

Supplementary Material for

Sensitive Dopamine Recognition by Boronic Acid Functionalized Multi-Walled Carbon Nanotubes

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S-1. Experimental Section

General

MWNTs were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). 2,2'-(Ethylenedioxy)diethylamine, Di-*tert*-butyl dicarbonate and *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) were obtained from Fluka. 4-Carboxyphenylboronic acid was obtained from Aldrich. Dopamine and L-Ascorbic acid were purchased from Sigma and Acros, respectively. All other reagents and solvents were obtained from commercial suppliers and used without further purification. XPS analyses were carried out on Surface Analysis PHI5600. TGA was recorded on TGA7 Perkin Elmer. TEM observations were conducted on JEOL2010F microscope operating at 200 kV. SEM analyses were performed on JEOL6700 at an accelerating voltage of 5 kV. The electrochemical measurements were performed with a three-electrode system. The GC and MWNTs modified GC electrodes were used as the working electrodes. A Pt-wire electrode served as the counter electrode, and a saturated KCl-Ag|AgCl electrode was used as the reference. All electrochemical experiments were carried out using CHI610B (Austin, USA) in the 0.1 M phosphate buffer (pH = 7.0) solutions that were thoroughly deaerated with high purity nitrogen before use at ambient temperature. CVs were measured at a scan rate of 100 mV s⁻¹. DPV were recorded under the following input parameters: scan rate 20 mV s⁻¹, pulse amplitude 50 mV, pulse width 50 ms, pulse period 200 ms.

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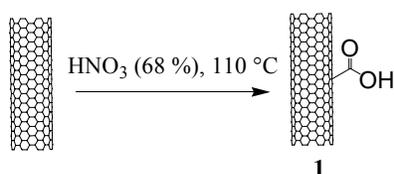
^b Beijing Normal University.

Electrode Preparation

A glassy carbon (GC) disk (3 mm diameter) was used as the working electrode. To clean the electrode, the surface of the GC electrode was polished with chamois leather soaked with alumina slurry and washed in an ultrasonic bath for a few minutes. Thereafter, the electrode was electrochemically cleaned by cycling with potentials between 1.6 and -0.4 V in a 0.5 M H₂SO₄ solution until a stable voltammogram was obtained. The GC electrode was used after washing with water by sonication. For preparation of the pristine MWNTs or MWNTs **3** modified GC electrodes, 1 mg/ml suspension of the corresponding MWNTs in acetone was prepared. The GC electrode was then cast with 10 μ l of the obtained MWNTs or MWNTs **3** suspension and dried in air before use. Both MWNTs and MWNTs **3** modified electrodes are very stable in the process of measurement.

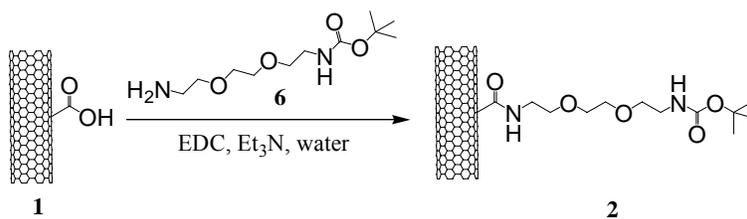
Synthesis

1. Oxidization of MWNTs



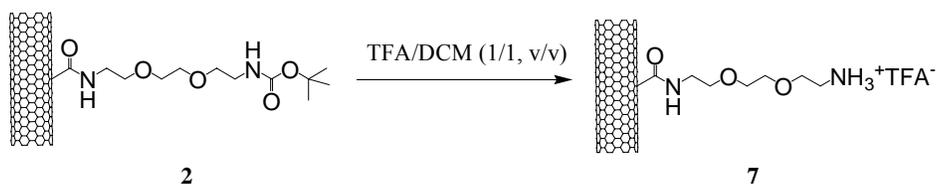
200 mg of MWNTs were suspended in 30 ml of HNO₃ (68 %) by sonication. The resultant mixture was stirred at 110 °C for 12 hr. After dilution with water, the mixture was filtered through a polycarbonate filter (Whatman, pore size 200 nm) and rinsed thoroughly with water. MWNTs **1** were obtained as a suspension in water.

2. Derivatization of MWNTs



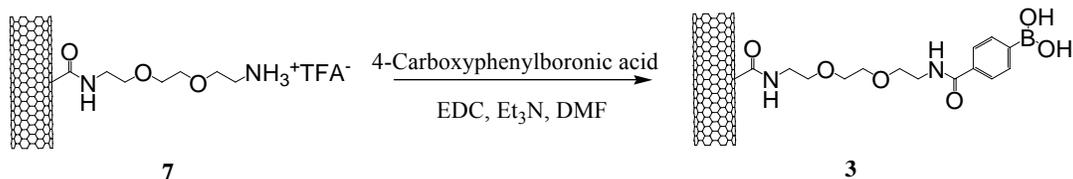
To a suspension of 20 mg of oxidized MWNTs **1** in 5 ml of water, were added 74.7 mg of **6**¹, 57.5 mg of EDC and 50 μ l of triethyl amine (Et₃N). The mixture was stirred at room temperature overnight under argon. After evaporation of the water under vacuum, the excessive of **6** was removed by washing with methanol several times and the removal was monitored by thin-layer chromatography (TLC) (eluant: dichloromethane (DCM)/methanol/Et₃N 8/2/0.1).

3. Cleavage of the *tert*-butyloxycarbonyl (Boc) groups from MWNTs 2



18 mg of MWNTs 2 were added to a solution of 3 ml of trifluoroacetic acid (TFA) in 3 ml of DCM. After sonication for few minutes, the resulting mixture was stirred at room temperature under argon for 5 hr. After removal of the solvents by evaporation under vacuum, the black solid was washed with methanol several times.

4. Functionalization of MWNTs with boronic acid



37.3 mg of 4-carboxyphenylboronic acid, 43.1 mg of EDC and 10 μ l of triethyl amine were added to a suspension of 15 mg of MWNTs 7 in 5 ml of *N,N*-Dimethylformamide (DMF). The resultant mixture was stirred at room temperature under argon overnight. After evaporation of the solvent under vacuum, the solid was washed with methanol thoroughly by centrifugation. The MWNTs 3 were afforded as a black solid.

References

- (1) Kordatos, K.; Ros, T. Da; Bosi, S.; Vazquez, E.; Bergamin, M.; Cusan, C.; Pellarini, F.; Tomberli, V.; Baiti, B.; Pantarotto, D.; Georgakilas, V.; Spalluto, G.; Prato, M. *J. Org. Chem.* **2001**, *66*, 4915-4920.

S-2. Additional Data

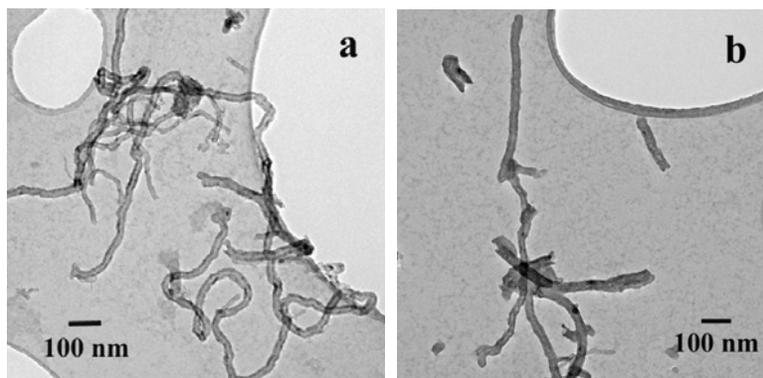


Figure S1. TEM images of pristine MWNTs (a) and MWNTs **1** (b).

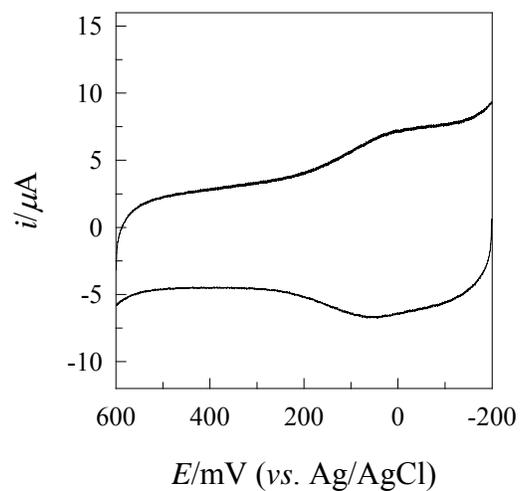


Figure S2. Cyclic voltammogram of MWNTs **3** modified GC electrode in 0.1 M phosphate buffer (pH = 7.0).

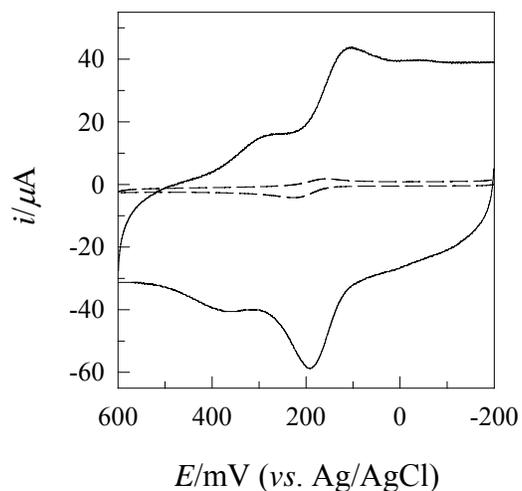


Figure S3. Cyclic voltammograms of 0.1 mM DA in 0.1 M phosphate buffer (pH = 7.0) on a bare GC electrode (dash line) and MWNTs **3** modified GC electrode (solid line).

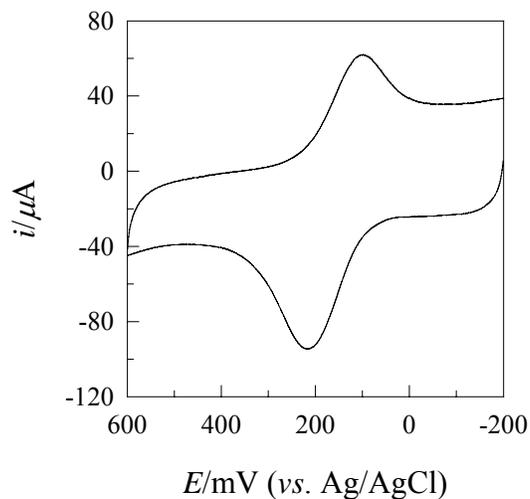


Figure S4. Cyclic voltammogram of 0.5 mM DA in 0.1 M phosphate buffer (pH = 7.0) on a pristine MWNTs modified GC electrode.

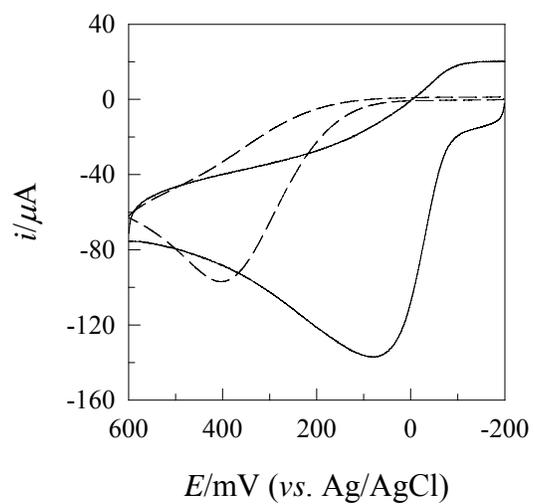


Figure S5. Cyclic voltammograms of 5 mM L-AA in 0.1 M phosphate buffer (pH = 7.0) on a bare GC electrode (dash line) and MWNTs **3** modified GC electrode (solid line).