

Supporting Information for

Confining Pt Nanoparticles in Mesoporous Carbon

Structure for achieving Durable Electrochemical

Performance

Chunzhen Yang,^{a,} Ming Zhou,^a Qian Xu^{b,*}*

^a CYM Chemistry Building, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong S.A.R.

Address correspondence to chunzhenxp@gmail.com

^b School of Energy and Power Engineering, Jiangsu University, Zhenjiang, P.R. China

Address correspondence to hawkingxq@hotmail.com

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Experimental

Synthesis of SCMS SiO₂ spheres

A two-step synthesis procedure was used to prepare the solid core-mesoporous shell (SCMS) silica spheres as described in previous work.¹ SiO₂ solid spheres were first prepared by the Stöber method² as follows: concentrated ammonium solution (7 ml) was added into a mixture of ethanol (180 ml) and water (14 ml). Then tetraethoxysilicate (TEOS, 10 ml) was added and stirred for 6 hrs. In order to grow the mesoporous silica shell onto the solid silica spheres, a solution of cetyltrimethylammonium bromide (CTAB, 2.4 g) in water (40 ml) and ethanol (20 ml) was added into the above mixture and stirred for 12 hrs. Then TEOS (4.1 ml) was introduced and stirred for another 12 hrs. The above procedure can be repeated for several times to increase the mesoporous shell thickness. Finally, the product was collected by filtration and treated at 500 °C in air for 3 hrs to remove CTAB. Three SCMS silica spheres with the same core diameter (300 nm) and stepwise increased shell thickness (50 nm, 80 nm, and 150 nm) were synthesized using above procedure.

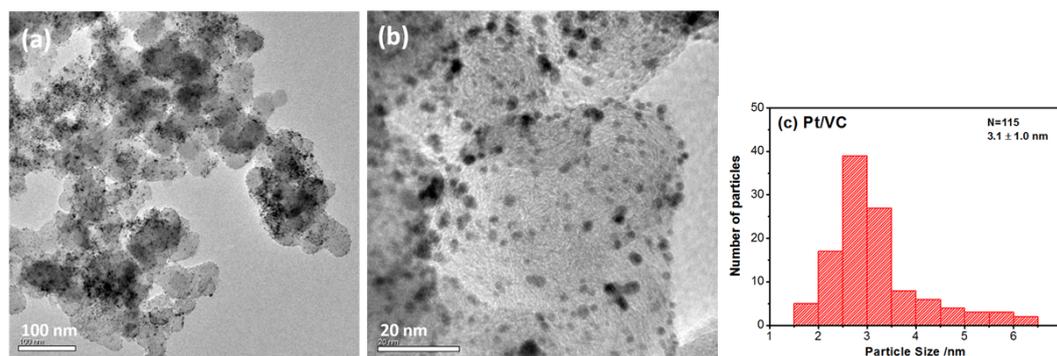


Fig. S1 (a-b) TEM images of commercial E-TEK Pt/VC catalyst, (c) particle size distribution profile of Pt NPs in the E-TEK Pt/VC catalyst measured from the TEM images.

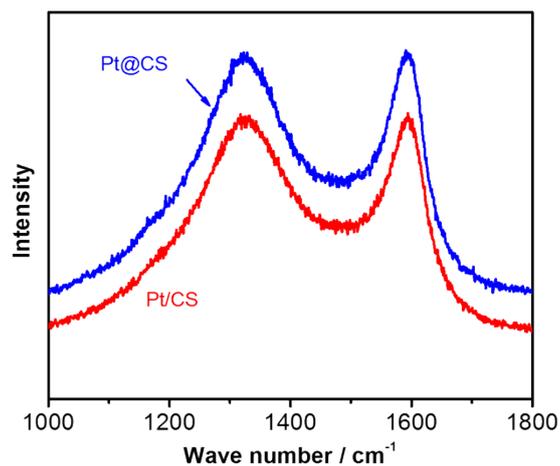


Fig. S2 Raman spectroscopy of Pt@CS and Pt/CS. Two characteristic peaks at 1340 cm⁻¹ and 1590 cm⁻¹, corresponding to disordered graphite (D-band) and graphite (G-band) respectively, were observed, indicating the bulk structure of HCMS carbon spheres was composed of two different carbon phases. The intensity ratio between the D-band and G-band (I_D/I_G) reflected the ratio of the amorphous to graphitic carbon content. Therefore, both of the Pt@CS and Pt/CS catalysts supported on HCMS carbon spheres exhibited a similar hydrophilic/hydrophobic character of the carbon support.

