Electronic Supplementary Material (ESI) for Analyst.
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Supporting information

Electrochemical Sensor for Detection of *p*-Nitrophenol Based on Cyclodextrin Decorated Gold Nanoparticles-Mesoporous Carbon Hybrid

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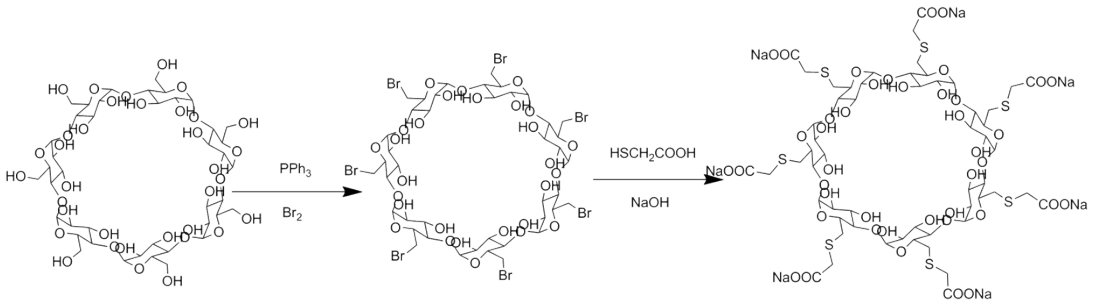
Content



Scheme S1. Synthesis of per-6-deoxy-per-6-(2-carboxy-methyl)thio-*β*-cyclodextrin

Synthesis of per-(6-deoxy-6-bromo)-*β*-cyclodextrin

Triphenylphosphine (28 g, 106 mmol) was dissolved in anhydrous DMF (60 mL) and placed in a three-necked flask, and bromine (2.8 mL, 106 mmol) was placed in a constant pressure dropping funnel, and drip into the solution at a rate of 3 to 4 seconds per drop. The temperature was controlled below 15 °C. When the addition was completed, the reaction solution was stirred for 30 min, and then *β*-cyclodextrin (6.8 g, 6 mmol) was dissolved in 30 mL of DMF solution and and placed in a constant pressure dropping funnel. The temperature was adjusted to 70 ° C for 14 hours, and nitrogen gas was continuously supplied during the reaction until the reaction was completed. After the reaction is completed, the reaction solution is stirred in an ice water bath at 0 to 5 ℃ and the sodium methoxide solution is added dropwise to adjust the pH to 8, and then 1000 mL of methanol is added to stir to precipitate a solid, which is filtered to obtain a crude product. DMF/H_2O was recrystallized twice and vacuum dried to give per-[6-deoxy-6-bromo]-*β*-cyclodextrin.(product weight: 7.13 g; yield: 75%) ^{1}H NMR (400 MHz, DMSO) δ 6.02 (d, J = 6.7 Hz, 7H), 5.89 (d, J = 1.9 Hz, 7H), 4.98 (d, J = 3.4 Hz, 7H), 4.00 (d, J = 9.9 Hz, 7H), 3.82 (t, J = 9.0 Hz, 7H), 3.74 – 3.56 (m, 14H), 3.39 (dd, J = 12.8, 6.4 Hz, 14H).

Synthesis of per-6-deoxy-per-6-(2-carboxy- methyl)thio-*β*-cyclodextrin[1]

Sodium hydroxide (4.0 g, 100 mmol) was dissolved in 30 mL of distilled water, and mercapto acetic acid (3.68 g, 40 mmol) was added and reacted for 8 h. Then 20 mL of dissolved per-[6-deoxy-6-bromo]-*β*-cyclodextrin (3.16 g, 2 mmol) in DMF was added, pass nitrogen protection, and raise the temperature to 60 °C with stirring. When the initial addition, a white solid precipitated, but as the reaction progressed, the white solid disappeared and the solution became transparent. At this time, heating was stopped, and the reaction was completed. The reaction solution was cooled to room

