Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Soft X-ray emission spectroscopy for electronic state of water molecules influenced by plasma-treated multi-wall carbon nanotubes

Noritaka Sakakibara[1,2], Kenichi Inoue[1,2], Shion Takahashi[1], Taku Goto[1,2], Tsuyohito Ito[1,2], Keishi Akada[3,4], Jun Miyawaki[1,3,4], Yukiya Hakuta[2], Kazuo Terashima[1,2,*], and Yoshihisa Harada[1,2,3,4,**]

[1] *Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan*

[2] *AIST-UTokyo Advanced Operando-Measurement Technology Open Innovation Laboratory (OPERANDO-OIL), National Institute of Advanced Industrial Science and Technology (AIST), 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8589, Japan*

[3] *Institute for Solid State Physics, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

[4] *Synchrotron Radiation Research Organization, The University of Tokyo, 1-1-1, Koto, Sayo, Hyogo 679-5148, Japan*

Corresponding authors: * kazuo@plasma.k.u-tokyo.ac.jp, ** harada@issp.u-tokyo.ac.jp

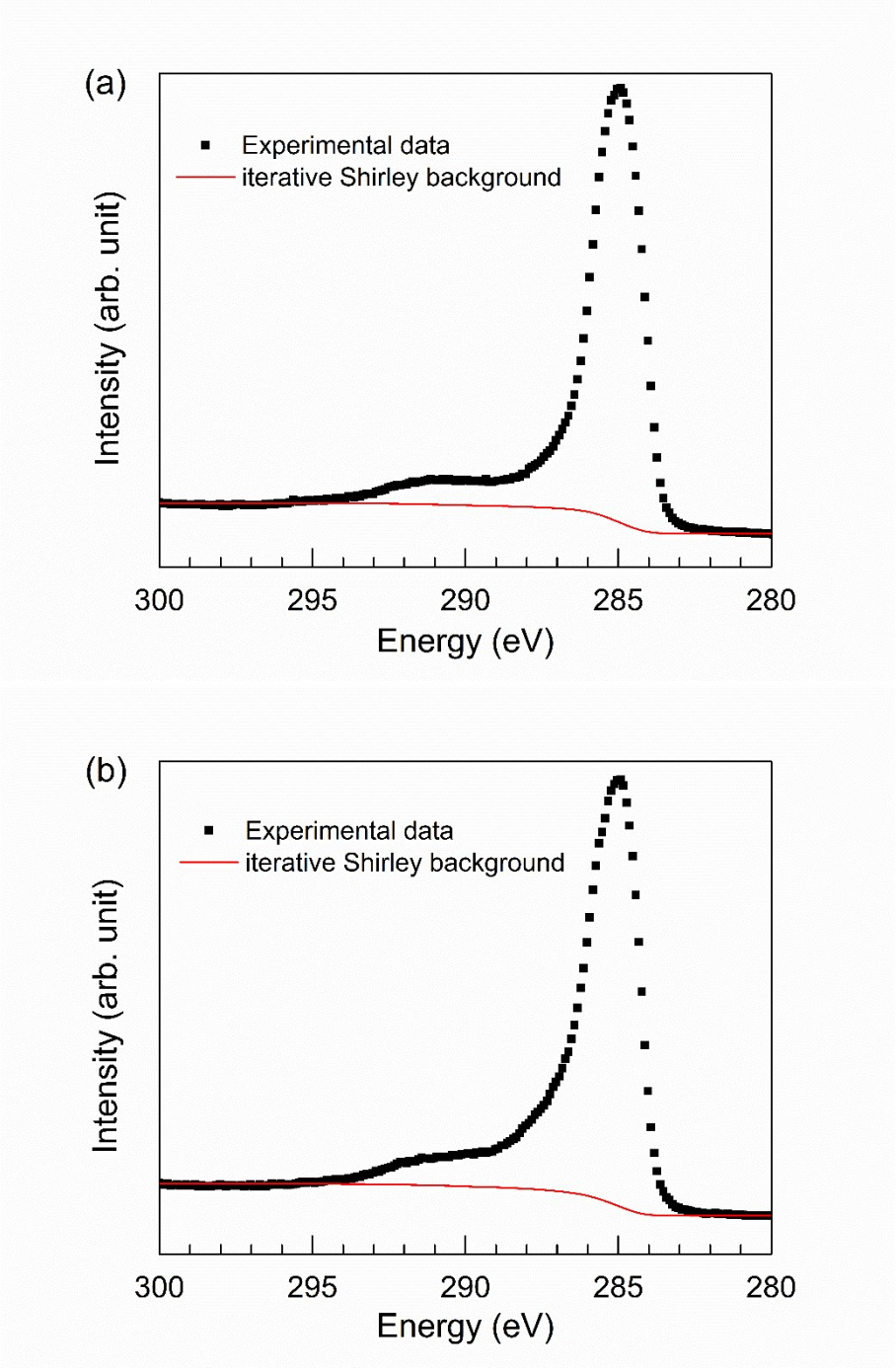

Figure S1. Originally obtained XPS spectra (black plot) and the subtracted iterative Shirley background of (a) as-purchased MWCNT and (b) plasma-MWCNT.

