

Electronic Supplementary Information (ESI)

Highly dispersive Ag nanoparticles on functionalized graphene for excellent electrochemical sensor of nitroaromatic compounds

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Experimental Section

Chemicals.

Graphene generated by the direct current arc discharge method were purchased from JIANSIN Scientific & Trading Company (Beijing, China) and used as received, and the purity was over 95%. Nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols and water) was obtained from Sigma (USA) and used as received. Other reagents including azodiisobutyronitrile(AIBN), toluene, sodium hydroxide, methanol, silver nitrate(AgNO_3), sodium borohydride (NaBH_4), Sodium Chloride, Nitrobenzene, 2,4-dinitrotoluene and 2,4,6-Trinitrotoluene were of analytical grade and were used as received. Millipore Milli-Q water ($18.2 \text{ }\Omega\text{M}$) was used throughout the experiment.

Apparatus.

All electrochemical measurements were carried out using a CHI 660C

electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). A three-electrode system was employed, comprising a glassy carbon electrode (GCE) ($\phi=3$ mm diameter) or a modified electrode as the working electrode, a platinum wire coil electrode as the auxiliary electrode, and an Ag/AgCl (sat. KCl) electrode as the reference electrode. All potentials were referred to the reference electrode.

The morphologies of the Ag/CS-G were observed through the high-resolution transmission electron microscope (HTEM) (JEM-2010, Japan Electron Optics Laboratory Co., Ltd). The powder X-ray diffraction (XRD) measurements of the samples were recorded on a D/Max-2400 with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) operating at 40 kV, 100 mA with scattering angles (2θ) of 5-90°. X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI-5702 spectrometer with Al $K\alpha$ X-ray radiation as the X-ray source for excitation. UV-vis detection was carried out on a UV-1102 spectrophotometer.

Synthesis of carboxylic sodium functionalized graphene and Ag NPs/CS-G

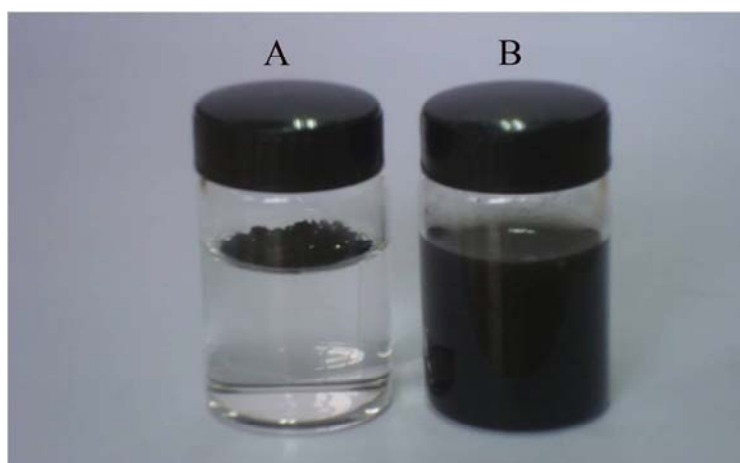


Fig S1. Photographs of aqueous solution of graphene (A) and CS-G(B).

100 mg graphene were dispersed in 100 mL of toluene by sonication. Subsequently, 20 mL of toluene solution containing 6.40 g AIBN was added to the dispersion under strong stirring. The resulting dispersion was heated at 75 °C for 4h in a Ar atmosphere, the product was washed with toluene repeatedly and dried in vacuum at 40 °C overnight, then the graphene-cyano (graphene-CN) was produced. 50mg graphene-CN was dispersed in a mixture of methanol and 10 M sodium hydroxide, the resultant dispersion was subjected to refluxing at 60 °C for 48h, the product was washed with distilled water for several times. Finally, the purified carboxylic sodium functionalized graphene (CS-G) was dried in vacuum at 40 °C overnight. and finally the CS-G was obtained¹.

