

# Supporting Information

## A novel electrochemical sensor based on nafion stabilized Au(I)-Alkanethiolate nanotubes modified glassy carbon electrode for detection of Hg<sup>2+</sup>

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### 1. Experimental section

#### Reagents and apparatus

Stock solution of 0.01 M Hg(NO<sub>3</sub>)<sub>2</sub> was prepared in deionized water. The other used metal salts, i.e. Ba(NO<sub>3</sub>)<sub>2</sub>, CoCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, FeCl<sub>3</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> were of analytical grade and used as received without further purification. All the voltammetric determinations were carried out with a CHI 660D electrochemical workstation. A conventional three-electrode system was used that consisted of glassy carbon electrode (GCE, 5.0 mm diameter), a platinum wire auxiliary electrode and a Ag/AgCl reference electrode.

#### Synthesis of Au(I)-nanotubes

Au(I)-nanotubes (Au(I)NTs) was prepared according to the previous report.[1] Typically, 1 mL of a tetrachloro-aurate trihydrate (HAuCl<sub>4</sub>, 0.03 M, in deionized water) mixed with 1 mL of 1-dodecanethiol (DDT, C<sub>12</sub>H<sub>25</sub>SH, 0.1 M, in ethanol), and the mixture was foggy due to the presence of strongly hydrophobic C<sub>12</sub>H<sub>25</sub>SH. Afterwards, 1 mL NaOH (1 M, in deionized water) was added under vigorous stirring conditions. After vigorous stirring for 2 h, pale-yellow products were separated by centrifugation, and washed by ethanol to remove the excess surfactants. The residue was resolved in ethanol, and the concentration is a about 6 mg/mL. The structure and the average size of the as-prepared Au(I)NTs were characterized by TEM.

#### Preparation of electrode

A bare GCE (5.0 mm diameter) was polished to a mirror like surface with 0.3 and 0.5 μm alumina powder followed by rinsing thoroughly with deionized water, then sonicated in 1:1 nitric acid (V/V for HNO<sub>3</sub>:H<sub>2</sub>O) and deionized water, then dried at room temperature. The cleaned electrode was modified with nafion stabilized Au(I)NTs by a simple casting method. Typically, 5

1  $\mu\text{L}$  0.5 wt% nafion ethanol solution and 10  $\mu\text{L}$  prepared Au(I)-nanotubes solution were mixed,  
2 then the mixture was cast on the electrode surface and the electrode was allowed to dry at room  
3 temperature to obtain a Nf-Au(I)NTs modified electrode. The surface of the bare GCE and the  
4 modified electrode were characterized by SEM.

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### 6 **Detection of $\text{Hg}^{2+}$**

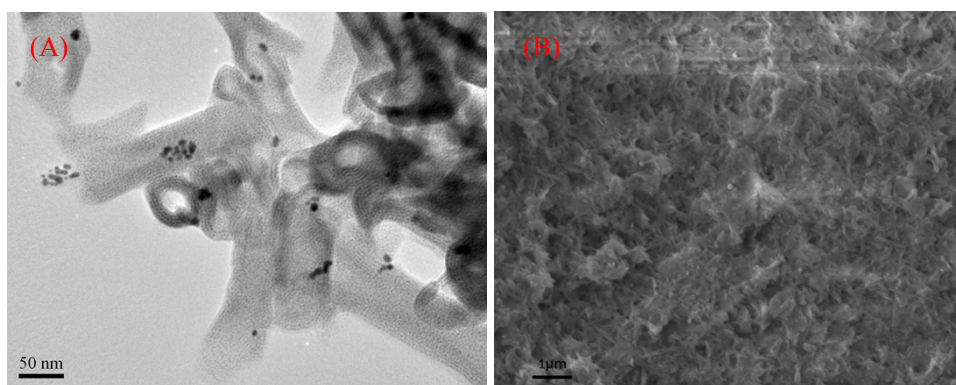
7 Different concentrations of  $\text{Hg}^{2+}$  solution were prepared in 0.1 M  $\text{HNO}_3$  solution, and then  
8 accumulated at  $-0.60$  V for 500 seconds while stirring the solution. The solution was then left for  
9 30 s and the square wave anodic stripping voltammetry (SWASV) measurements were performed  
10 in the potential range from  $-1.0$  to  $+0.60$  V with a frequency of 30 Hz, amplitude of the square  
11 wave of 25 mV, and a potential step of 4 mV. The peak heights were measured at  $-0.20$  V. All  
12 experiments were conducted at room temperature.

