Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2006
Paper submitted to *Chem. Commun.* by Shou-Heng Liu et al.

Electronic supplementary information

1. Characterization methods

The concentrations of platinum in various samples were analyzed by flame atomic absorption (AA, Hitachi Z-8200) spectroscopy. The powdered X-ray diffraction (PXRD) patterns of various samples were recorded on a PANalytical (X'Pert PRO) instrument using CuKα radiation (λ = 0.1541 nm). X-ray photoelectron spectra (XPS) were measured through the energy analyzer with pass energy 20 eV followed by irradiating a 6-mm-in-diameter sample pellet with the monochromatic Al-Kα (1486.6 eV) X-ray in an ultra-high vacuum system. Nitrogen adsorption/desorption measurements were done at 77 K on a Micromeritics ASAP 2010 apparatus. For transmission electron microscopy (TEM) studies, each sample was first suspended in acetone (99.9 vol.%) by ultrasonication, then the suspension was deposited on a lacey carbon grid, and the experiments were performed at room temperature (298 K) using a 200 kV electron microscope (JEOL JEM-2100).

2. Pt dispersion measurements

The dispersions of platinum on various samples were measured by hydrogen chemisorption. For each run, ca. 0.2 g of Pt-CMM sample were pretreated by outgassing at 623 K for one hour, then, the first H_2 adsorption isotherm was measured after the sample was cooled to 305 K, followed by outgassing for one hour to obtained a second H_2 adsorption isotherm under the same conditions.

3. CO tolerance tests

CO tolerance tests were done by competitive adsorption with H_2 on an automated chemisorption apparatus (Micromeritics, AutoChem II 2920). First, ca. 500 ppm of CO was pre-adsorbed onto the sample at 328 K for 0.5 h, then H_2 (10%) was pluse-injected with Ar carrier gas till a saturated coverage of H_2 was achieved.

4. Evaluation of electrocatalytic performances

Electrocatalytic activity of various Pt-CMMs and the commercial Johnson Matthey Pt/C sample (20 wt.% Pt on Vulcan XC-72) were performed on a μ Autolab potentiostat at a scan rate of 10 mV/s. The glossy carbon thin-film electrode was prepared by the following steps: first, ca. 5 mg of Pt-loaded carbon sample was added into 2.5 mL deionized water followed by ultrasonic treatment for 0.5 h. Then, ca. 20 μL of the resultant suspension mixture was withdrawn and injected onto the glassy carbon electrode followed by drying in air at 333 K for 1 h. Finally, 20 μL of 5% Nafion solution was added as a binder under N_2 environment. Electrooxidation of MeOH was carried out with an electrolyte of 0.5 M H_2SO_4 and 1 M MeOH between –0.2 and 1.0 V at room temperature.

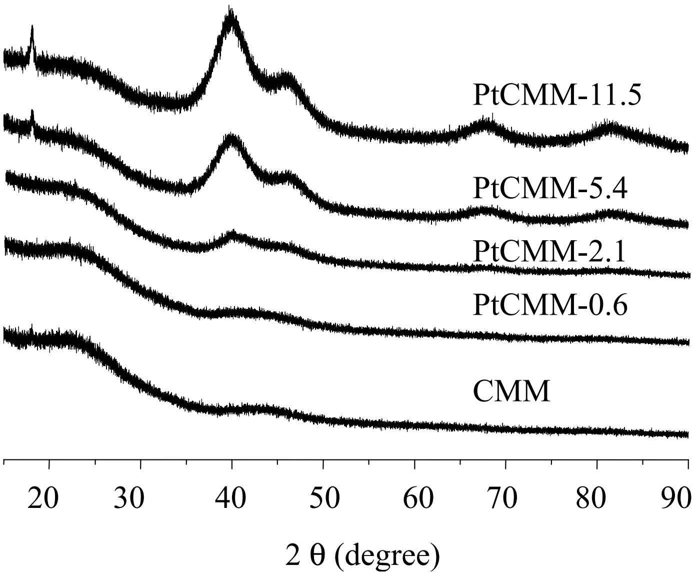

Fig. S1. Large-angle PXRD patterns of CMM and various Pt-CMMs. The size of Pt particle can be deduced by Scherrer formula: $d = k\lambda/\beta_{1/2}\cos\theta$, where k is the coefficient taken as 1, λ is the wavelength of X-ray radiation, and $\beta_{1/2}$ is the full-width half-maximum linewidth.

