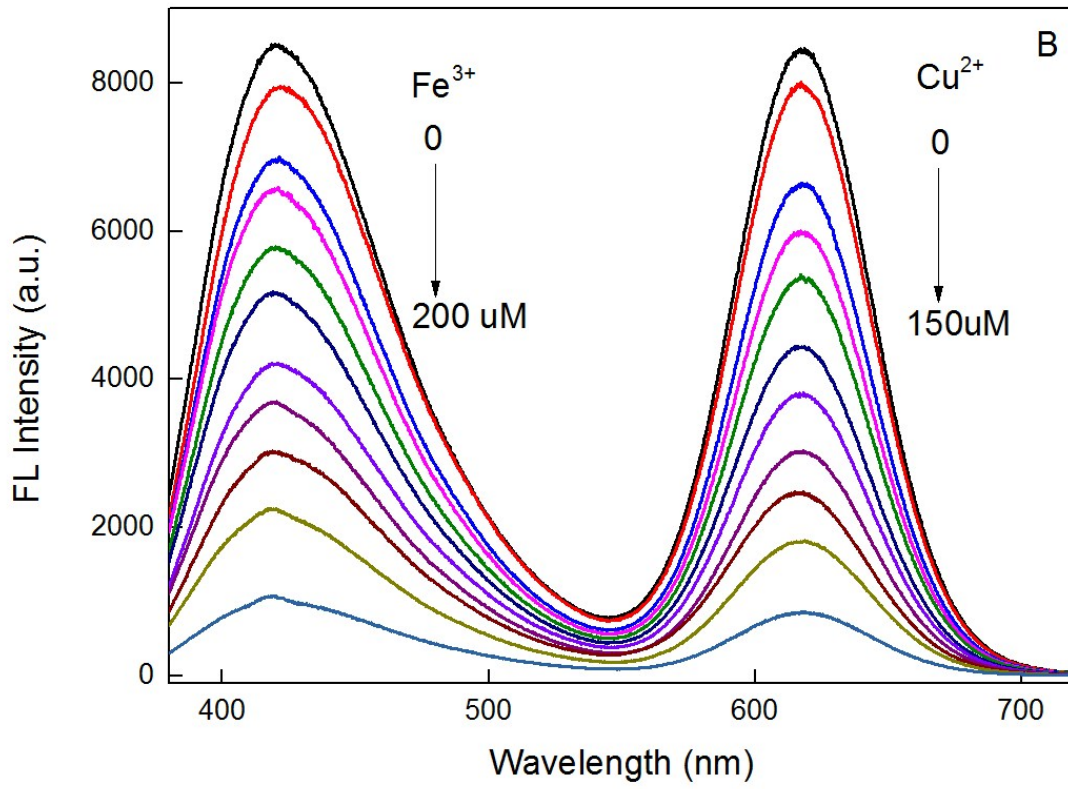
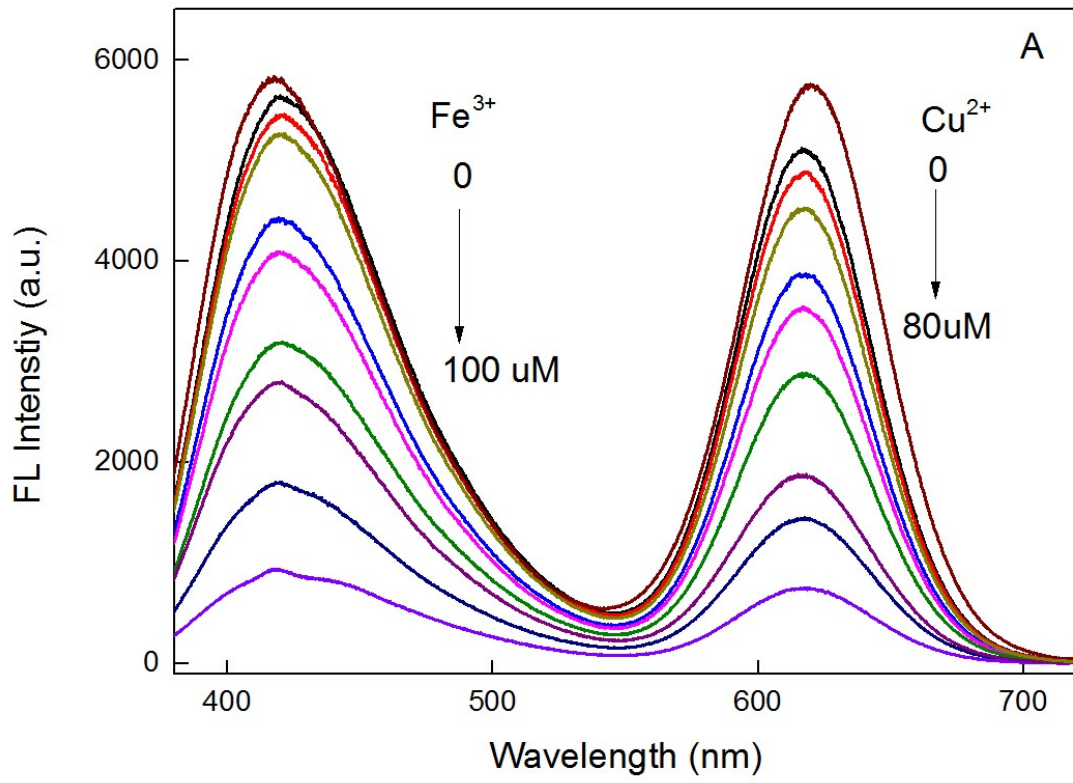


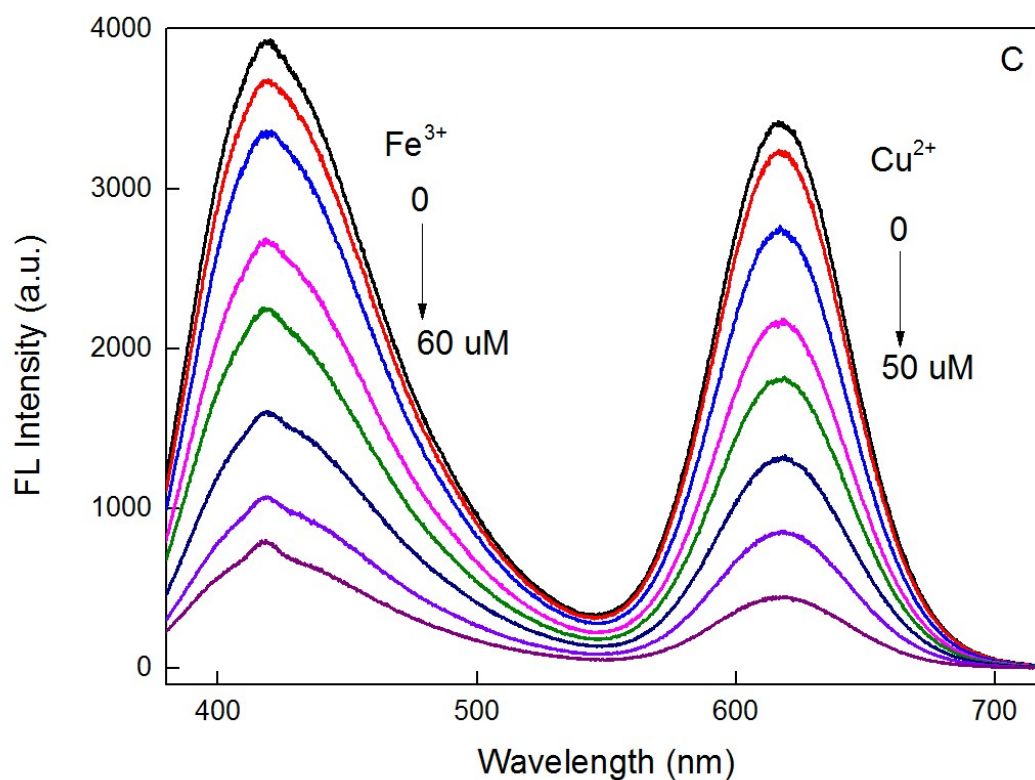
Figure S1 The fluorescence spectrum of CDs, QDs and the mixture of CDs and QDs (A); The fluorescence spectrum of CDs (B) and QDs (C) to various metal ions. The concentration of ions was 10  $\mu$ M, respectively.



