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Supporting Information for:

Chemiresistive Metal-Stabilized Thiyl Radical Films as Highly Selective Ethylene Sensors

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Fabrication and cleaning of electrode device before deposition of films

Two Au electrodes separated by 23 µm were fabricated in a clean room facility by photolithography on a Si/SiOx substrate. Wire leads were attached to the Au contact pads with Ag epoxy (cured 12 h, 80 degree celcius), which was further insulated with an overlayer of Torr-seal epoxy (cured 12 h, 80 degree celcius). The electrodes were cleaned by rinsing in acetone, ethanol, and 2-propanol before drying under N_2. The device was then placed in a UVO ozone cleaner (Jelight Company Inc., Irvine, CA) for 10 min prior to film deposition.

Drop casting at Au - electrode device surface

A 3mM **[Re-1]**$^+$ complex solution is prepared inside the dry box to avoid oxygenation of *cis* sulfur centers. A 3mM burgundy red solution is made with 2 ml of dry degasified dichoromethane and **[Re-1]** (6.39mg, 6.01µmoles). Then added the Ferrocenium hexafluorophosphate (1.99 mg , 6.01µmoles) that oxidizes **[Re-1]** neutral complex to deep blue solution of **[Re-1]**$^+$ complex that reversibly binds ethylene. Thereafter the solution is dropped on the electrode device and evaporated. Before ethylene sensing, the electrode device is kept for an hour in the dry box to ensure solvent evaporation. The quality of the electrode is dependent on the thickness and uniformity of the drop cast film. Using the method above, we obtain consistent responses at least one of every four attempts. Failed films may be electrode using dichloromethane allowing the electrode device to be recycled.

Chronoamperometry measurements for ethylene detection

Electronic measurements were performed with a CH Instruments 660A (Austin, TX) electrochemical workstation operating in chronoamperometry (CA) mode. One electrode device lead was connected to the working electrode lead, and the other electrode was connected to both the counter and reference electrode leads. The current was monitored at a potential of -1.0 V, while the device was exposed to alternating flows of pure N_2 carrier gas and C_2H_4 mixed with carrier gas. The C_2H_4 concentration was varied by mixing C_2H_4 and N_2 at different flow rates controlled by Cole Parmer flow meters located between the sample and the gas cylinders and operated by a three-way valve. All samples were exposed to 100 towards 1 % C_2H_4 for 1000 s to monitor the electronic response to C_2H_4.

Solution phase experiment set up

All electrochemical measurements were performed using a PAR 273 potentiostat/ galvanostat with a three-electrode cell (glassy carbon working electrode, platinum wire counter electrode, and Ag/Ag ion reference electrode), Figure S9. Reported potentials are scaled versus a ferrocenium/ ferrocene (Fc^+/Fc) standard (0.00 V), which was determined using ferrocene as an internal standard. A 1 mM solution of **Re-1** was prepared in dry, degassed methylene chloride with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte.

Electrochemical measurements were collected under a nitrogen/ethylene atmosphere with relative ethylene concentrations regulated using calibrated flow meters. Prior to each run, nitrogen gas was bubbled through the solution to refresh the atmosphere. The solution was then purged for 30 seconds with an ethylene/nitrogen mixture. Relative ethylene concentrations investigated were 0%, 10%, 25%, 30%, 40%, 50%, 60%, 70%, 75%, 80%, 90%, and 100%. A potential of 0.7V or 1.4V was then applied for 120 seconds to oxidize **Re-1** to **[Re-1]**$^+$ or **[Re-1]**$^{2+}$, respectively. A squarewave potential sweep from the positive holding potential to a final potential of -200 mV was then applied.

Current response was plotted as the difference in the cathodic and anodic peak intensity. Relative peak areas for each redox couple were determined by curve fitting of the voltammogram assuming Gaussian peak shapes. Data were then plotted to obtain a calibration curve.

