Supporting Information for

Modular "click" chemistry for electrochemically and photoelectrochemically active molecular interfaces to tin oxide surfaces

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Scanning electron microscopy of synthesized SnO$_2$ nanoparticles:

Samples for scanning electron microscopy were prepared by suspending a small amount of the SnO$_2$ nanopowder in acetone and spin-coating onto a heavily doped (conductivity <0.001 Ωcm) silicon wafer. Figure 1 shows the nanopowder consists of particles with roughly cubic shapes and an average diameter of ~50 nm, ranging from 20-100 nm. SEM images were acquired using a LEO Supra55 VP field-emission scanning electron microscope (Carl Zeiss NTS, Peabody, MA) using the standard in-lens detector.

Figure S1: Top-view SEM image of as-synthesized SnO$_2$ nanoparticles
X-ray powder diffraction of synthesized SnO₂ nanoparticles:

X-ray diffraction (XRD) measurements were performed using a Siemens STOE X-ray diffractometer. Figure S2 shows the XRD spectrum of our synthesized nanoparticles. For comparison we also show a reference spectrum for the cassiterite phase, from the Joint Committee on Powder Diffraction Standards (PDF) reference spectrum card JCPDS 04-003-0974.

![X-ray diffraction data](image)

Figure S2. X-ray diffraction data of synthesized SnO₂ nanoparticles and comparison with reference spectrum of cassiterite

Scanning electron microscopy of sintered SnO₂ films:

Scanning electron microscopy was used to characterize the shape of the nanoparticles and the overall structure of the nanoparticle films after sintering. Figure S3 shows an SEM image of a SnO₂ film that was fabricated on a fluorinated tin oxide / glass substrate and then sintered as described in the primary manuscript. The sample was then fractured to facilitate imaging from the side. This particular film is ~1 µm thick. Top-view and side-view SEM images show shows that the film consists of ~50 nm diameter particles sintered together into a dense film. This structure leads to increased surface area due to the nanometer-scale roughness of the surface, but minimizes penetration of the liquid reagents into the film and avoids potential difficulties associated with possible reactions at the underlying substrates, which are completely protected by
the SnO$_2$ sintered film. Consequently the film has low porosity to liquid reagents and the analytical measurements probe the near-surface region only.

Preparation and characterization of Azide-Terminated SnO$_2$ nanocrystalline films: To prepare azide-terminated SnO$_2$ films, the nanocrystalline sintered SnO$_2$ films were exposed to neat 3-buten-1-ol and sealed in an argon environment inside a stainless steel cell with a fused silica window. The cell was then placed under ultraviolet light from a low-pressure mercury lamp (254 nm, ~10 mW/cm$^2$) for 15 hours. The SnO$_2$ nanocrystalline thin-films were then rinsed with methanol (MeOH), CHCl$_3$, and isopropyl alcohol (IPA) for 30 seconds each. The films were stored in IPA until further use. Mesylation of the terminal –OH group was carried out in an ice bath with a 10:1:1 (by volume) dichloromethane (DCM): triethylamine (NEt$_3$): methanesulphonyl chloride (MsCl) mixture for 1 hour. The films were then rinsed with DCM, MeOH, and IPA for 30 seconds each. The films were immediately sealed in a solution of supersaturated NaN$_3$ in DMSO for 15 hours at 80°C. The films were then rinsed with deionized H$_2$O for one minute then IPA for 30 seconds. The films were stored in IPA until further use.

Figure S4 shows FTIR spectra of SnO$_2$ sintered film after each of the functionalization steps to achieve the azide terminated surface. After grafting of 3-buten-1-ol the FTIR spectrum shows peaks at 2860 and 2923 cm$^{-1}$ from the C-H vibrations of the grafted molecules and also shows a large, broad –OH peak from ~3100-3400 cm$^{-1}$. The intensity of this peak has been reduced by a factor of 3 in Figure S3a. After treatment with methylsulfonylchloride, the OH stretch is no
longer present and two sharp peaks appear at 1174 and 1352 cm$^{-1}$. These frequencies are similar to the values of 1176 and 1353 cm$^{-1}$ reported for methyl methane sulfonate (CH$_3$SO$_2$-OCH$_3$) and attributed to the symmetric and asymmetric stretching vibrations of the SO$_2$ group.$^1$ After treatment with NaN$_3$, the S=O stretches disappear and the spectrum shows a sharp feature at 2096 cm$^{-1}$ from the azide group. A small OH peak is seen that most likely arises from adsorbed water after the reaction NaN$_3$ reaction and subsequent rinsing. It is important to note that the CH$_2$ stretch is present unchanged after each of the subsequent functionalizations, proof that the carbon chain remains intact and all reactions occur at the terminal functional group.

Figure S4. FTIR spectra of SnO$_2$ film at successive stages of functionalization a) after grafting of 3-butene-ol, b) after mesylation step, and c) after treatment with NaN$_3$. Note that the intensity of the 3000-3700 cm$^{-1}$ region containing the O-H peak been reduced three-fold for the butenol spectrum only.
Electrochemical stability of ferrocene covalently grafted to SnO$_2$ nanocrystalline film:

The stability of ferrocene grafted to SnO$_2$ was measured in 1.0 M HClO$_4$. The graph below shows the 1$^{st}$ and 100$^{th}$ cyclic voltammograms measured at a rate of 1 V/s. At longer times the film showed signs of degradation.

![Graph showing 1st and 100th cyclic voltammograms](image)

Figure S5: 1st and 100th cyclic voltammograms of ferrocene grafted to SnO$_2$ sintered nanocrystalline film, measured at a scan rate of 1 V/s in 1.0 M HClO$_4$.

References: