

Supporting Information

Electrochemical determination of trace pesticide residues based on multiwalled carbon nanotube grafted acryloyloxy ferrocene carboxylates with different spacers

Feng Xu*, Zhuo-Miao Cui, He Li, Yan-Ling Luo*

(Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry
and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China)

Contact details for corresponding authors

Feng Xu and Yan-Ling Luo

Fax: +86 29 81530727

E-mail address: fengxu@snnu.edu.cn (F. Xu) and luoyanl@snnu.edu.cn (Y. L. Luo)

Affiliations: Key Laboratory of Macromolecular Science of Shaanxi Province, School
of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062,
People's Republic of China

Fax: +86 29 81530727

1. Preparation and ^1H NMR of monomers

2-Acryloyloxyethyl ferrocene carboxylate (AEFC) was prepared via esterification reaction of FCA with HEA using DMAP as a catalyst and DCC as a dehydration agent, with the molar ratio of 1:1.2:1.2:1. In a sealed 500 ml three-neck flask, FCA (9.2 g, 40 mmol) was dissolved in a mixture of dried CH_2Cl_2 (50 ml), HEA (6.64 ml, 48 mmol) and DMAP (5 g, 40 mmol). Under the condition of N_2 atmosphere, DCC (10 g, 48 mmol) dissolved in desiccative CH_2Cl_2 of 30 ml was dropwise added to the mixed solution at $0\text{ }^\circ\text{C}$ at a speed of 3-4 drop s^{-1} and the reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 2 h. The reaction proceeded at room temperature overnight. The resulting solution was filtered to remove the sediment 1,3-dicyclohexylurea (DCU). The filtrate was extracted twice by using saturated sodium bicarbonate solution and deionized water, respectively, to remove DMAP and unreacted FCA until the supernatant is colorless. After the concentration, the extract was purified by column chromatography using a mixture of *n*-hexane and ethyl acetate ($v/v=10/1$) as an eluent to give an orange solid product with a yield of 76%. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 6.38-6.44 (dd, 1H), 6.07-6.16 (dd, 1H), 5.79-5.83 (dd, 1H), 4.75 (s, 2H, *meta*-H in $-\text{C}_5\text{H}_4$), 4.41 (t, 4H, $-\text{OCH}_2-\text{CH}_2\text{O}-$), 4.34 (s, 2H, *ortho*-H in $-\text{C}_5\text{H}_4$), 4.13 (s, 5H, C_5H_5).

4-Acryloyloxybutyl ferrocene carboxylate (ABFC) was prepared through a similar

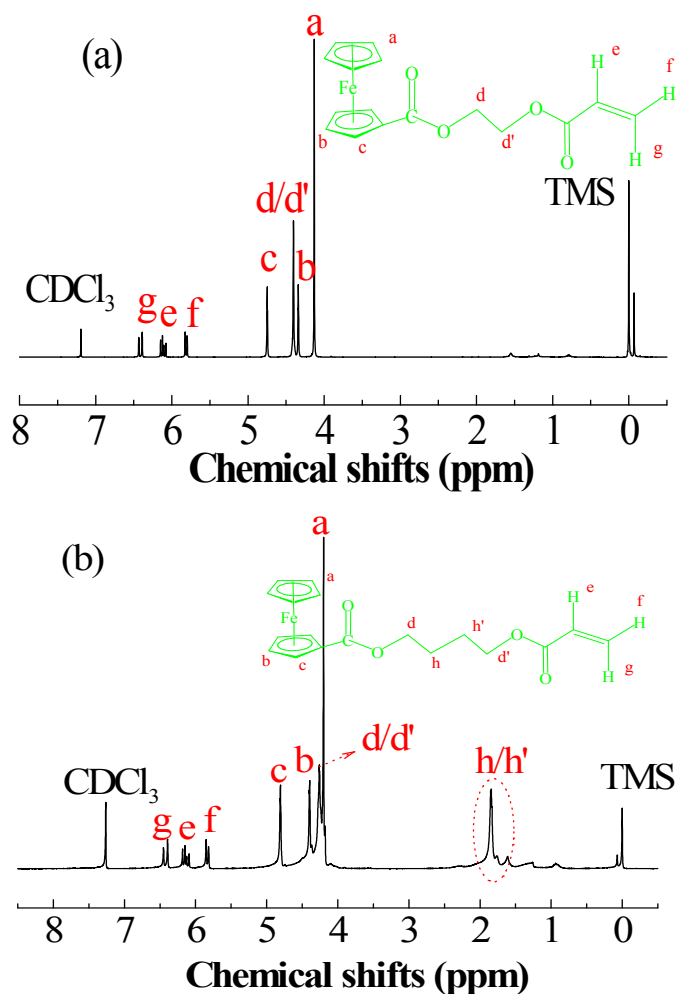


Figure S1 ^1H NMR spectra of AEFC and ABFC.

