Supporting Information

An all-solid-state imprinted polymer-based potentiometric sensor for determination of bisphenol S

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Reagents and materials

Bisphenol S (BPS), 4,4'-sulfonyldiphenol, acetonitrile (ACN), sodium hydroxide, methanol, benzyl alcohol, zinc chloride and tetrahydrofuran (THF) were obtained from Guoyao Chemical Reagent Co., Ltd (Shanghai, China). Methacrylic acid (MAA), ethylene glycoldimethacrylate (EGDMA), 4-vinylpyridine (4-VP) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Aladdin Shanghai Reagent Company. High molecular weight poly(vinyl chloride) (PVC), dioctylphthalate (DOP), tridodecylmethylammoniumchloride (TDMAC) and tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) were purchased from Sigma-Aldrich. MAA and THF were distilled prior to use. All other reagents were analytical grade and used as received. Aqueous solutions were prepared by dissolving the appropriate salts in the freshly de-ionized water (18.2MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system.

Synthesis of the molecularly imprinted polymer (MIP)

The BPS MIP beads were synthesized by the precipitation polymerization method as described elsewhere.[1,2] The template BPS (1 mmol), MAA (2mmol), 4-VP (2 mmol), EGDMA (10 mmol) and AIBN (50 mg) were dissolved in ACN (25 mL) in a 50 mL flask. The solution was degassed with N_2 for 10 min and then sealed under N_2 atmosphere. The polymerization was performed by placing the flask in an oil bath at 60 °C for 18 h. After polymerization, the polymer particles were added to a mixture of methanol/1 M NaOH (75:25, *v*/*v*), and heated in reflux with stirring for 20 h to remove the template. The non-imprinted polymer (NIP) was synthesized by the similar procedures except for omission of the template. The obtained MIP and NIP beads were characterized by scanning electron microscopy (SEM; Hitachi, S-4800).

Fabrication of the nanoporous gold (NPG) film

The NPG film was fabricated by the multicyclic electrochemical alloying/dealloying method as described before.[3,4] Briefly, the alloying/dealloying process was carried out in a benzyl alcohol solution containing $ZnCl_2$ with a three-electrode system controlled by CHI 660C Electrochemical Workstation (CH Instruments Inc.). A freshly polished gold electrode was used as the working electrode. A Zn wire was utilized as the reference electrode, and a Zn plate served as the auxiliary electrode. The electrochemical cycles were first recorded at 120 °C from the open circuit potential to -0.72 V and then

repeatedly scanned in the potential range from -0.72 to 1.88 V (*vs* Zn). The obtained NPG film-based electrodes were finally washed with benzyl alcohol, ethanol, and de-ionized water in sequence.

Cyclic voltammetry (CV) was conducted in 0.5 M H_2SO_4 to characterize the real surface areas of the Au/NPG electrodes using a conventional three-electrode cell comprising the NPG film-based gold electrode as the working electrode, a Ag/AgCl/3 M KCl electrode as the reference electrode and a platinum wire as the auxiliary electrode.

Preparation of the solid-contact electrodes

The membrane cocktail was prepared by dissolving 360 mg of components in 4.5 mL THF: MIP or NIP (6.0 wt%), TDMAC (1.5 wt%), ETH 500 (2.0 wt%), PVC (35.9 wt%), and DOP (54.6 wt%), and then degassed by sonication for 10 min. 100 μL membrane cocktail was drop-cast onto the NPG film-based electrode and allowed to dry for 2 h. For comparison, the coated-wire electrode (CWE) was fabricated with the membrane cocktail directly casted on the polished gold electrode. For potentiometric detection of deprotonated BPS, the electrodes were conditioned in 10^{-4} M BPS in 30 mM $NaHCO_3/Na_2CO_3$ buffer of pH 10.2 for one day, while for neutral BPS, the electrodes were conditioned in 30 mM phosphate buffer solution (PBS) buffer with a pH of 5.0 for one day.

Electromotive force (EMF) measurements

All measurements of EMF were performed at 20 ± 1°C using a PXSJ-216L pH meter (Leici, Shanghai) with a saturated calomel electrode (SCE) as reference electrode in the galvanic cell: SCE//sample solution/ISE membrane/NPG film/bare gold electrode. For determination of deprotonated BPS, the EMF values were corrected for the liquid-junction potential according to the Henderson equation. The ion activity coefficient was calculated from the modified Debye-Hükel equation.[5]

References for the Supporting Information:

1. K. Yoshimatsu, K. Reimhult, A. Krozer, K. Mosbach, K. Sode and L. Ye, *Anal. Chim. Acta*, 2007, **584**, 112-121.
2. L. J. Kou, R. N. Liang, X. W. Wang, Y. Chen and W. Qin, *Anal. Bioanal. Chem.*, 2013, **405**, 4931-4936.
3. F. L. Jia, C. F. Yu, Z. H. Ai and L. Z. Zhang, *Chem. Mater.*, 2007, **19**, 3648-3653.
4. T. J. Yin, D. W. Pan and W. Qin, *Anal. Chem.*, 2014, **86**, 11038-11044.
5. S. Kamaata, A. Bhale, Y. Fukunaga and H. Murata, *Anal. Chem.*, 1988, **60**, 2464-2467.

