Supplementary Information

1. Experimental Section

Chemicals and Reagents. 3-aminopheylboronic acid (APBA), N-(3-Dimethy-laminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI) and Alizarin Red S (ARS) were obtained from Sigma-Aldrich Chemical Co., USA. MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). Astragaloside IV, ononin and formononetin were bought from Chenming Reagent Co., Ltd. (Sichuan, China). In addition, glucose and sucrose were obtained from Sinopharm Chemical Regent Co., Ltd.. All other reagents and solvents were of analytical grade and used without further purification. Double-distilled water was used for preparation of all solutions and for washing.

Apparatus and Instruments. FT-IR spectra were obtained from Nicolet Nexus 670 spectrometer. TEM analyses were carried out with JEOL-JEM2010 electron microscope. And UV-vis absorption spectra were recorded on CARY-50 Conc spectrometer. Electrochemical measurements were performed at 25℃ on CHI660C electrochemical workstation (Shanghai Chenhua Instruments Co., Shanghai, China). A three-electrode configuration was employed, consisting of a bare, MWCNTs-COOH or APBA/MWCNTs modified GC electrode (d=3mm) as the working electrode, a platinum wire and a saturated calomel electrode (SCE) (Jiangsu Electroanalytical Instruments Factory, China) as the auxiliary electrode and reference electrode, respectively. To clean the bare GC electrode, the surface of the electrode was polished with alumina slurry firstly, and then soaked alternately in HNO_3, alcohol and distilled water using an ultrasonic bath for 3 minutes for each. After that, the electrode was electrochemically cleaned by cycling with potentials between 0.2 and -1.2V in 0.1 M PBS solution (pH=7.4) until a stable voltammogram was obtained. Furthermore, the 10 mg/ml suspension of the corresponding MWCNTs-COOH or APBA/MWCNTs in DMF (50μL) and chitosan (150μL) was prepared and 2.5 μl of the obtained mixture was casted on the cleaned GC. Then, the modified electrode was dried under the infrared lamp for 10 min. Both MWCNTs-COOH and APBA/MWCNTs modified electrodes were achieved for the following experiments. Electrochemical measurements to characterize APBA/MWCNTs materials and detect astragoloside IV were all carried out in 0.1 M phosphate buffer solution (PBS, pH=7.4) at room temperature (25℃). Cyclic voltammetry was performed from 0.2 to -1.2 V at a scan rate of 100 mV/s.

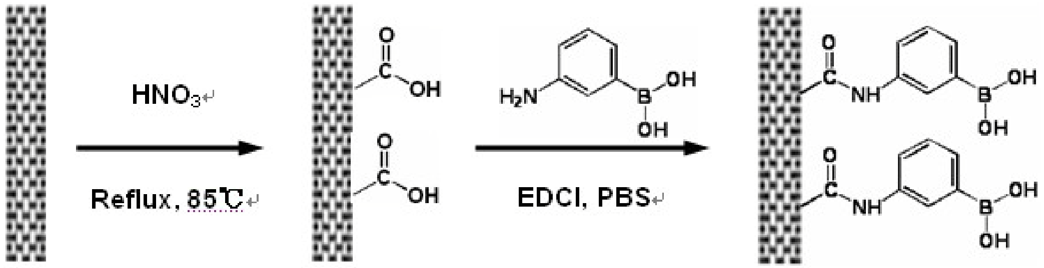
Preparation of the APBA/MWCNTs probe. The boronic acid-functionalized MWCNTs (APBA/MWCNTs) was synthesized as Scheme S1. Firstly, the carboxylic acid- functionalized MWCNTs (MWCNTs-COOH) were obtained according to the reference.[1] Then APBA (0.1g, 0.6mM) was added to the solvent of 15mL of PBS (pH=4.8) in a three-necked flask purged with N_2 under magnetic stirring and cooled to 4℃ in the ice bath. After MWCNTs-COOH (1.35g, 0.6mM) was dispersed in 15mL of PBS (pH=4.8) and cooled to 4℃ in refrigerator, it was added into the above three-necked flask. Followingly, EDCI (0.115g, 0.6mM) was also added into the flask. The mixture was firstly stirred for 1h in ice bath and then for another 12h at room temperature. At last, the mixture was filtrated, washed with distilled water for 5 times and the resulting solid was dried overnight in a vacuum oven. As a result, the boronic acid- functionalized MWCNTs were obtained. FT-IR spectrometer and transmission electron microscopy (TEM) were employed to confirm the success of boronic acids modification to the surface of MWCNTs.

In real medicine detection. Bao’erning Keli and Huang Qi Jing are chosen as the medicine samples, which are the Chinese patent medicines that are usually used to cure the weakness of spleen and stomach. Both of the medicines contain astragaloside IV as the active ingredient. The medicine samples were purchased from drugstore. Prior to determination, pretreatment of the real samples was necessary. 10 g of the materials of Bao’erning Keli were dissolved in 30mL of methanol in 50mL iodine flask. The mixture solutions were ultrasonicated for 30 min and then filtered through a 0.45μm polycarbonate membrane. By reduced pressure distillation, the solvent was removed from the filtrate and a little solid residue was obtained. Then the residue was dissolved in 15mL of distilled water and leached by 20mL of water saturated butanol four times. The extractions were merged and washed by 30mL of ammonia two times. After that, the butanol was removed by reduced pressure distillation after the removal of ammonia and a little solid was obtained. Finally, it was dissolved in 60 μL methanol, and 1μL of the solution was added into 5 mL PBS (pH=7.4) before detection.

Reference:

(1) X. W. Kan; Y. Zhao; Z. R. Geng; Z. L. Wang. J. J. Zhu; J. Phys. Chem. C **2008**, *112*, 4849-4854

2. Functionalization of MWCNTs with APBA



Scheme S1. Chemical routes for the preparation of APBA functionalized MWCNTs.

3. FT-IR spectra

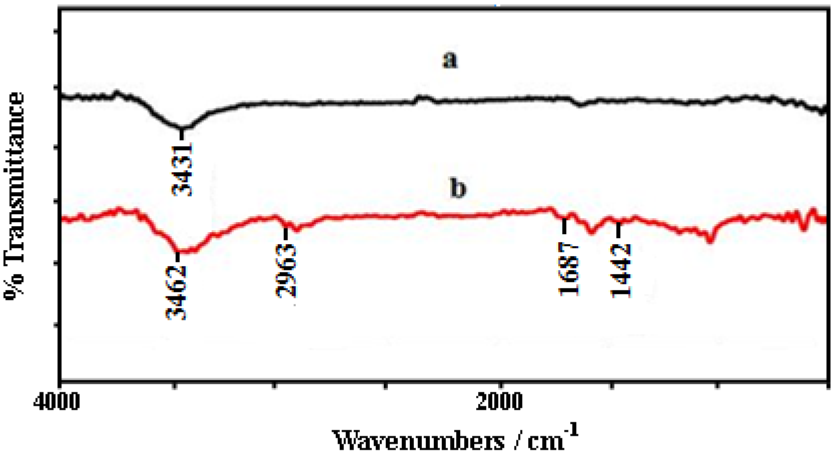


Figure S1. FT-IR spectra of (a) MWCNT-COOH; (b)APBA/MWCNTs.

The MWCNTs-COOH and APBA/MWCNTs were characterized by FTIR. A broad band at ～3431 cm^{-1} (curve a) is attributed to the hydroxyl stretching vibration, which confirmed the oxidation process of MWCNTs. Appearance of band at ～3300-3600 cm^{-1} (curve b) is due to the N-H stretch overlapped with O-H stretching vibration and the brand at ～2963 is attributed to the C-H stretching vibration of phenyl ring. The confirmation of the binding between MWCNTs-COOH and APBA is the presence of new bands at ～1687 cm^{-1} and ～1442 cm^{-1}, corresponding to amide carbonyl C=O and C-N bond stretching .

4. Electrochemical behavior of APBA and ARS

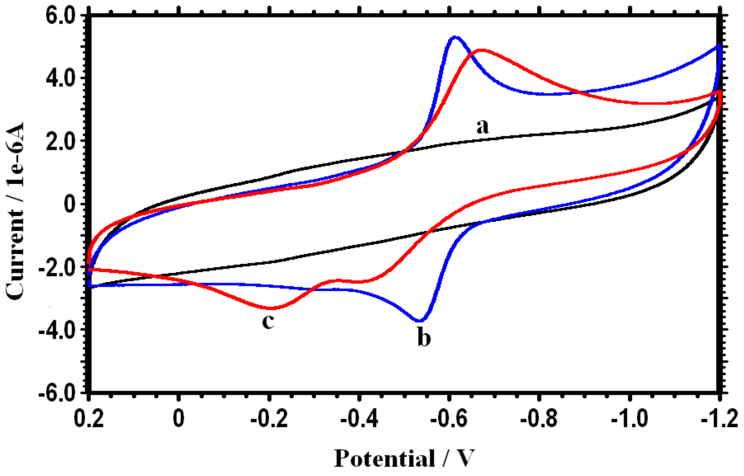


Figure S2. Cyclic voltammograms of a) 0.4 mM APBA, b) 0.4 mM ARS, c) 0.4mM APBA and 0.4 mM APBA in 0.1M PBS (pH=7.4) on bare electrode.