Figure S1: Design of electrode device

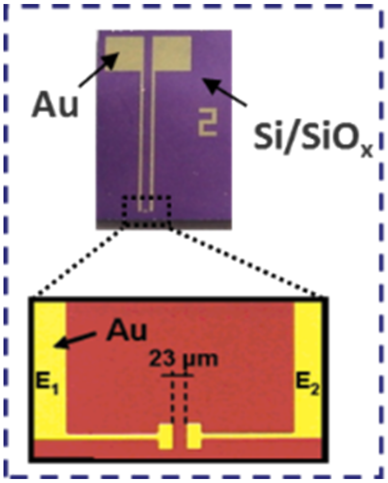

Figure S2: Chronoamperometry measurements for ethylene detection

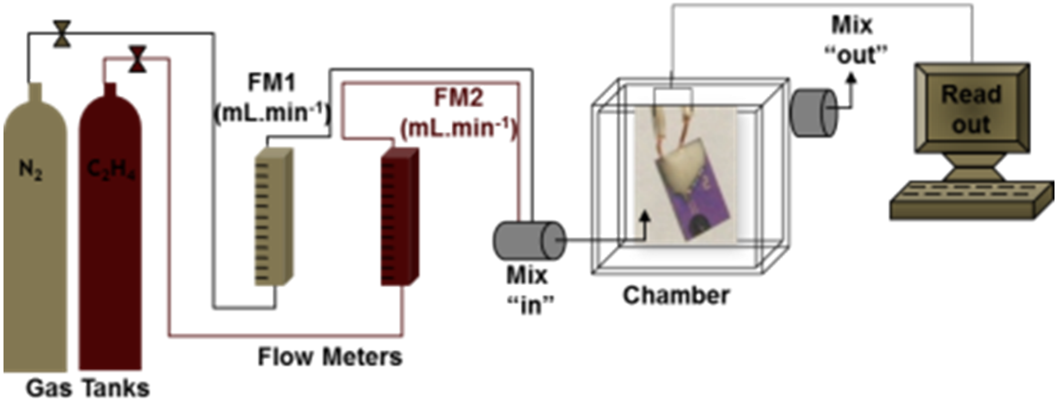

Figure S3: Chronoamperometry measurement for gaseous 31.6% ethylene detection with the solid-state [Re-1]+ coated Au microgap electrode.

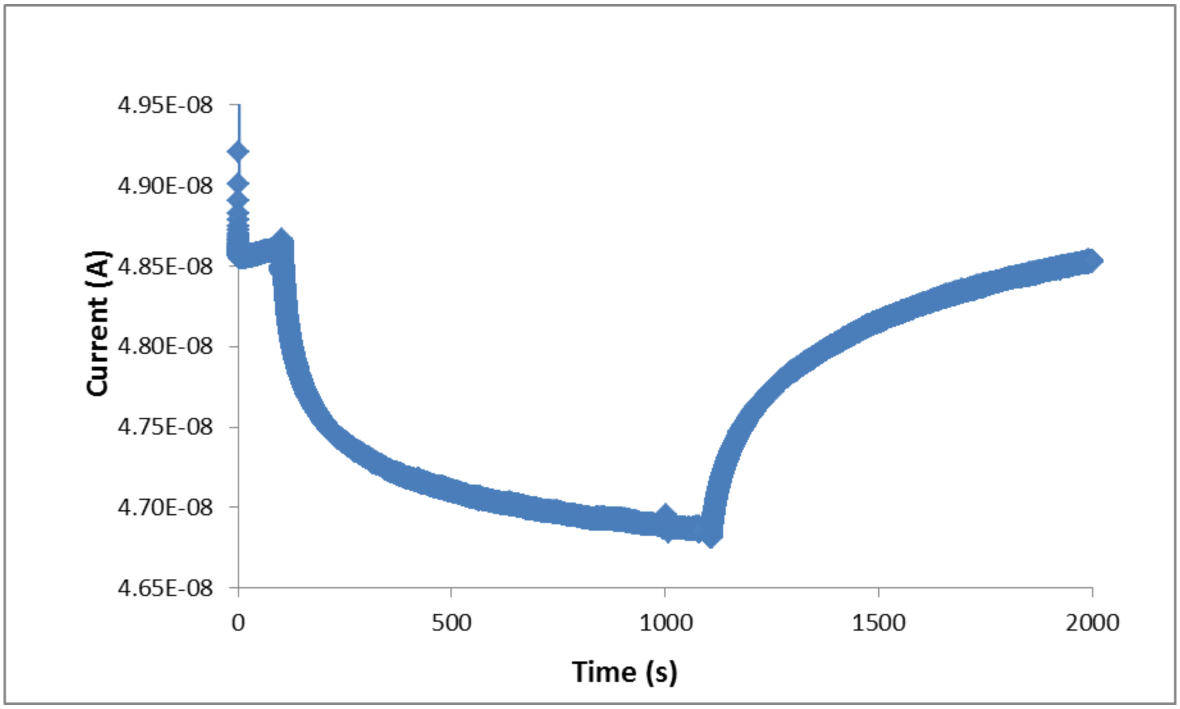

Figure S4: Chronoamperometry measurement for gaseous 26.3% ethylene detection with the solid-state [Re-1]+ coated Au microgap electrode.

