# Electronic Supporting Information

## On the chemistry of activating commercial carbon-supported PtRu electrocatalyst for methanol oxidation reaction

De-Jun Chen,[1,2] Shi-Gang Sun,[2]* and YuYe J. Tong[1]*

[1] *Department of Chemistry, Georgetown University, 37th & O Streets, NW, Washington, DC 20057. Email: yyt@georgetown.edu*
[2] *Departments of Chemistry and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005 P R China. Email: sgsun@xmu.edu.cn*

### *Experimental:*

***Chemicals and materials***: All materials used herein were purchased commercially unless specified otherwise. Pt/C (40 wt%) and PtRu/C (60 wt.%, Pt:Ru=1:1) were courtesy of Johnson Matthey). Ru/C (60 wt.%) was purchased from E-TEC. $HClO_4$ (70%, Cl < 0.1 101 ppm) was from GFS chemicals and MeOH (>99.8%) from Sigma-Alorich, A.C.S. Reagent. They were used as purchased. High-pure Milli-Q $H_2O$ (18.2MΩ, TOC<2ppb) was used to make all the solutions.

***Electrochemistry and Electrochemical ATR-SEIRAS***: All electrochemical (EC) experiments were carried out in a conventional three-electrode EC-IR cell (Fig. S2) using a CHI-660D potentiostat in 0.1 M $HClO_4$ + 0.5 MeOH. Large surface-area Pt gauze and Ag/AgCl (3 M) (Bioanalytical) were used as counter and reference electrodes, respectively. While all potentials were measured physically with respect to this Ag/AgCl reference electrode during the experiments, the potentials used in the paper were converted to with respect to reversible hydrogen electrode (RHE). All attenuated-total-reflection surface enhanced infrared adsorption spectroscopy (ATR-SEIRAS) data acquisitions were carried out on a Bruker Vector-22 Fourier transform IR spectrometer equipped with a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector. A home-made EC-IR cell with a triangular Si prism and an optical reflection accessory (incident angle of >60◦ enabling total attenuation reflection) was used for in situ measurements (Fig. S2). The geometric area, 1.13cm$^2$, was limited by the hole of the sealing O-ring. 100 μL of well-sonicated PtRu/C (60wt.%) suspension with a concentration of 1 μg/μL was drop-casted onto the hole area and air-dried. As Au film and carbon support do not have any methanol oxidation activity within the potential range of the experiments, the detected species must come from the used PtRu/C electrocatalyst. Although ATR-SEIRAS is highly sensitive

with the surface adsorbed species due to surface enhancement effect, the two layer structure (Au film+catalyst) with many small pin-holes between NPs created a micro-porous structure that can hold some reactant or product (such as $CO_2$) for infrared detection. No Nafion® solution was used in order to eliminate all influence by sensitive infrared measurement. The spectral resolution was 4 $cm^{-1}$. The obtained spectra were shown in the absorbance units defined as $-\log(I/I_0)$ where I and $I_0$ are the single-beam spectral intensities at the measuring potential and the reference potential, respectively.

***Catalyst Characterizations***: The surface morphology and composition of catalysts were examined by field emission scanning electron microscopy (FE-SEM) combined with Oxford EDS (Zeiss SUPRA55-VP, 20 kV, Carl Zeiss Inc., Germany). The crystal structure of catalysts was measured by X-Ray diffractometer (Rigaku, Ultima IV, 40kV, 44mA). The TEM characterization was performed on JEOL JEM-2100 LaB6 transmission electron microscope at 100 kV. The samples were prepared in carbon-coated copper grids (400 meshes, Electron Microscopy Science). The nanoparticle sizes were measured using Image-J program.

## *Supporting Figures:*

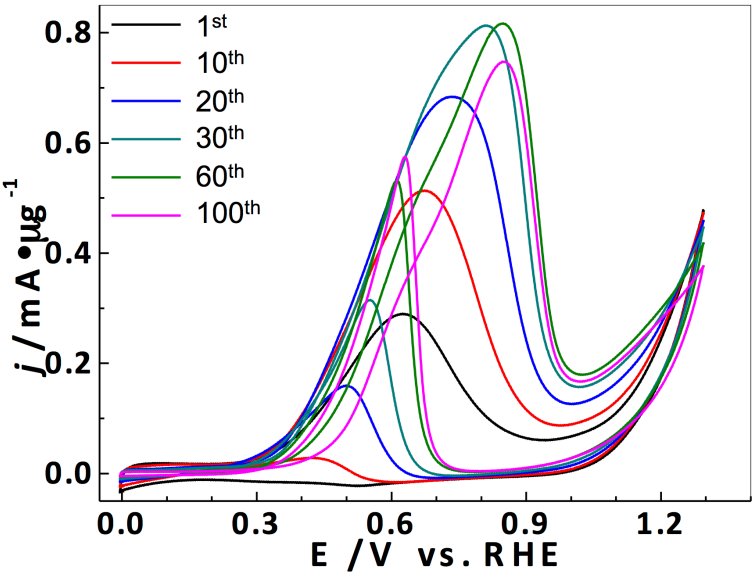


**Fig. S1.** The activating-deactivating CVs for the PtRu/C on a glassy carbon (GC) electrode in 0.1 M $HClO_4$ + 0.5 M MeOH.

