Supporting Material to: Flexible to Rigid: IR Spectroscopic Investigation of a Rhenium-Tricarbonyl-Complex at a Buried Interface

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(Dated: January 26, 2021)

I. MATERIALS AND METHODS

This study utilizes the fact that the Rhenium tricarbonyl molecule specifically adsorbs to the ZrO_2 scaffold in a monolayer. Since the ZrO_2 particle solution we have used has a distribution of particle sizes (Solaronix Z-SP) we calculate the absorbance for 3 cases of particles with 20, 30 and 40 nm in diameter. Previously, the layer thickness could be measured by profilometry [1], however for the thinner layers applied here, we decided to utilize scanning electron microscopy to see the films. The sensitized sample without ALD deposited ZrO_2 was measured to estimate the coverage with rhenium carbonyl molecules.

II. SCANNING ELECTRON MICROSCOPY

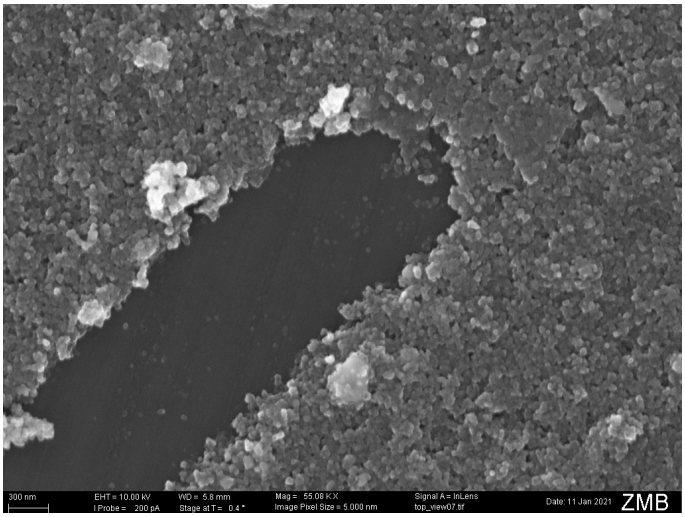

FIG. 1. SEM of sample without ALD layer, top view with scratch to show layer thickness.

Imaging was performed with a field emission scanning electron microscope (Zeiss Supra 50 VP or Zeiss Gemini 450) equipped with an in-lens secondary electron detector. The samples were prepared by thermal evaporation of 5 – 7 nm of carbon using a high-vacuum sputter coating device (Safematic CCU-010 HV) with an CT-010 Carbon Thread Head.

SEM images were taken after all measurements were completed (the sample had to be broken into pieces) with a top view (Fig. 1) after scratching the surface to show the underlying CaF_2 window. It can be seen there that the size of the particles roughly varies between 20-40 nm, some of them larger. A cross section of the sample is shown in Fig. 2. The mesoporous ZrO_2 film is between 130 and 310 nm thick, the average is 215±13 nm (P=95%). This value was obtained by digitization of the image in Fig. 2 with OriginPro 2020.

III. SURFACE COVERAGE ESTIMATION

From weight and height measurements of thicker films (1.8 μm) combined with their geometric area we found the porosity of the deposited ZrO_2 layers to be around 51%. As such the measured density was about 2.8 g cm^{-3} compared

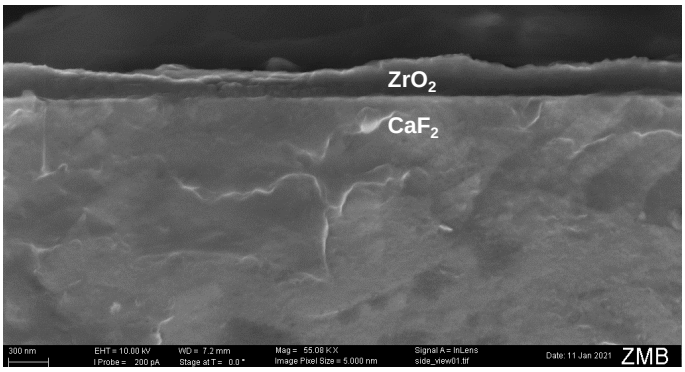

FIG. 2. SEM of sample without ALD layer, cross section.

to the theoretical value for solid ZrO_2 with 5.68 g cm^{-3}. We used the obtained porosity value also for the thinner films and estimated the amount of particles with 20, 30 and 40 nm diameter per area of a 215 nm thick film. From that, the total surface area can be calculated, assuming perfect spheres. The footprint of the molecule is about 1 nm^2 [2] and the absorbance coefficient of the a'(1) mode (in solution) is 2650 cm^{-1} M^{-1}.[1]. Using these values the expected absorbance of the a'(1) mode on the samples are 14, 9 and 7 mOD, depending on the assumed particle diameter. The particles are 20-40 nm in size, the majority of them are larger than 30 nm (see Fig.1). The measured absorbance is well within that range for uncovered ZrO_2, it gets lower and the signal gets much broader when the molecule is covered with ALD layers. With the measured absorbance of 6-8 mOD, there is on average one monolayer of Re molecules on the surface.

[1] K. Oppelt, R. Fernández-Terán, R. Pfister, and P. Hamm, Geminate Recombination versus Cage Escape in the Reductive Quen-ching of a Re(I) Carbonyl Complex on Mesoporous ZrO_2, The Journal of Physical Chemistry C **123**, 19952 (2019).
[2] K. Oppelt, M. Mosberger, J. Ruf, R. Fernández-Terán, B. Probst, R. Alberto, and P. Hamm, Shedding Light on the Molecular Surface Assembly at the Nanoscale Level: Dynamics of a Re(I) Carbonyl Photosensitizer with a Coadsorbed Cobalt Tetrapyridyl Water Reduction Catalyst on ZrO_2, The Journal of Physical Chemistry C **124**, 12502 (2020).