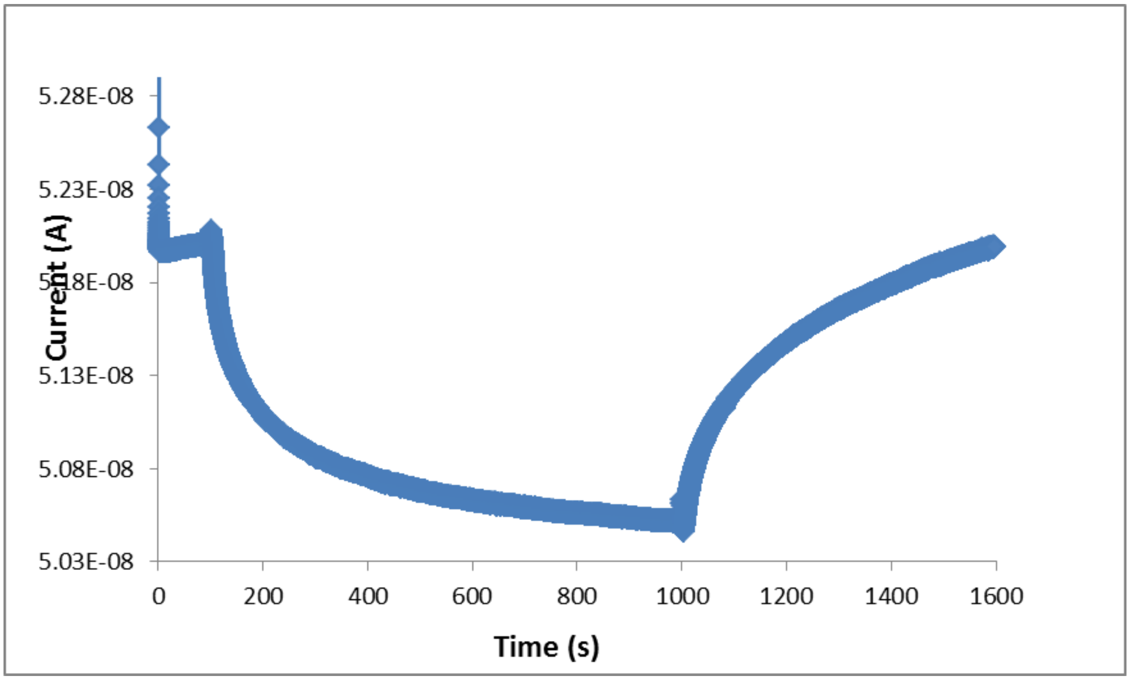

Figure S5: Chronoamperometry measurement for gaseous 11.12% ethylene detection with the solid-state [Re-1]+ coated Au microgap electrode.

