

## Supporting information- B404918G

### **Spherical carbon capsules with hollow macroporous core and mesoporous shell structures as a highly efficient catalyst support in direct methanol fuel cell**

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#### **Experimental**

SCMS silica template was synthesized by the reported method<sup>1</sup> and the following procedure describes the synthesis of SCMS silica with a core diameter of 220 nm and a shell thickness of 40 nm. 3.14 mL of aqueous ammonia (32 wt. %) was added to a solution containing 74 mL of ethanol and 10 mL of deionized water. 6 mL of tetraethoxysilane (TEOS) was added to the above-prepared mixture at 303 K with vigorous stirring and the reaction mixture was stirred continuously for one hour to yield uniform silica spheres. A mixture solution containing 5 mL of TEOS and 2 mL octadecyltrimethoxysilane (C<sub>18</sub>-TMS) was added to the colloidal solution containing the silica spheres and further reacted for one hour. The resulting octadecyl group incorporated silica shell/solid core nanocomposite was retrieved by centrifugation, and further calcined at 823 K for 6 hours under an oxygen atmosphere to produce the final solid core/mesoporous shell (SCMS) silica material. Aluminum was incorporated into the silicate framework through an impregnation method. 1 g of SCMS silica was added to an aqueous solution containing 0.27 g of AlCl<sub>3</sub>·6H<sub>2</sub>O in 0.3 mL of water and the resulting slurry was stirred for 30 min. The powder was dried in air at 353 K. Finally,

the Al-impregnated SCMS silica was calcined at 823 K for 5 hours in air to yield SCMS aluminosilicate.

The typical synthetic procedure for HCMS carbon capsules is as follows.<sup>2</sup> 0.374 g of phenol per gram of SCMS aluminosilicate template was incorporated into the mesopores by heating at 373 K for 12 hours under static vacuum. The resulting phenol-incorporated SCMS aluminosilicate was reacted with paraformaldehyde (0.238 g) under static vacuum at 403 K for 24 hours to yield a phenol-resin/SCMS aluminosilicate nanocomposite. The nanocomposite was heated at 1 K min<sup>-1</sup> to 433 K and held at that temperature for 5 h under a nitrogen flow. The temperature was then ramped at 5 K min<sup>-1</sup> to 1223 K and held at that temperature for 7 h to carbonize phenol resin inside the mesopores of the SCMS aluminosilicate, in order to obtain a carbon/aluminosilicate nanocomposite. The dissolution of the SCMS aluminosilicate template using 2.0 N NaOH in 1:1 mixture of EtOH and H<sub>2</sub>O generated hollow core/mesoporous shell carbon. Temperature gravimetric analysis combined with EDX analysis indicated that the carbon contained about 0.5 wt % of residual silicon in the framework, demonstrating virtual complete removal of all the silica.

Carbon supported Pt-Ru alloy catalysts were synthesized at room temperature using H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O (Aldrich) and RuCl<sub>3</sub>.xH<sub>2</sub>O (Aldrich) as metal precursors and NaBH<sub>4</sub> as a reducing agent.<sup>3</sup> Equal moles (2x10<sup>-3</sup> mole) of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O and RuCl<sub>3</sub>.xH<sub>2</sub>O were dissolved in deionized water. The required amount of carbon substrates (HCMS or Vulcan-72 carbon) was suspended in deionized water and stirred to form homogeneous carbon slurry. Then the metal salt solution was added into the carbon slurry. Excess of NaBH<sub>4</sub> solution (NaBH<sub>4</sub>/metal mole ratio of ~ 10) was quickly poured into the carbon-metal salt mixed solution under vigorous stirring to reduce the metal salts for 2 h at

ambient temperature. 60 wt% metal loading was made with the Vulcan XC-72 carbon like in the commercial E-TEK catalyst, while 80 wt% with the HCMS carbon capsule. Since the HCMS carbons have a higher surface areas than Vulcan XC-72, it was possible to have higher metal loading of 80 wt% as well as the same metal loading of 60 wt%. This also gives an extra benefit that the amount of carbon support used can be decreased to half for the HCMS carbon.