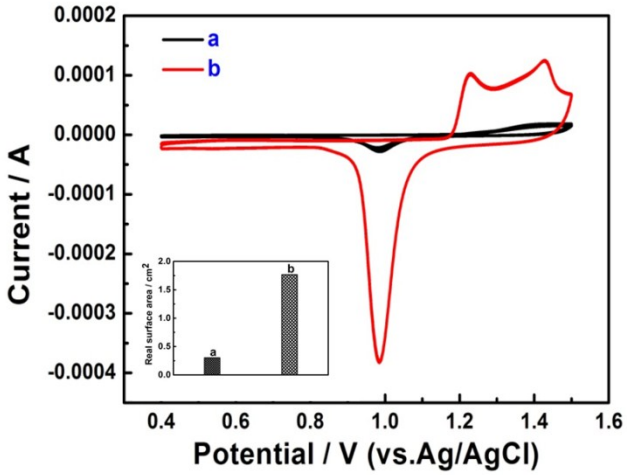

Fig. S1 CVs for the bare Au electrode (a) and the Au/NPG electrode (b) recorded in 0.5 M H_2SO_4at a scan rate of 10 mV/s.

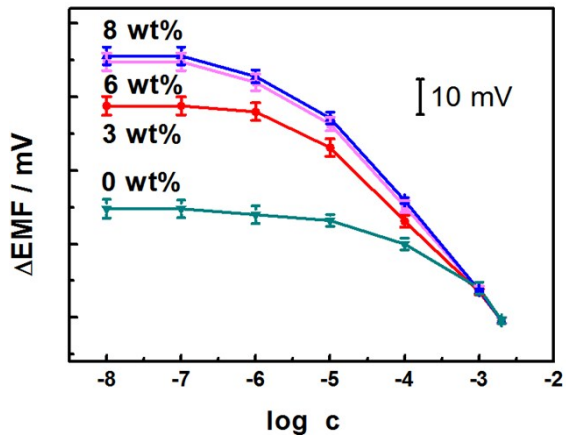

Fig. S2 Effect of the amount of MIP on the potential response to deprotonated BPS. Experimental conditions: detection background, 30 mM $NaHCO_3/Na_2CO_3$ buffer of pH 10.2; conditioning solution, 10^{-4} M BPS in 30 mM $NaHCO_3/Na_2CO_3$ buffer of pH 10.2. Error bars represent one standard deviation for three measurements.

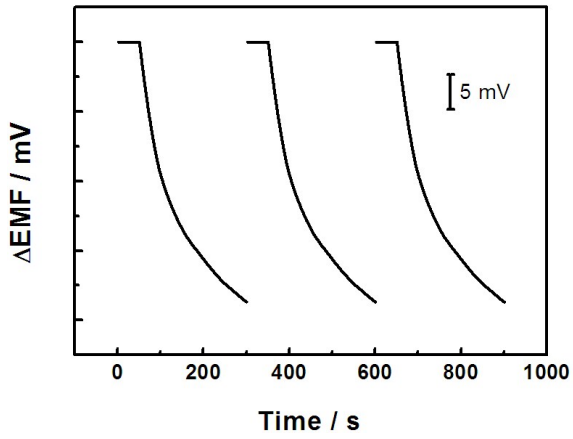

Fig. S3 Recycle potential response profiles for 10 μM neutral BPS. Experimental conditions: detection background, 30 mM PBS with a pH of 5.0; conditioning solution, the same as the detection background.

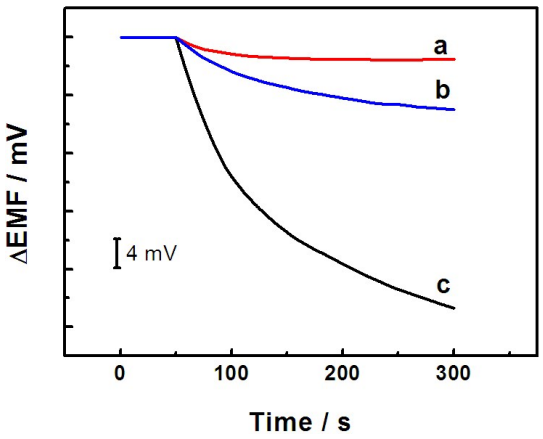

Fig. S4 Dynamic potential responses to neutral BPS of 10 μM using the blank (a), NIP (b) and MIP (c) membrane-based electrodes. Membrane ingredients (in wt%): (1) blank membrane, 1.5 % TDMAC, 2.0 % ETH 500, 38.3 % PVC and 58.2 % DOP; (2) NIP membrane, 1.5 % TDMAC, 2.0 % ETH 500, 35.9% PVC, 54.6 % DOP and 6.0 % NIP; (3) MIP membrane, 1.5 % TDMAC, 2.0 % ETH 500, 35.9% PVC, 54.6 % DOP and 6.0 % MIP. Other conditions are as given in Fig. S3.

Table S1 Application of the proposed sensor to determination of neutral BSA in BPA-free baby bottles

Sample	Proposed sensor (μM)[a]	HPLC (μM)[a]	Recovery results		
			Added (μM)	Found (μM)[a]	Recovery (%)
Sample 1	0.18 ± 0.04	0.22 ± 0.05	0.40	0.59 ± 0.04	95
			0.60	0.80 ± 0.03	98
			0.80	1.03 ± 0.01	101
Sample 2	0.26 ± 0.01	0.24 ± 0.03	0.40	0.60 ± 0.05	94
			0.60	0.83 ± 0.01	99
			0.80	1.05 ± 0.02	101

[a] Average of three measurements ± standard deviation.