temperature and poured into 900 mL of methanol. Solids were precipitated, filtered under reduced pressure, and the hobtained solid was dissolved with as little water as possible. The pH of the solution was adjusted to 2 with 3 mol/L hydrochloric acid, and the solid was slowly precipitated and centrifuged. The solid was obtained and washed three times with distilled water, and recrystallized twice in a mixed solvent of C_2H_5OH/H_2O to give a white product per-6-deoxy-per-6-(2-carboxy-methyl)thio- *β*-cyclodextrin sodium salt. (product weight: 2.04 g; yield: 62%) ^{1}H NMR (400 MHz, D_2O) δ 5.07 (d, J = 3.5 Hz, 7H), 4.09 – 3.95 (m, 7H), 3.89 (t, J = 9.5 Hz, 7H), 3.67 (t, J = 9.2 Hz, 7H), 3.60 (dd, J = 10.0, 3.4 Hz, 7H), 3.33 (q, J = 15.3 Hz, 14H), 3.11 (d, J = 13.8 Hz, 7H), 3.03 – 2.71 (m, 14H); LC-MS:m/z 1651.4 $[M-H]^-$.

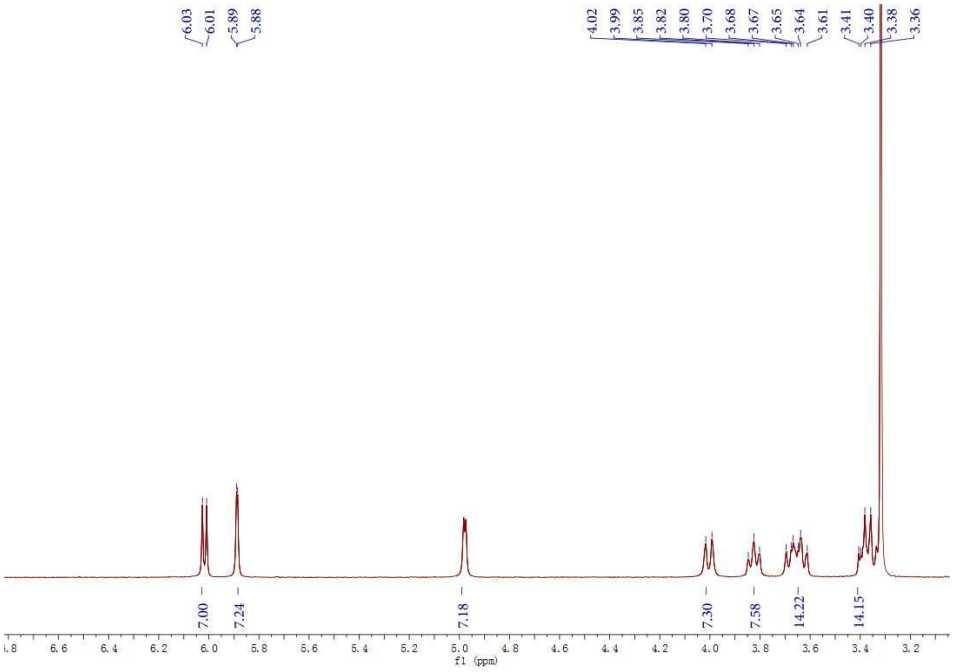


Figure S1. The ^{1}H-NMR spectrum of per-(6-deoxy-6-bromo)-*β*-cyclodextrin

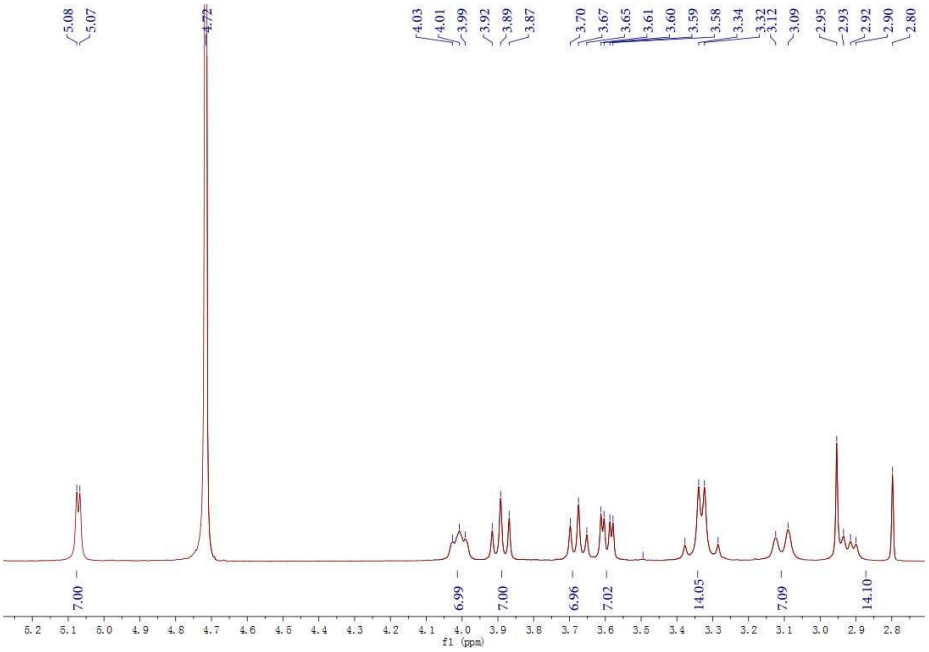


Figure S2. The [1]H-NMR of per-6-deoxy-per-6-(2-carboxy-methyl)thio-*β*-cyclodextrin

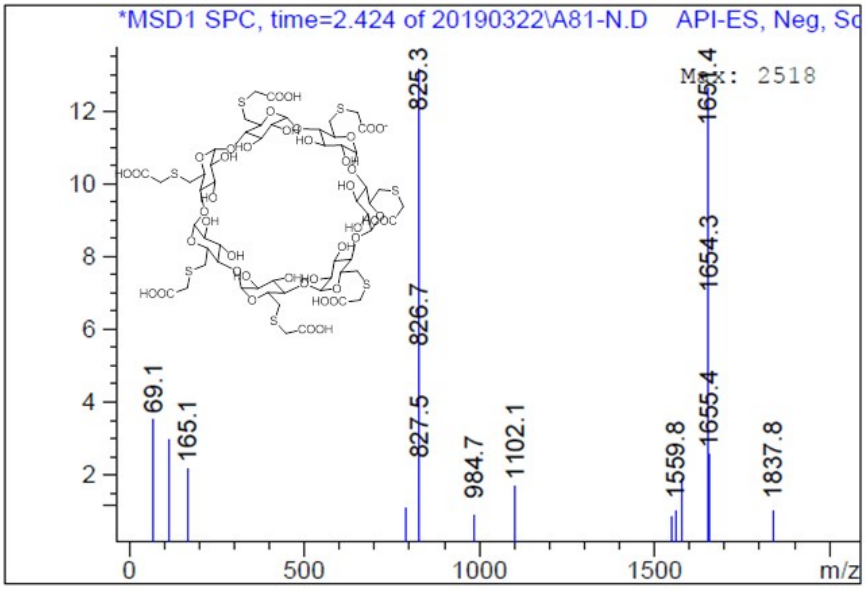


Figure S3. The mass spectrometry of per-6-deoxy-per-6-(2-carboxy-methyl)thio- *β*-cyclodextrin

