

Supporting Information

Hydroxylation of Indium Tin Oxide Electrode Promoted by Surface Bubbles

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General Considerations

Materials. Unless noted otherwise, all chemicals are of analytical grade and used as received. Deionized water ($>18 \text{ M}\Omega \text{ cm}^{-1}$) was used to prepare solution, for electrochemical reactions, and in surface cleaning procedures. Sodium hydroxide (NaOH, AR), potassium hydrogen phthalate (AR), ammonium molybdate (AR), ethanol (99.7%), methanol ($\geq 99.8\%$), ferroceneacetic acid (Fc-COOH, 97%), tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%), (3-aminopropyl)triethoxysilane (APTES, 98%), and acetonitrile (99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. O-phenylenediamine (OPD, 98%), potassium iodide (99.5%), and dihydroethidium (DHE, $\geq 95\%$) were purchased from Shanghai Macklin Biochemical Co., Ltd. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (AR, EDC) and 4-dimethylaminopyridine (AR, DMAP) were obtained from Adamas-Beta. ITO glasses (resistivity $< 10 \text{ ohm/sp}$) were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Spiral platinum wire (Pt) electrode with size of $0.5 \times 230 \text{ mm}$ and silver/silver chloride (Ag/AgCl) electrode were

purchased from Gaoss Union Photoelectric Technology Co., Ltd. Commercial hydrogen peroxide (H₂O₂) test paper was purchased from Runbo Tstcheck.

Surface Modification. ITO slides were cut into pieces (approximately 1.5 × 2 cm²), followed by ultrasonic cleaning in deionized water, ethanol, and deionized water, respectively. Air bubbles were deposited on the cleaned ITO using a gas dispersion tube with 10 – 20 μm porosity (Z408727, Sigma Aldrich). The ITO-OH surface was produced upon applying +1.0 V to the bubbles-adherent ITO surface. Silanization was used to attach APTES to the hydroxylated active ITO surface. To a reaction vial containing the ITO-OH surfaces was added 0.5% ethanol solution of APTES. Reactions were carried out in air at room temperature overnight. The silanized electrodes were rinsed with ethanol to remove non-bonded silane molecules and dried under a stream of nitrogen. The details of the linking of the Fc-COOH to silanized ITO are as follows. The freshly silanized surface samples were then transferred to a 10 mL ethanol containing 5 mM EDC and 5 mM DMAP, leaving this reaction overnight. After conjugation, the ITO slides were washed thrice using ethanol and dried with nitrogen.

Characterization. Electrochemical experiments were performed using a one-compartment three-electrode glass cell under the control of a CHI 760E electrochemical workstation. In brief, the electrochemical cell holding the ITO electrode was initially filled with electrolyte, then the air flow was forced across the liquid, and after having visually inspected the ITO slide to confirm the presence of adherent gas bubbles, the resulted ITO served as the working electrode. The Pt coil and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. All potentials are reported versus the Ag/AgCl. The contact angle is measured by an optical contact Angle gauge (KSV CM200, KSV Instruments Ltd), every test was repeated six times independently. XPS were obtained on an ESCALAB 250 Xi spectrometer. All energies are binding energies expressed in electronvolts, obtained by applying to all samples a rigid shift to bring the energy of the C1s peak to a value of 284.8 eV. The optical

absorption spectra were measured using a Shimadzu UV-3600i Plus UV-visible spectrometer. Electron spin resonance (ESR) spectra was carried out by a Bruker A-300 spectrometer using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping agent, the results were recorded after 30 min reaction. The fluorescence spectra were measured using the fluorescence spectrometer (FS5, Edinburgh Instruments Ltd).

