Supporting Information For

Thiol-ene chemistry guided preparation of thiolated polymeric nanocomposite for anodic stripping voltammetric analysis of Cd^{2+} and Pb^{2+}

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Outline

Table 1S Performance of Bi film modified electrodes for simultaneous determination of Cd^{2+} and Pb^{2+} by anodic stripping techniques.*

Electrode	Cd^{2+}			Pb^{2+}		
	S / μA μg^{-1} L	LDR / μg L^{-1}	LOD /μg L^{-1}	*S* / μA μg^{-1} L	LDR / μg L^{-1}	LOD /μg L^{-1}
Bi/Nafion/DMcT-PANI/MWCNTs/GCE (This work)	3.44	0.02~20	0.01	1.63	0.08~31	0.04
Bi/Nafion/DMcT-$PANI_e$/MWCNTs/GCE (This work)	2.92	0.10~30	0.04	1.28	0.20~35	0.1
Bi/Nafion/PDMcT-MWCNTs/GCE[1]	3.53	0.05~20	0.03	2	0.1~22	0.05
Bi/Nafion/PANI-MES/GCE[2]	1.10	0.1~20	0.04	0.766	0.1~30	0.05
Bi/ABTS-MWCNTs/GCE[3]	0.812	0.5~35	0.2	0.532	0.2~50	0.1
Bi/Nafion/GCE[4]	2.37	1~20	0.1	2.66	1~20	0.1
Bi/C/GCE[5]	0.26	–	0.49	0.71	–	0.41
Bi-CPE[6]	–	10~100	1.2	–	10~100	0.9
Bi/poly(*p*-ABSA)/GCE[7]	0.311	2.5~85	0.63	0.191	3~113	0.80
Bi-CpmEs[8]	–	1.1~112	0.15	–	2.1~207	0.17

* PDMcT: poly(2,5-dimercapto-1,3,4-thiadiazole); MES: 2-mercaptoethanesulfonate; ABTS: 2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonate) diammonium salt; MWCNTs: multiwalled carbon nanotubes; GCE: glassy carbon electrode; CPE: carbon paste electrode; poly(*p*-ABSA): poly(*p*-aminobenzene sulfonic acid); CPmEs: carbon paste mini-electrodes.

Table 2S Determination of Cd^{2+} and Pb^{2+} in tap water (1), spring water (2) and river water (3) (n = 5).

Sample	Original Cd^{2+} / μg L^{-1}	Original Pb^{2+} / μg L^{-1}	Added Cd^{2+} / μg L^{-1}	Added Pb^{2+} / μg L^{-1}	Cd^{2+}			Pb^{2+}		
					Found /μg L^{-1}	Recovery / %	RSD / %	Found /μg L^{-1}	Recovery / %	RSD / %
1	–	1.53	10.0	10.0	9.30	93	4.2	11.6	101	5.4
2	1.35	2.26	10.0	10.0	11.7	103	5.1	11.5	94	4.8
3	1.52	4.71	10.0	10.0	10.8	94	2.3	14.1	96	3.5