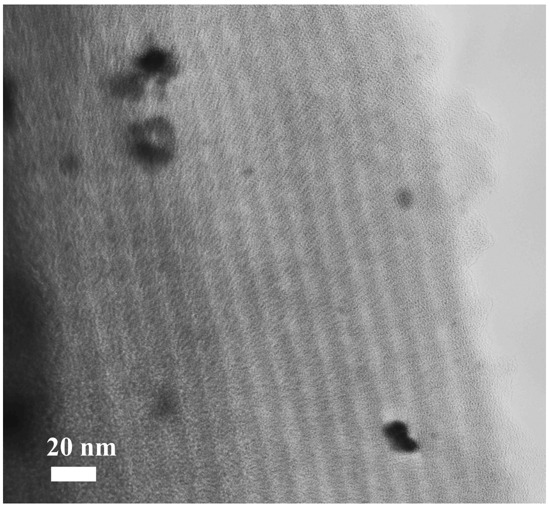

Fig. S2. TEM image of the Pt/CMM-0.6I sample prepared by conventional impregnation method.

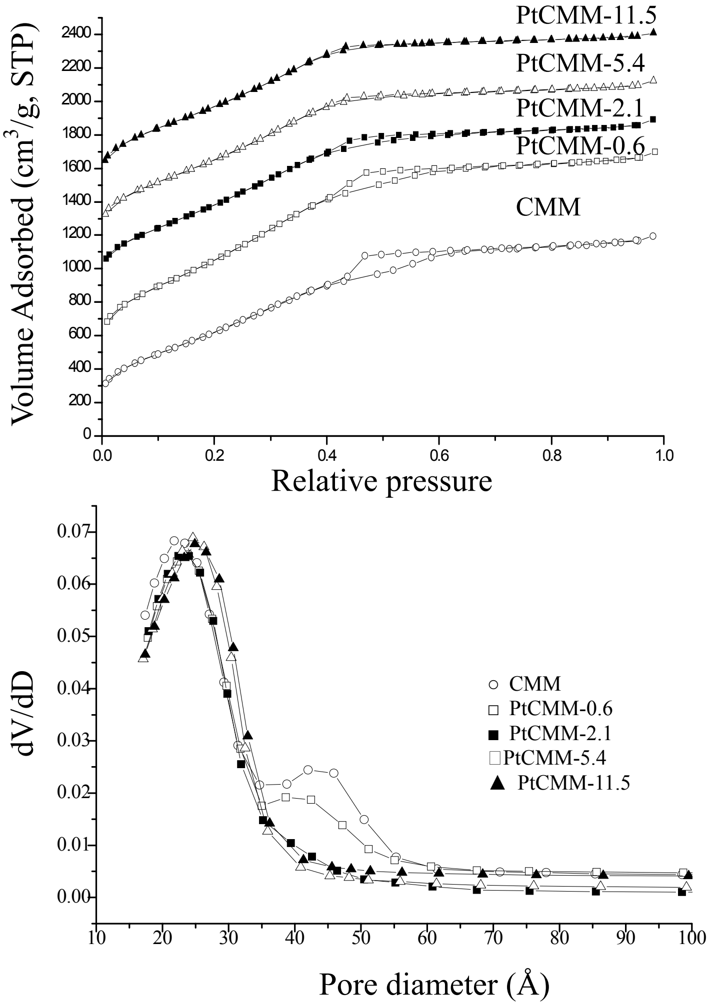

Fig. S3. N_2 adsorption/desorption isotherms (top) and BJH pore size distribution (bottom) for CMM and various Pt-CMMs.

