

## Supplementary Information

### Tuning the reactivity of nanostructured indium tin oxide electrodes toward chemisorption

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#### Materials and Methods.

**Chemical reagents.** Chemicals (solvent, buffers) and riboflavin 5'-monophosphate sodium salt (i.e., Flavin mononucleotide FMN) were purchased from Sigma-Aldrich.

**GLAD electrodes.** The ITO substrates were deposited by electron beam evaporation in a glancing angle deposition (GLAD) process. Source ITO material (91%In<sub>2</sub>O<sub>3</sub>, 9% SnO<sub>2</sub>) was purchased from Cerac. Thickness of 1- $\mu$ m of ITO were deposited at a constant glancing angle of  $\alpha = 70^\circ$  as previously described.<sup>9,16</sup> Immediately following deposition, the ITO films were non transparent and modestly conductive, and therefore, a post-process anneal procedure was implemented to improve these properties. The samples were first annealed in an air environment at 500°C for 90 minutes to incorporate oxygen and improve crystallinity, followed by a second anneal at 375°C for 60 minutes in a forming gas (H<sub>2</sub>/N<sub>2</sub> 5/95) environment under gas flow rates ranging from 10 to 300 sccm. Once prepared, the substrates were cutted in rectangular pieces of 0.8 x 2.5 cm<sup>2</sup> for further studies.

**XPS.** ULTRA spectrometer (Kratos Analytical) was used with base pressure in the analytical chamber lower than  $4 \times 10^{-8}$  Pa. Monochromatic Al K $\alpha$  source ( $h\nu = 1486.6$  eV) was run at a power of 210 W. The analysis spot was 300 x 700  $\mu$ m. The resolution of the instrument is 0.55 eV for Ag3d and 0.70 eV for Au4f peaks. The survey scans were collected for binding energy spanning from 1100 eV to 0 with analyzer pass-energy of 160 eV and a step of 0.4 eV. For the high-resolution spectra the pass-energy was 20 eV with a step of 0.1 eV. Since samples were conducting no charge neutralizer was required and the data presented are as collected, without calibration for the binding energy.

Instrument software Vision-2 was used for data processing. Linear background and instrument relative sensitivity factors (RSF) were applied. Major photoelectron lines were used for calculating the composition from the high-resolution spectra. When only one peak of the doublet spectra were used (2p<sub>3/2</sub> or 3d<sub>5/2</sub>) then the RSF value was adjusted accordingly.

**Surface functionalization.** Prior functionalization, the GLAD- ITO electrodes were cleaned by a sequential immersion of the electrodes in trichloroethylene, acetone and then ethanol for 15 min each and at a temperature maintained at 50 °C. After cleaning, a portion of the ITO surface was delimited by a nail varnish insulating layer in such a way to have a square working electrode area of  $0.25 \pm 0.05$  cm<sup>2</sup>. The ITO electrodes were then functionalized by dipping the active electrode area in a pure

aqueous solution containing 100  $\mu\text{M}$  FMN in milliQ water (pH~5). After 15-20 h immersion in the adsorption solution, the electrodes were thoroughly rinsed first with milliQ water and then immersed for 30 minutes in a heated (50  $^{\circ}\text{C}$ ) buffer solution (45 mM Hepes, 0.32 M KCl, pH 7.25) to desorb the poorly adsorbed FMN fraction.