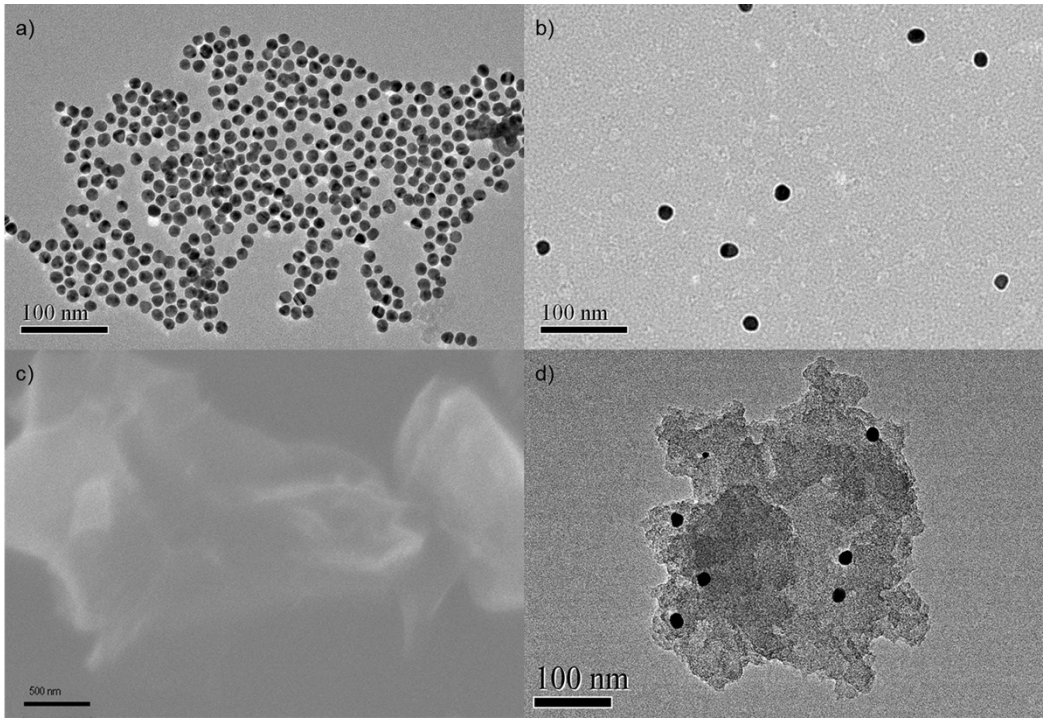


Figure S4. (a) TEM image of AuNPs; (b) TEM image of AcSCD-AuNPs; (c) SEM image of AcSCD-AuNPs-MC; (d) TEM image of AcSCD-AuNPs-MC

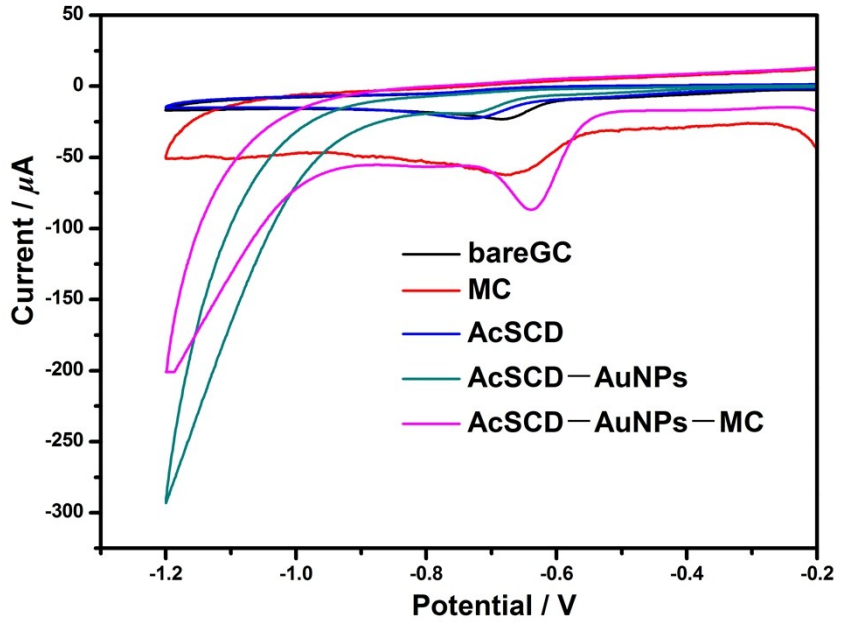


Figure S5. CVs of 100 μM p-nitrophenol at bare GC electrode, MC/GC, AcSCD/GC, AcSCD-AuNPs/GC, AcSCD-AuNPs-MC/GC electrodes

