

Supporting Information

Hierarchical Self-Assembly of Cyclodextrin and Dimethylamino-Substituted Arylene-Ethynylene on N-doped Graphene for Synergistically Enhanced Electrochemical Sensing of Dihydroxybenzene Isomers

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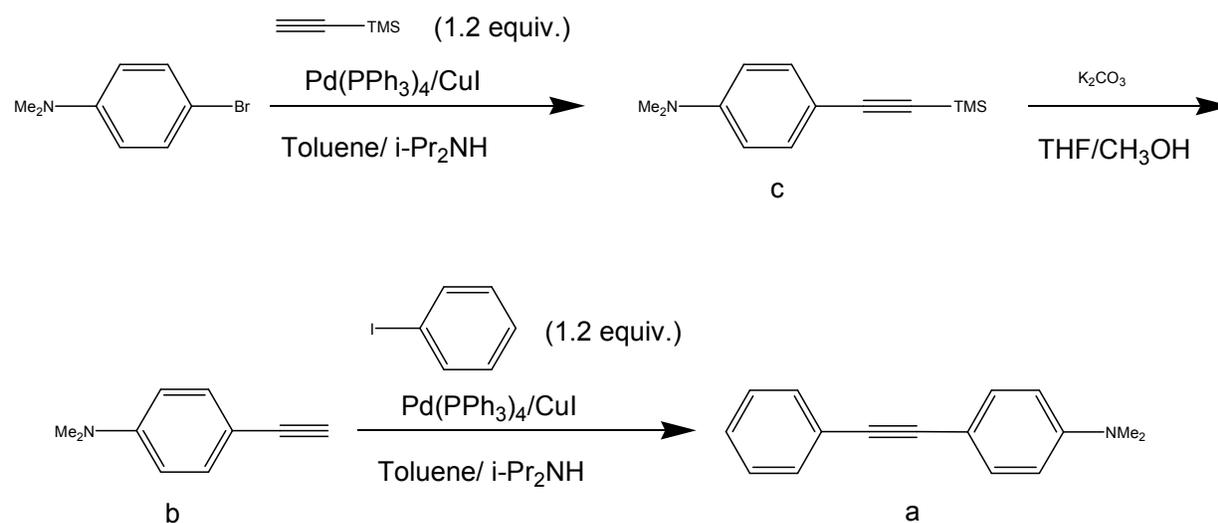
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1. Materials and methods

Catechol (CT), resorcinol (RS), hydroquinone (HQ) and ammonia solution (25-28 wt%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). These solutions were prepared fresh prior to use. Nafion solution (5%) was purchased from Alfa Aesar. Citrate phosphate buffer solutions (0.1 M, pH 3-7) were prepared using 0.1 M citric acid and 0.2 M Na₂HPO₄. Natural graphite was obtained from Qingdao Zhongtian Company. Other chemicals not mentioned here are of analytical grade and used as received without further purification. Doubly distilled water was used throughout the whole experiments. All the measurements were carried out at room temperature.



Preparation of *N,N*-dimethyl-4-((trimethylsilyl)ethynyl)aniline (**c**).¹

To a flask were added 4-bromo-*N,N*-dimethylaniline (400 mg, 2.0 mmol), (trimethylsilyl)acetylene (236 mg, 2.4 mmol), Pd(PPh₃)₄ (116 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), diisopropylamine (5 mL) and toluene (15 mL), and the mixture was stirred at 80 °C overnight. Then the reaction mixture was

poured into aqueous NH_4Cl and extracted with CH_2Cl_2 , the organic layer was washed with brine and dried over MgSO_4 . After filtration, solvents were evaporated. The crude product was subjected to column chromatography (SiO_2 ; eluent, hexane/ CH_2Cl_2 , 3:1) to give **c** as pale yellow powder, yield 74.2%, m.p. 86-88°C. ^1H NMR (500 MHz, CDCl_3): δ 0.23(s, 9H), 2.97(s, 6H), 6.59(d, J 9.0 Hz, 2H), 7.34(d, J 9.0 Hz, 2H).

Preparation of 4-ethynyl-*N,N*-dimethylaniline (b).¹

To a flask were added **3a** (326 mg, 1.5 mmol), K_2CO_3 (2.073 g, 15.0 mmol), THF (5 mL) and MeOH (5 mL), and the mixture was stirred at room temperature for 2 h. Then the reaction mixture was poured into water and extracted with CH_2Cl_2 , the organic layer was washed with brine and dried over MgSO_4 . After filtration, solvents were evaporated. The crude product was subjected to column chromatography (SiO_2 ; eluent, hexane/ CH_2Cl_2 , 3:1) to give **b** as pale yellow powder, yield 98.2%, m.p. 50-51°C. ^1H NMR (500 MHz, CDCl_3): δ 2.96(s, 6H), 2.97(s, 1H), 6.62(d, J 9.0 Hz, 2H), 7.36(d, J 9.0 Hz, 2H).

