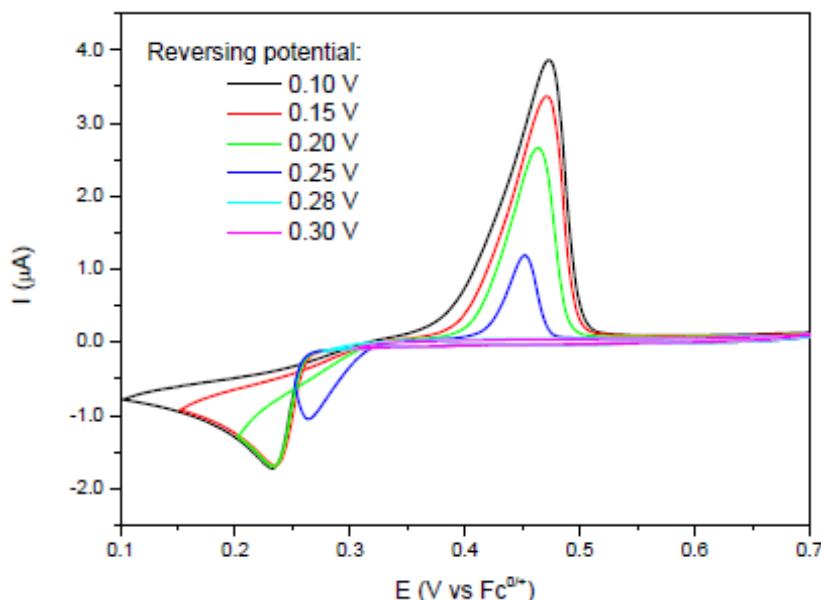
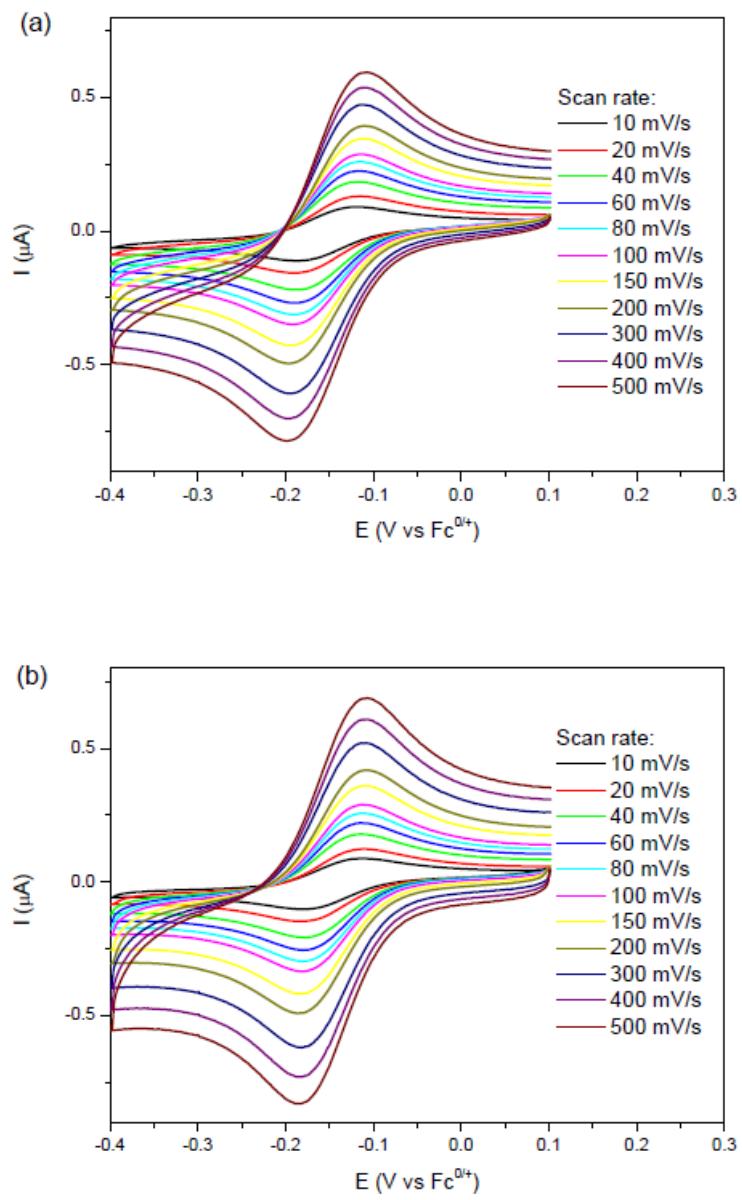