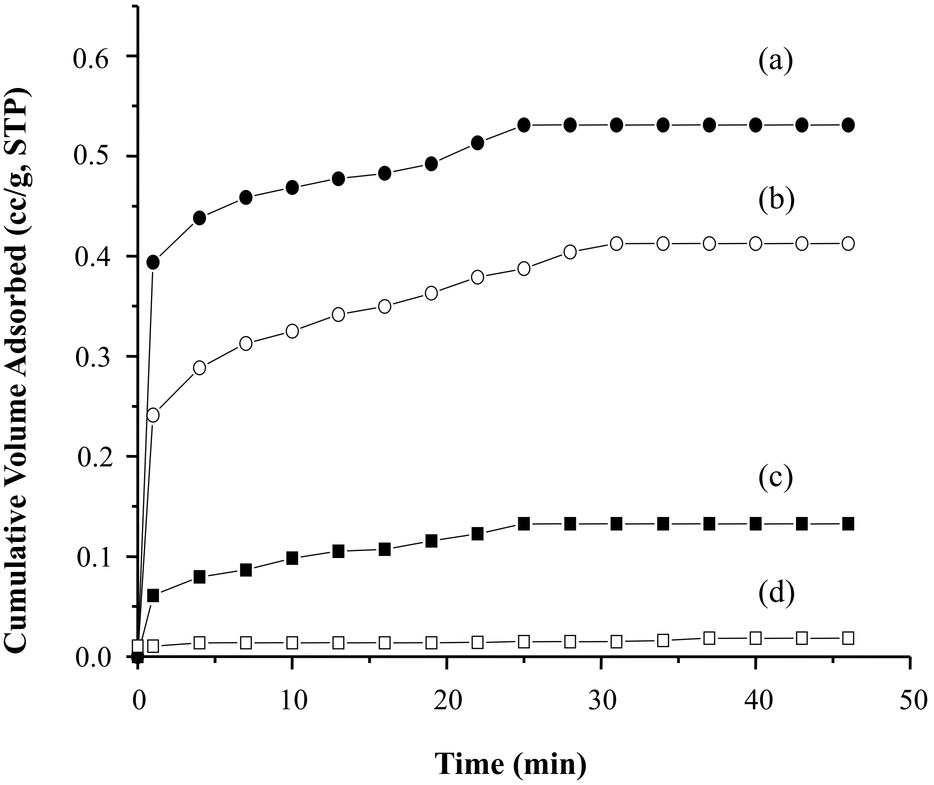

Fig. S4. Pulsed H_2 chemisorption profiles of Pt-CMM-0.6 (circular symbols) and Pt/CMM-0.6I (square symbols) samples (a), (c) without and (b), (d) with pre-adsorption treatment by CO (500 ppm).

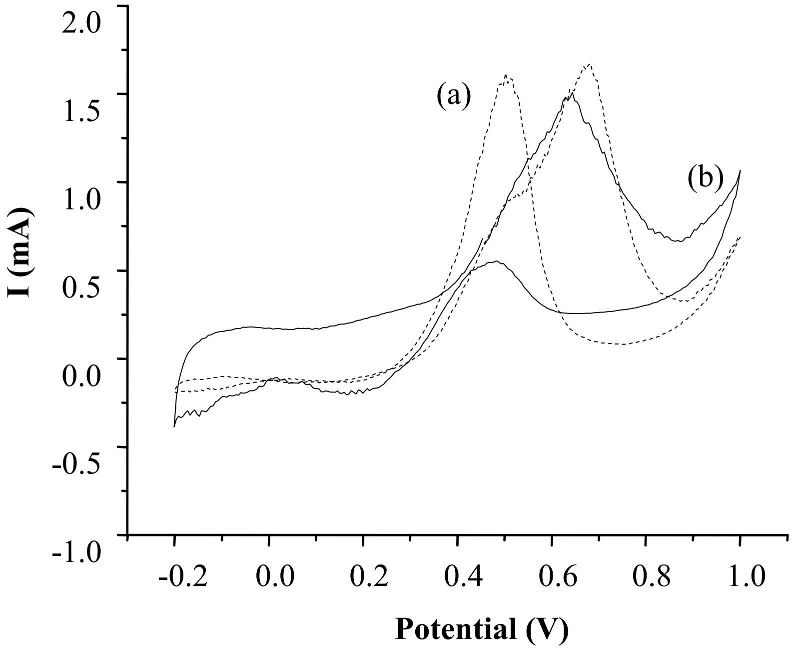

Fig. S5. Cyclic voltammograms of methanol oxidation on (a) commercial Johnson Matthey Pt/C and (b) Pt-CMM-11.5 catalysts in 0.5 M H_2SO_4 and 1 M MeOH at 10 mV/s.