Preparation of *N,N*-dimethyl-4-(phenylethynyl)aniline (a).¹

To a flask were added **4a** (145 mg, 1.0 mmol), iodobenzene (245 mg, 1.2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol), diisopropylamine (3 mL) and toluene (10 mL), and the mixture was stirred at room temperature overnight. Then the reaction mixture was poured into aqueous NH_4Cl and extracted with CH_2Cl_2 , the organic layer was washed with brine and dried over MgSO_4 . After filtration, solvents were evaporated. The crude product was subjected to column chromatography (SiO_2 ; eluent, hexane/ CH_2Cl_2 , 3:1) to give **a** as pale yellow powder, yield 87.9%, m.p. 107-109°C. ^1H NMR (500 MHz, CDCl_3): δ 2.97(s, 6H), 6.65(d, J 9.0 Hz, 2H), 7.25-7.32(m, 3H), 7.40(d, J 9.0 Hz, 2H), 7.49(d, J 9.0 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 40.2, 87.3, 90.6, 110.1, 111.9, 124.2,

127.4, 128.2, 131.3, 132.7, 150.1. Anal. calcd for C₁₆H₁₅N: C, 86.84; H, 6.83; N, 6.33; found C 86.56, H 6.85, N 6.27.

2. Instrumentation

All electrochemical experiments including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectra (EIS) were performed with a CHI660E Electrochemical Workstation from Shanghai Chenhua Instrument (Shanghai, China). The conventional three-electrode cell was employed with platinum wire and a saturated calomel electrode (SCE) as the auxiliary electrode and the reference electrode, respectively, a bare GCE ($\Phi = 3$ mm) or modified electrode as working electrode. EIS was performed in 5.0 mM Fe(CN)₆^{3-/4-} redox couple with 0.1 M KCl as supporting electrolyte over a frequency range of 0.1 Hz to 10⁵ Hz. The charge transport process of the electrodes can be described by monitoring charge transfer resistance (R_{ct}) through the electrode/electrolyte interface. The value of R_{ct} was estimated by the semicircle diameter of EIS at higher frequency corresponding to the electron-transfer limited process. Its value can provide information on the impedance changes of the electrode surface during the modification process. Fourier transform infrared (FT-IR) spectra for the various samples were recorded on a Nicolet IS-10 FT-IR spectrometer using Ge crystal. Thermogravimetric analysis (TGA) was carried out by using a Mettler TGA/SDTA851e thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ from 50 to 800 °C in nitrogen atmosphere. And the patterns are obtained by Bruker D8 Advance diffractometer with Cu-K α radiation. The defect sites of different samples were performed Raman spectroscopy on a LabRAM ARAMIS (HORIBA Jobin Yvon S.A.S.) using an excitation wavelength of 532 nm.

3. Supporting figures

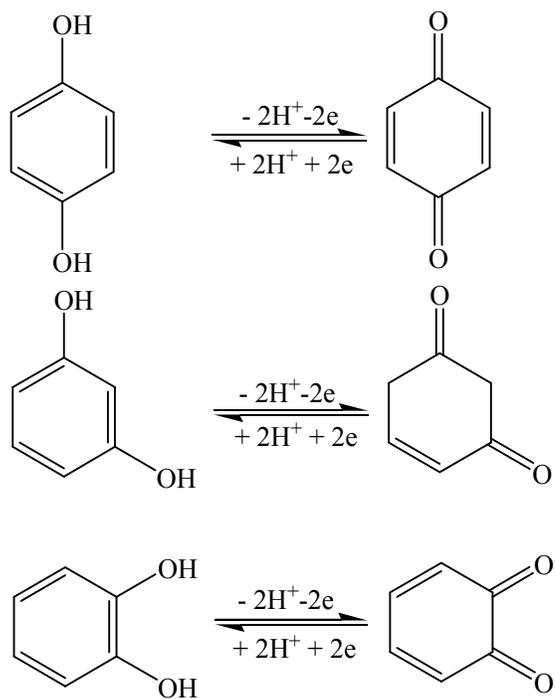


Figure S1. The mechanisms of electron generation for CT, RS and HQ at CD-MPEA-NG/GCE.