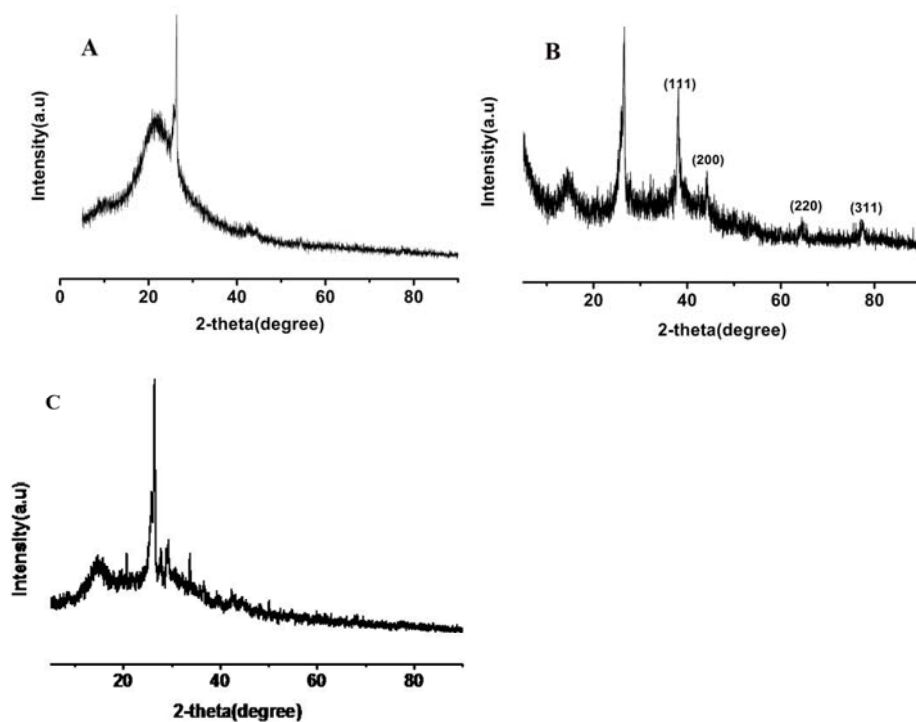


Fig S2. The XRD pattern of graphene(A), Ag/CS-G (B) and CS-G (C).

As shown in fig S2, the diffraction peak at 14.3° in X-ray diffraction (XRD) also reveals the successfully functionalization of graphene with carboxylic sodium groups, the sharp diffraction peak at about 26.4° may be from pristine graphite², which exists in the raw graphene prepared by the direct current arc discharge method.

In a typical synthesis of highly dispersive Ag NPs³ on the CS-G (Ag/CS-G), as-synthesized CS-G was ultrasonically dispersed in aqueous solution to form a homogenous suspension (0.5 mg mL^{-1}). Then homogeneous CS-G suspension ($5 \text{ mL } 0.5 \text{ mg mL}^{-1}$) and AgNO_3 ($3 \text{ mL } 1 \text{ mM}$) aqueous solution was kept in a vial under vigorous stirring for 30 min at room temperature. Under continuous stirring, NaBH_4 ($3 \text{ mL } 40 \text{ mM}$) was slowly added to the mixture for 1 h at room temperature. Finally, the reaction mixture was washed with pure water and centrifuged to remove the remaining reagents. Before the preparation of the catalysts modified GCE, the GCE was polished with 0.3 and $0.05 \text{ }\mu\text{m}$ $\alpha\text{-Al}_2\text{O}_3$, sequentially. As-synthesized Ag/CS-G was ultrasonically dispersed in 0.05% Nafion solution to form a homogenous suspension (1g/L). The Ag/CS-G modified GCE was prepared by casting $5\mu\text{L}$ of Ag/CS-G suspension on the electrode surface and drying at room temperature.