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### 14 **2. Characterization of Au(I) alkanethiolate nanotubes**

15 Fig.S1A shows the TEM image, the diameter of the as papered Au(I)NTs is about 15-35nm, and  
16 the ends of the nanotubes are open. As illustrated in Fig.S1B, the surface of the nafion stabilized  
17 Au(I)NTs modified electrode are evenly coated with the nanomaterials.

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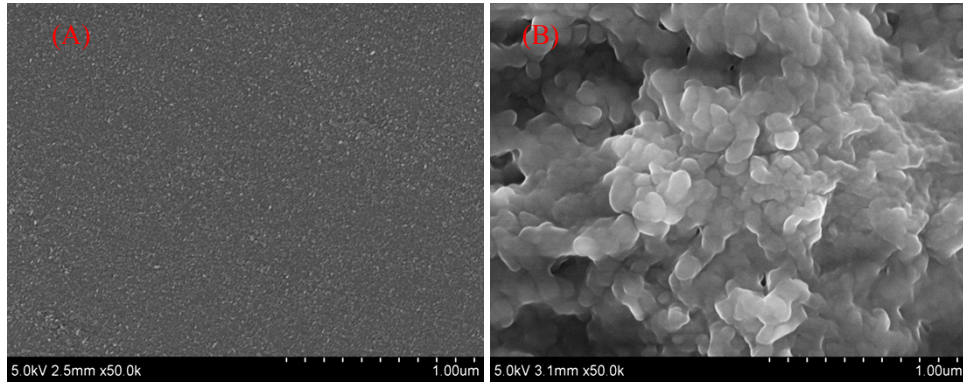
20 **Fig. S1** Typical TEM images of Au(I) alkanethiolate nanotubes(A), and the surface of the nafion  
21 stabilized Au(I)NTs (B).

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### 23 **3. Characterization of the modification of GCE**

24 Fig. S2 shows the SEM images of GCE before (Fig.S2A) and after (Fig.S2A) the modification.  
25 As shown in Fig. S2, the Nf-Au(I)NTs composite can greatly enhance the electrochemically active  
26 surface area of the modified electrode.

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**Fig. S2** Typical SEM images of bare GCE (A), and the surface of the Nf-Au(I)NTs modified electrode (B).

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5 **4. The reproducibility of current response at different modified electrodes**

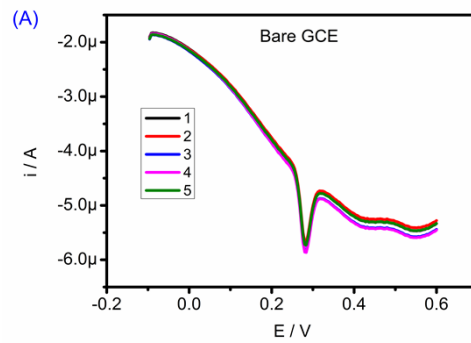
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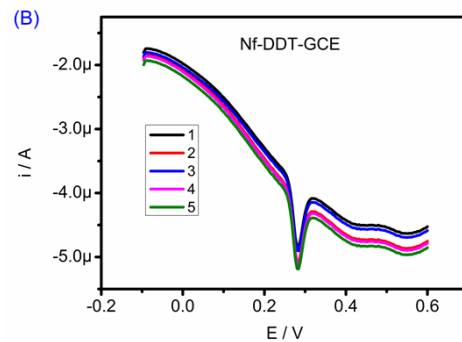
Fig. S3 shows five independent measurements of SWASV response for 50 nM  $\text{Hg}^{2+}$  at bare (A), Nf-DDT- (B) and Nf-Au(I)NTs- (C) modified GCE. These results indicate that our proposed approach has a good reproducibility for the detection of  $\text{Hg}^{2+}$ .