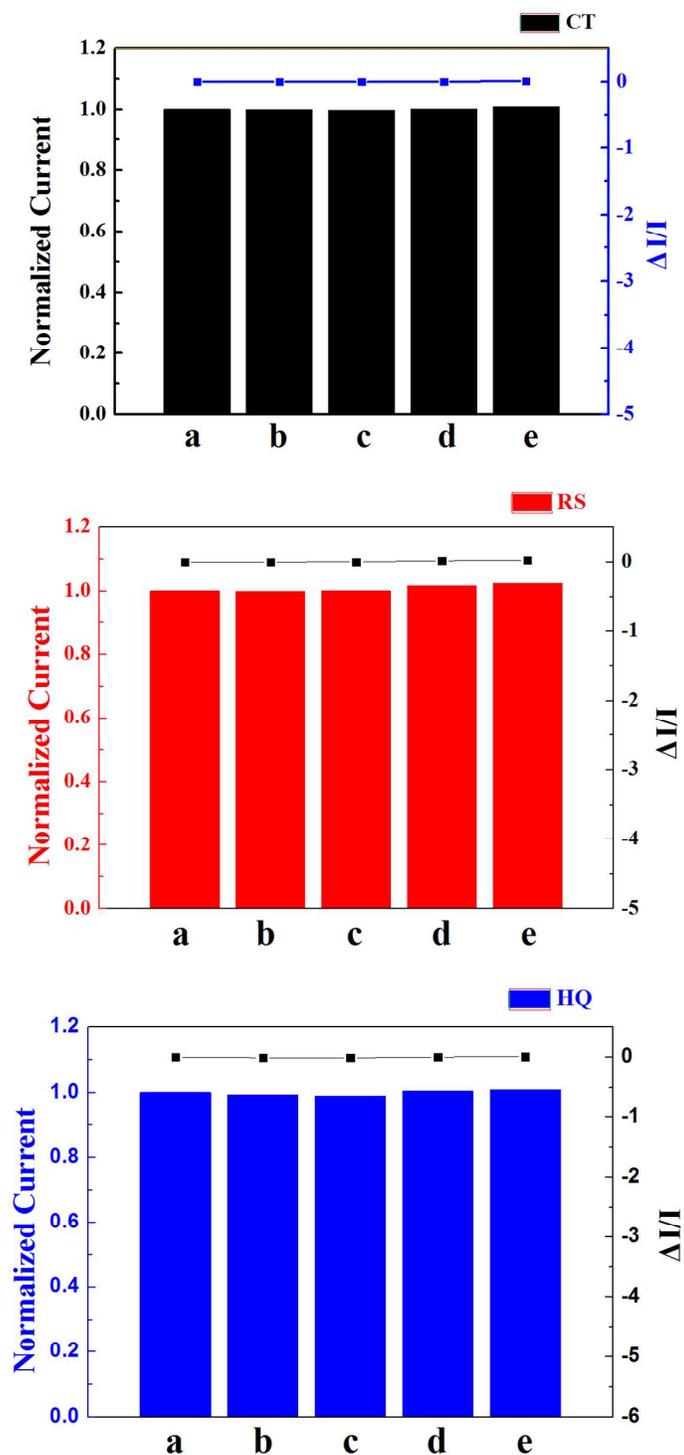


Figure S2. The DPV oxidation currents of 5 μM of CT, RS and HQ in the absence (a) and presence of 10-fold concentration of interfering species (from b to e): glucose, ascorbic acid, bisphenol A, p-chlorophenol.

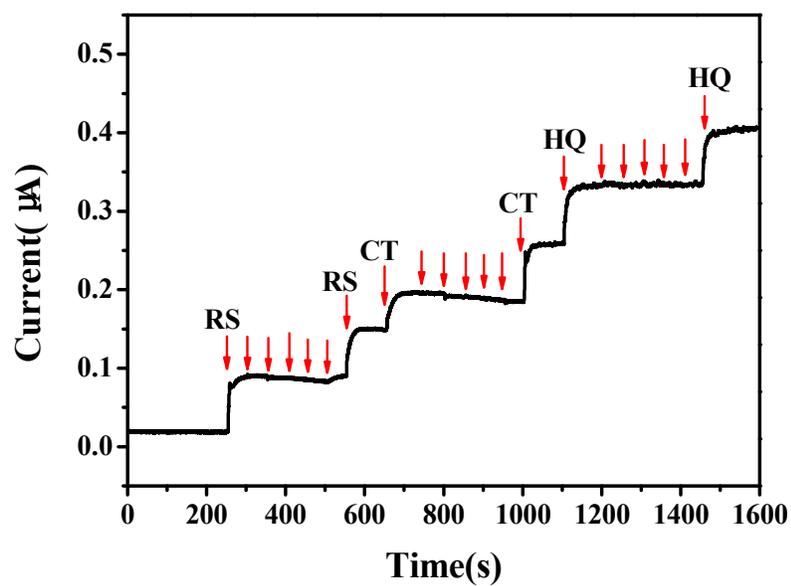


Figure S3. Amperometric response at CD-MPEA-NG/GCE to the subsequent addition of 4 μM RS, KNO_3 , ZnSO_4 , NaAC, CaCl_2 , $\text{Cu}(\text{NO}_3)_2$, 4 μM RS, 2 μM CT, KNO_3 , ZnSO_4 , NaAC, CaCl_2 , $\text{Cu}(\text{NO}_3)_2$, 2 μM CT, 2 μM HQ, KNO_3 , ZnSO_4 , NaAC, CaCl_2 , $\text{Cu}(\text{NO}_3)_2$, 2 μM HQ.