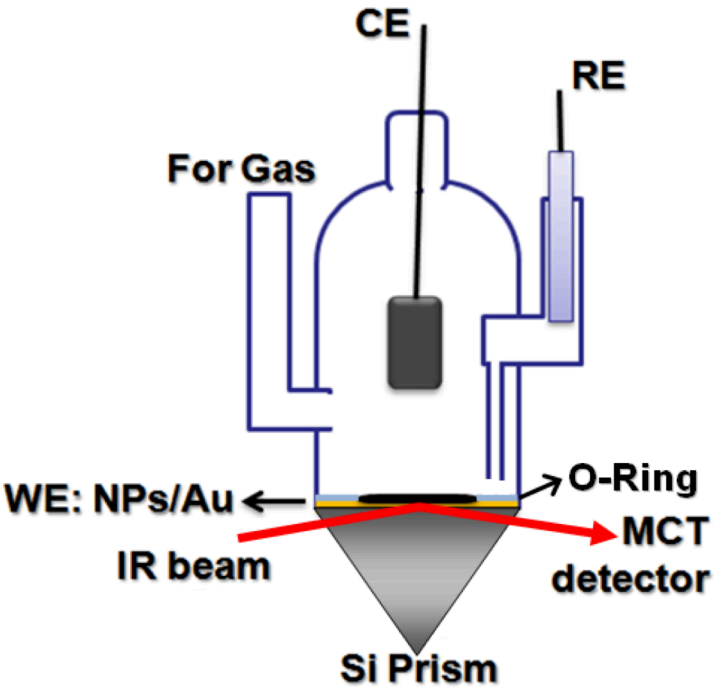


**Fig. S2.** The schematic of the IR cell used in acquiring ATR-SEIRAS spectra

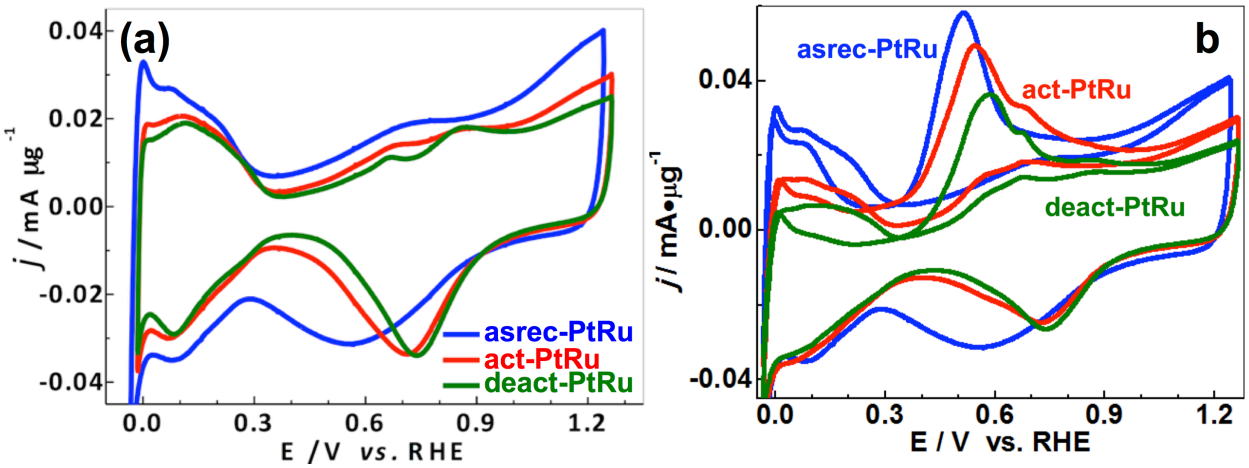


**Fig. S3.** The normal (a) and M-$CO_L$ (b) stripping CVs of the as-received, the best activated, and the worst deactivated PtRu/C samples in pristine 0.1 M $HClO_4$ electrolyte. The graduate reduction of the double-layer current is a good indication of less and less surface Ru.

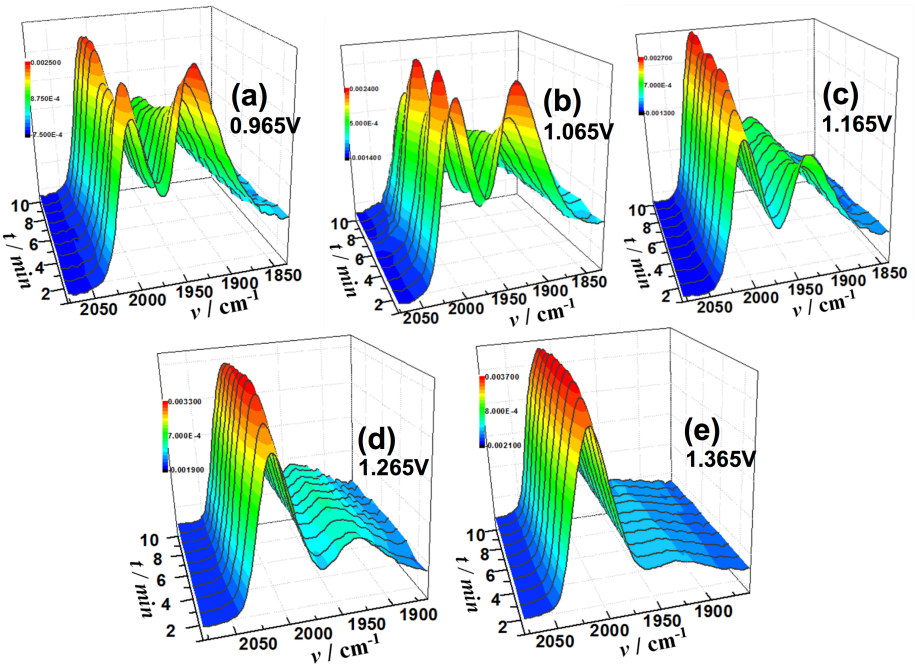


**Fig. S4.** The time-dependent SEIRAS spectra acquired during the SPS with different SP values: (a) 0.965 V, (b) 1.065 V, (c) 1.165 V, (d) 1.265 V, and (e) 1.1365 V.