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Supplementary Information

Generalized strategy for small-molecule-functionalized electrodes exhibiting aqueous stability for use in artificial photosynthesis

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Materials and Methods. Complexes Ru(bpy)$_2$Cl$_2$[1] and **Ru2-Cl**[2] were synthesized by previously published procedures. Trimethoxyoctylsilane was purchased from ArkPharm and used as received. Tetraethoxysilane was purchased from Alfa Aesar and used as received. Trimethoxy(propyl)silane, 3-aminopropyltrimethoxysilane, and trimethoxyphenylsilane were purchased from TCI and used as received. (3-chloropropyl_trimethoxysilane was purchased from Aldrich Chemical and used as received. Hydrothane (HPU, AL25-70A) and Tecoflex (TPU, SC-80A) polyurethanes were purchased from AdvanSource Biomaterials and Lubrizol, respectively. HPU/TPU solutions were made by dissolving 10 wt% HPU and TPU in THF. All other reagents were ACS grade and purchased from Millipore Sigma. Microwave reactions were carried out in a CEM Discover SP system.

UV-vis spectra were recorded on an Agilent Technologies Model 8454 diode-array spectrophotometer. SEM images were taken using a JEOL 6360 LV SEM. Electrochemical measurements and analyses were performed on a CH Instruments model 660E potentiostat/galvanostat. Working and reference electrodes were purchased from BASi. A 3 mm glassy carbon disk was used as the working electrode and a Ag/AgCl (3 M NaCl) was used as the reference electrode in all experiments. Experiments were conducted in 0.1 M phosphate solutions made by mixing the appropriate ratios of phosphoric acid, monobasic, dibasic, and tribasic phosphate salts. Final pH values were adjusted using either phosphoric acid or concentrated sodium hydroxide. RRDE experiments were performed with a Pine Instruments bipotentiostat and rotator. The working electrode was prepared as described. The reference electrode was a standard Ag/AgCl electrode (Pine) mounted in a Vycor-tipped glass tube. The counter electrode was a platinum wire coil in an isolated glass tube with fine glass frit separator (Pine). Solutions were deaerated by bubbling nitrogen and the disk potential was scanned from 0.0 V to 1.70 V *vs* Ag/AgCl at a scan rate of 10 mV/s while the ring potential was held at a constant −0.55 V to detect O_2.

Synthesis of Ru1. Ru(bpy)$_2$Cl$_2$ (0.300 g, 0.62 mmol) and 2,2'-bipyridine (0.106 g, 0.68 mmol) were added to a 30-mL CEM microwave reaction vessel with 15 mL of a 1:1 EtOH/H_2O mixture. The reaction was heated at 150 °C for 20 minutes, then gravity filtered hot. Solvent was removed on a rotary evaporator and the solid was collected and washed with Et$_2$O to give a bright orange solid (0.357, 90%). Characterization matched what was previously reported.

Synthesis of sol-gel solutions. A 0.1 M aqueous solution of **Ru1** or **Ru2-Cl** was mixed with trimethoxyoctylsilane (0.5 mL, or appropriate amount of other silane), water (4.2 mL), and concentrated HCl (3.9 µL). Absolute ethanol was then added to make a total of 20 mL of solution. Resulting solutions were made to keep the total molar ratio of Ru:silane:water:HCl at 0.05:1.0:120:0.3. The solution was stirred at room temperature overnight. Solutions were stored in sealed scintillation vials at 8 °C after synthesis.

Film formation. A 15 µL aliquot of sol-gel solution was added to a freshly polished GC electrode which was then placed in a 50% relative humidity chamber. After drying for 5 minutes, a second 15 µL drop of sol-gel solution was added. Following an additional 10 minutes of drying at 50% relative humidity, a 10-µL drop of 50/50 HPU/TPU in THF was added. It was important that the electrodes were not fully dried before addition of the HPU/TPU layer. The resulting electrodes were allowed to dry at 50% relative humidity for 24 hours. Prior to use, electrodes were soaked in 0.1 M phosphate buffer for 10 minutes. To prepare films that contained electrolyte solution, the same procedure was followed with the exception of the addition of a 15-µL drop of 0.5 M phosphate buffer (aqueous) between the drops of sol-gel solution.