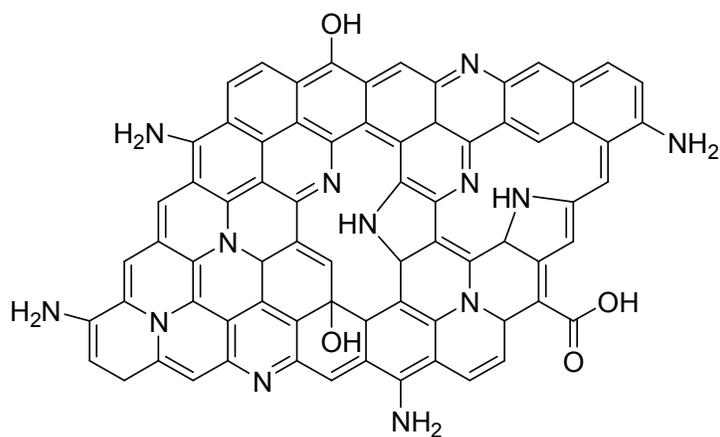


Figure S4. Chemical structure of NG.²

Table S1Charge transfer resistance (R_{ct}) for the different electrodes.

Electrodes	GCE	GO/GCE	NG/GCE	MPEA-NG/GCE	CD-NG/GCE	CD-MPEA-NG/GCE
R_{ct} (Ω)	91.4	92.8	72.1	88.7	104.2	107.8

Table S2

Total energies and binding energies of MPEA-NG dimers at wB97XD/LanL2DZ level *

Species	E	$\Delta E_{\text{Relative}}$	$\Delta E_{\text{Binding}}$
Dimer1	-4450.99791430	-4.29821	-134.91
Dimer2	-4451.00284640	-17.2474	-147.86
Dimer3	-4451.00234840	-15.9399	-146.55
Dimer4	-4450.99627720	0.00	-130.61

* E in a.u., ΔE in kJ/mol

Table S3

Comparison of the proposed sensor for three isomers detection with other reported electrodes.

Sensors	Method	Linear range (μM)			Detection limit (μM)			Ref.
		CT	RS	HQ	CT	RS	HQ	
ER(GO-TT-CNT) ^a /GCE	DPV	0.5-200		0.1-100	0.0049		0.035	3
N ^b -GCE	DPV	5-260		5-260	0.2		0.2	4
NiO/MWCNT/GCE	DPV	7.4-56		7.4-56	0.015		0.039	5
AuNPs/EGP ^c	DPV	0.5-100		0.07-100	0.027		0.041	6
CNF ^d /GCE	DPV	1-250	1-200	5-300	0.5	0.8	0.4	7
VOTPRu ^e -GCE	DPV	2-38		2-38	0.41		0.55	8
Pt/ZrO ₂ -RGO/GCE	DPV	1-400		1-1000	0.4		0.4	9
graphene-SPE ^f	DPV	1-38.1	1-50	1-35	1.7	2.4	2.7	10
CD ^g /r-GO/GCE	DPV	1-950	5-600	0.5-1000	0.28	1	0.17	11
MWCNTs/CDs ^g /MWCNTs/GCE	DPV	4-200	3- 400	1-200	0.06	0.15	0.07	12
Ph-rGO-GCE	DPV	4-50	10-180	10-170	0.18	2.62	0.08	13

AuNPs-MPS ⁱ /CPE	SWV	1-400		1-400	1.2	0.95	14	
Cu-MOF-199 ^j /SWCNTs/GCE	DPV	0.1-1150		0.1-1453	0.1	0.08	15	
CD-MPEA-NG/GCE	DPV	0.25-50, 50-1400	0.5-14, 14-620	0.5-60, 60-1400	0.009	0.019	0.01	This work

^a electrochemically reduced GO-terthiophene-CNT;

^b nitrogen-introduced;

^c exfoliated graphite paper;

^d carbon nano-fragment;

^e {VOTPyP[RuCl₃(dppb)]₄} porphyrin;

^f screen-printed electrodes;

^g carbon dot;

^h porous;

ⁱ mesoporous silica;

^j Cu₃(BTC)₂ (BTC = 1,3,5-benzenetricarboxylic acid).

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