# Underpotential and Overpotential ElectrocrySTALLIZATION of Semiconducting Silver-Tetracyanoquinodimethane onto Gold Substrates from an Ionic Liquid

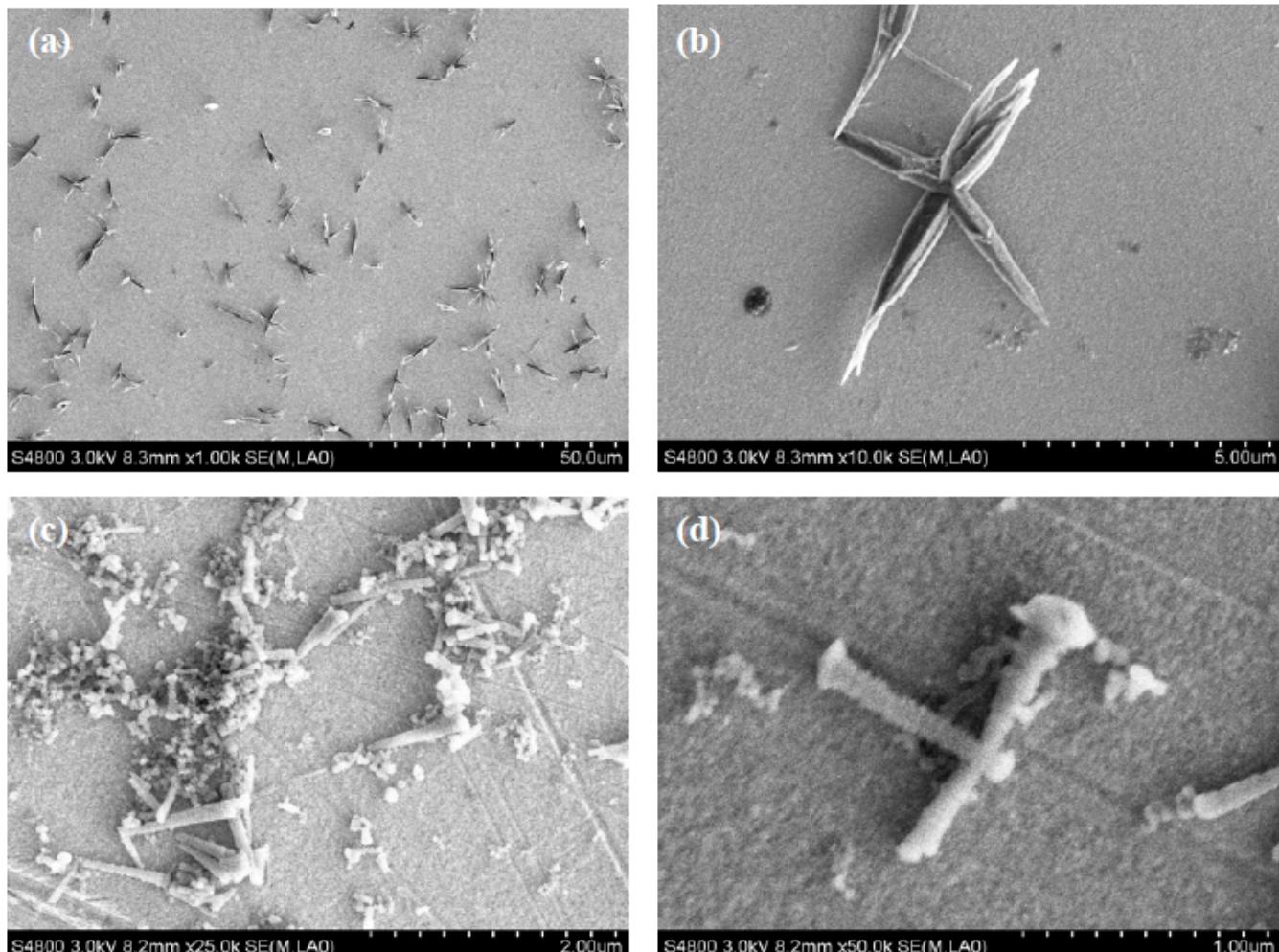
Huan Wang,<sup>†,‡</sup> Xiaohu, Qu,<sup>‡</sup> Jia-Xing Lu,<sup>†</sup> Alan M. Bond<sup>‡, \*</sup> and Chuan Zhao<sup>§, \*</sup>