Subtraction of the contribution of oxygen atoms on plasma-MWCNT

To extract the information regarding the modulation of the valence electronic state of water molecules in the plasma-MWCNT aqueous dispersion, the contribution of the oxygen atoms on the plasma-MWCNTs to the XES spectrum (dashed-lines in Fig. S2) was subtracted from the as-obtained XES spectrum of 1 wt% plasma-MWCNT aqueous dispersion (a purple solid line in Fig. S2). First, the dry-plasma MWCNT spectrum with 2.92×10^{-4} times area ratio (a blue dashed line in Fig. S2) in comparison with the absolute integration of the as-obtained XES spectrum was subtracted from the as-obtained XES spectrum of 1 wt% plasma-MWCNT aqueous dispersion. The resulted spectrum is depicted with a blue solid line in Fig. S2, which is same as the XES spectrum of liquid H_2O in the 1 wt% plasma-MWCNT aqueous dispersion as shown with a blue solid line in Fig 4. The as-obtained spectrum (a purple solid line) is overlapped with the subtracted spectrum (a blue solid line).

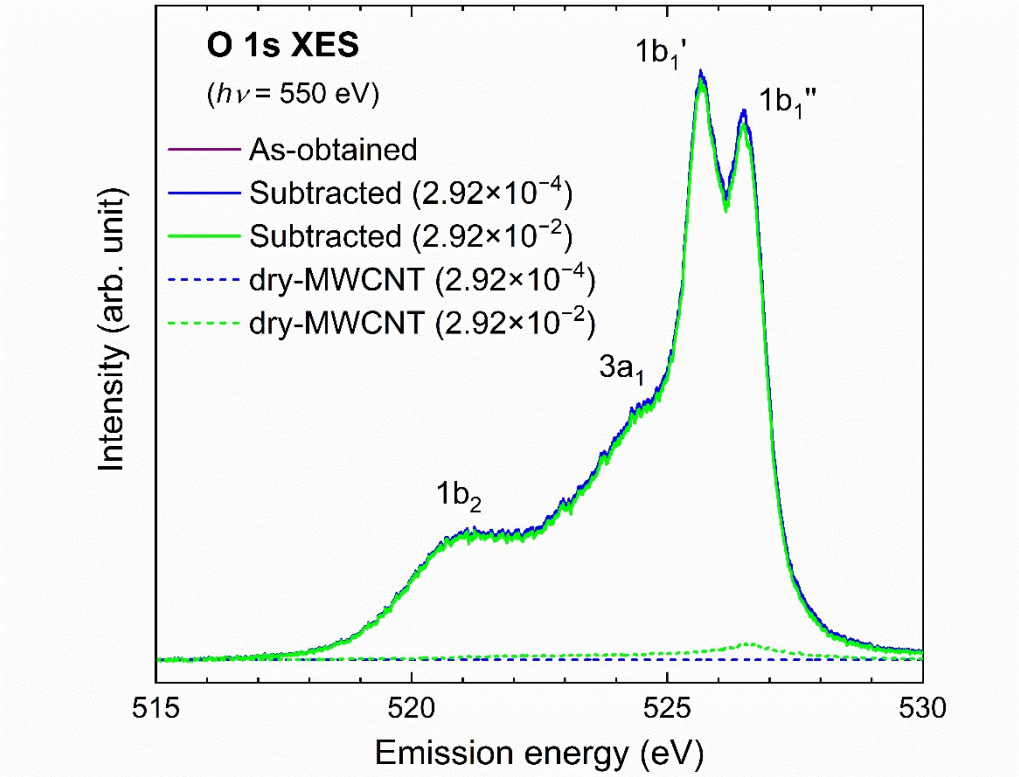

Figure S2. O 1s XES spectra of 1 wt% plasma-MWCNT aqueous dispersion with different subtraction ratios of the contribution of oxygen atoms on plasma-MWCNT. A purple solid line indicates the as-obtained spectrum, blue and green solid lines indicate the subtracted spectra with 2.92×10^{-4} and 2.92×10^{-2} subtraction ratio, respectively. The purple solid line is overlapped with the blue solid line. O 1s XES spectra of dry-MWCNT for the subtraction with different ratios are also depicted. Blue and green dashed lines indicate the dry-MWCNT spectra with 2.92×10^{-4} and 2.92×10^{-2} times area ratio, respectively, in comparison with the absolute integration of the as-obtained XES spectrum (the purple line).

Estimation of the inner diameter of plasma-MWCNT

The BET specific surface area of the plasma-MWCNT (S_{BET}) is expressed by the surface area (S_{CNT}) and weight (W_{CNT}) of one plasma-MWCNT as follows,

$$S_{BET} = \frac{S_{CNT}}{W_{CNT}} = \frac{\pi(R_{out} + R_{in})L}{W_{CNT}}, \quad \text{(S1)}$$

$$W_{CNT} = \sum_{k=1}^{m} \left(\frac{\pi(R_{out} - kd_l)L}{S_G} \times N_{CG} \times \frac{12}{N_A} \right), \quad \text{(S2)}$$

$$m = \frac{R_{out} - R_{in}}{d_l}, \quad \text{(S3)}$$

where R_{out} = 20–30 nm is the outer diameter, R_{in} in the inner diameter, and L = 1 μm is the typical length of the plasma-MWCNT, and d_l = 0.34 nm is the interlayer distance [47] and of carbon nanotube. From the Eqs. (S1), (S2) and (S3), R_{in} is calculated to be 4–18 nm to satisfy the S_{BET} value of 66.4 m^2/g.

