## **Supporting Information**

## PtNi Nanocrystals Supported on Hollow Carbon Spheres: Enhancing the Electrocatalytic Performance through High Temperature Annealing and Electrochemical CO Stripping Treatments

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**Figure S1** The size distribution histograms of PtNi nanoparticles in PtNi NCs-PVP@HCS (A) and PtNi NCs@HCS (B).



**Figure S2** XPS spectra of O 1s and Ni 2p in PtNi NCs-PVP@HCS (A, C) and PtNi NCs@HCS (B, D).

Table S1 The surface atomic ratios of Pt and Ni in PtNi NCs-PVP@HCS and PtNi NCs@HCS measured by XPS

| Samples<br>At.%<br>Elements | PtNi NCs-PVP@HCS | PtNi NCs@HCS |
|-----------------------------|------------------|--------------|
| Pt                          | 0.27             | 0.99         |
| Ni                          | 0.03             | 0.05         |



Figure S3 Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of the hollow carbon spheres.



Figure S4 Raman spectra of PtNi NCs-PVP@HCS and PtNi NCs@HCS.



**Figure S5** (A-C) TEM images of PtNi nanocrystals synthesized at 130 °C for 5 h with different Pt and Ni precursor ratios (A) 3:1, (B) 2:1, and (C) 1:1; (D-F) TEM images PtNi nanocrystals synthesized at different solvothermal temperatures for 5 h at the Pt/Ni ratio of 1:1 (D) 130 °C, (E) 150 °C, and (F) 180 °C; (G-I) TEM images of PtNi nanocrystals supported on hollow carbon spheres synthesized at different solvothermal temperatures for 5 h at the Pt/Ni ratio of 1:1 (G) 130 °C, (H) 150 °C, (I) 180 °C.



**Figure S6** TEM images of PtNi nanocrystals supported on hollow carbon spheres prepared at 130 <sup>o</sup>C with different Pt/Ni ratios (A) 1:1; (B) 1:2; (C) 1:3; and (D) 2:1.



**Figure S7** (A) CV curves of the PtNi NCs@HCS(COS) in 0.1 M N<sub>2</sub>- and O<sub>2</sub>-saturated HClO<sub>4</sub> solution. (B) CV curves of ORR on the as-synthesized PtNi NCs-PVP@HCS (black curve), acid washed (blue curve) and CO-stripping treated (red curve) PtNi NCs-PVP@HCS with a potential scan rate of 50 mV/s.



**Figure S8** ORR polarization curves obtained from PtNi NCs-PVP@HCS synthesized at different conditions. (A) At different temperatures (130, 150 and 180  $^{\circ}$ C) with a fixed Pt/Ni ratio of 1:1; (B) With different Pt/Ni ratios (1:1, 2:1,1:2 and 1:3 ) at 130  $^{\circ}$ C; (C) PtNi NCs-PVP@HCS, PtNi NCs@HCS and PtNi NCs@C. All the measurements were carried out in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution with the potential scan rate of 10 mV/s and rotation rate of 1600 rpm.



**Figure S9** (A) LSVs of ORR on commercial Pt/C in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> at different rotation rates with a scan rate of 10 mV/s; (B) The corresponding K-L plots at different potentials.



**Figure S10** CO stripping curves of commercial Pt/C (A), PtNi NCs-PVP@HCS (B); and PtNi NCs@HCS(COS) (C) in 0.1 M HClO<sub>4</sub> with a potential scan rate of 20 mV/s.