Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Information

“One-Drop-of-Blood” Electroanalysis of Lead Level in Blood Using Foam-Like Mesoporous Polymer of Melamine-Formaldehyde and Disposable Screen-Printed Electrodes

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Experimental Section

Materials and Instruments

Chemical reagents

Melamine, paraformaldehyde, and lead nitrate were obtained from Aladdin Reagent Co. (Shanghai, China). Dimethylsulfoxide (DMSO), acetone, tetrahydrofuran (THF), and dichloromethane, sodium chloride and all other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and were of analytical grade. Deionized water (>18 Mohm) used was obtained from an Ultra-pure water system (Pall, USA).

Apparatus

All electrochemical experiments were carried out with a CHI830 electrochemical workstation (Chenhua

Instruments Co., Shanghai, China). Screen-printed carbon electrodes (SPEs) were obtained from Pine Instrument Company (PE, USA). Each of the SPEs consists of a miniaturized three-electrode system including an Ag/AgCl pseudo-reference electrode, and two carbon electrodes acting as working (3 mm diameter) and counter electrode, respectively.

Synthesis and modification of mPMF on SPEs

The mPMF was synthesized using a modified procedure reported previously [29-32]. Briefly, 0.756 g melamine and 0.324 g paraformaldehyde were dissolved in 10.0 mL anhydrous DMSO at 100 °C. The mixture was then sealed in the 25-mL Teflon container for the hydrothermal treatment at 170 °C for 72 h. Furthermore, after being cooled to room temperature, the product was crushed and filtered, followed by washing separately with DMSO, acetone, THF, and dichloromethane. Subsequently, the resulting white powder was dried at 80 °C for 24 h under vacuum. The so obtained product was characterized by using transmission electron microscopy (TEM, FEI Tecnai G20, USA).

An aliquot of 2.0 mg of mPMF was dispersed by ultrasoniction in 1.0 mL of chitosan (0.50 %, w/v) in acetic acid (2.0 %, v/v). The suspension (5.0 μL) was separately dropped on the surface of bare SPEs to be dried overnight at room temperature. The prepared mPMF-modified SPEs were used for the electroanalysis experiments. Characterizations of the mPMF-modified SPEs were performed by using scanning electron microscopy (SEM, Hitachi E-1010, Japan). In addition, the chitosan-modified SPEs were prepared accordingly by using 0.50 % chitosan (5 μL) for the comparison tests.

Electrochemical measurements

The Pb^{2+} detections were performed by electrochemical square wave voltammetry (SWV) by anodic stripping with optimized parameters. An aliquot of 50 μL standard solution or blood sample of Pb^{2+} ion with different concentrations was separately dropped onto the SPE covering all three electrodes. The accumulation potential (- 1.2 V) was applied to the SPE for 120 s. After a 10-sec quiet period at - 1.0 V, the potential was scanned from – 1.0 V to 0 V, showing the peak of Pb^{2+} ions at - 0.56 V, at a frequency of 25 Hz with a pulse amplitude of 25 mV and a potential step height of 2.0 mV. All of the experiments were conducted at room temperature.

