Supporting Information

Versatile grafting chemistry for creation of stable molecular layers on oxides

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Calculations of surface coverage of the molecular layers on SiO$_2$ and TiO$_2$ by XPS

The overall number of the atoms of interest (X) per unit area of TiO$_2$, for example, can be calculated from the using:

$$N(X) = \frac{A(X)s(Ti)\rho(Ti, TiO_2)\sin(\theta)\exp\left(\frac{t}{\lambda(X, organic)\sin(\theta)}\right)}{A(Ti)s(X)\exp\left(\frac{t}{\lambda(Ti, organic)\sin(\theta)}\right)}$$

where $N(X)$ is number of atoms per unit area, $A(X)/A(Ti)$ is the ratio of integrated XPS peak areas, $s(Ti)/s(X)$ is sensitivity factor ratio between titanium and atom of interest, $\rho(Ti, TiO_2)$ is number of Ti atoms per unit volume in SiO$_2$, $\lambda(Ti, TiO_2)$ is inelastic mean free path (IMFP) of Ti photoelectrons in TiO$_2$, $t$ is thickness of the layer, $\lambda(X, organic)$ and $\lambda(Ti, organic)$ are IMFPs of X and Ti in organic films, respectively.$^1$ The angle $\theta$ is the take-off angle of photoelectrons with respect to the sample plane ($\theta = 45^\circ$). Neglecting the surface roughness$^2$ and using similar approximation of IMFPs of organic self-assembled monolayers from previous studies [$\lambda(A^\circ) =$...
9.0 + 0.022*E(eV)] where E(eV) is the kinetic energy in electron volts, \(\lambda(X, \text{organic}) \sim 2.8-3.5\) nm and \(\lambda(\text{Ti, TiO}_2) \sim \lambda(\text{Ti 2p, organic}) = 3.3\) nm. Since \(\lambda(X, \text{organic}) \sim \lambda(\text{Ti 2s, organic})\) and \(t < \lambda\) for thin organic layer approximation, we conclude that 
\[
\exp\left(\frac{t}{\lambda(\text{Ti,organic})\sin(\theta)}\right) \approx 1.
\]

Using \(p(\text{Ti, TiO}_2) = 2.6 \times 10^{22}\) atoms/cm\(^3\), \(s(\text{N 1s}) = 0.477\), \(s(\text{Cl 2p}) = 0.891\), and \(s(\text{Re 4f}) = 3.961\), the surface coverage of bipyridine and rhenium-bipyridine complex on TiO\(_2\) was calculated. For the calculation of surface coverage of organic layers on SiO\(_2\), \(p(\text{Si, SiO}_2) = 5.0 \times 10^{22}\) atoms/cm\(^3\) and \(s(\text{Si 2s}) = 0.399\) were used.

**Synthesis of ReOH**

ReOH was synthesized using the literature procedure.\(^4\) To a 50-mL round bottom flask, BipyOH (0.24 g, 1.3 mmol), Re(CO)\(_5\)Cl (0.47 g, 1.3 mmol), and methanol (20 mL) were added. The reaction mixture was heated at 60 °C overnight. After cooling down to room temperature, the mixture was precipitated in hexane and then filtered and washed with cold hexane and cold methanol to yield the ReOH (0.48 g, 75%). \(^1\)H NMR (300 MHz, DMSO-d\(_6\), \(\delta\) in ppm): 8.99 (d, J=5 Hz, 2H), 8.93 (d, J=9 Hz, 1H), 8.70 (d, J=8 Hz, 1H), 8.61 (s, 1H), 8.31 (dt, J=1, 8 Hz, 1H), 7.74 (dt, J=1, 8 Hz, 1H), 7.69 (d, J=6 Hz, 1H), 5.81 (t, J=6 Hz, 1H, -OH), 4.74 (d, J=6 Hz, 2H, -CH\(_2\)-). \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\), \(\delta\) in ppm): 197.8, 190.1, 156.8, 155.2, 154.7, 152.9, 152.6, 140.3, 127.8, 124.8, 124.1, 121.2, 61.4.
$^1$H-NMR of BipyOH

Aromatic CH's

CDCl$_3$

$^1$H-NMR of ReOH

Aromatic CH's

$^1$C-NMR of ReOH
The IRRAS spectrum of grafted rhenium-bipyridine complex (BipyOH-Re) on TiO\textsubscript{2} is similar to that on SiO\textsubscript{2}. Three C≡O stretching bands, one at 2024 cm\textsuperscript{-1} corresponding to the symmetric stretching mode of metal carbonyl groups and two overlapping asymmetric stretching bands at 1905 cm\textsuperscript{-1} were observed indicating the presence of rhenium-bipyridine complex on TiO\textsubscript{2} surface.
NMR spectra of Bipy(OH)$_2$: before and after heating at 160°C for 48 h showing no change in the spectrum. This rules out self-condensation or degradation upon thermal annealing on the substrate to form multilayers. Hence, the higher surface coverage of Bipy(OH)$_2$ is primarily due to bidentate anchoring to the substrate via ether bond formation.

Reference:

