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Electronic Supplementary Information

An effective electrochemical sensing plat-form for fluoride ion based on fluorescein isothiocyanate-MWCNT composite

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Figure S1. (A) Absorption spectra of FITC (0.065 μ M, in DMF), FITC-OSi (0.065 μ M, in DMF), and FITC-OSi (0.065 μ M) + F⁻ (60 μ M) in DMF



Fig. S2. ¹H-NMR spectrum of FITC-OSI in DMF-d₇



Fig. S3. Bode phase (A) and bode impedance modulus (B) plot of FITC-OSi-p-mwcnt-GCE prepared using L-B-L-M and M-D-M. Conditions: pH=7, FITC-OSi (0.06 μ M), p-mwcnt (0.22 gL⁻¹).



Fig. S4. Raman spectroscopy results performed on FITC-OSi-p-mwcnt composite. The spectrum of p-mwcnt is also present for comparison.



Fig. S5. (A) Peak current intensity change of FITC-OSi-p-mwcnt-GCE prepared using L-B-L-M with 5 μ L FITC-OSi (0.062 mM) and 5 μ L p-mwcnt (0, 0.07, 0.11, 0.15, 0.19, 0.22, and 0.26 gL⁻¹). 5 μ L of 60 μ M F was dropcast on the electrode prior to the CV scan and (B) Peak current derived from CV scans of FITC-OSi-p-mwcnt-GCE after addition of 5 μ L of 60 μ M F- and incubating for 5, 10, 15, and 20 min.



Fig. S6. CV scans of FITC-OSi-p-pmwcnt-GCE in presence of 5 μ L of varying F⁻ concentrations (1, 3, 5, 10, 20, 40, 60, and 100 μ M). The mole equivalent between Si-O bonds and F⁻ at each concentration is displayed. The saturation point can clearly be seen after equivalent mole reaction was achieved. 2.43 μ L of FITC-OSi (0.062 mM in DMF), L-B-L-M, and p-mwcnt loading (0.22 gL-1) were used to fabricate the electrode. Tris-HAc buffer (pH=7, 0.1M) was used as electrolyte. The dropcast F⁻ solution and the electrode were allowed to react for 15 min before CV scans were taken.



Fig. S7. (Black line) CV scan of FITC-OSi-p-mwcnt-GCE (L-B-L-M) electrode in the presence of 5 μ L of F⁻ (60 μ M) after 15 min of reaction. Tris-HAc buffer solution (0.1M, pH=7) was used as the electrolyte. (Red line) CV scan of FITC-OSi-p-mwcnt-GCE (L-B-L-M) electrode in Tris-HAc (0.1 M, pH=7) containing 0.3 nmoles of fluoride ion. The CV scan was taken after after 35 min of reaction. In both electrodes, p-mwcnt and FITC-OSi loading of 0.22 gL⁻¹ and 5 μ L of 0.062 mM FITC-OSi in DMF were used, respectively.



Fig. S8. A picture depicting two competing reactions on the electrode surface after F⁻ is dropcast: (left image) precipitation of FITC-OSi out of solution controlled by a rate constant r_1 and (ii) cleavage of Si-O bonds to generate phenolate ions controlled by a rate constant r_2 . The picture on the right shows the resulting solution composition when $r_2 > r_1$ and vice versa.

Table S1 Comparison of the upper detection limit and current response of electrode prepared using different FITC-OSi loading

Stock	Volume	Moles of Si-	Concentration of	Volume of	Moles of F-	Current
concentration of	dropcast on	O sites in	F^{-} solution (μM)	F ⁻ solution	in dropcast	response
FITC-OSi (mM)	GCE (µL)	dropcast	tested	dropcast	solution	(mA)
		solution		(µL) on	(nmole)	
		(nmole)		electrode		
0.062	2.43	0.30	60	5	0.30	0.0233
0.062	4.04	0.50	100	5	0.50	0.0288

Table S2 Detection of F⁻ in tap water using FITC-OSi-p-mwcnt-GCE via cyclic voltammetry

F- added(µM)	F- detected(µM)	AcO ⁻ added (µM)	RSD(%)	Recovery (R%)
0	0.25	-	0.9	-
20	19.91	-	2.1	98.32
20	19.50	20	3.0	96.29
60	60.29	-	1.8	100.06
	F- added(μM) 0 20 20 60	F-added(μM) F-ceeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeee	F- added(µM)F- cetected(µM)AcO- added (µM)00.25-2019.91-2019.50206060.29-	F-detected(µM)AcO- added (µM)RSD(%)00.25-0.92019.91-2.12019.50203.06060.29-1.8