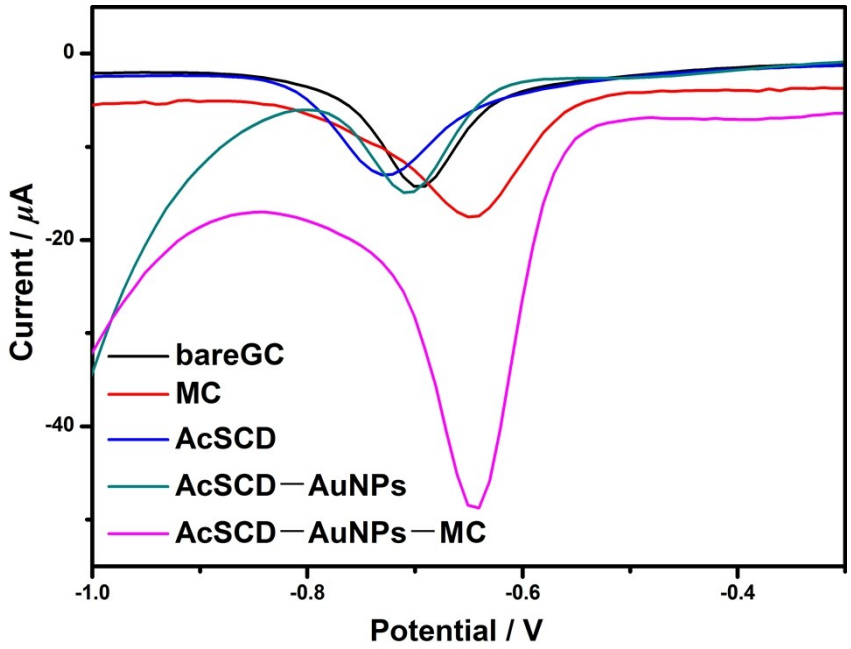


Figure S6. DPV response for 100 μM p-nitrophenol at bare GC electrode, MC/GC, AcSCD/GC, AcSCD-AuNPs/GC, AcSCD-AuNPs-MC/GC electrodes

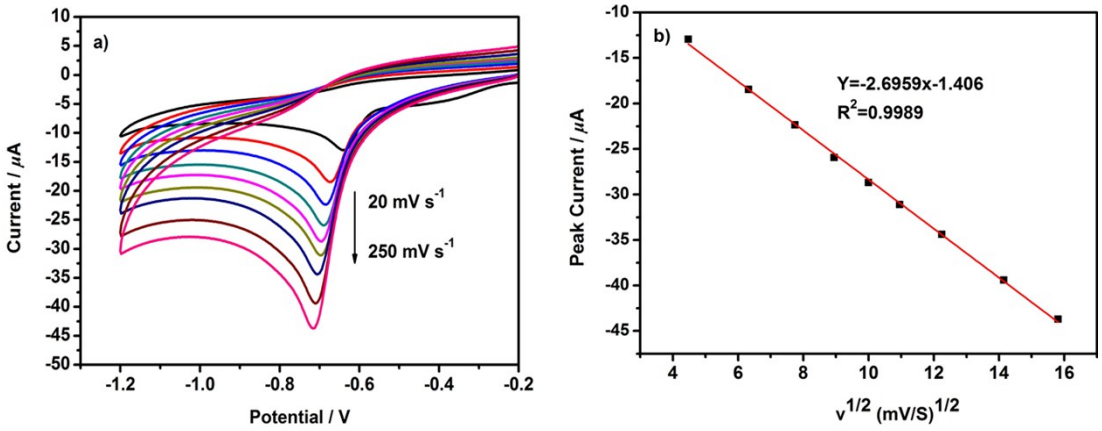


Figure S7. (a) CVs of bare GC electrode in 0.1 M PBS electrolyte containing 100 μM *p*-NP with different scan rate values (scan rate:20、40、60、80、100、120、150、200、250 mV s^{-1}) at pH=6.5; (b) A Plot of peak current against square root of scan rate