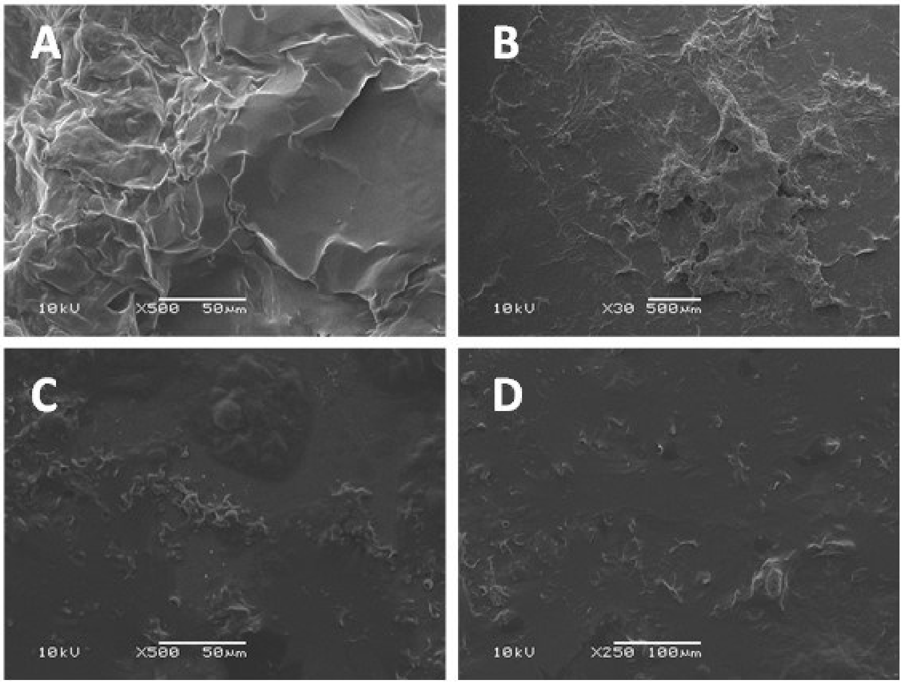

Figure S1. SEM images of octyl siloxane xerogel films of **Ru1** (A and B) and **Ru2-Cl** (C and D).

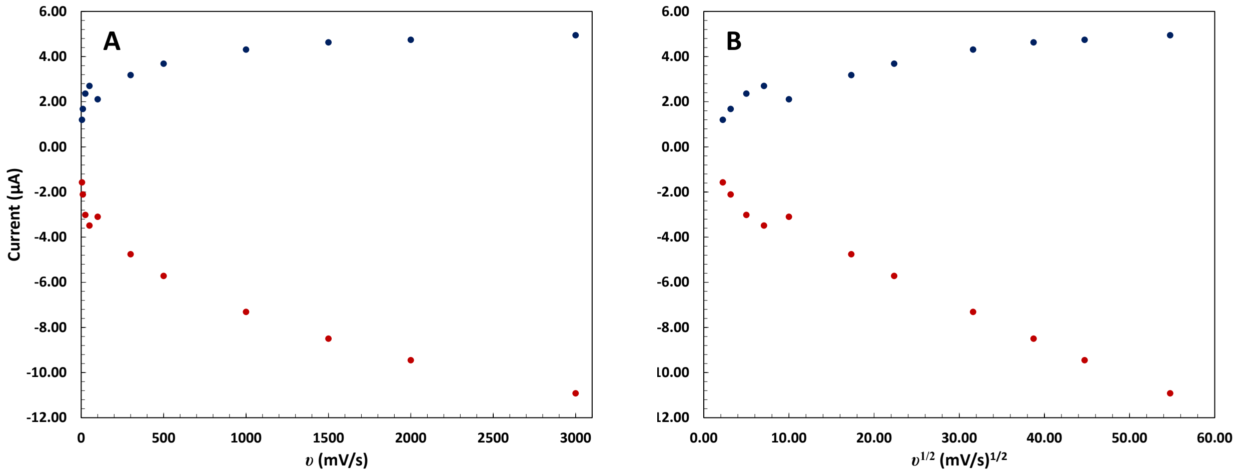

Figure S2. Plots of the dependence of both cathodic and anodic current on the scan rate for a TEOS film containing electrolyte. A: plot of current *vs* scan rate and B: plot of current *vs* square root of the scan rate. Neither show a linear dependence which is often observed for electron hopping/covalent attachment or diffusion controlled processes, respectively.

1 M. R. Norris, J. J. Concepcion, C. R. K. Glasson, Z. Fang, A. M. Lapides, D. L. Ashford, J. L. Templeton and T. J. Meyer, *Inorg. Chem.*, 2013, **52**, 12492–12501.

2 J. J. Concepcion, J. W. Jurss, M. R. Norris, Z. Chen, J. L. Templeton and T. J. Meyer, *Inorg. Chem.*, 2010, **49**, 1277–1279.