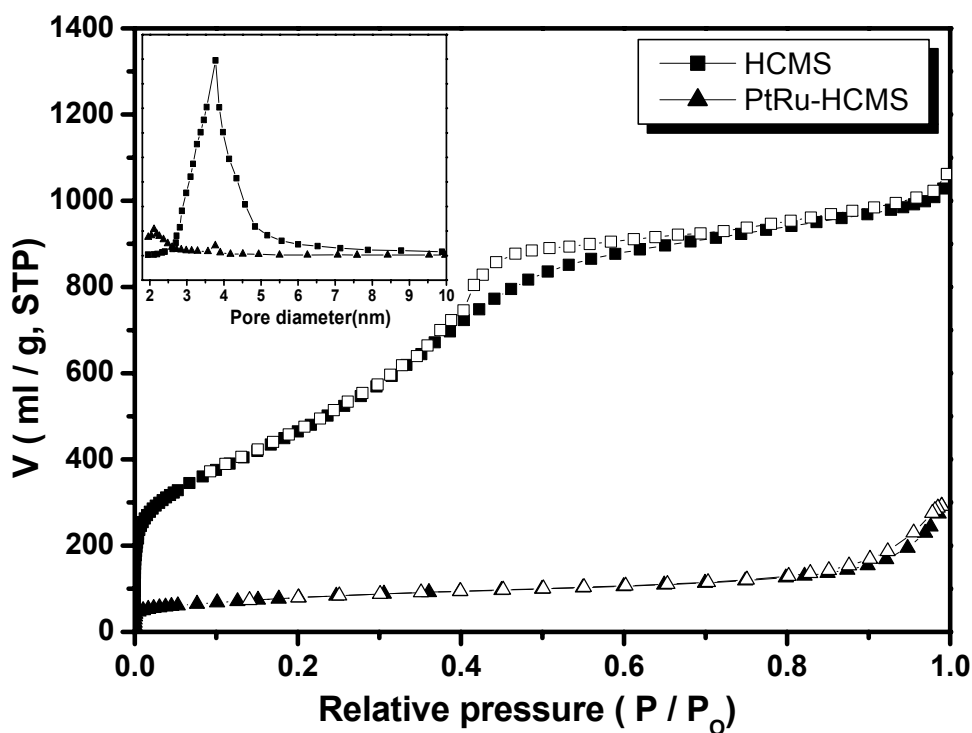
Unit cell performance was evaluated using a DMFC unit cell with a 2 cm<sup>2</sup> cross-sectional catalyst area, and measured with a potentiometer (WMPG-1000), which recorded cell potentials under constant current condition. The MEA (membrane electrode assembly) was fabricated by hot-pressing (130 °C, 1000 psi, 3 min) a pretreated Nafion<sup>®</sup> 117 (Du-Pont) with anode and cathode catalysts on each side. 5 wt% Nafion solution (Aldrich) corresponding to 20 and 7 wt% of anode and cathode catalysts, respectively was added to each of the catalyst inks for proton transfer. The catalyst loadings at anode and cathode based on metal only were 3.0 mg/cm<sup>2</sup> (supported Pt-Ru alloy) and 5.0 mg/cm<sup>2</sup> (unsupported Pt from Johnson-Matthey), respectively. The Nafion<sup>®</sup> 117 membrane was pretreated by boiling in 3 wt % H<sub>2</sub>O<sub>2</sub> for 1 h and then in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 1 h. The single cell test fixture was composed of two copper end plates and two graphite plates with rib-channel patterns allowing the passage of methanol to the anode and oxygen gas to the cathode. 2.0 M methanol solution was supplied to the anode by a Masterflex liquid micro-pump at a rate of 1.0 mL/min, while dry O<sub>2</sub> was fed to the cathode at a rate of 300 mL/min using a flowmeter.

