Supporting information

Size Dependent Electrochemical Detection for Trace Heavy Metal Ions

Based on Nano-Patterned Carbon Sphere Electrodes

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Part I:



Fig. S1 (a) Photograph of the dispersed solution of HCSs. (b) Representative DLS curves of the HCS-188-44. (PDI=polydispersity index).



Fig. S2. SEM images of the self-assembled HCSs.



Fig. S3 Nyquist plots of HCS-188-55 modified GCE. Solid red line, measurement data; dot green line, fitting data.



Fig. S4 Schematic illustration of electron transfer pathways.



Fig. S5. N_2 sorption isotherms of HCS-x-y samples. Note: the isotherms of samples HCS-188-55, HCS-188-44, and HCS-188-33 are vertically offset by 10, 20, 30 cm³ g⁻¹, respectively.

-	Sample	S _{BET}	\mathbf{S}_{mic}	V _{total}	V_{mic}
		$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$
-	HCS-265-33	588	537	0.30	0.24
	HCS-188-33	607	541	0.32	0.25
	HCS-188-44	603	554	0.32	0.26
	HCS-188-55	600	544	0.31	0.25
	HCS-188-79	580	531	0.25	0.23

Table S1. Textural properties of HCS-x-y samples^a

 ${}^{a}S_{BET}$ = specific surface area calculated by the BET method, S_{mic} = micropore surface area calculated by the t-plot method, V_{total} = total pore volume at P/P₀ = 0.90, and V_{mic} = micropore volume calculated by the t-plot method.

	Sample	D _{PS} ^a	Phenol	HMT	T _{HCS} ^b	$\mathrm{D}_{\mathrm{void}}^{\mathrm{c}}$
		(nm)	(mg)	(mg)	(nm)	(nm)
	HCS-265-33	280	141	105	32	265
	HCS-188-33	200	188	140	33	188
	HCS-188-44	200	235	175	44	188
	HCS-188-55	200	282	210	55	188
	HCS-188-79	200	376	280	79	188

Table S2. Synthesis conditions and structure parameters of HCSs

^aD_{PS}: the diameter of PS template. ^bT_{HCS}: the shell thickness of HCSs. ^cD_{void}: the void diameter of HCSs.

Part II:

The contact points between HCSs and GCE can be calculated as following:

We assume that HCSs have hexagonal close-packed structure on the surface of GCE. When HCS-188-44 modified GCE, the number of contact points between HCS and GCE :

$$n = \frac{S_{GCE}}{a_u} = \frac{4\pi R_{GCE}^2}{\sqrt{3}R_{HCS}D_{HCS}} = \frac{4\pi (2 \times 10^{-3})^2}{2\sqrt{3}(138 \times 10^{-9})^2} = 7.62 \times 10^8$$

Where n is the number of contact points between HCS and GCE, S_{GCE} is the area of GCE; a_u is the area of each unit; R_{GCE} is the radius of GCE; R_{HCS} , D_{HCS} is the radius and diameter of HCSs.