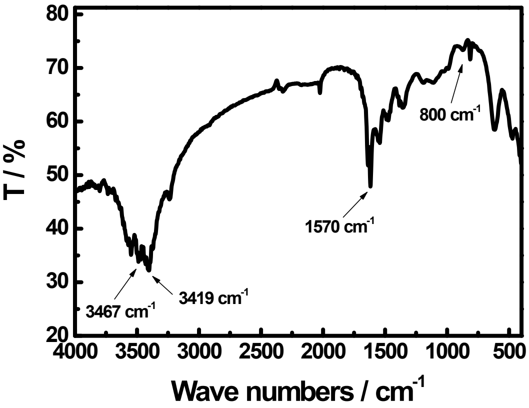

Fig. S1 IR spectrum of mPMF

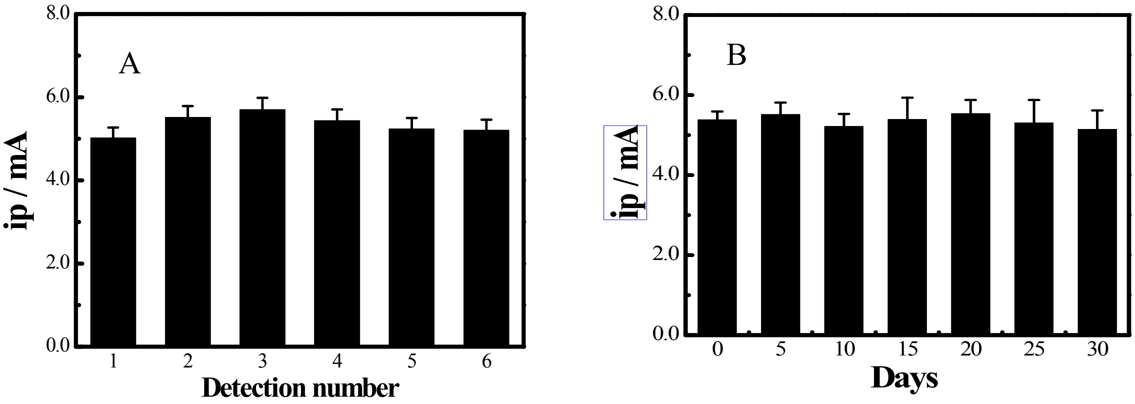

Fig. S2 (A) The detection reproducibility of the mPMF-modified SPEs for Pb^{2+} ions (40 μg L^{-1}) among six repetitions, and (B) the storage stability of the developed SPEs for sensing Pb^{2+} ions (40 μg L^{-1}) over different time intervals of storage.

Table S2 Comparison of the results of the electrochemical Pb^{2+} detection among the developed method and other anodic stripping techniques at the modified SPEs.

Materials modified on SPEs	**Method**[a]	**Deposition Potential (V)**	**Deposition Time (s)**	**Linear Range (μg L^{-1})**	**Detection Limit (μg L^{-1})**	**Ref.**[b]
Gold	SWV	- 0.5	120	0 - 50	0.50	1
ntimony and tin	DPV	- 1.4	240	5.0 - 45	0.90	2
4-Carboxy-phenyl diazonium	DPV	- 1.4	120	0 - 40	0.90	3
Bismuth	SWV	- 1.2	300	0.050 - 30	0.030	4
Bismuth /crown ether/Nafion	SWV	-1.2	180	5-600	1.1	5
Bismuth/graphene/poly(sodium 4-styrenesulfonate)	DPV	-1.3	120	0.5-120	0.089	6
Bismuth/graphene/ionic liquid	SWV	-1.2	120	1.0-80.0	0.10	7
Reduced graphene oxide/Bismuth	SWV	-1.2	150	1-60	0.80	8
Carbon nanotubes	SWV	-1.4	180	2-100	0.2	9
mPMF	SWV	-1.2	120	1.0-100.0	0.10	This work

[a] Differential pulse voltammetry (DPV) and square wave voltammetry (SWV).

[b] References:

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Table S1 Comparison of the recovery results of the detection Pb^{2+} ions in blood between the developed method and the AAS method in the clinical laboratory (n = 6).

Blood samples	Added (μg L^{-1})	Found (μg L^{-1})[a]	Recovery (%)[a]	Found (μg L^{-1})[b]
1	0	10.39 ± 0.43	–	9.51 ± 0.35
	20	32.36 ± 1.12	109.9 %	33.38 ± 0.53
2	0	N. D. [c]	–	N. D. [c]
	20	21.63 ± 0.75	108.2 %	23.24 ± 0.42
3	0	15.40 ± 0.52	–	16.22 ± 0.29
	20	34.73 ± 1.06	96.7 %	32.16 ± 0.48

[a] The developed method.

[b] The AAS method.

[c] Not detectable.