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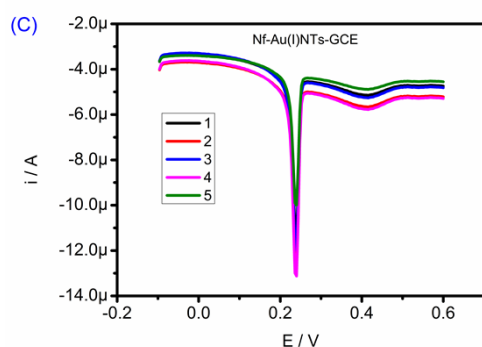
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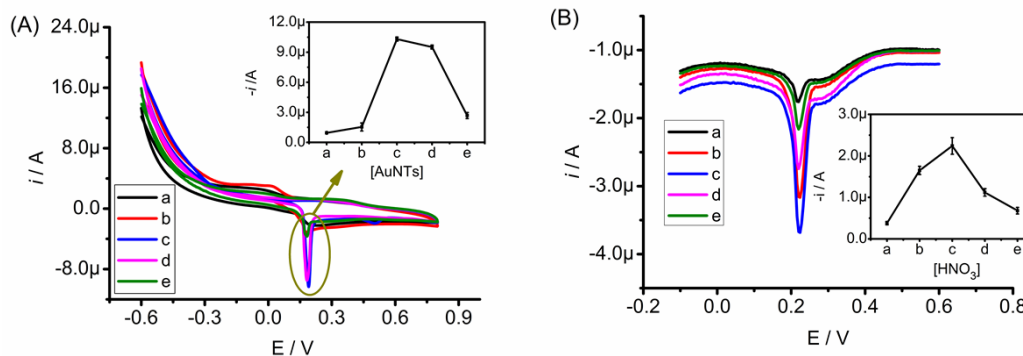


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2 **Fig. S3** Five independent measurements of SWASV response for 50 nM  $\text{Hg}^{2+}$  at bare (A), Nf-  
 3 DDT- (B) and Nf-Au(I)NTs- (C) modified GCE. SWASV conditions: quiet time, 10 s; frequency,  
 4 30 Hz; potential increment, 4 mV; amplitude of the square wave, 25 mV.

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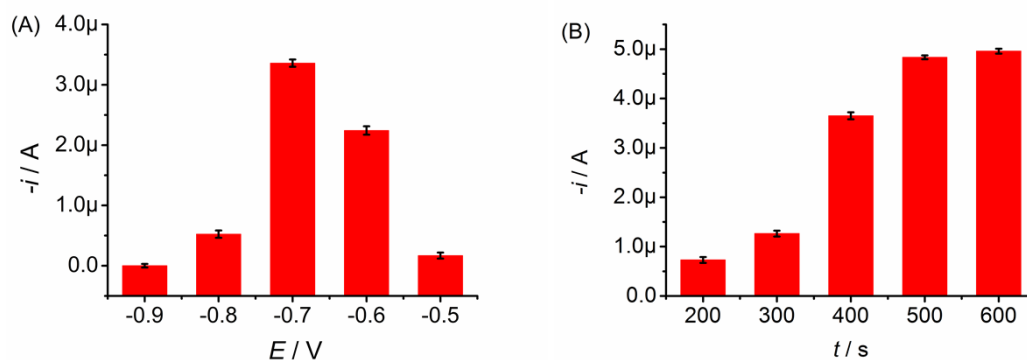
## 6 5. Conditions optimization



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8 **Fig. S4** (A) CV response for 10  $\mu\text{M}$   $\text{Hg}^{2+}$  solution using different volume of AuNTs (a~e: 0, 5, 10, 20,  
 9 40  $\mu\text{L}$ ) modified electrodes; (B) SWASV response for 50 nM  $\text{Hg}^{2+}$  at different concentration of  $\text{HNO}_3$   
 10 (a~e: 0, 0.05, 0.1, 0.25, 0.5 M) using GCE/Nf-DDT.

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12

13 **Fig. S5** Effects of (A) deposition potential and (B) deposition time on the peak currents of 50 nM  
 14  $\text{Hg}^{2+}$  at GCE/Nf-Au(I)NTs in 0.1 M  $\text{HNO}_3$  solution. SWASV conditions: quiet time, 10 s;  
 15 frequency, 30 Hz; potential increment, 4 mV; amplitude of the square wave, 25 mV.