5. Electrochemical behavior MWCNTs-COOH and APBA/MWCNTs-COOH

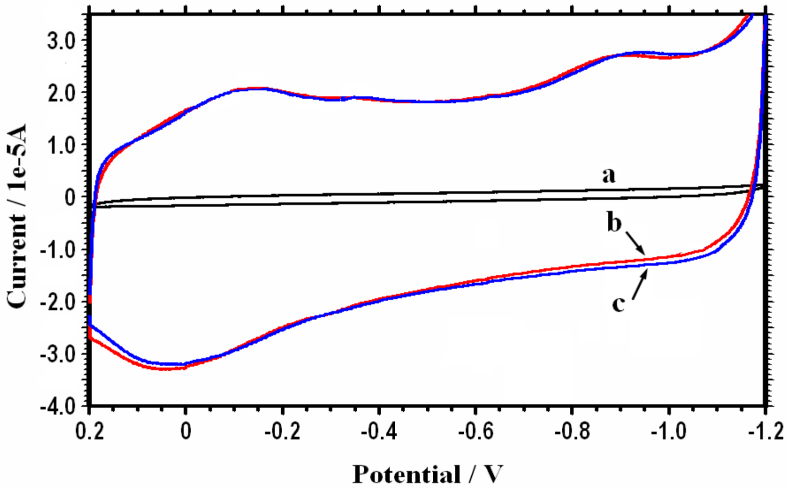


Figure S3. Cyclic voltammograms of a) bare GC electrode, b) MWCNTs-COOH and c) APBA/MWCNTs modified GC electrodes in 0.1M PBS (pH=7.4).

6. Structure of the five compounds

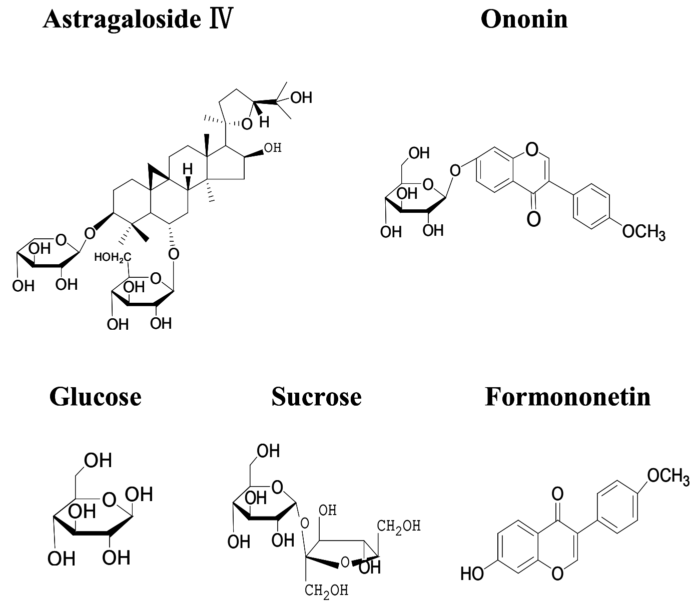


Figure S4. Structure of the five compounds

7. Linearity of Electrochemical Sensor for Astragaloside IV

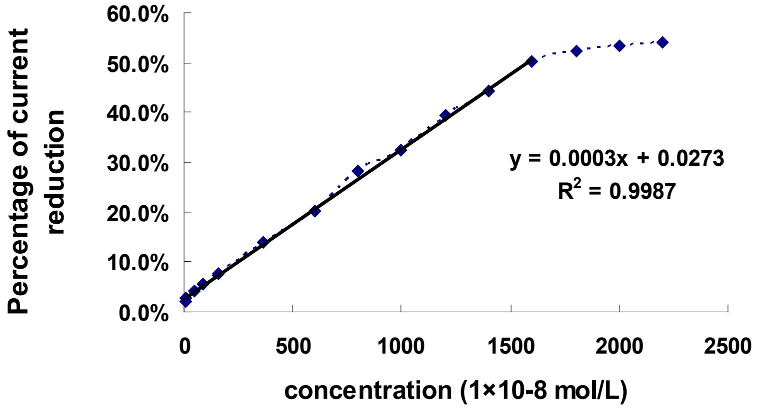


Figure S5. Calibration curve of astragaloside IV concentration was 0.04, 0.08, 0.5, 0.9, 1.6, 3.6, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 22.0 μM, (from bottom to top), respectively.

8. The application of the sensor in real medicine detection

Table S1. Detection of astragaloside IV in real medicine samples

Samples	**Current Reduction (%)**	**Concentration**	**Concentration (Literature data)**	**RSD**
Bao'erning Keli	**9.18**	**6.4×10^{-8} mol/g**	**6.8×10^{-8} mol/g**	**3.3%**
Huangqi Jing	**19.2**	**1.64×10^{-4} mol/L**	**1.70×10^{-4} mol/L**	**3.8%**