# Molecular unravelling of the mechanism of overpotential change at the carbon nanotubes-modified gold electrode surface

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# **Electronic Supplementary Information**

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#### **Experimental Details**

#### Fabrication Details of the microfluidic electrochemical devices

The high-vacuum compatible microfluidic electrochemical devices for *in situ* liquid SIMS measurements were fabricated on a polyether ether ketone (PEEK) block according to our previous design<sup>1-2</sup> with some adaptations. Within the devices, the gold (Au) film or that modified with carbon nanotubes served as the working electrode (WE), and two platinum wires as the counter electrode (CE) and pseudo reference electrode (RE), respectively. At first, a liquid chamber (6.0 mm in length, 5.2 mm in width and 1.0 mm in height), two punched holes for fixation of platinum wires (0.5 mm in diameter) on the bottom of the liquid chamber and two channels for fixation of tubes that were used to introduce electrolytes were machined on the PEEK block. The key design of the device is the use of a silicon frame (200  $\mu$ m thick, 7.5 mm  $\times$  7.5 mm) with a silicon nitride (SiN) membrane window (100 nm thick,  $0.5 \text{ mm} \times 0.5 \text{ mm}$ ) on top of the liquid chamber. Before fabrication of the frame, we prepared the gold film working electrode by sputter-coating an adhesion layer of 5 nm Ti for better attachment and then a gold layer of 50 nm in thickness on the SiN membrane window. A narrow strip of the gold film was extended to the edge of the silicon frame for connection with a copper wire which further connected with an electrochemical workstation. Then, the silicon frame with the modified SiN membrane window was placed on the top of the chamber and fixed with epoxy. Aqueous electrolyte solutions of 10 mM sodium phosphate buffer (NaH<sub>2</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub>) at pH=7.0 in the absence or presence of 10 mM ascorbate were introduced into the liquid chamber and sealed with unions and fittings. Afterwards, the device was loaded onto a ToF-SIMS sample holder and introduced into the SIMS main chamber for further operando analysis.

### Electrode modification with carbon nanotubes

Single-walled carbon nanotubes (SWCNTs, <2 nm in diameter and 0.5-50  $\mu$ m in length) purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China) were purified by refluxing in 2.6 M nitric acid for 5 h, which was followed by centrifugation, resuspension and filtration and evaporation of the solvent. The purified SWCNTs were further heated under vacuum at 500 °C for 2 h and then dispersed into N,N-dimethylformamide to obtain a 2 mg/mL of the SWNTs dispersion. Aliquot (2.0  $\mu$ L) of the dispersion was drop-casted onto the gold film electrode and then air-dried to evaporate the solvent to obtain the SWCNTs modified gold film electrode.

#### **Electrochemical measurements**

A CHI660E electrochemical workstation (CH Instruments, TX, USA) was used for applying electrode potentials to the microfluidic electrochemical devices. To verify the electrochemical performance of the devices under high vacuum, cyclic voltammetry (CV) scanning was performed in the potential range of 0 V to 0.9 V when using the gold film working electrode or -0.3 V to 0.6 V when using the SWCNTs modified gold film working electrode, respectively. Scan rate: 25 mV/s.

## In situ liquid SIMS analysis

To investigate the electrochemical interfacial chemistry, we chose the characteristic step potentials of 0 V, 0.3 V, 0.5 V, 0.7 V and 0.9 V or -0.3 V, 0 V, 0.2 V, 0.4 V and 0.6 V in the anodic direction when using the gold film electrode without or with modification of SWCNTs, respectively. As soon as a specific constant potential value was applied to the working electrode, we conducted in situ and operando liquid SIMS measurements. The detailed experimental parameters of *in situ* liquid SIMS were similar to our previous report <sup>1</sup>with some adaptations. In brief, a pulsed 10 kHz 30 keV Bi<sub>3</sub><sup>+</sup> primary ion beam was focused to  $\sim$ 300 nm in diameter, and rastered on a round area with 2 µm in diameter on SiN membrane. The pulse width of the Bi<sub>3</sub><sup>+</sup> beam was set as 500 ns (the corresponding beam current was about 1.50 pA) and it needed for about 65 s in the negative ion mode or 50 s in the positive mode to drill through the SiN membrane and form a small aperture. Then, the pulse width was first quickly set to 0 ns and then changed to 100 ns for better mass resolution and the corresponding beam current was about 0.15 pA. After further sputtering of ~100 s (a slight variance may occur), a sudden increase in the interface related signals involving both the electrode and the electrolyte indicated the *in situ* analysis on the exposed electrochemical interface. The vacuum pressure in the main chamber during measurements was about  $5 \times 10^{-7}$  mbar. ToF-SIMS data from the time period when signals from the electrochemical interface were relatively stable were reconstructed and the resulting spectra were mass calibrated using  $CH_3^+$  (m/z 15), Si<sup>+</sup> (m/z 28), and Bi<sup>+</sup> (m/z 209) ions in the positive ion mode, and C<sup>-</sup> (m/z 12), Si<sup>-</sup> (m/z 28), PO<sub>2</sub><sup>-</sup> (m/z 63), PO<sub>3</sub><sup>-</sup> (m/z 79), and Au<sub>3</sub><sup>-</sup> (m/z 591) ions in the negative ion mode. All the spectra were normalized to the total ion intensity.



Fig. S1 The scanning electron microscope (SEM) image of the SWCNTs.



**Fig. S2** Cyclic voltammograms (CVs) obtained at the gold film electrodes without (a) and with (b) modification with SWCNTs in 10 mM phosphate buffer (pH 7.0) in the absence of ascorbate in fabricated microfluidic electrochemical devices. When using the Au working electrode, we clearly observed a pair of peaks with the oxidation and reduction peak values at +0.65 V and +0.25 V, respectively (a). If using the SWCNTs-modified Au electrode, interestingly no peaks were observed (b).



**Fig. S3** (a-b) Schematic illustration of in situ liquid SIMS analysis of the Au-electrolyte interface: (a) The electrolyte was protected from a high vacuum using a thin silicon nitride (SiN) membrane. At the initial stage of the liquid SIMS analysis, the primary ion beam only bombarded the SiN membrane and only SiN-related signals could be detected. (b) As soon as the primary ion beam drilled through the SiN membrane, a tiny aperture of  $\sim 2 \mu m$  formed. Due to the pressure difference between the inside and outside, the electrolyte permeated through the porous Au film and formed a thin liquid layer on the upper side of the Au film. Hence, signals of the Au-electrolyte interface could be detected in situ. (c) The representative dynamic SIMS depth profiles in the negative ion mode for analysis of Au-electrolyte interface when applying a potential of 0 V to the working electrode. The phosphate buffer in the absence of ascorbate was used as the electrolyte. The highlighted time region in the blue square refers to the stage where the primary ion beam drilled through the SiN membrane and bombarded the Au-electrolyte interface. The mass spectra and 2D images reflecting interfacial information were reconstructed from this time region.



**Fig. S4** (a) Dropping of SWCNTs dispersion on the Au nanofilm which was pre-sputtered on the silicon nitride membrane window. (b) During drying process, the SWCNTs dispersion infiltrates into the porous Au nanofilm layer through the inside channels. (c) After drying, not only a SWCNTs film layer forms on the upper side of the Au film, but also the inside channels of the Au nanofilm is filled with SWCNTs.



**Fig. S5** A schematic illustration of in situ liquid SIMS analysis of the Au/SWCNTs-electrolyte interface. (a) The electrolyte is protected from a high vacuum using a thin silicon nitride (SiN) membrane. At the initial stage of the liquid SIMS analysis, the primary ion beam only bombards the SiN membrane and only SiN-related signals could be detected. (b) As soon as the primary ion beam drills through the SiN membrane, a tiny aperture of ~2  $\mu$ m formed. Due to the pressure difference between the inside and outside, the electrolyte permeates through the SWCNTs film as well as the Au/SWCNTs composite film, resulting in the formation of a thin electrolyte layer on the upper side of the Au/SWCNTs composite layer. Hence, signals of the Au/SWCNTs-electrolyte interface could be detected in situ.