## References

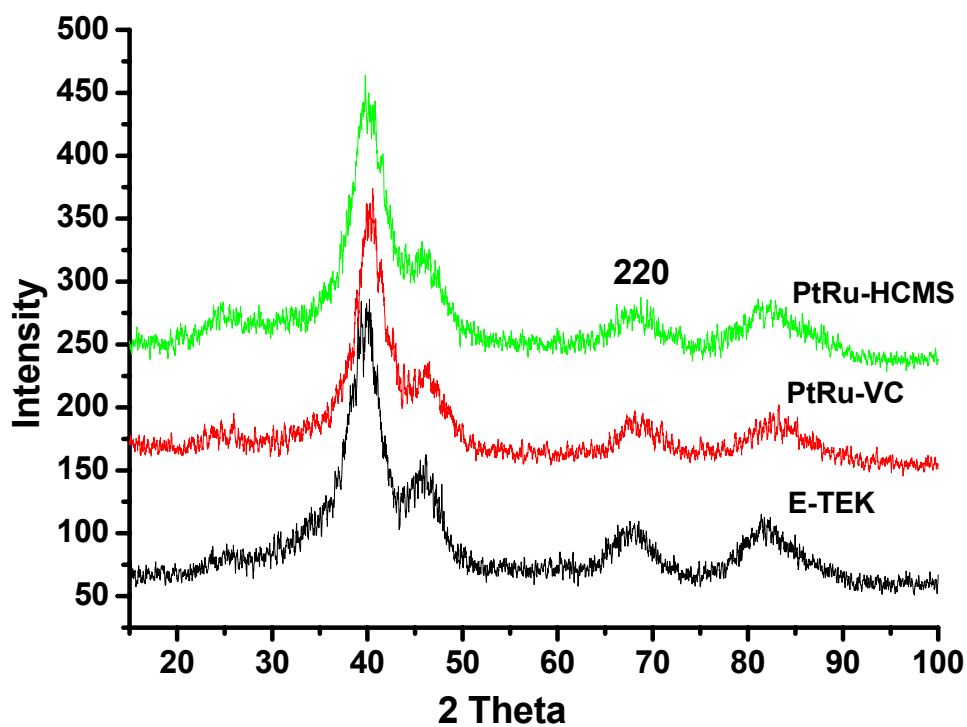
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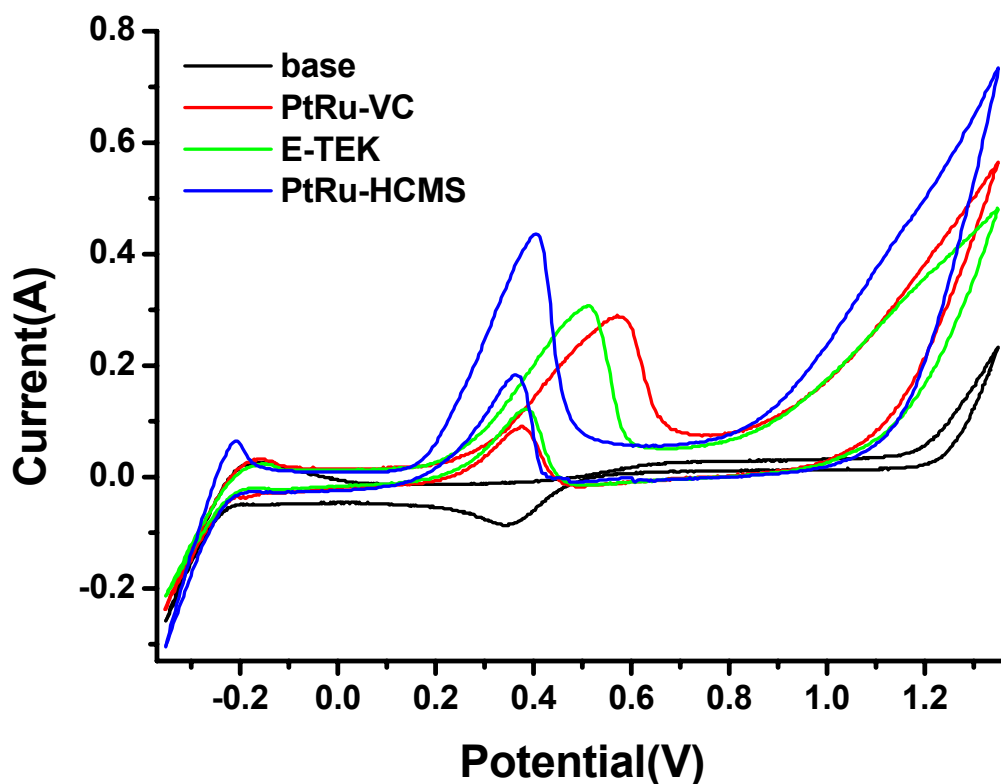
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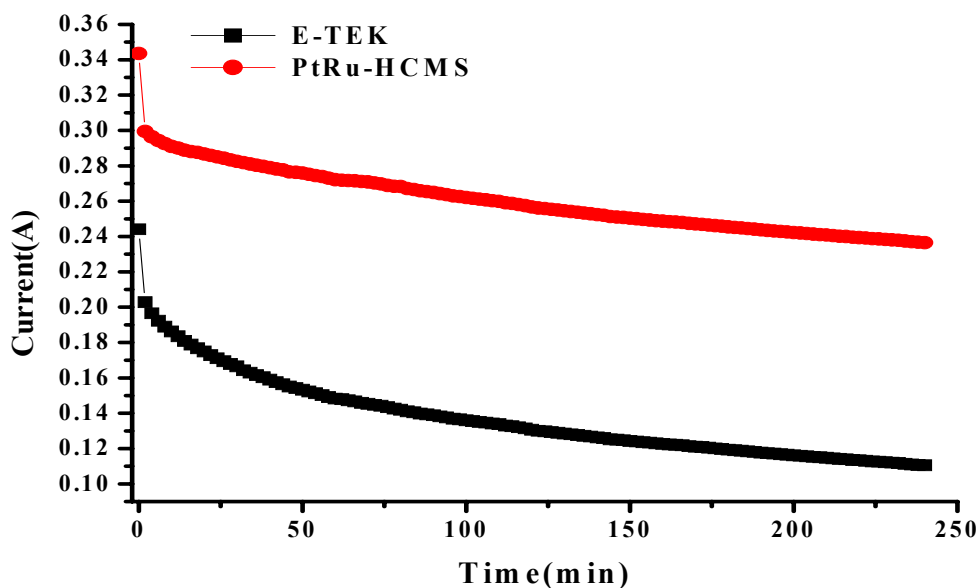
**Fig. S1.** N<sub>2</sub> adsorption (filled line) and desorption (unfilled line) isotherms of HCMS carbon capsule (■) and the corresponding carbon with loaded Pt-Ru catalyst (▲). The corresponding pore size distribution curves of the HCMS carbon capsules before and after catalyst loading (inset) were calculated from the adsorption branch of the nitrogen isotherm by BJH method. Micropore volumes were also calculated from the analysis of the adsorption branch of the nitrogen isotherm using Horvath-Kawzoe method. The isotherms were measured at 77 K on a KICT SPA-3000 Gas Adsorption Analyzer after the carbon was degassed at 423 K to 20 μTorr for 4 h.