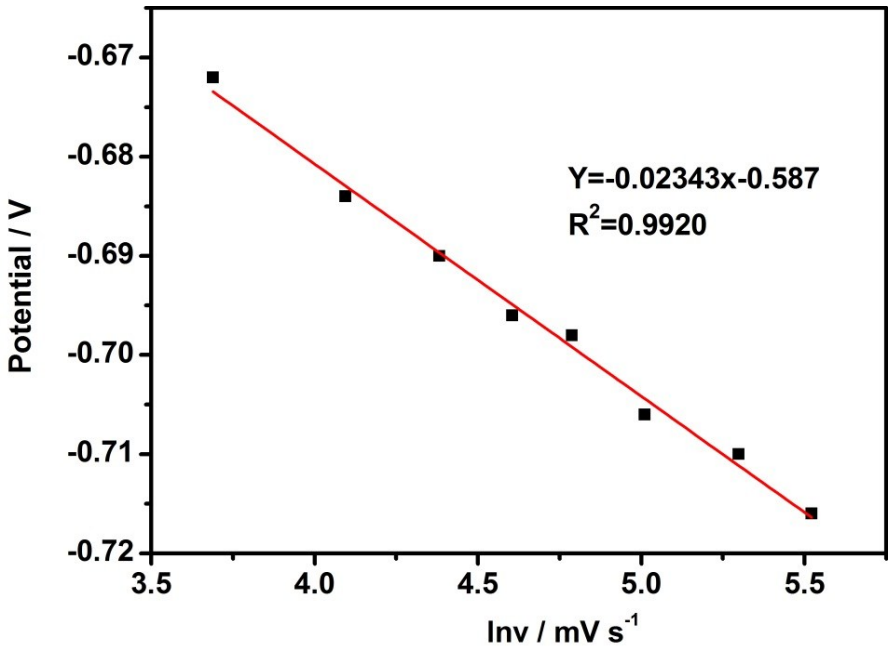


Figure S8. A plot of potential against logarithm of scan rate on bare GC electrode

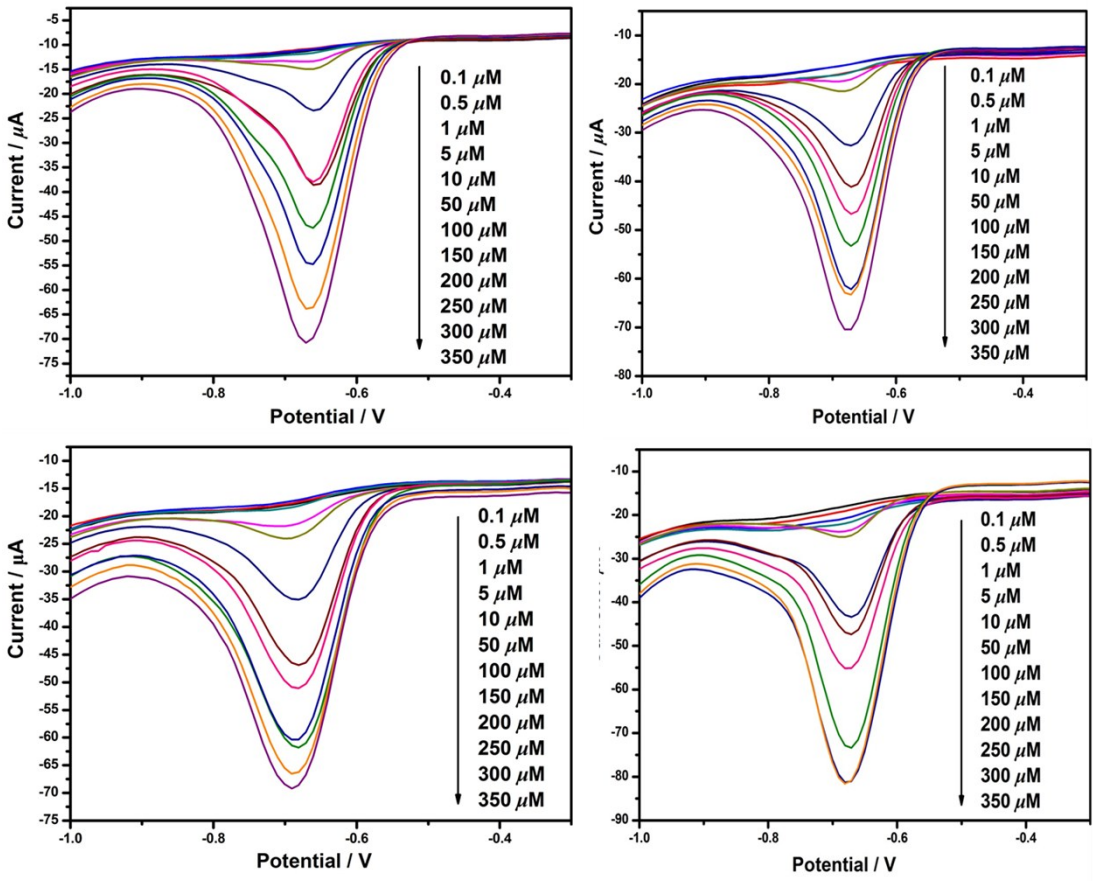


Figure S9. Differential pulse voltammograms response for the different concentrations of p-nitrophenol at four individual AcSCD-AuNPs-MC electrodes