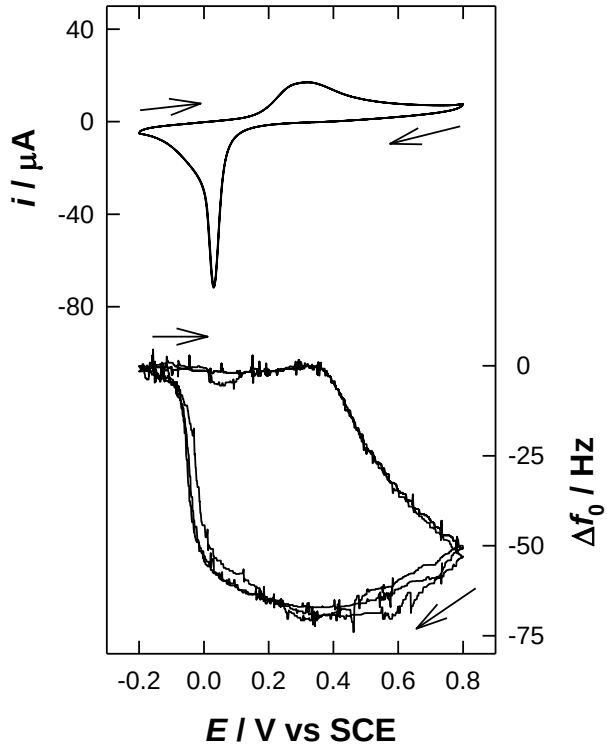

Fig. 1S Electrochemical QCM responses during potential cycling of a bare Au electrode in 0.05 mg mL^{-1} DMcT + 0.1 mol L^{-1} H_2SO_4 + ethanol (v/v 1:1) aqueous solution. Scan rate: 30 mV s^{-1}.

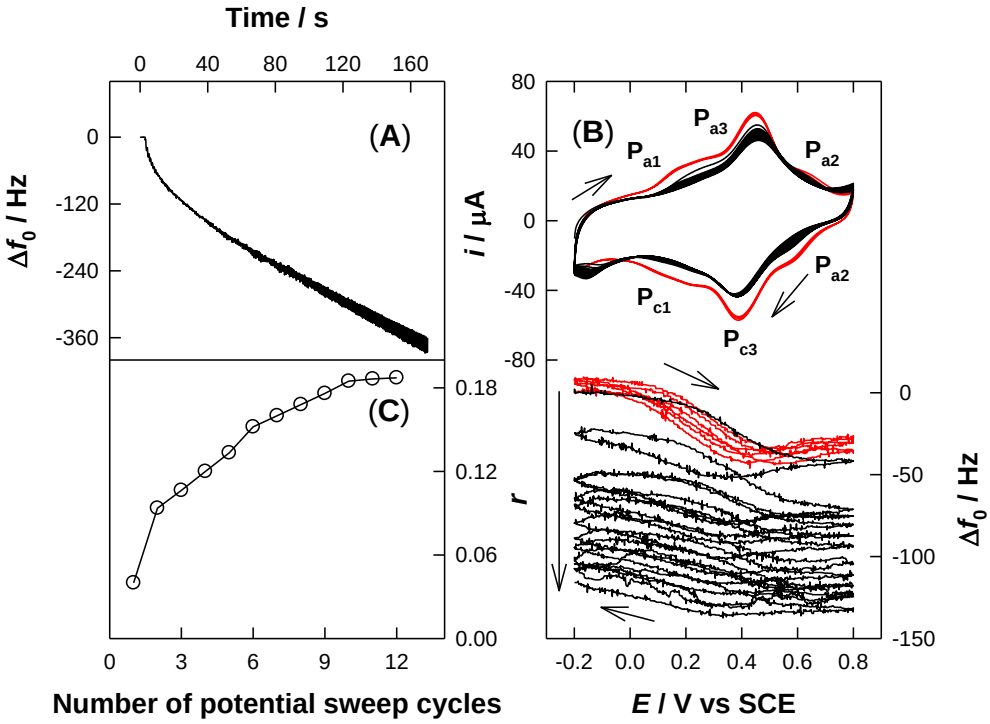

Fig. 2S (A) Electrochemical QCM responses to $PANI_e$ deposition by multipulse potentiostatic perturbation that was started at time zero. (B) Electrochemical QCM responses during potential cycling (30 mV s^{-1}) of a MWCNTs/$PANI_e$ film in 0.1 mol L^{-1} H_2SO_4 + ethanol (v/v 1:1) (red curves) and in 0.05 mg mL^{-1} DMcT + 0.1 mol L^{-1} H_2SO_4 + ethanol (v/v 1:1) (black curves). (C) The relationship of *r* with number of potential sweep cycles.