**Fig. S2.** X-ray diffraction patterns of supported Pt<sub>50</sub>Ru<sub>50</sub> alloy catalysts. XRD analysis was carried out on the catalysts with a Rigaku 1200 using a Cu K $\alpha$  radiation, a Ni  $\beta$ -filter and operating at 40 kV and 20mA. All catalyst samples exhibit the characteristic peaks of the Pt f.c.c. structure.



**Fig. S3.** Cyclic voltammograms for supported Pt<sub>50</sub>Ru<sub>50</sub> alloy catalysts. The CV measurements were carried out in a three-compartment cell with Ag/AgCl reference electrode and platinum gauge counter electrode. The reference electrode contacted the electrolyte via a Luggin capillary. All cyclic voltammograms were obtained at room temperature at a scan rate 20 mV/s in a mixed solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M CH<sub>3</sub>OH from -0.35V to +1.35 V vs. Ag/AgCl using an EG&G 362 potentiostat. Base line curve was obtained in the same condition without CH<sub>3</sub>OH solution. The effective geometric area of the working electrode was 1 cm<sup>2</sup> and the electrode had a catalyst loading of 2.5 mg/cm<sup>2</sup> (metal base). PtRu-HCMS started the methanol oxidation activity on the lower voltage than E-TEK catalyst and PtRu-VC catalyst based on their on-set potentials which correspond to starting points of methanol oxidation. The PtRu-HCMS catalyst also exhibited higher specific methanol oxidation current of 174 mA/mgcm<sup>2</sup> at 0.4V (verse Ag/AgCl, in saturated KCl), compared with 80 mA/mgcm<sup>2</sup> for the E-TEK catalyst and 60 mA/mgcm<sup>2</sup> for the PtRu-VC catalyst. This corresponds to significant improvement of the PtRu-HCMS catalyst over E-TEK one by about 117 % and PtRu-VC one by about 190 %.



**Fig. S4** Chronoamperograms for supported Pt<sub>50</sub>Ru<sub>50</sub> alloy catalysts. The electrodes were first optimized by applying several voltammetric cycles (20 mV/s, from -0.35V to +1.35V, 0.5 M H<sub>2</sub>SO<sub>4</sub>) until a reproducible response was reached. Then, the cyclic voltammograms were recorded at room temperature at a scan rate 20 mV/s in N<sub>2</sub> degassed mixed solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M CH<sub>3</sub>OH from -0.35V to +1.35 V vs. Ag/AgCl using a WMPG-1000 potentiometer. Chronoamperograms were obtained at a fixed potential of 0.4V vs Ag/AgCl reference electrode for 4 h in the mixed solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M CH<sub>3</sub>OH. The effective geometric area of the working electrode was 1 cm<sup>2</sup> and the electrode had a catalyst loading of 2.5 mg/cm<sup>2</sup> (metal base).