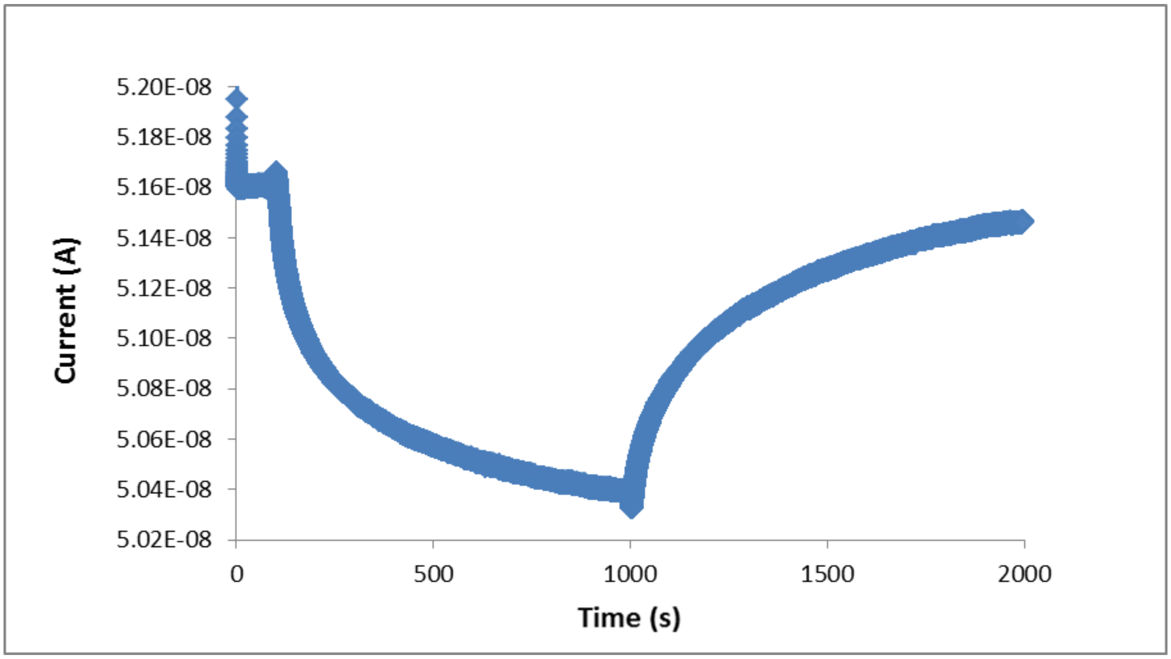

Figure S6: Chronoamperometry measurement for gaseous 3.96% ethylene detection with the solid-state [Re-1]+ coated Au microgap electrode.

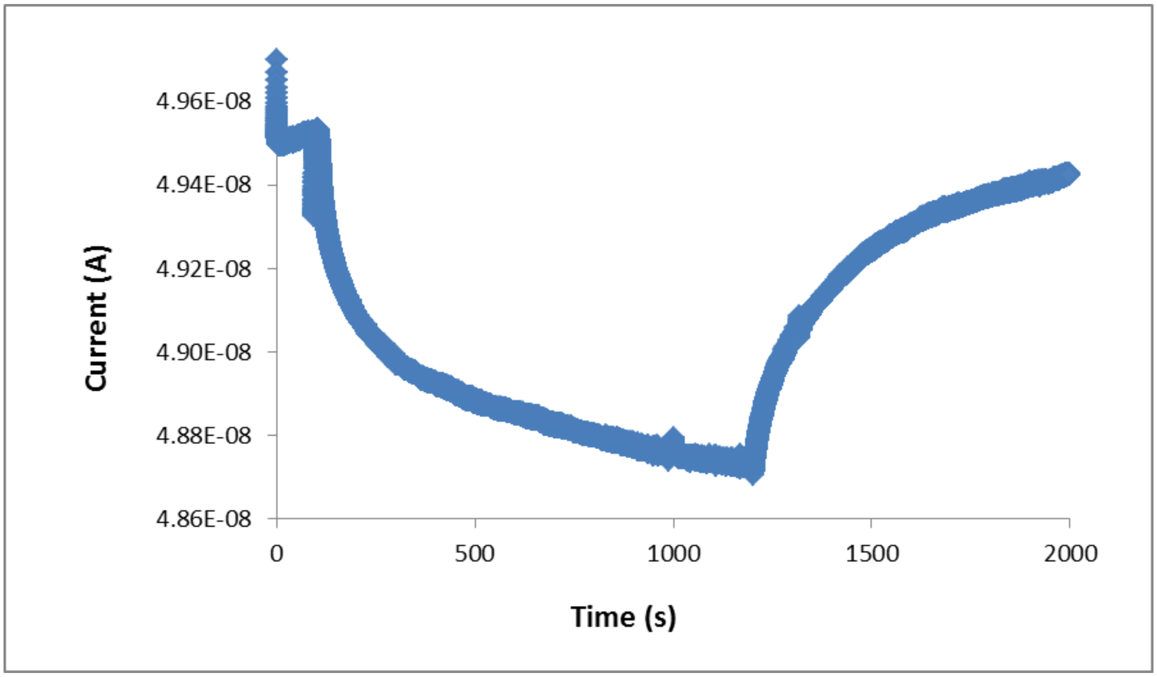

Figure S7: Chronoamperometry measurement for gaseous 2.82% ethylene detection with the solid-state [Re-1]+ coated Au microgap electrode.

