## **Supplementary Material for**

# Nanoscale chemical imaging and spectroscopy of individual RuO<sub>2</sub> coated carbon nanotubes

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#### 1. Preparation of RuO<sub>2</sub>/MWCNT and RuO<sub>2</sub> nanoparticles

RuO<sub>2</sub> coated multi-walled carbon nanotubes (RuO<sub>2</sub>/MWCNT) and RuO<sub>2</sub> nanoparticles were prepared by a sol-gel method. The details of preparation can be found elsewhere (ref 14 in the paper). Briefly, the MWCNTs (diameters of 60-100 nm) were first treated by refluxing in nitric acid (40%) to generate surface oxygen-containing functional groups, and are henceforth denoted MWCNTs. MWCNTs were then dispersed in a 0.1 M RuCl<sub>3</sub> solution. A 0.3 M NaHCO<sub>3</sub> aqueous solution was then added slowly to the above mixture under stirring until the pH of the solution reached 7. The black sediments were then washed several times with distilled water, and then dried in air flow at room temperature. The black powder thus obtained was annealed at 150  $^{\circ}$ C for 19 h in air and the final product is henceforth denoted RuO<sub>2</sub>/MWCNT. RuO<sub>2</sub> nanoparticles were prepared following a similar sol-gel process in 0.1 M RuCl<sub>3</sub> in the absence of MWCNTs. It was also annealed at 150  $^{\circ}$ C for 19 h in air and paper).

#### 2. STXM sample preparation

In order to measure spectro-microscopy for individual CNTs,  $RuO_2/MWCNT$  and MWCNT need to be dispersed before deposition onto  $Si_3N_4$  window; the solvent casting method was used. First, a few milligrams of each sample was added into methanol to prepare a ~1% suspension, then it was sonicated for 15 minutes. After the suspension was well dispersed, one can start to prepare STXM sample. On a STXM sample plate, a carbon double-side tape was

used to tape a blank Si<sub>3</sub>N<sub>4</sub> window (1 mm x 1 mm x 75 nm (length x width x thickness) Si<sub>3</sub>N<sub>4</sub> window membrane on a 5 mm x 5 mm x 200  $\mu$ m silicon wafer frame, Norcada Inc.) onto one of the six sample holes. Then a tiny drop of sample suspension (~1  $\mu$ L) was placed onto the Si<sub>3</sub>N<sub>4</sub> window membrane by a micropipette and allowed to dry in air. After solvent was evaporated, the sample was transferred into the STXM chamber for pumping to coarse vacuum (~0.25 torr) , then the chamber was filled with ~1/6 atm helium for STXM measurement. RuO<sub>2</sub> nanoparticles were deposited onto a blank Si<sub>3</sub>N<sub>4</sub> window directly by a small spatula without the dispersion procedure, since only spectroscopic measurement was needed.

#### 3. STXM measurement

STXM measurement was conducted using the STXM at the SM beamline of the Canadian Light Source (CLS). In order to achieve the best spatial resolution, a 25 nm outer-zone zone plate (CXRO, Berkeley Lab) was used. The diffraction-limited spatial resolution for this zone plate is 30 nm. Circularly polarized soft X-ray beam generated from SM elliptically polarized undulator (EPU) was used to remove the linear dichroism effect originated from different orientations of the CNTs in the plane of the Si<sub>3</sub>N<sub>4</sub> window membrane<sup>1</sup>. A 250 l/mm plane grating monochromator (PGM) was used for both C and O K-edge measurements. The incident photon flux (Io) was tuned to be ~20 MHz as read by the STXM detector in a hole of the STXM sample plate at 320 eV with exit slits at 35/35  $\mu$ m (dispersive/non-dispersive) for the C K-edge, and at 560 eV with slits at 25/25  $\mu$ m for the O K-edge. X-ray photon energy at C and O K-edge was calibrated using the gas phase XANES of CO<sub>2</sub>, and literature values for the transitions: C 1s  $\rightarrow$  3p at 294.96 eV<sup>2</sup>, O 1s  $\rightarrow \pi^*$  at 535.4 eV<sup>3</sup>, respectively. Image sequence (stack) scans over a range of photon energies were acquired for all three samples at both C K-

edge (including Ru  $M_{5,4}$  edge) and O K-edge. The C K-edge stacks covered an energy range of 280 - 340 eV with energy step as fine as 0.1 eV around the XANES peaks and coarser, 0.4 - 1.0 eV, in the pre-edge and continuum. The O K-edge stacks scanned an energy range of 525 - 560 eV with the finest energy step of 0.2 eV. The stack scan size was defined to include CNT sample region of interest, normally a few microns depending on the size of CNTs. In addition, the scan area often contained some blank region for Io measurement. The pixel size and dwell time for each image of a stack scan was adjustable to optimize the total scan time consumption and data statistics. In this work typical pixel size was 20 - 30 nm with 1 ms dwell time per pixel.