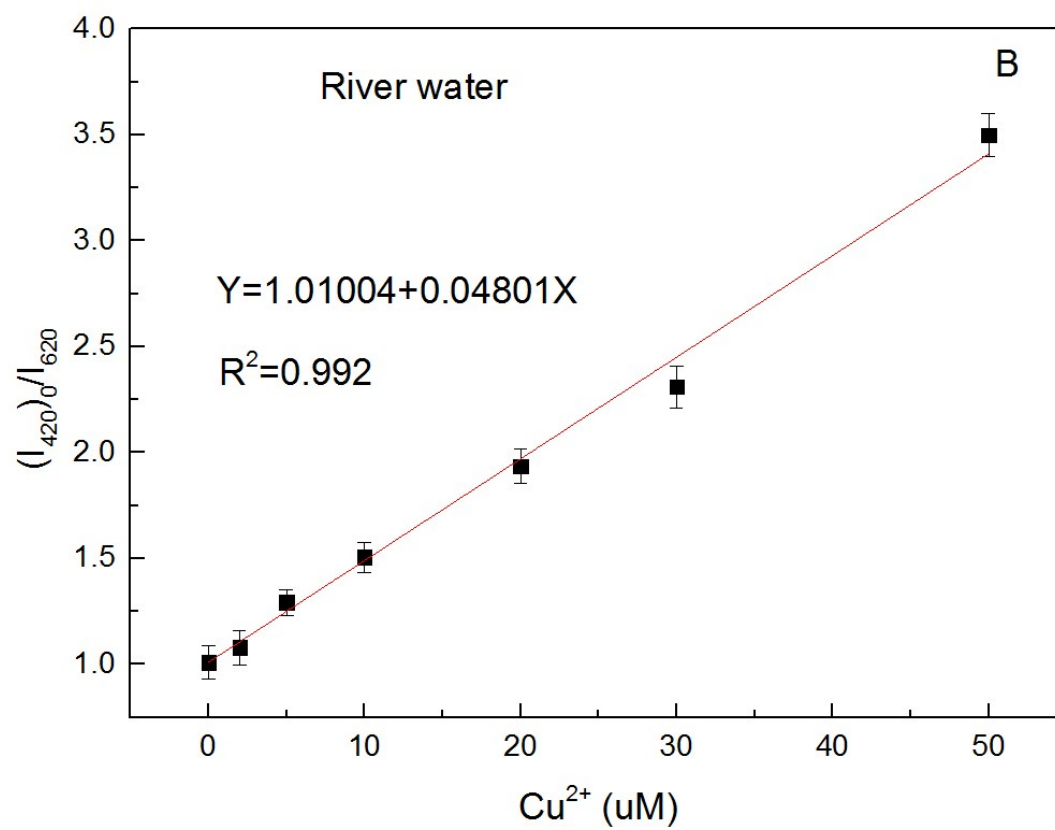
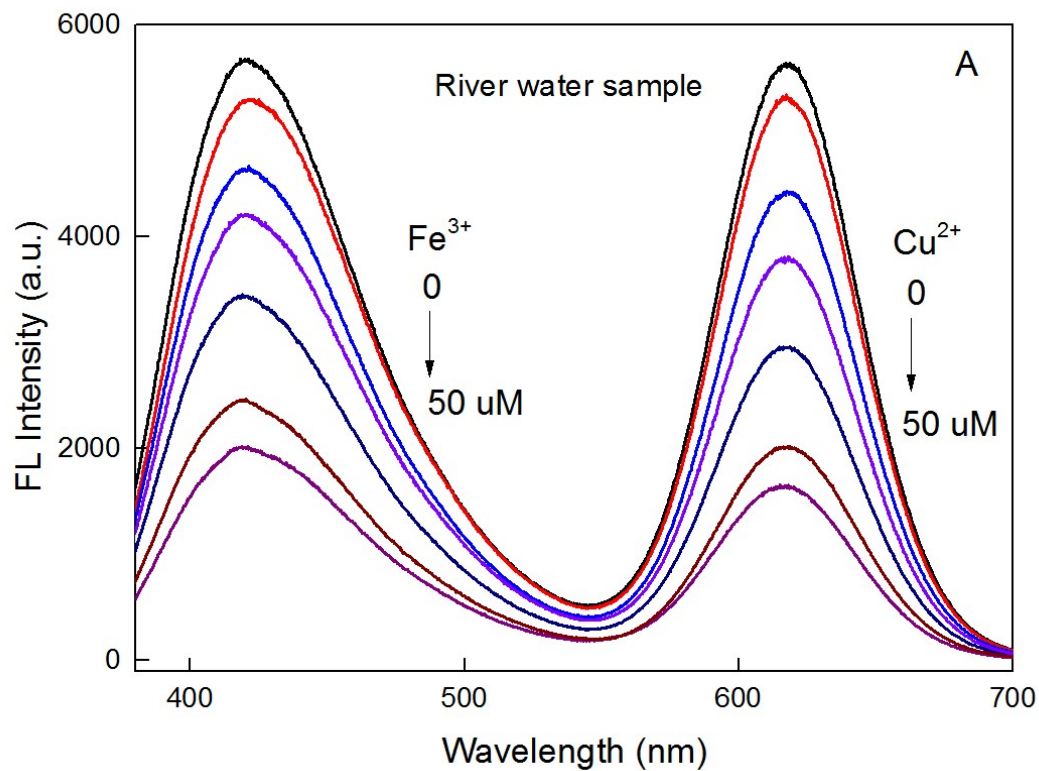