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## 17 6. Determination of $\text{Hg}^{2+}$ in tap water

1 For tap water, the sample was collected after discharging tap water for about 20min.

2 **Table S1.** Detection of Hg<sup>2+</sup> in tap water samples using the proposed method (n = 5).

Sample	Background	Concentration		Recovery	RSD
	content /nM	Added / nM	Found / nM	/ %	/ %
Tap water 1	ND	20	23	115.0	5.2
Tap water 2	ND	50	46	92.0	4.7
Tap water 3	ND	200	187	93.5	3.6
Tap water 4	ND	500	492	98.4	4.2

3 ND: Not Detected

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## 5 **7. Comparison of reported electrochemical methods with the present method for** 6 **Hg<sup>2+</sup> detection**

7 Table S2 shows the comparison of this method for the detection of Hg<sup>2+</sup> with some other  
8 electrochemical techniques. As can be seen, the limit of LOD of this method is 0.5 nM, which is  
9 satisfactorily lower than the guideline value of 6 ppb in drinking water given by the World Health  
10 Organization. More importantly, the preparation of this modified GCE is very simple, and this  
11 method shows high selectivity for detection Hg<sup>2+</sup>.

12 **Table S2** Comparison of reported electrochemical methods with the present method for Hg<sup>2+</sup>  
13 detection

Detection method	Technique in detail	Linear range (nM)	Detection limit (nM)	Selectivity [Ion]/[Hg <sup>2+</sup> ]	RSD (%)	Ref.
DPV <sup>a</sup>	GCE <sup>b</sup> /AuNPs <sup>c</sup> -GO <sup>d</sup> -IL <sup>e</sup>	0.1–100.0	0.03	50	2.66–9.07	[2]
DPV	ITO <sup>f</sup> /GO-AuNPs-MTU <sup>g</sup>	5.0–110.0	0.78	50	3.3–5.2	[3]
DPV	GCE/IIP <sup>h</sup> -MWCNTs <sup>i</sup>	10-	5.0	100–500	1.9	[4]
SWASV <sup>j</sup>	GCE/PPy <sup>k</sup> -RGO <sup>l</sup>	10.0-	15.0	40–70	-	[5]
SWASV	GCE/Nf <sup>m</sup> -Au(I)NT <sup>n</sup>	1-100 100-1000	0.5	100	3.6-5.2	<b>This method</b>

14 <sup>a</sup> DPV (differential pulse voltammetry), <sup>b</sup> GCE (glassy carbon electrode), <sup>c</sup> AuNPs (gold  
15 nanoparticles), <sup>d</sup> GO (graphene oxide), <sup>e</sup> IL (ionic liquid), <sup>f</sup> ITO (indium tin oxide), <sup>g</sup> MTU (5-  
16 methyl-2-thiouracil), <sup>h</sup> IIP (ion imprinted polymeric nanobeads), <sup>i</sup> MWNTs (multi-wall carbon  
17 nanotubes); <sup>j</sup> SWASV (square wave anodic stripping voltammetry), <sup>k</sup> PPy (polypyrrole), <sup>l</sup> RGO  
18 (reduced graphene oxide), <sup>m</sup> Nf (Nafion), <sup>n</sup> Au(I)NT (Au(I)-alkanethiolate nanotubes)

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## 21 **Reference**

22 [1] Y. X. Zhang, H. Ch. Zeng, *Adv. Mater.*, 2009, **21**, 4962;

23 [2] N. Zhou, J. Li, H. Chen, C. Liao, L. Chen, *Analyst*, 2013, **138**, 1091;

24 [3] N. Zhou, H. Chen, J. Li, L. Chen, *Microchim Acta*, 2013, **180**, 493;

25 [4] H. R. Rajabi, M. Roushani, M. Shamsipur, *J. Electroanal. Chem.*, 2013, **693**, 16;

1 [5] Z.-Q. Zhao, X. Chen, Q. Yang, J.-H. Liu, X.-J. Huang, *Chem. Commun.*, 2012, **48**, 2180.