#### 4. Data analysis

#### 4.1 Reference spectra

For quantitative analysis of the RuO<sub>2</sub>/MWCNT stack, reference spectrum of each pure material is needed. First XANES spectra of pure RuO<sub>2</sub> and MWCNT were acquired through stack scans in both the C K-edge (including Ru  $M_{5,4}$  edge) and O K-edge. In the absence of absorption saturation, XANES spectra are obtained through the transmitted light intensity and the incident beam intensity (recorded in the absence of sample region of the same stack) using the Beer-Lambert law:

$$OD = A = -\ln T = \ln(\frac{I_0}{I}) = \mu \rho l$$
(S1)

where OD is the optical density, also called absorbance (*A*), *T* is the transmittance,  $I_0$  and *I* are the incident and transmitted X-ray photon flux (photons/s) respectively,  $\mu$  is the energy dependent mass absorption coefficient (cm<sup>2</sup>/g),  $\rho$  is the density (g/cm<sup>3</sup>) of the material, and *l* is the sample thickness (cm or nm). Then these spectra were converted to absolute linear absorbance scales (i.e. optical density per nm thickness sample). This was manipulated using the software package aXis $2000^4$  by scaling the XANES spectra of the pure material to match that of the linear X-ray absorption for the elemental composition of the material. For a specific compound, the elemental linear X-ray absorption, which neglects interactions such as bonding among the atoms, is calculated by aXis2000 using **Equation S1** and **S2** (which computes sum of the weighted atomic photoabsorption cross sections<sup>5</sup>) with a known density,

$$\mu = \frac{N_A}{M} \sum_i x_i \sigma_{ai} \tag{S2}$$

where  $N_A$  is the Avogadro's number, M is the molecular weight of a compound containing  $x_i$  atoms of type *i*,  $\sigma_{ai}$  is the atomic photoabsorption cross section (cm<sup>2</sup>/atom) for type *i* atom.

Specifically, RuO<sub>2</sub> reference spectra were obtained by fitting the original XANES spectra to match its calculated elemental linear X-ray absorption profile (which was based on actual formula RuO<sub>2</sub>.0.5H<sub>2</sub>O, estimated density = 5.0 g/cm<sup>3</sup>, and thickness = 1 nm) in the pre-edge and continuum. MWCNT C K-edge reference spectrum was generated similarly assuming its composition was carbon and density was 1.8 g/cm<sup>3</sup>. MWCNT was slightly oxidized after nitric acid treatment, but the oxygen content might vary among different CNTs, so the O K-edge reference spectrum of MWCNT was an average of a few individual MWCNT spectra without scaling to the unknown elemental linear X-ray absorption profile. The reference spectra of RuO<sub>2</sub> and MWCNT and their elemental linear X-ray absorption profiles are shown in **Figure S1**.

#### 4.2. Chemical mapping

Before fitting the image stacks with reference spectra, all images as a function of photon energy must be aligned such that the spatial features can be accurately superimposed from one image to the other. The automated stack alignment method in aXis2000/Zimba is based on 2 dimensional Fourier transform cross-correlation technique. Manual corrections of the alignment will be applied if automatic alignment is not satisfied. Then the aligned image stacks are converted to optical density image stacks by normalization to the Io spectrum usually collected at a blank region on the same stack. Afterwards, stack fit with multiple reference spectra can be performed using aXis2000. It computes a least squares fit of the optical density at each pixel of an image at energy *E*,  $OD_{(x,y,E)}$ , to a linear combination of reference spectra for each chemical component  $OD1_{(i,E)}$  (optical density per nm thickness of component *i* at energy *E*) based on **Equation S3** below:

$$OD_{(x,y,E)} = Constant_{(x,y)} + \sum_{i} a_{(x,y,i)} OD1_{(i,E)}$$
(S3)

 $a_{(x,y,i)}$ , the absolute thickness in nm of component *i* at each pixel, is the quantitative result of each chemical component map. A color composite map can be created by superimposing multiple component maps. Note for RuO<sub>2</sub>/MWCNT O K-edge stack fit, since the MWCNT reference spectrum is an average of oxygen content before RuO<sub>2</sub> coating, the fitting result means a comparison of oxygen content of MWCNT before and after RuO<sub>2</sub> coating. Stack fit can also be used to determine the thickness distribution for a pure material system, as demonstrated in **Figure S2**, which shows the thickness distribution of the MWCNT sample. The gray scale represents the absolute thickness distribution in nanometers.



**Figure S1** Reference spectra and elemental linear X-ray absorption profiles of  $RuO_2$  and MWCNT. (a)  $RuO_2 Ru_{M5,4}$  edge (thick line: optical density spectrum of 1 nm thickness, thin red line: elemental linear X-ray absorption profile based on formula  $RuO_2.0.5H_2O$ , density = 5.0 g/cm<sup>3</sup>, and thickness = 1 nm); (b)  $RuO_2 O K$ -edge; (c) MWCNT C K-edge (elemental linear X-ray absorption profile based on formula C, density = 1.8 g/cm<sup>3</sup>, and thickness = 1 nm); (d) MWCNT O K-edge (reference spectrum was an average of a few individual MWCNT spectra).



**Figure S2** Thickness distribution of the MWCNT sample as derived from the STXM C 1s stack fit. The right grey scale represents the thickness of MWCNT in nm.

### References

- 1. Najafi, E.; Hernandez, D.; Obst, M.; Hitchcock, A.P.; Douhard, B.; Prreaux, J.J.; Felten, A.; Small, 2008, 4(12) 2279-2285.
- 2. Ma, Y.; Chen, C.T.; Meigs, G.; Randall, K.; Sette, F.; Phys. Rev. A, 1991, 1848-1858.
- 3. Hitchcock, A.P.; Ishii, I.; J. Electron Spectrosc. Relat. Phenom, 1987, 42, 11-26.

4. aXis2000 is an application written in Interactive Data Language. It is available free for noncommercial applications at <u>http://unicorn.mcmaster.ca/aXis2000.html</u>

5. Henke, B.L.; Gullikson, E.M.; Davis, J.C.; At. Data Nucl. Data Tables, 1993, 54, 181-342.