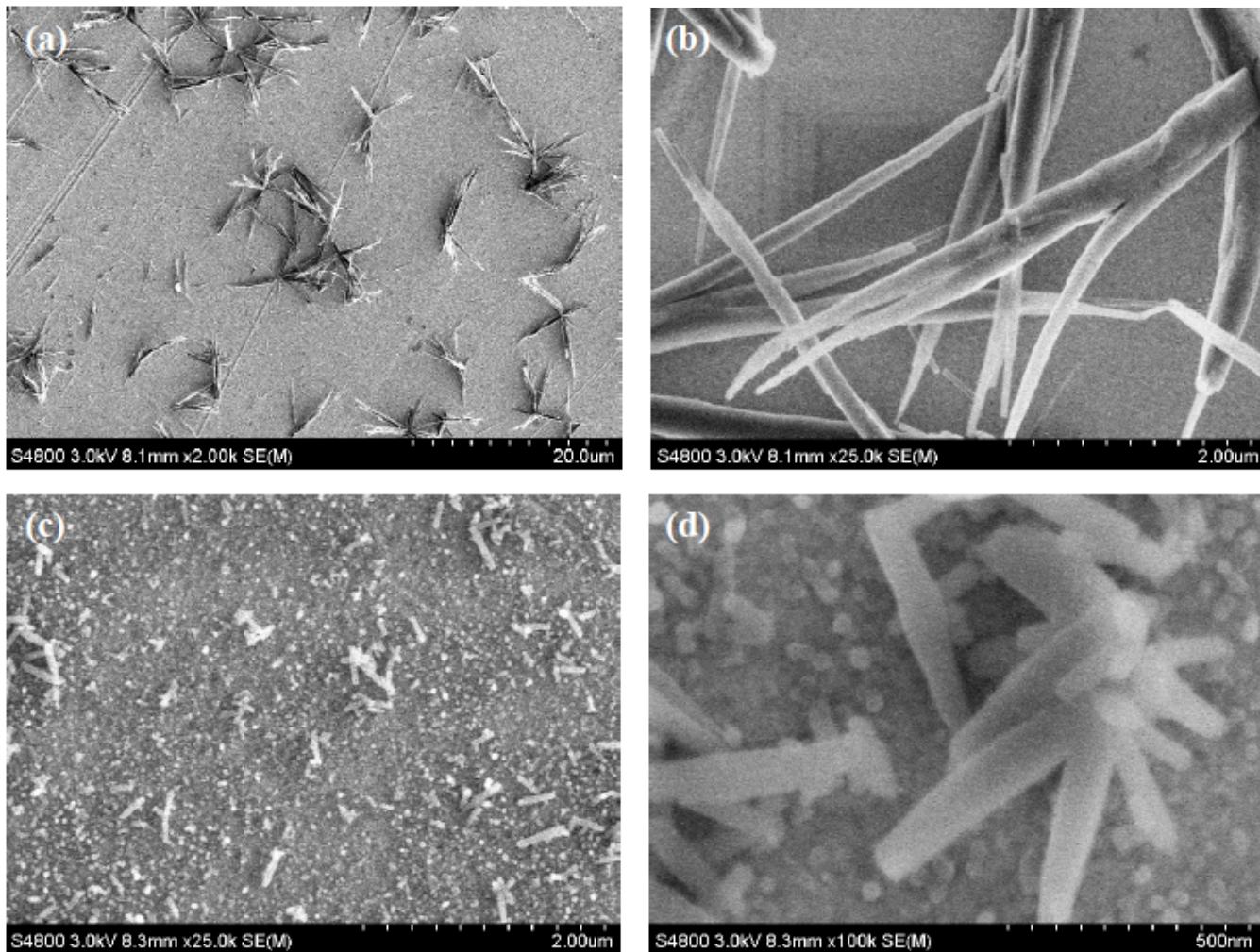
**Figure S1.** Cyclic voltammogram obtained at a Pt electrode for reduction of a 5 mM  $\text{Ag}^+$  in BMIMBF<sub>4</sub> at a scan rate of 20 mV s<sup>-1</sup> when the switching potential is varied from 0.10 to 0.30 V.



