## *In situ* Raman Spectroscopic Measurement of Surface pH Value Changes during Electrochemical Reactions

De-Jun Chen and YuYe J. Tong

Department of Chemistry, Georgetown University, 37th & O Streets, NW, Washington, DC 20057, USA. E-mail: yyt@georgetown.edu

## **Experimental:**

**Chemicals and Materials:** The Pt black (~10 nm, ~20 m<sup>2</sup>/g) was purchased from Johnson-Matthey. HClO<sub>4</sub> (70%, Cl < 0.1 101 ppm, GFS chemicals), MeOH (>99.8%, Sigma-Alorich, A.C.S. Reagent) and High-Pure Milli-Q H<sub>2</sub>O (18.2 M $\Omega$ , TOC<2ppb) were used to make the solutions. Ultrapure Ar (GTS•Welco, 99.999%, THC<0.5ppm) and O<sub>2</sub> gas (GTS•Welco, 99.993%, THC<1ppm) were used as-received to make anaerobic pristine, MeOH-containing, or O<sub>2</sub>-saturated electrolyte solutions.

**Electrochemistry:** All electrochemical (EC) experiments were carried out in a three-electrode EC-Raman flow cell (see Figure 1 and pictures below of which the left is the pump-flowing system and the right is the EC-Raman flow cell mounted in the Raman scope) using a CHI-601D potentiostat. A Pt wire loop and Ag/AgCl (1 M, 0.290 V with respect to RHE in 0.1 M HClO<sub>4</sub>, Bioanalytical) were used as counter and reference electrodes, respectively.



The electrolyte was circulated by a Masterflex Peristaltic Pumps (HV-07528-30) with speed control of  $\pm 0.25\%$  (left picture in Figure S1). The Raman spectra were obtained using a

confocal microprobe Raman system (Renishaw RM1000) equipped with a deep depletion CCD peltier cooled down to  $-70 \circ$ C. The microscope attachment is based on an Olympus BH2-UMA system and uses a 50× objective. A holographic notch filter was used to filter the excitation line, and 1200 g/mm selective holographic grating was employed depending on the spectral resolution required. The excitation wavelength was 785 nm from a diode laser with a maximum power of 100 mW. The focused laser spot by objective was about 3 µm.

**Spectral Normalization:** The Raman spectra presented in this Communication are the normalized spectra defined by  $\Delta R/R = (R_s - R_{ref})/R_{ref}$  where  $R_s$  and  $R_{ref}$  are the spectra taken at the measuring and reference potentials, respectively. Therefore, upward/downward peaks in these normalized spectra reveal the increasing/decreasing in the amount of  $ClO_4^-$  as compared to those at the reference spectrum. The reference was chosen at the potentials at which no reactions take place. Consequently, the normalized spectra reflect the local near surface acidity change during the oxidation and reduction reactions with respect to the reference potential because of the local ionic electroneutralitiy ( $[H^+]=[ClO_4^-]$ ) in the HClO<sub>4</sub> electrolyte.



## **Supporting Figures:**

**Figure S1** 

Figure S1a and S1b show the raw and normalized (vs. the spectrum taken at the HClO<sub>4</sub> concentration of 0.1 M) Raman spectra of  $ClO_4^-$  as a function of the bulk concentration of HClO<sub>4</sub> from 0.01 to 0.5 M. The inset shows the Beer's Law-like linear relationship [H<sup>+</sup>] and the integration Raman band intensity (see Table S1 for the numeric data) for the bulk concentration of HClO<sub>4</sub> from 0.01 to 0.5 M.

[HCIO <sub>4</sub> ] / M	[H⁺] / mM	l(ClO₄⁻) / cts	∆I(ClO <sub>4</sub> ⁻) / a.u.
0.01	10	2329.9	-2.2200
0.02	20	3820.8	-2.1807
0.05	50	15396.7	-1.5784
0.1	100	35161.2	0
0.2	200	75589.6	2.9417
0.5	500	197436.5	11.7181

**Table S1.** The proton concentration [H<sup>+</sup>] and integrated Raman band intensity.



Figure S2

Figure S2 presents the CVs of the Pt black NPs in 0.01 (purple), 0.02 (pink), 0.05 (green), 0.1 (black), 0.2 (blue) and 0.5 (red) mol/L HClO<sub>4</sub>.



Figure S3

Figure S3 shows the forward (a) and backward (b) current transients of MOR on Pt black electrode in 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH. The integrated charge of each current transient is shown in Figure 2c.



Figure S4

**Figure S4** presents the current transients of ORR on Pt black in the flow cell circulating  $O_2$ -saturated 0.1 M HClO<sub>4</sub> at 4 ml/min. The generated reduction current depends on the applied potentials and the charges are displayed in Fig. 3c.