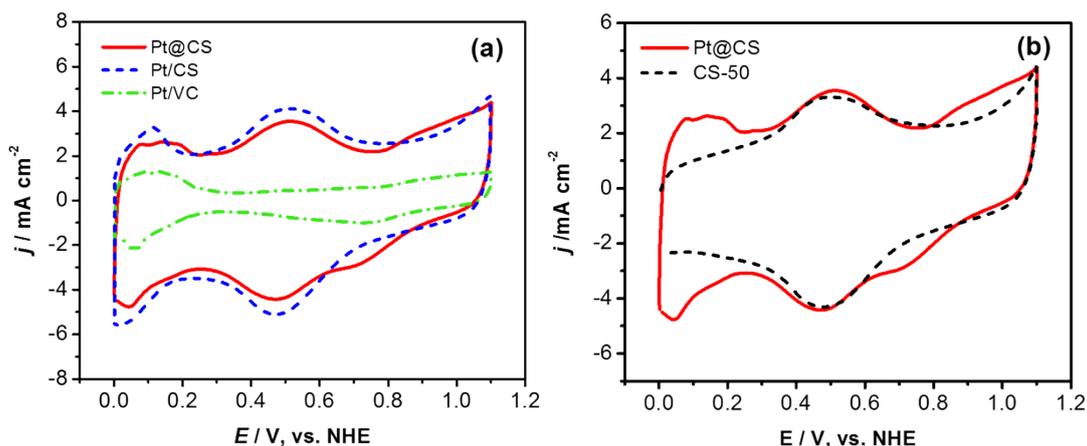


Figure S3. (a) Cyclic voltammetry of the examined Pt catalysts in 0.5 M H₂SO₄ electrolyte at a scan rate of 20 mV s⁻¹. (b) CV curves of Pt@CS and carbon spheres (CS-50) in 0.5 M H₂SO₄ electrolyte at a scan rate of 20 mV s⁻¹ with equal mass loading of carbon on GC electrodes (0.57 mg cm⁻²). The current was normalized by the electrode surface area.

Cyclic voltammetry of carbon spheres (CS-50) was measured in H₂SO₄ electrolyte at the same scan rate (20 mV s⁻¹) as background. The area under the hydrogen desorption region between 0.05 V and 0.4 V vs. NHE subtracted the background currents contributed from carbon support was integrated as the charge associated with H⁺ desorption (Q_H).³⁻⁵ The ECSA of Pt was then calculated according to the following equation:

$$\text{ECSA} = \frac{Q_H}{0.21 \times [Pt]}$$

where Q_H (mC) is the charge due to the hydrogen desorption in the potential region of 0.05 – 0.4 V of the CVs, 210 μC cm⁻² is the electrical charge associated with monolayer adsorption of hydrogen on Pt surface, and [Pt] is the loading of Pt on the working electrode.

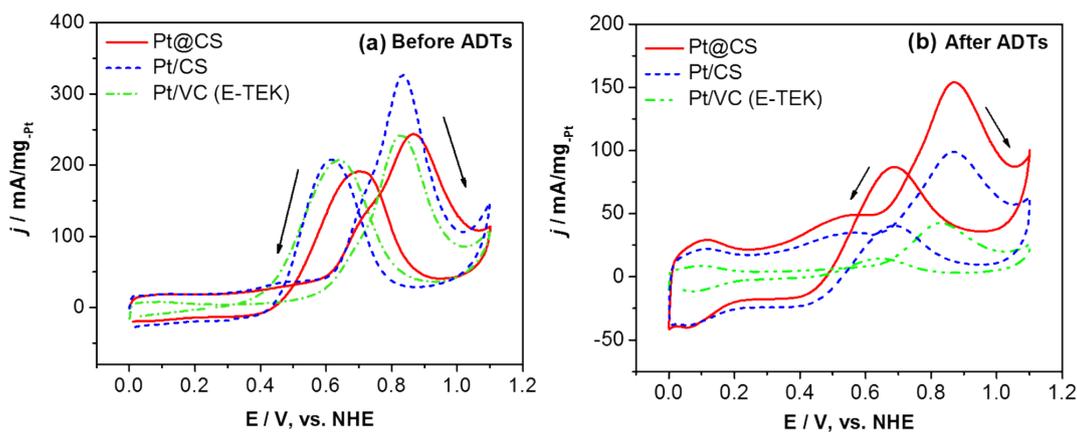


Fig. S4 (a) CV curves of the Pt@CS, Pt/CS and E-TEK Pt/VC catalysts in 1.0 M CH₃OH + 0.5 M H₂SO₄ solution at a scan rate of 20 mV s⁻¹. (b) CV curves of the degraded Pt catalysts after 2000 cycles of ADTs in 1.0 M CH₃OH + 0.5 M H₂SO₄ solution at a scan rate of 20 mV s⁻¹. The current was normalized by Pt mass loaded on the GC electrodes.

References

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