## 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. $\mathrm{N}_{2}$ 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 $10,20,30 \mathrm{~cm}^{3} \mathrm{~g}^{-1}$, respectively.

Table S1. Textural properties of HCS-x-y samples ${ }^{\text {a }}$

| Sample | $\mathrm{S}_{\text {BET }}$ <br> $\left(\mathrm{m}^{2} \mathrm{~g}^{-1}\right)$ | $\mathrm{S}_{\text {mic }}$ <br> $\left(\mathrm{m}^{2} \mathrm{~g}^{-1}\right)$ | $\mathrm{V}_{\text {total }}$ <br> $\left(\mathrm{cm}^{3} \mathrm{~g}^{-1}\right)$ | $\mathrm{V}_{\text {mic }}$ <br> $\left(\mathrm{cm}^{3} \mathrm{~g}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| 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 |

${ }^{a} S_{\text {BET }}=$ specific surface area calculated by the BET method, $\mathrm{S}_{\text {mic }}=$ micropore surface area calculated by the $\mathrm{t}-$ plot method, $\mathrm{V}_{\text {total }}=$ total pore volume at $\mathrm{P} / \mathrm{P}_{0}=0.90$, and $\mathrm{V}_{\text {mic }}=$ micropore volume calculated by the t-plot method.

Table S2. Synthesis conditions and structure parameters of HCSs

| Sample | $\mathrm{D}_{\mathrm{PS}}{ }^{\mathrm{a}}$ | Phenol | HMT | $\mathrm{T}_{\mathrm{HCS}}{ }^{\mathrm{b}}$ | $\mathrm{D}_{\text {void }}{ }^{\mathrm{c}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $(\mathrm{nm})$ | $(\mathrm{mg})$ | $(\mathrm{mg})$ | $(\mathrm{nm})$ | $(\mathrm{nm})$ |
| 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 |

${ }^{a} \mathrm{D}_{\mathrm{PS}}$ : the diameter of PS template. ${ }^{\mathrm{b}} \mathrm{T}_{\mathrm{HCS}}$ : the shell thickness of $\mathrm{HCSs} .{ }^{\mathrm{c}} \mathrm{D}_{\text {void }}$ : 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 :
$n=\frac{S_{G C E}}{a_{u}}=\frac{4 \pi R_{G C E}^{2}}{\sqrt{3} R_{H C S} D_{H C S}}=\frac{4 \pi\left(2 \times 10^{-3}\right)^{2}}{2 \sqrt{3}\left(138 \times 10^{-9}\right)^{2}}=7.62 \times 10^{8}$

Where n is the number of contact points between HCS and GCE, $\mathrm{S}_{\mathrm{GCE}}$ is the area of GCE; $\mathrm{a}_{\mathrm{u}}$ is the area of each unit; $\mathrm{R}_{\mathrm{GCE}}$ is the radius of GCE; $\mathrm{R}_{\mathrm{HCS}}, \mathrm{D}_{\mathrm{HCS}}$ is the radius and diameter of HCSs.