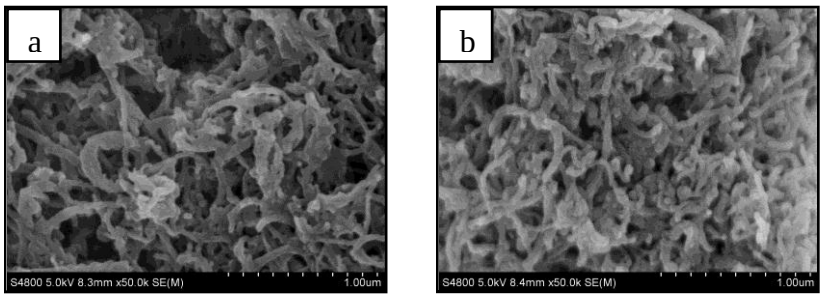

Fig. 3S SEM pictures of Bi/Nafion/DMcT-PANI/MWCNTs (a) and Bi/Nafion/DMcT-PANI$_e$/MWCNTs (b).

Pretreatment of the DMcT-PANI/MWCNTs/GCE

As shown in **Fig. 1S**, the oxidation current peak of DMcT occurred at 0.3 V, and reduction current peak of dimer or oligomers of DMcT occurred at 0.05 V during potential cycling of bare Au electrode in 0.05 mg mL^{-1} DMcT + 0.1 mol L^{-1} H_2SO_4 + ethanol (v/v 1:1) aqueous solution, and the simultaneously recorded frequency increased and then decreased with intercycle-recoverable frequency values, giving negligible net frequency shift. The dimer or oligomers of DMcT could be cathodically detached from the electrode surface at -0.2 V, as similarly reported previously.[9] Thus, the pretreatment of the DMcT-PANI/MWCNTs/GCE was conducted potentiostatically at -0.2 V for 120 s to remove the physically adsorbed or doped dimer and oligomers of DMcT which were probably formed by the interaction of oxidized PANI/MWCNTs and DMcT.

Electrochemical QCM study on DMcT-$PANI_e$/MWCNTs nanocomposite film

A $PANI_e$ film was electrodeposited on a MWCNTs modified QCM Au electrode, and the $PANI_e$ deposition led to continuous QCM frequency decrease (**Fig. 2S**). As shown in **Fig. 2S**, in DMcT-free 0.1 mol L^{-1} H_2SO_4 + ethanol (v/v 1:1) aqueous solution, the frequency decreased in the first oxidation process (P_{a1}/P_{c1}, leucoemeraldine to emeraldine, anion doping) and then somewhat increased in the second oxidation process (P_{a2}/P_{c2}, emeraldine to pernigraniline, partial release of doped anions to the solution from the film) on the positive potential scan, and the negative potential scan well reversed the frequency response (decreased and then increased).[10] The P_{a3}/P_{c3} redox peaks result from the nonideal structures of PANI.[10] In 0.05 mg mL^{-1} DMcT +

0.1 mol L^{-1} H_2SO_4 + ethanol (v/v 1:1) aqueous solution, all the redox peaks (P_{a1}/P_{c1}, P_{a2}/P_{c2} and P_{a3}/P_{c3}) and the frequency decreased cycle by cycle. The net frequency decrease (vs. the absence of the thiol) was observed only at the oxidized states of PANI of alkenes-like electron-conjugate structure, rather than at its fully reduced state, coinciding with the thiol-ene chemistry.

The binding molar ratio (*r*, thiol vs. aniline unit of PANI) for the thiolated PANI film is estimated as follows,

$$r = \frac{\Delta f_{0,\text{thiol}} M_{\text{W(aniline unit)}}}{\Delta f_{0,\text{PANI}} M_{\text{W}(RS^-)}} \quad (1)$$

where $M_{\text{W}(RS^-)}$ and $M_{\text{W(aniline unit)}}$ are the molar weight values of the thiol anion and the aniline unit of the fully reduced $PANI_e$, respectively, $\Delta f_{0,\text{thiol}}$ denotes the frequency shift after the thiol-$PANI_e$/MWCNT interaction (load of thiol anion), and $\Delta f_{0,\text{PANI}}$ denotes the frequency shift after the $PANI_e$ electrodeposition (load of reduced $PANI_e$). The optimized *r* (r_{opt}=0.19±0.01, three parallel experiments) of DMcT-$PANI_e$/MWCNTs for Cd^{2+} and Pb^{2+} determination was obtained here from the interactions of -360 Hz $PANI_e$ with 0.05 mg mL^{-1} DMcT for 12 potential cycles, and the potential cycle-dependent *r* value is shown in **Fig. 2S**.

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