**Figure S2** The stability of the as prepared imprinted probe against UV light (A), various anions (B), and pH (C); and (D) was the fluorescent quenching effect IIPs during 20 min; the concentration of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions was both  $50 \mu\text{M}$ . For  $\text{Cu}^{2+}$ , fluorescent intensity was recorded at 620 nm, For  $\text{Fe}^{3+}$ , fluorescent intensity was recorded at 420 nm.

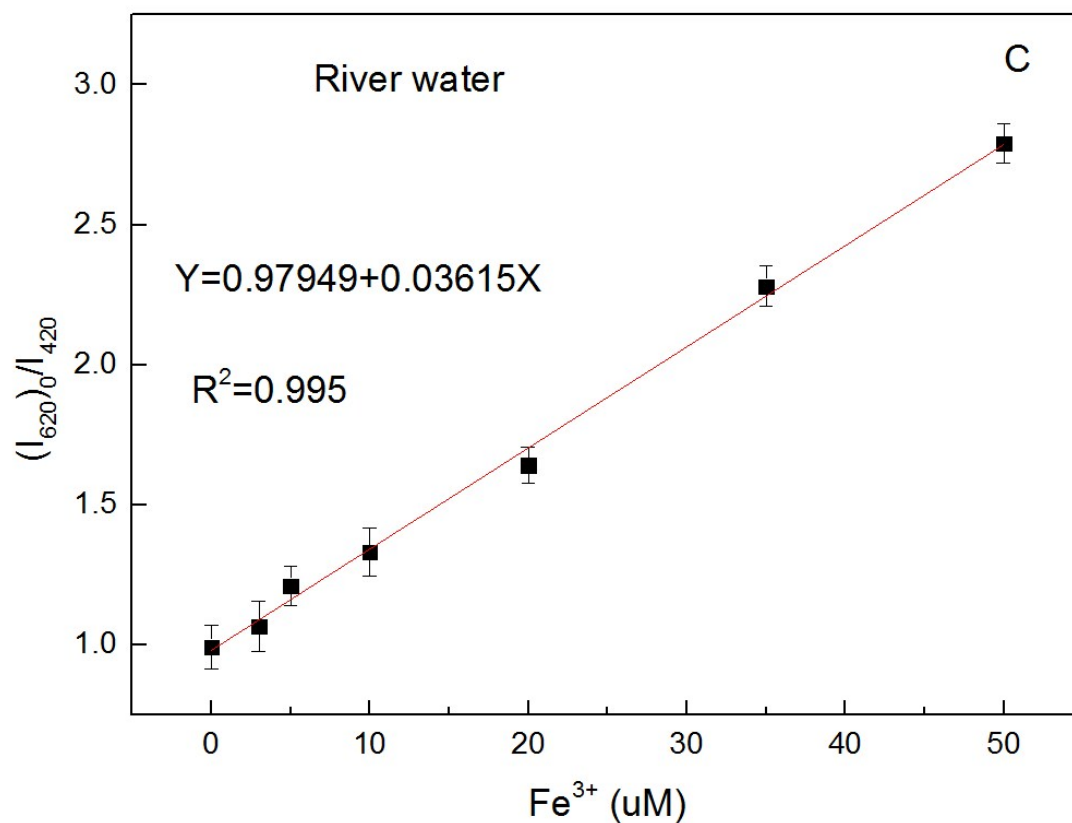