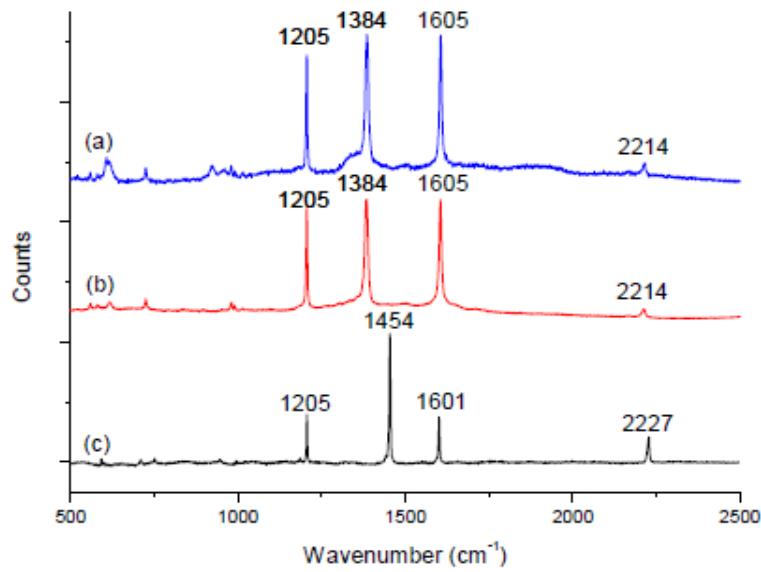
**Figure S2** Cyclic voltammograms obtained at Au (a) and Pt (b) electrodes for reductions of a 3 mM TCNQ in BMIMBF<sub>4</sub> with scan rates of 10-500 mV/s.



**Figure S3.** SEM images of AgTCNQ formed by electrocrystallization from BMIMBF<sub>4</sub> containing 4.9 mM Ag(MeCN)<sub>4</sub>BF<sub>4</sub> and 4.8 mM TCNQ onto a Au electrode when the potential is held at 0.3 V (a,b) and -0.2 V (c,d) vs Fc<sup>0/+</sup> for 300 s.



**Figure S4.** SEM images of AgTCNQ formed by electrocrystallization from BMIMBF<sub>4</sub> containing 6.6 mM Ag(MeCN)<sub>4</sub>BF<sub>4</sub> and 4.8 mM TCNQ onto a Au electrode when the potential is held at 0.3 V (a,b) and -0.2 V (c,d) vs Fc<sup>0/+</sup> for 300 s.



**Figure S5.** Raman spectra of (a, b) electrocrystallized AgTCNQ on a Au electrode from BMIMF<sub>4</sub> containing 10.0 mM Ag(MeCN)<sub>4</sub>BF<sub>4</sub> and 4.8 mM TCNQ at (a) 0.3 V and (b) -0.2 V vs FeC<sup>0/+</sup>, (c) TCNQ crystals.