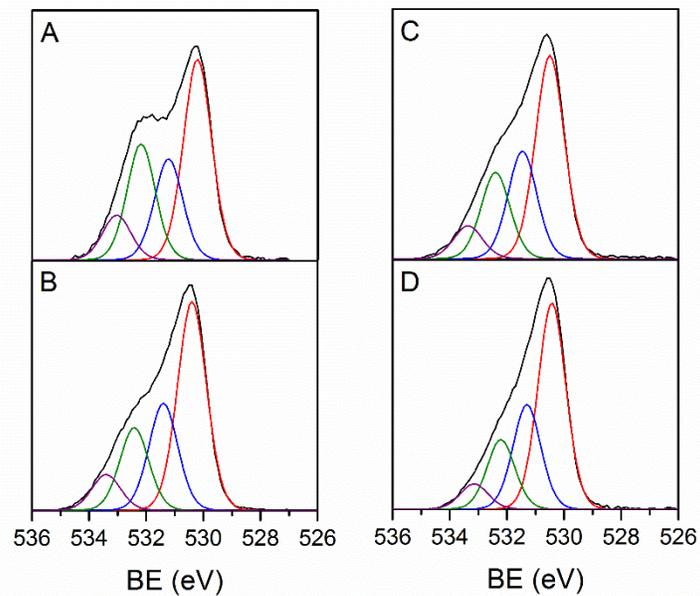
**Electrochemistry.** The cyclic voltammetry experiments were carried out with an Autolab potentiostat (PGSTAT-12) under ohmic drop compensation in a thermostated double-jacket electrochemical cell (20 $^{\circ}\text{C}$ ) under inert atmosphere (argon). The reference electrode is an SCE electrode and the counter electrode is a platinum wire. Desorption experiments were performed at 20 $^{\circ}\text{C}$  in a buffer solution at pH 7.25 (45 mM Hepes, 0.32 M KCl). Experiments conducted at different pH were performed in a buffer solution containing a mixture of Mes, Hepes, TABS and acetic acid (55 mM each) and 320 mM KCl which pH was shifted from 4 to 12 by gradual addition of concentrated solutions of HCl and NaOH.

**Real-time spectroelectrochemistry.** The experiments were conducted under argon atmosphere in a home-made spectroelectrochemical cell (1-cm optical length) thermostated at 20 $^{\circ}\text{C}$  in 1.5 mL buffer solution at pH 7.25 (45 mM Hepes, 0.32 M KCl). The reference electrode is an Ag/AgCl/KCl 3M electrode (WPI) and the counter electrode is a platinum wire. UV- visible absorption spectroscopy was carried out on a TORUS-50 diode array spectrometer (Ocean Optics) equipped with a balanced deuterium tungsten source (Micropack). The cell was thermostated to 20 $^{\circ}\text{C}$  using a Peltier-controlled cuvette holder (Quantum Northwest).

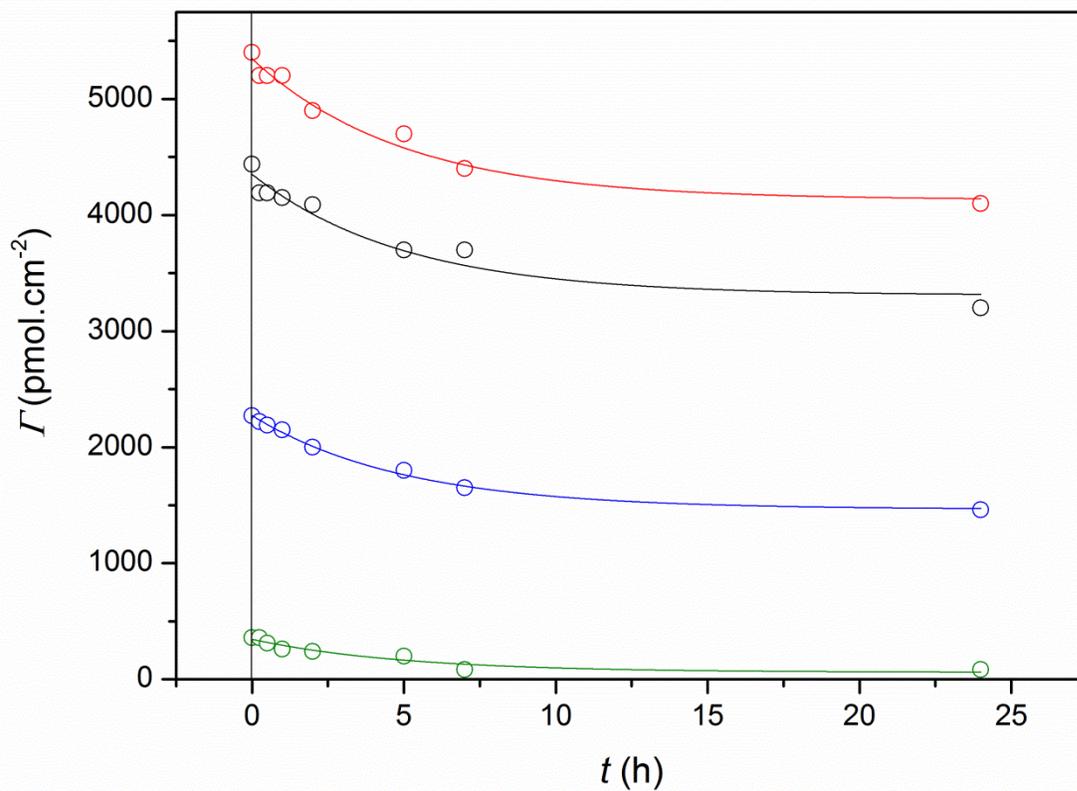
**Table S1.** XPS data, transmittance, surface concentration  $\Gamma_{\chi}$  of the chemisorbed FMN fraction and corresponding midpoint potential values determined by cyclic voltammetry at pH 7.25, of GLAD ITO electrodes submitted to 10, 30, 100 and 300 sccm forming gas flow rates.