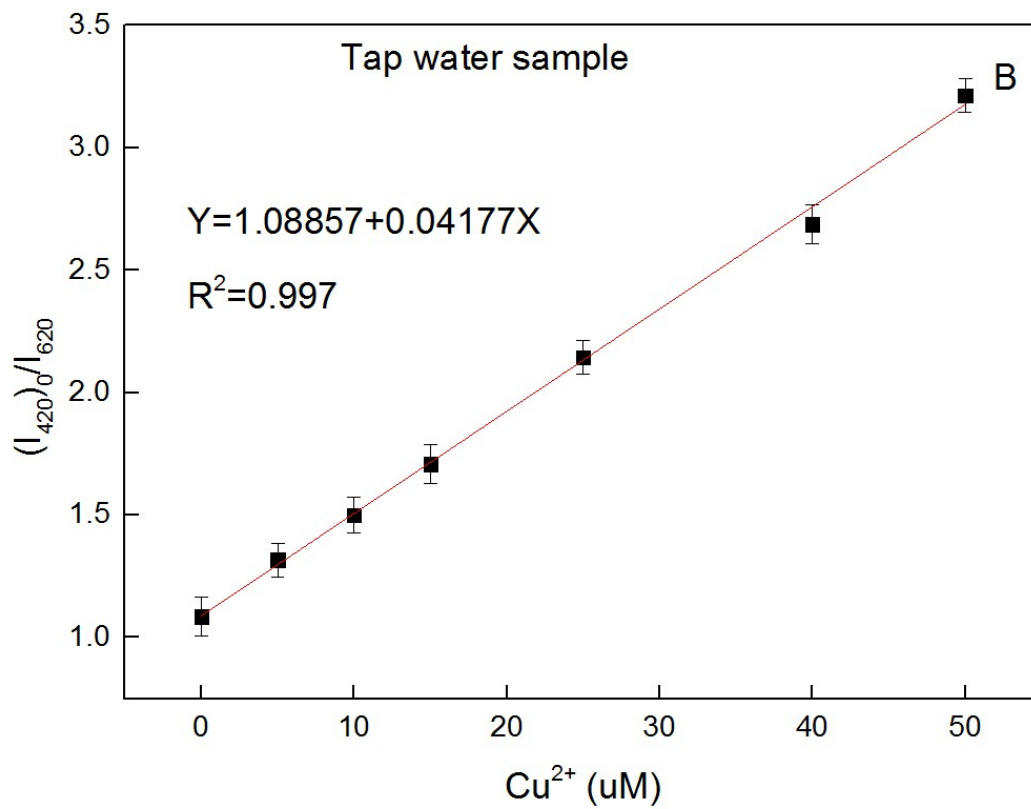
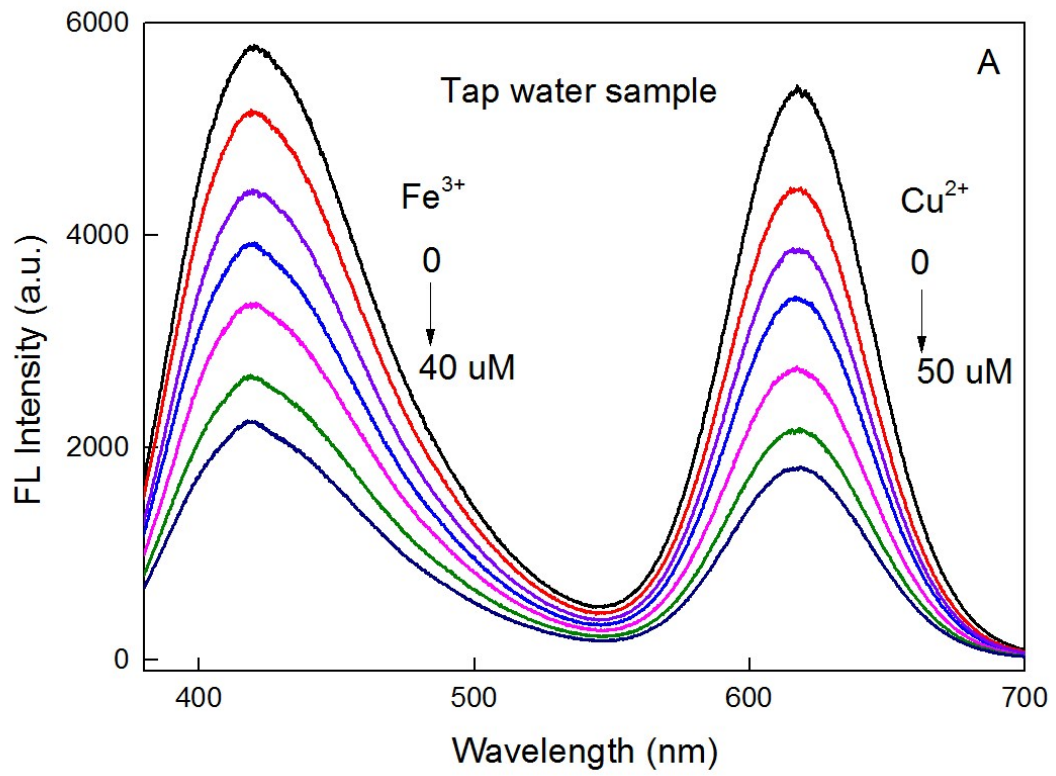
**Figure S3** Different amount of imprinted polymers (A: 100 mg/L; B: 150 mg/L; C: 50 mg/L) exposure to different concentrations of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ . The experimental conditions were pH=7.0 under room temperature; excited wavelength at 345 nm and the slit widths of emission and excitation were 5 nm ( $n = 5$ ); reaction time was 20 min.