reaction to AEFC. 9.20 g (40 mmol) FCA, 6.65 ml (48 mmol) HBC, 4.88 g (40 mmol) DMAP, and 9.89 g (48 mmol) DCC were used for the reaction, and the crude product was purified by column chromatography using a mixture of *n*-hexane and ethyl acetate ($v/v=15/1$), giving dark orange oily liquid with a yield of 68%. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 6.40-6.46 (dd, 1H), 6.10-6.19 (dd, 1H), 5.82-5.87 (dd, 1H), 4.71 (s, 2H, *meta*-H in $-\text{C}_5\text{H}_4$), 4.40 (s, 2H, *ortho*-H in $-\text{C}_5\text{H}_4$), 4.26 (t, 4H, $-\text{OCH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{O-}$), 4.20 (s, 5H, C_5H_5). 1.62-1.85 (m, 4H, $-\text{OCH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{O-}$).

2. Pre-treatment of glass carbon electrodes (GCEs)

For pre-treatment of GCEs, the bare GCEs were polished using 0.05 and 0.3 μm alumina slurry in sequence and rinsed with deionized water, sonicated with ethanol and deionized water for 5 minutes each procedure.

3. High-resolution XPS spectra of MWCNTs-COOH and the related composites

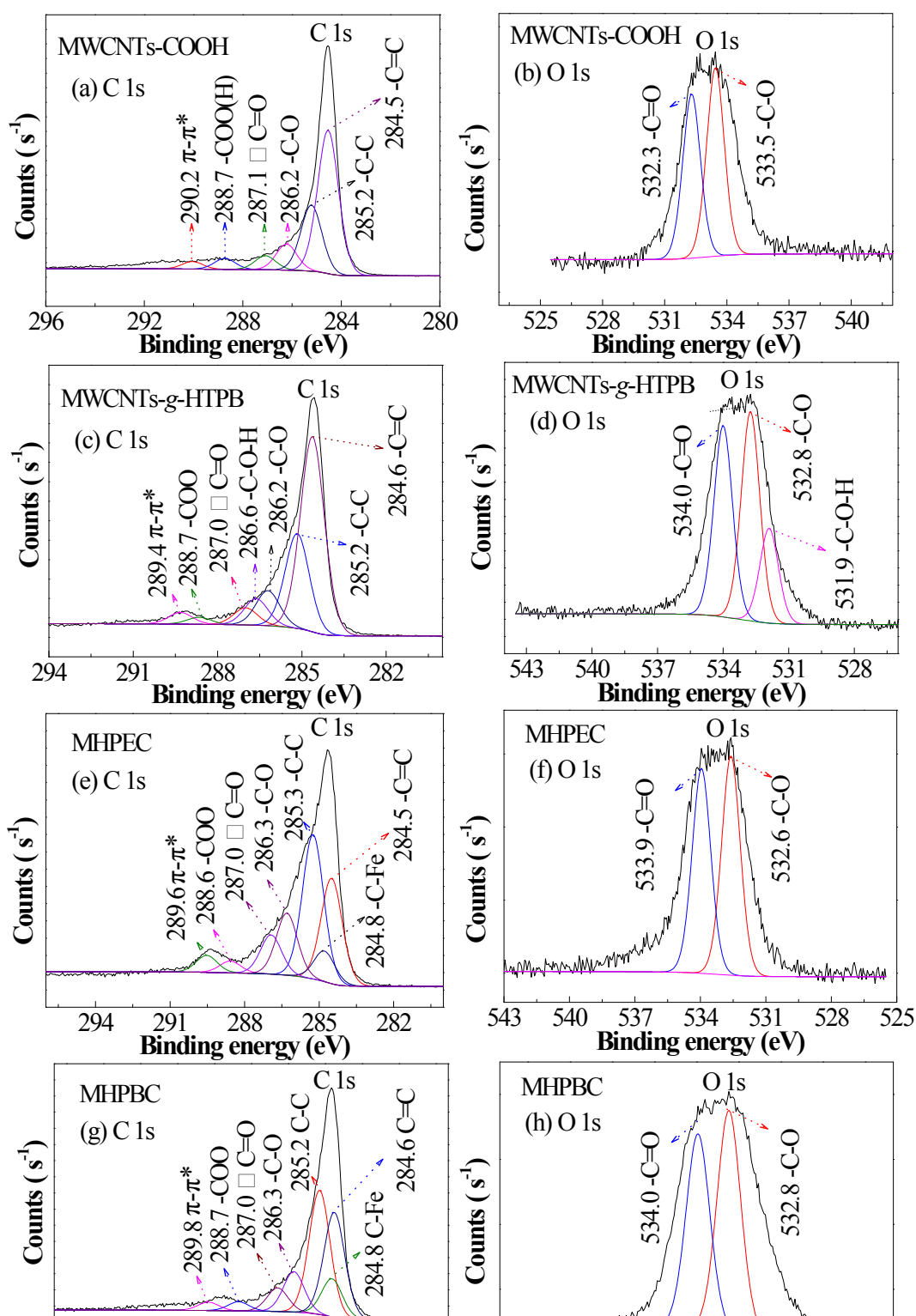


Table S1 Mass ratios in different materials

Samples	C, %	O, %	Fe, %
MWCNTS	95.98	4.02	0
MWCNTs-g-HTPB	93.15	6.85	0
MWCNTs-g-HTPB-b-PAEFC	89.63	9.42	0.95
MWCNTs-g-HTPB-b-PABFC	91.75	7.49	0.76

4. CVs of MHPEC modified electrodes

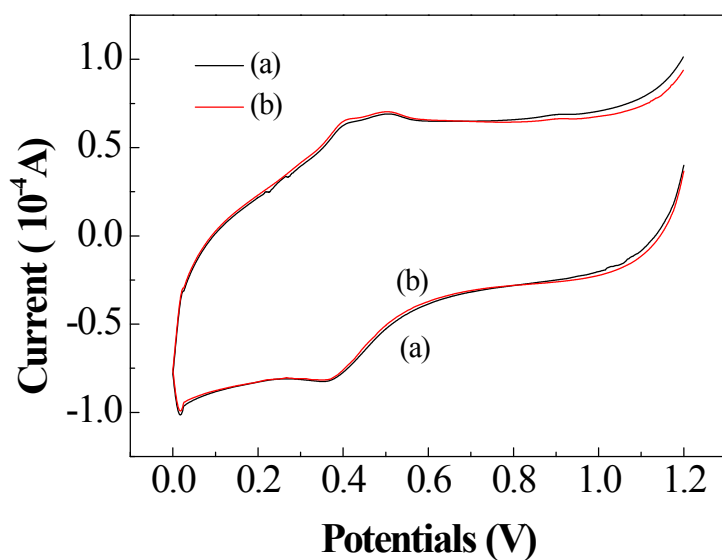


Figure S3 CVs of the MHPEC modified electrodes: (a) in the absence of and (b) in presence of 1×10^{-3} melamine in 1 M H_2SO_4 solution at a scan rate of 50 mV s^{-1} .

5. Detection of the residues of melamine in real milk

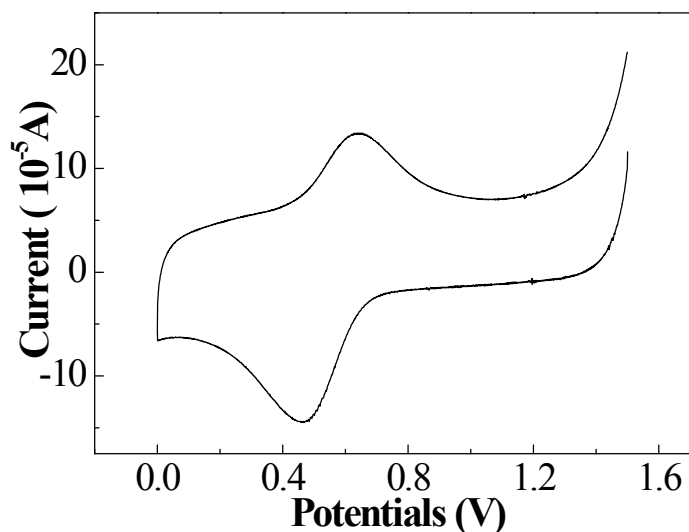


Figure S4 CVs of the MHPEC modified electrodes for detection of the residues of melamine in real milk.

6. Stability of MHPBC modified electrodes by CV

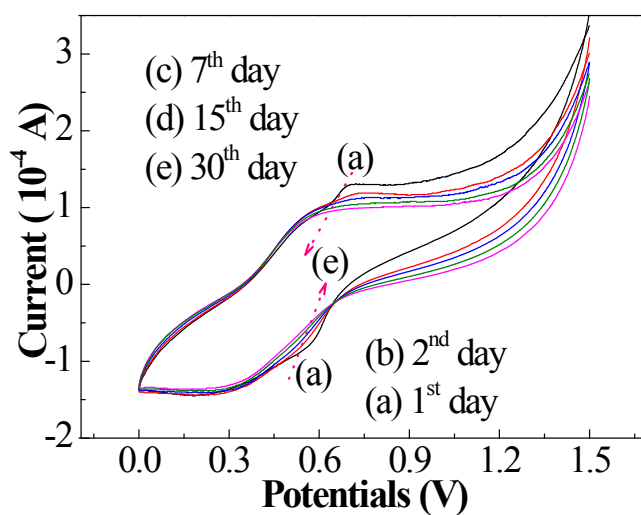


Figure S5 CVs of the MHPBC modified electrode sensors at various time intervals: (a) the 1st day, (b) the 2nd day, (c) the 7th day, (d) the 15th day, and (e) the 30th day, in PBS of pH 7.0 at a scan rate of 50 mV s⁻¹ (Melamine concentration: 4.2×10^{-6} mol l⁻¹).