Supporting Figures

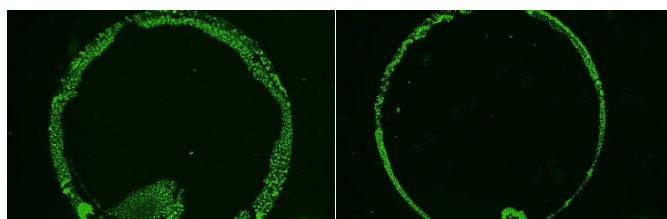


Fig. S1 In order to further confirm the generation of $\bullet\text{OH}$ at the triple frontier gas-water-ITO, we introduced coumarin into the electrolyte, a compound known to react with $\bullet\text{OH}$ to generate highly fluorescent substances (7-hydroxycoumarin). Using an inverted fluorescence microscope (Olympus, IX73), we observed patterns resembling coffee rings on the ITO surface. Such patterns are invisible by naked eyes, which can be attributed to the fact that the effect of $\bullet\text{OH}$ on the surface of ITO occurs at the molecular level, rendering it imperceptible at a macroscopic level.

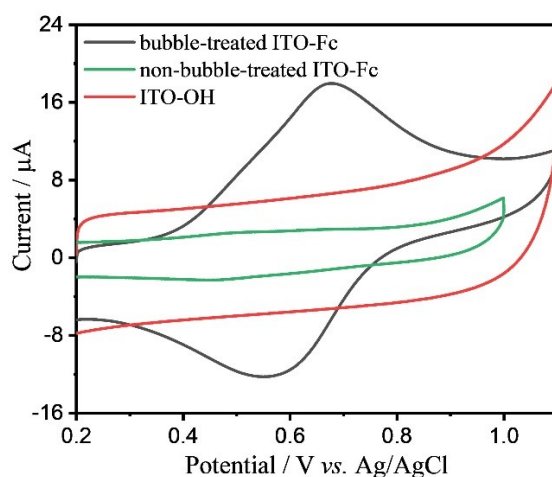


Fig. S2 During our research, both bubble-treated and non-bubble-treated ITO samples were subjected to Fc modification. Cyclic voltammetry was conducted in a

tetrabutylammonium hexafluorophosphate solution, revealing distinct differences between these two samples. In the case of the non-bubble-treated ITO electrode, no obvious redox signal was observed. However, upon modification of the bubble-treated ITO electrode, noticeable redox signals were observed. This suggests the successful attachment of Fc molecules to the surface of the ITO electrode through chemical bonding. These findings highlight the effectiveness of bubble treatment in enhancing the functionalization of the ITO-OH surface with ferrocene molecules.

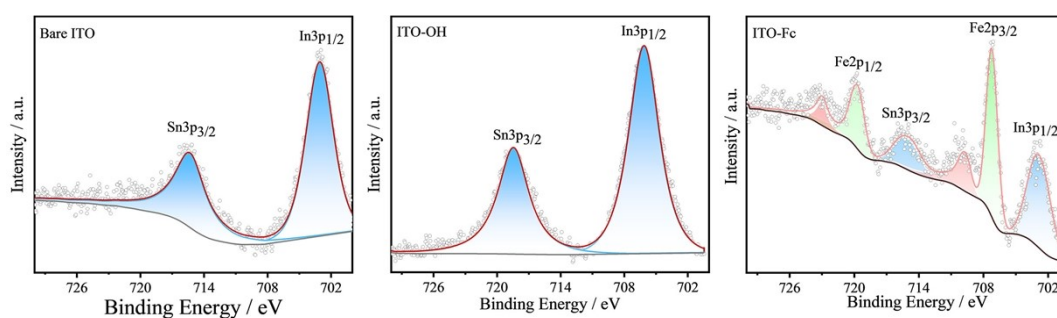


Fig. S3 We compared the XPS Fe2p region of the bare ITO sample with those of ITO-OH and ITO-Fc samples. Obviously, Fe2p components are observed only in the Fc-modified ITO samples. Further analysis of the Fe2p high-resolution spectrum confirms the presence of two distinct peaks at 707.3 and 719.8 eV, corresponding to Fe2p_{3/2} and Fe2p_{1/2}, respectively. The peaks at 703.1 and 715.4 eV are attributed to In3p_{1/2} and Sn3p_{3/2}. The XPS spectra of the Fe2p region of bare ITO and ITO-OH exhibit peaks attributed to In3p_{1/2} and Sn3p_{3/2} but do not display any Fe2p features. These binding energy values are consistent with those reported in the literature for immobilized ferrocene units on electrode surfaces. In summary, both the XPS and electrochemical results (Fig. 4a) provide strong evidence for the presence of ferrocene units on the ITO surface.