GLAD ITO	Sn/In	O/ (Sn+In)	O <sub>A</sub> / (Sn+ In)	O <sub>B</sub> / (Sn+ In)	O <sub>C</sub> / (Sn+ In)	O <sub>D</sub> / (Sn+ In)	% T <sub>550 nm</sub>	$\Gamma_{\chi}$ (nmol.cm <sup>-2</sup> )	E <sub>m,7.5</sub> (V) vs. SCE
10 sccm	0.07	1.94	0.84	0.42	0.49	0.19	87	0.1	-0.45
30 sccm	0.07	1.80	0.87	0.44	0.34	0.15	85	1.4	-0.45
100 sccm	0.07	1.76	0.83	0.44	0.35	0.13	80	3.3	-0.46
300 sccm	0.07	1.57	0.80	0.40	0.27	0.10	0	4.1	-0.45
2D-ITO*	0.14	1.62	0.85	0.35	0.25	0.10	nd	0.076	-0.45

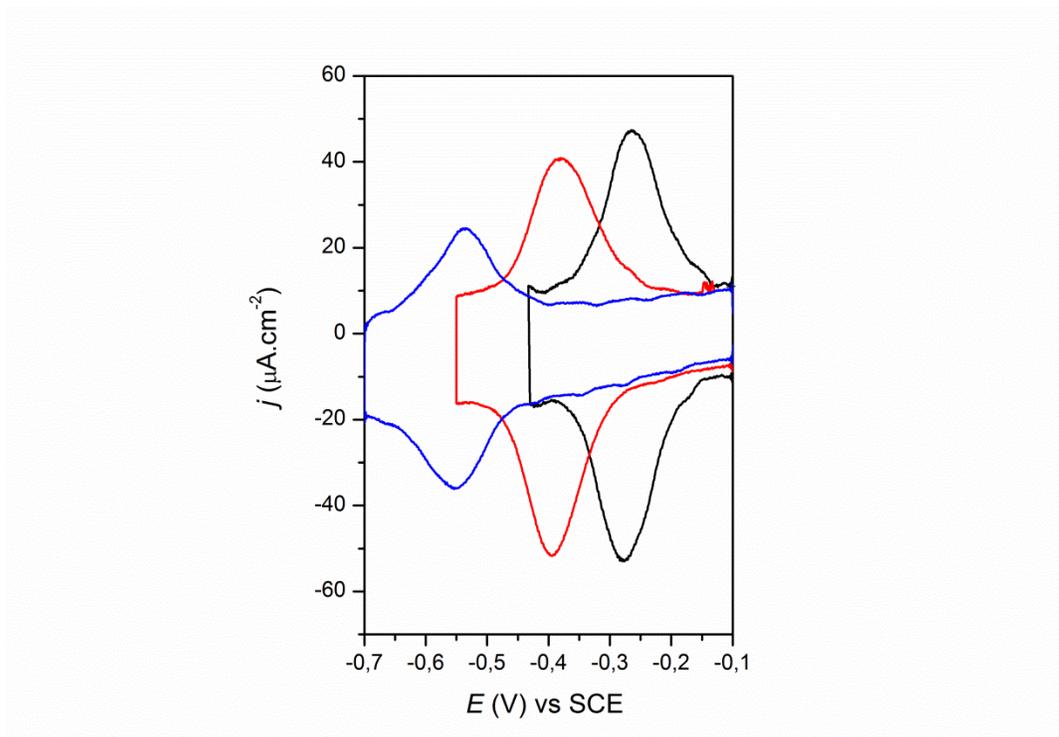
\* Data from ref 13.