Subtraction of the 100 times higher contribution of oxygen atoms on plasma-MWCNT

Next, to investigate the possibility of the segregation of plasma-MWCNTs to the window membrane during the XES measurement, 100 times higher (2.92×10^{-2} times area ratio) contribution of the oxygen atoms on the plasma-MWCNTs (a green dashed line in Fig. S1) were subtracted from the as-obtained XES spectrum of 1 wt% plasma-MWCNT aqueous dispersion (the purple solid line in Fig. S2). The resulted spectrum is depicted with a green solid line in Fig. S2. The green solid line is almost overlapped with the blue solid line. Furthermore, the normalized spectrum with an equal integrated area intensity and its difference spectrum from the bulk H_2O water in the case of 100 times higher subtraction (a green solid line in Fig. S3(a) and a red solid line in Fig. S3(b), respectively) are also almost overlapped with those in the case of the original subtraction with 2.92×10^{-4} times area ratio (a blue solid line in Fig. 5(a) and S3(a), and a black solid line in Fig. 5(b) and S3(b), respectively). Therefore, the 100 times higher subtraction considering the segregation of plasma-MWCNTs does not influence on the results and discussion described in the main text.

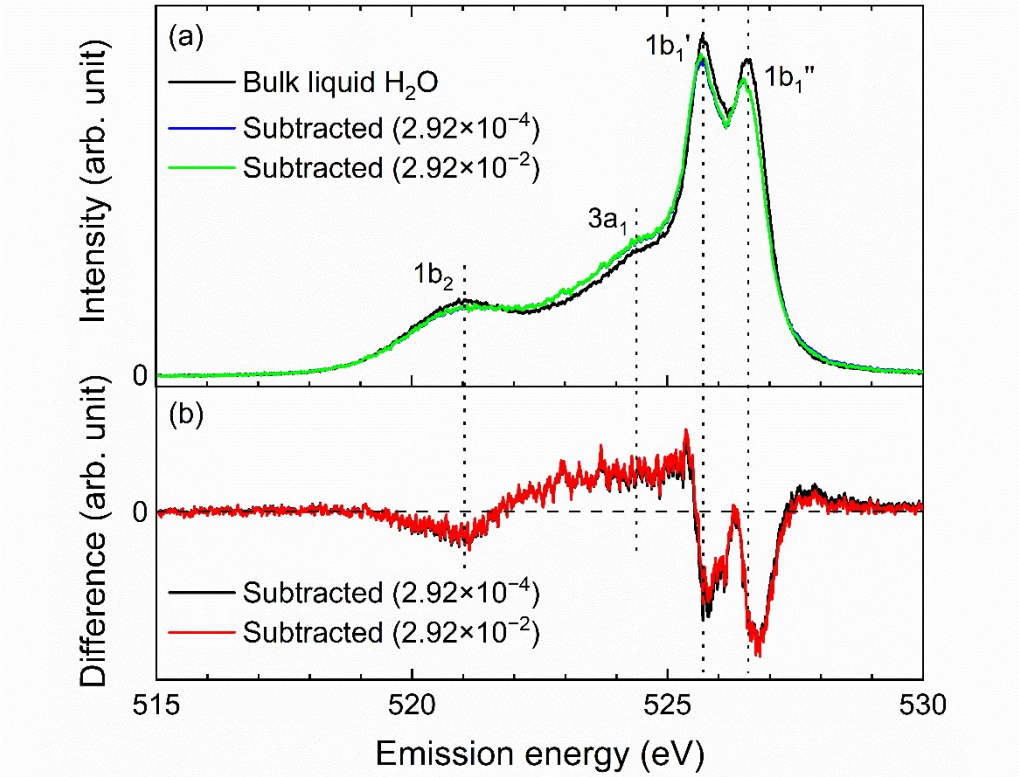

Figure S3. (a) O 1s XES spectra of liquid H_2O in pure water (black) and in the 1 wt% plasma-MWCNT aqueous dispersion with the different subtraction ratios (blue and green), all of which are normalized with an equal integrated area intensity between 515 and 530 eV. A blue solid line corresponds to the 2.92×10^{-4} subtraction ratio, whereas a green solid line corresponds to the 2.92×10^{-2} subtraction ratio. (b) Modulation of the valence electronic structure of liquid H_2O in the 1 wt% plasma-MWCNT aqueous dispersion from that in pure water. A black solid line corresponds to the 2.92×10^{-4} subtraction ratio, whereas a red solid line corresponds to the 2.92×10^{-2} subtraction ratio.