Table S1. Supplementary datum of the reduction peak currents (μA) for the different concentrations of p-nitrophenol (μM) at four individual AcSCD-AuNPs-MC electrodes

	Electrode 1	Electrode 2	Electrode 3	Electrode 4	Average
350	−70.77	−70.44	−67.71	−69.18	−73.27
300	−63.83	−63.26	−66.22	−66.50	−68.28
250	−54.75	−62.17	−35.90	−60.35	−64.64
200	−47.34	−53.30	−38.57	−61.82	−54.88
150	−37.95	−46.73	−32.35	−51.07	−44.64
100	−38.55	−41.15	−27.49	−46.91	−40.29
50	−23.39	−32.63	−20.71	−35.09	−31.04
10	−14.94	−21.47	−13.19	−24.03	−19.74
5	−13.42	−19.48	−9.98	−21.81	−17.71
1	−12.00	−18.27	−0.00	−18.99	−18.21
0.5	−11.37	−16.71	−10.46	−18.22	−15.97
0.1	−11.65	−18.65	−7.76	−18.71	−15.05

Table S2. Comparison of the different methods for p-nitrophenol determination

Electrode materials	Methods	Linear range (μM)	LOD (μM)	Ref.
OMC	DPV	2–90	0.1	[2]
rGO	DPV	50–800	42	[3]
AgNWs-PANI	DPV	0.6–32	0.052	[4]
DTD/AgNP	CV	1–100	0.25	[5]
AuNPs/RGO	SWV	0.05–2	0.01	[6]
NMP/Gr	Amperometry	0.5–5.6	0.15	[7]
AcSCD-AuNPs-MC	DPV	0.1–10 10-350	26.1 (3.63 μg/mL)	This work

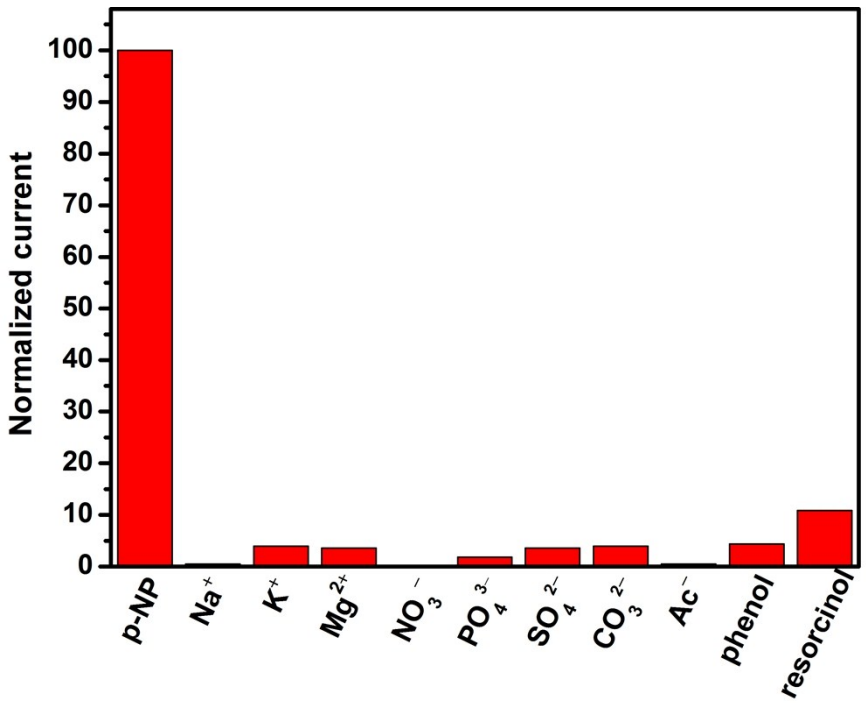


Figure S10. Normalized current of AcSCD-AuNPs-MC electrode for 100 μM p-nitrophenol in the presence of the high concentrations of possible interferents

Table S3. Determination of p-nitrophenol in real samples by standard addition method at AcSCD-AuNPs-MC electrode

Samples	Added (μM)	Average found (μM)	Recovery(%)
Tap Water1	0	0	0
Tap Water 2	30	30.94	103.15
Tap Water 3	100	103.94	103.94
Shangde Lake1	0	0	0
Shangde Lake2	50	47.62	95.25
Shangde Lake3	100	86.48	86.48

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