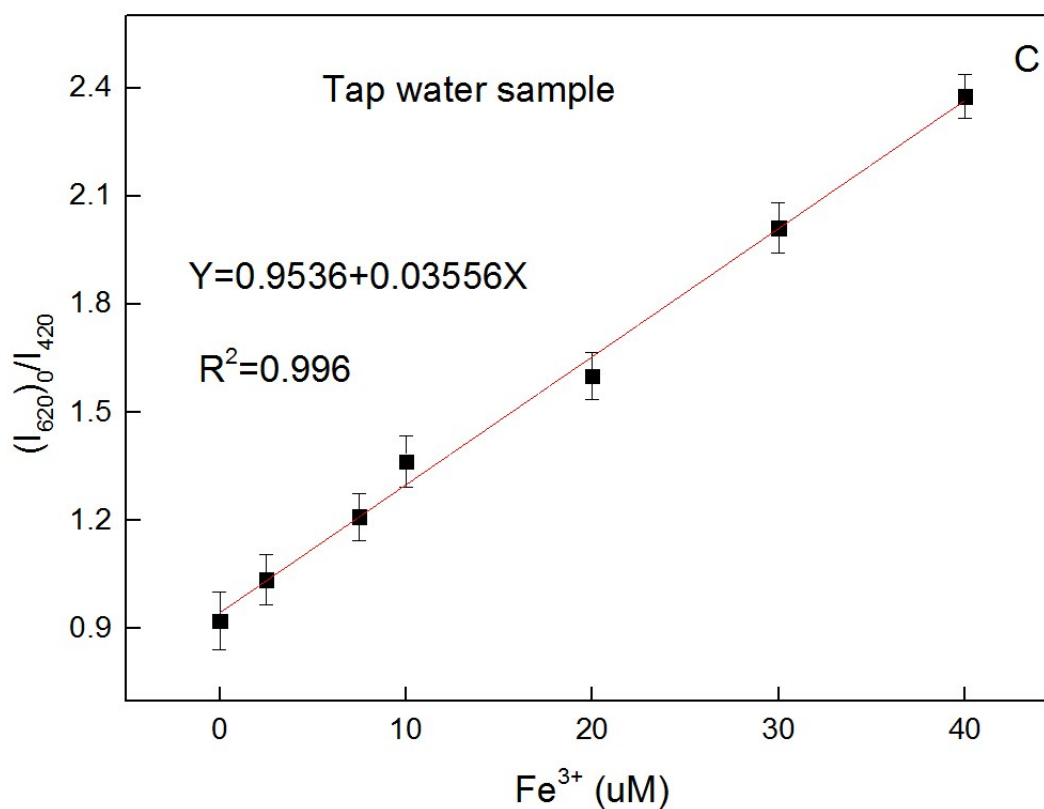






**Figure S4** The fluorescence spectra of IIFPs exposure to different concentrations of Cu<sup>2+</sup> and Fe<sup>3+</sup> in river water samples (A). B and C were the linear fitting curve of Cu<sup>2+</sup> and Fe<sup>3+</sup> detection in river water sample. The experimental conditions: excited wavelength at 345 nm and the slit widths of emission and excitation were 5 nm (n = 3); reaction time was 20 min, the concentration of IIFPs was 100 mg/L.





**Figure S5** The fluorescence spectrum of IIPs exposure to different concentrations of  $Cu^{2+}$  and  $Fe^{3+}$  in tap water samples (A). B and C were the linear fitting curve of  $Cu^{2+}$  and  $Fe^{3+}$  detection in tap water sample. The experimental conditions: excited wavelength at 345 nm and the slit widths of emission and excitation were 5 nm ( $n = 3$ ); reaction time was 20 min, the concentration of IIPs was 100 mg/L.

**Table S1** The linear range and LOD for Cu<sup>2+</sup> and Fe<sup>3+</sup> measured by different concentration of imprinted probes.

Concentration of probe (mg/L)	Cu <sup>2+</sup> detection		Fe <sup>3+</sup> detection	
	Linear range	LOD	Linear range	LOD
	( $\mu$ M)	(nM)	( $\mu$ M)	(nM)
50	0.5-30	156	1-50	322
100	0.5-50	130	1-100	340
150	2-100	526	4-150	1470

**Table S2** Detected concentration of Cu<sup>2+</sup> and Fe<sup>3+</sup> in river and tap water by this method and AAS.

sample	Cu <sup>2+</sup> ( $\mu$ M)		Fe <sup>3+</sup> ( $\mu$ M)	
	This method	AAS	This method	AAS
River water	5.34	5.41	2.78	2.68
Tap water	4.35	4.42	3.12	3.04