7. Stability and reproducibility of modified electrodes by DPV

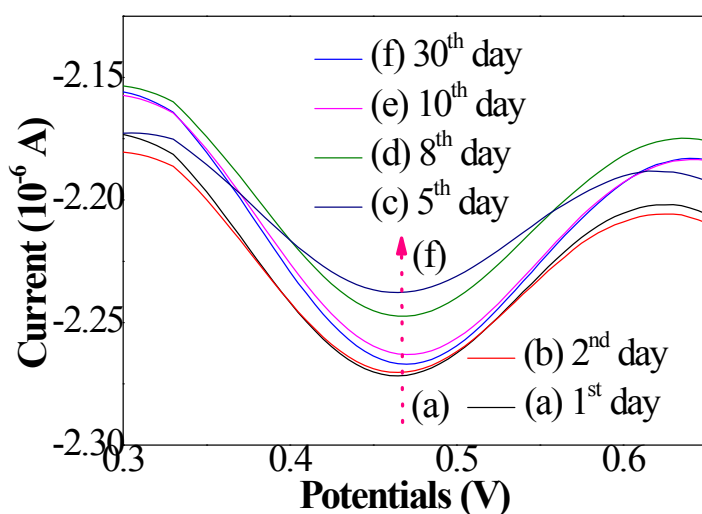


Figure S6 DPV profiles of the MHPBC sensors at various time intervals: (a) the 1st day, (b) the 2nd day, (c) the 5th day, (d) the 8th day, (e) the 10th day and (f) the 30th day, in PBS of pH 7.0 at a scan rate of 50 mV s^{-1} (Trichlorfon concentration: $1 \times 10^{-8} \text{ mol l}^{-1}$).

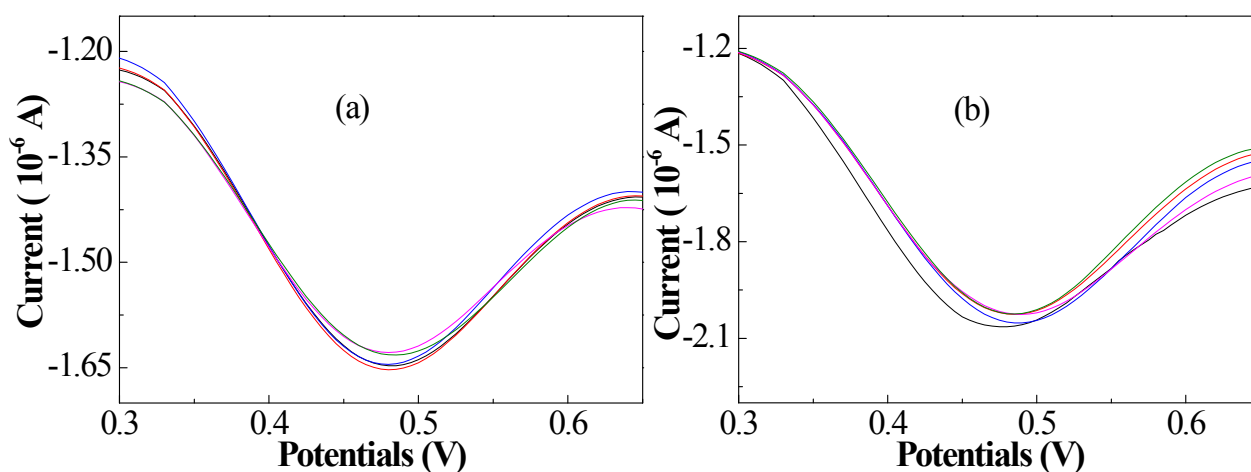


Figure S7 DPV profiles of (a) five measurements using the same MHPBC modified electrode in PBS of pH 7.0 (Trichlorfon concentration: $1 \times 10^{-12} \text{ mol l}^{-1}$) and (b) five MHPBC modified electrodes fabricated individually in PBS of pH 7.0 (Trichlorfon concentration: $1 \times 10^{-9} \text{ mol l}^{-1}$).

Table S2 Resistances (R) of the prepared nanohybrid composite samples with various spacers.

Samples	R1 (k Ω)	R2 (k Ω)	R3 (k Ω)	Mean R (k Ω)
MHPEC	10.62	10.58	10.55	10.58
MHPBC	2.56	2.53	2.52	2.54