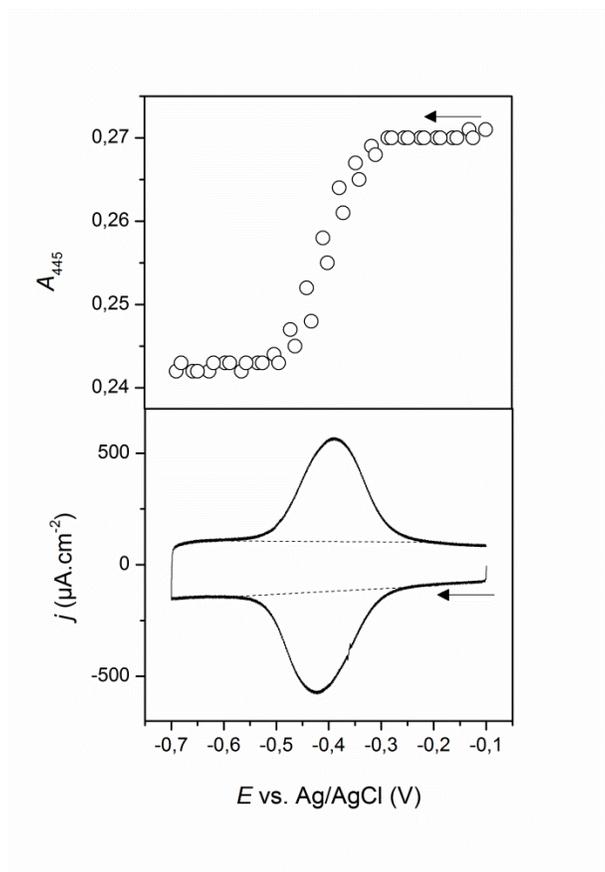
**Figure S1.** O(1s) XPS spectra recorded on GLAD ITO electrodes submitted to 10 (A), 30 (B), 100 (C) and 300 (D) sccm forming gas flow rates. The O(1s) peak was fitted according to four components the oxygen from the matrix directly linked to In or Sn (red line) and oxygen near vacancies (blue line), hydroxyls (green) and carbonyl oxygen (purple).



**Figure S2.** Surface concentration of FMN adsorbed in GLAD ITO electrodes (prepared under forming gas flux of (○) 10, (○) 30, (○) 100 and (○) 300 sccm) deduced from the characterization of the modified GLAD ITO electrodes by cyclic voltammetry in a FMN-free buffer solution as a function of the soaking time. Solid lines correspond to the fitting of the experimental data to a first-order desorption kinetic with desorption rates of  $4 \pm 1 \text{ h}^{-1}$  and  $\Gamma_{\infty}$  values reported in Table S1.



**Figure S3.** Cyclic voltammograms at pH 4 (black line), 6 (red line) and 10 (blue line) of a FMN-GLAD-ITO electrode (100 sccm) recorded after 24 hours desorption (scan rate  $0.01 \text{ V}\cdot\text{s}^{-1}$ ,  $T=20^\circ\text{C}$ ).



**Figure S4.** Cyclic voltabsorptogram monitored at 445 nm (up) and cyclic voltammogram (down) recorded simultaneously at a FMN-GLAD-ITO electrode (100 sccm) after 24 hours desorption ( $\Gamma_x = 3.3 \text{ nmol cm}^{-2}$ ). Scan rate  $0.1 \text{ V s}^{-1}$ , integration time 3 ms, scans to average 10,  $T=20^\circ\text{C}$ .