**Table S3 Recoveries of Cu<sup>2+</sup> and Fe<sup>3+</sup> in spiked river and tap water**

Type	Sample	ions	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (%)
Single spiking	River water	Cu <sup>2+</sup> (5.34)	0.50	6.07	104.0	3.6
			5.00	10.17	98.4	3.4
			20.00	25.16	99.3	2.4
		Fe <sup>3+</sup> (2.78)	1.00	3.63	96.0	3.9
			5.00	7.44	95.6	2.9
			20.00	22.89	100.5	2.4
	Tap water	Cu <sup>2+</sup> (4.35)	0.50	4.95	102.0	4.2
			5.00	9.09	97.2	3.4
			20.00	23.45	96.3	2.9
		Fe <sup>3+</sup> (3.12)	1.00	4.06	98.6	3.9
			5.00	7.75	95.4	3.1
			20.00	22.82	98.7	2.6
Mixed spiking	River water	Cu <sup>2+</sup> (5.34)	20.00	25.16	99.3	2.5
		Fe <sup>3+</sup> (2.78)	5.00	7.50	96.4	3.7
	Tap water	Cu <sup>2+</sup> (4.35)	20.00	19.76	98.8	2.9
		Fe <sup>3+</sup> (3.12)	5.00	8.93	110.8	3.7

**Table S4** Performance comparison with other reported fluorescence methods or IIP based detection method for Cu<sup>2+</sup> or Fe<sup>3+</sup> ions sensing

Detected method	Linear rang ( $\mu\text{M}$ )	LOD (nM)	Real sample	Ref.
Cu-IIP -FAAS	0.0157-1.57	1.6	Tap and well water	1
Cu-IIP-ICP-AES	0-15.7	5.9	drinking water	2
Dual emission CDs based ratiometric fluorescence probe	0-0.5	7.31	Tap water lake water	3
Dual emission QDs based ratiometric fluorescence probe	0.05-0.5	1.1	Lake water	4
Cu-IIFP	0–70.0.	110-140	Tap water, river water	5
Cu-IIFP chip	$1.7 \times 10^{-3}$ -0.913	0.551	Lake water; sea water	6
Cu-IIFP	0.5-50	130	River water, tap water	This work

Fe-IIFP	1.0-100	340	River water, tap water	This work
CDs for Fe <sup>3+</sup> detection	1--150	330	River water	7
nitrogen-doped CDs for Fe <sup>3+</sup> detection	2–25 μM	170	Drinking water	8

#### Reference

- [1] M. Shamsipur, A. Besharati-Seidani, J. Fasihi and H. Sharghi, *Talanta*, 2010, 83, 674-681.
- [2]. Hossein Hashemi, Mostafa Khajeh, Massoud Kaykhahi, *Anal. Methods*, 2013, 5, 2778-2783.
- [3] Y. Wang, M. Wu, S. Yu and C. Jiang, *RSC Adv.*, 2018, 8, 12708–12713.
- [4] J. Yao, K. Zhang, H. Zhu, F. Ma, M. Sun, H. Yu, J. Sun and S. Wang, *Anal. Chem.* 2013, 85, 6461–6468.
- [5] Z. Xu, P. Deng, J. Li, S. Tang, *Sensors and Actuators B* 255 (2018) 2095–2104.
- [6] J. Qi, B. Li, X. Wang, Z. Zhang, Z. Wang, J. Han, L. Chen, *Sensors and Actuators B* 251 (2017) 224–233
- [7] J. Shangguan, J. Huang, D. He, X. He, K. Wang, R. Ye, X. Yang, T. Qing and J. Tang, *Anal. Chem.* 2017, 89, 7477–7484.
- [8] X. Miao, X. Yan, D. Qu, D. Li, F. Feng Tao and Z. Sun, *ACS Appl. Mater. Interfaces* 2017, 9, 18549–18556.