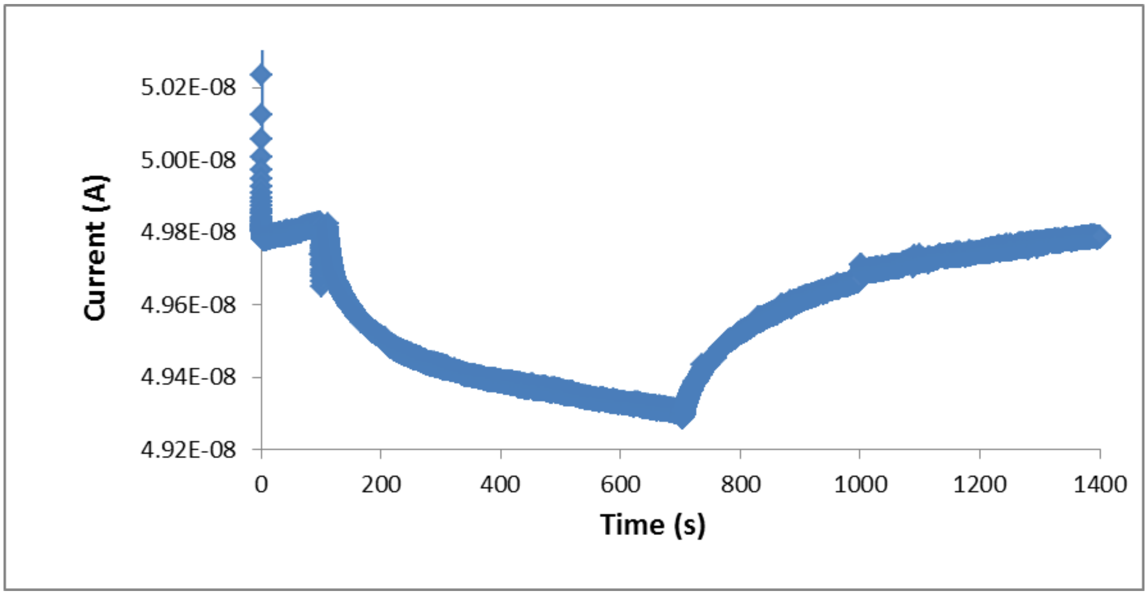

Figure S8: Chronoamperometry measurement for gaseous 0.86% ethylene detection with the solid-state [Re-1]+ coated Au microgap electrode.

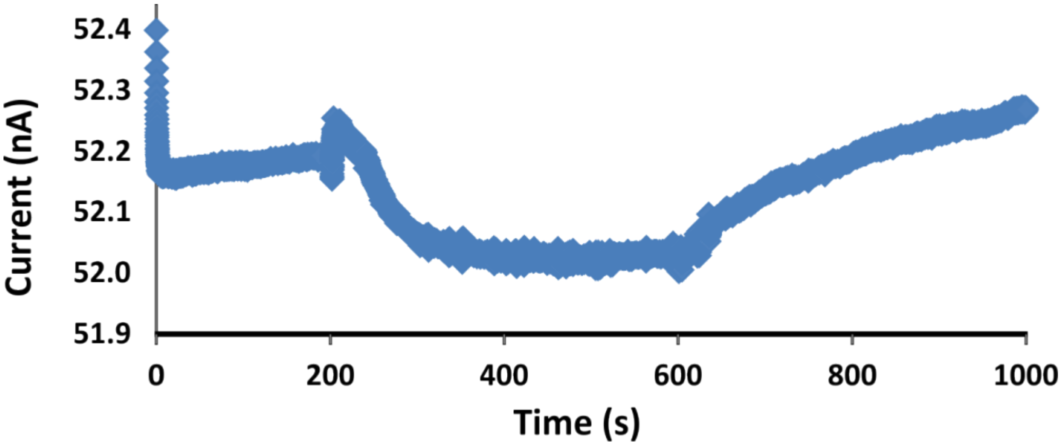

Figure S9: Solution phase Experiment set up

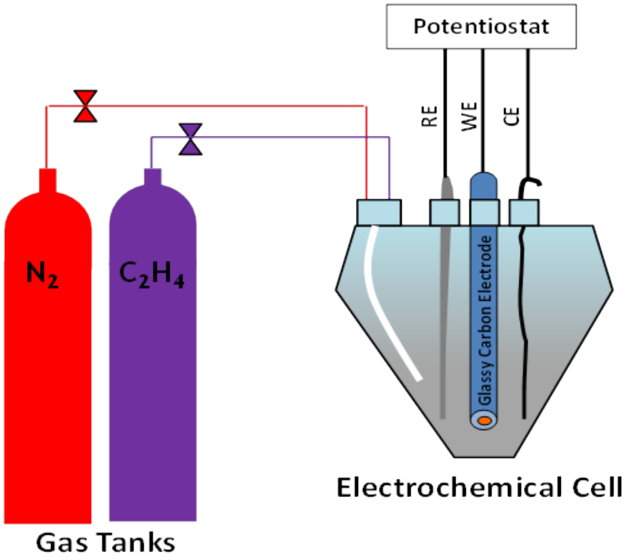

Figure S10. Square wave voltammogram of **[Re-1]** in dichloromethane with 0.1 M tetra-butylammonium hexafluorophosphate in the presence of ethylene (blue), nitrogen (red), and 1:1 ethylene:nitrogen (purple). Potentials scaled to the ferrocenium/ferrocene (Fc+/Fc) couple.