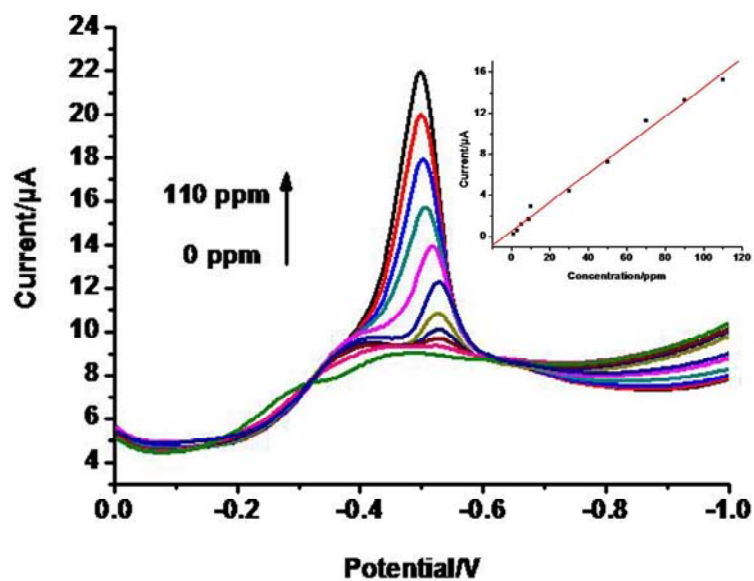


Fig S3. Differential pulse voltammetry for different concentrations of NB in 0.5 M NaCl on Ag/CS-G/GCE. NB concentration: 0, 1, 3, 5, 9, 10, 30, 50, 70, 90, 110 ppm. Inset: linear relationship between peak current and NB concentration.

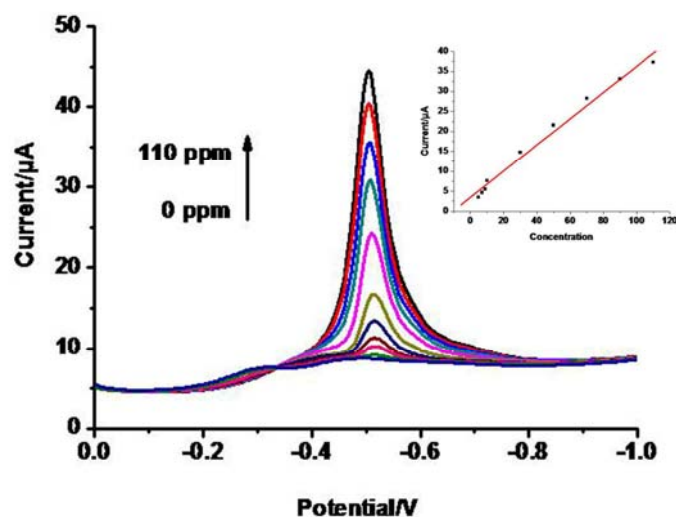


Fig S4. Differential pulse voltammetry for different concentrations of DNT in 0.5 M NaCl on Ag/CS-G/GCE. DNT concentration: 0, 1, 3, 5, 9, 10, 30, 50, 70, 90, 110 ppm. Inset: linear relationship between peak current and DNT concentration.

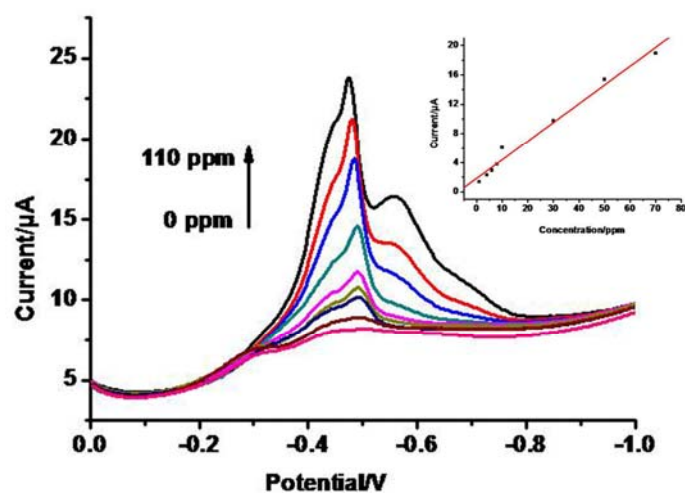


Fig S5. Differential pulse voltammetry for different concentrations of TNT in 0.5 M NaCl on Ag/CS-G/GCE. TNT concentration: 0, 1, 3, 5, 9, 10, 30, 50, 70 ppm. Inset: linear relationship between peak current and TNT concentration.

References

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2. X. Yan, J. Chen, J. Yang, Q. Xue and P. Miele, *ACS Appl. Mat. Interfaces*, 2010, **2**, 2521-2529.
3. Y.-S. Shon and E. Cutler, *Langmuir*, 2004, **20**, 6626-6630.