**Fig. S6** Representative normalized SIMS spectra in the negative mode, highlighting the different surface chemistry at the gold film electrode surface without (a) or with (b) modification of SWCNTs in 10 mM phosphate buffer.



**Fig. S7** Representative 2D chemical mapping of ions including  $PO_3^-$  at m/z 79 and  $Na(PO_3)_2^-$  ion at m/z 181 detected in the negative ion mode at the electrochemical interface using the (a) Au film or (b) Au/SWCNTs composite layer as the working electrode in 10 mM phosphate buffer.



**Fig. S8** Representative 2D chemical mapping of ions including Na<sup>+</sup> at m/z 23 and H(H<sub>2</sub>O)<sub>3</sub><sup>+</sup> ion at m/z 55 detected in the positive ion mode at the electrochemical interface using the (a) Au film or (b) Au/SWCNTs composite layer as the working electrode in 10 mM phosphate buffer.



Fig. S9 The normalized signal trends of  $PO_2^-$  (a and b) and  $PO_3^-$  (c and d) detected at the gold film electrode surface without (a and c) or with (b and d) modification of SWCNTs in 10 mM phosphate buffer.



**Fig. S10** Representative normalized SIMS spectra in the negative mode, highlighting the different surface chemistry at the gold film electrode surface without (a) or with (b) modification of SWCNTs in 10 mM phosphate buffer.



**Fig. S11** Representative 2D chemical mapping of the  $[C_6H_7O_6^{-}...H_2O]$  ion at m/z 193 detected in the negative ion mode at the electrochemical interface using the (a-b) Au film or (c-d) Au/SWCNTs composite layer as the working electrode in 10 mM phosphate buffer without (a and c) or with (b and d) ascorbate.



**Fig. S12** Representative normalized SIMS spectra in the negative (a and c) and positive (b and d) modes, respectively, revealing the different electrochemical interfacial chemistry in 10 mM phosphate buffer containing ascorbate using the gold film electrode without (a and b) or with (c and d) modification of SWCNTs.

The representative SIMS spectra in Fig. S12 highlighted the signals of  $PO_2^-$ ,  $PO_3^-$ ,  $Na(PO_3)_2^-$ ,  $Na^+$ and  $H(H_2O)_3^+$  detected in the phosphate buffer containing ascorbate using the gold film electrode without or with the modification of SWCNTs. (1) In the case of using the gold film electrode, in comparison to those in the ascorbate-free system (Fig. 3a, b), we observed the pronounced decrease in the signals of  $PO_2^-$ ,  $PO_3^-$ ,  $Na(PO_3)_2^-$ , and  $Na^+$  ions in presence of ascorbate (Fig. S12a, b), indicating that a significant portion of the adsorption phase at the gold surface was squeezed away by the electroactive ascorbate ions. This was further strengthened by the appearance of the apparent  $H(H_2O)_3^+$  signals (Fig. S12b). These results are in accordance with our recent report<sup>2</sup>. (2) In the case of using the SWCNTs-modified gold film electrode, the signals of  $PO_2^-$ ,  $PO_3^-$ ,  $Na(PO_3)_2^-$ , and  $Na^+$  ions were barely detected in presence of ascorbate (Fig. S12c, d), which is similar to those in the ascorbate-free system (Fig. 3c, d).



**Fig. S13** The dependence of the peak current for the ascorbate electrooxidation on the square root of scan rate. The CV data were measured in a traditional three-electrode assay using a bulk Au electrode without (a) or with (b) the SWCNTs modification as the working electrode, a Ag/AgCl electrode (KCl-saturated) as the reference electrode, and a Pt wire as the counter electrode. Scan rate: 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mV s<sup>-1</sup>. In contrast to the situation using a bulk Au working electrode (a), the peak current obtained for the ascorbate oxidation at the SWCNTs-modified bulk Au electrode was proportional to the square root of the potential scan rate in a range of 0.05-0.5 V s<sup>-1</sup> (b), suggesting a diffusion-controlled process of the ascorbate oxidation at the SWCNTs-modified Au electrode surface. These results also indicate a significantly reduced electrode fouling during the irreversible oxidation process of ascorbate at the SWCNTs-modified Au electrode surface<sup>3</sup>.

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