Supporting Information to:

Spatially-Resolved Sources of Dark Current from TiO_2 Nanoparticle Electrodes

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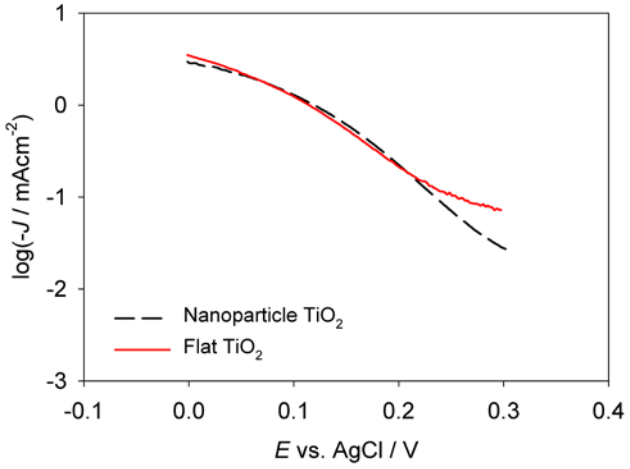
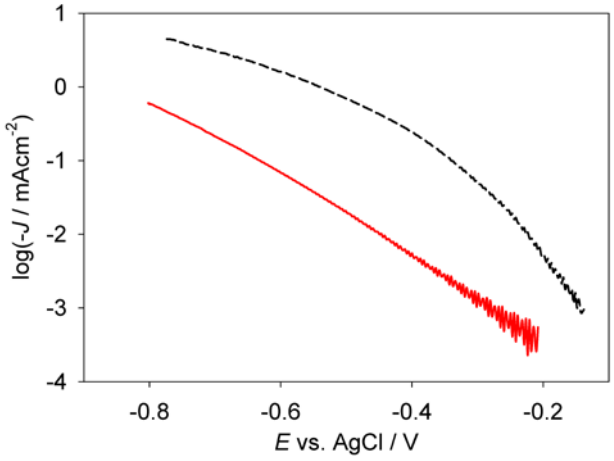
J-E curves for two different electrodes, FTO coated with a TiO_2 blocking layer and FTO coated with a TiO_2 blocking layer and a nanoparticle TiO_2 film, were measured with the $[Ru(bpy)_2(MeIm)_2]^{3+/2+}$ and $[Co(t\text{-}bu_2bpy)_3]^{3+/2+}$ shuttles. The log(-*J*) vs. *E* plots are shown in figure S1. The expected behavior is a linear increase in current density as the surface area increases. Figure S1a demonstrates that there is no difference in the magnitude of dark current using the $[Ru(bpy)_2(MeIm)_2]^{3+/2+}$ redox shuttle with only a TiO_2 blocking layer or with a blocking layer and nanoparticle film. This result is explained by the nanoparticle film remaining largely insulating at the potentials shown, < 0 V vs. AgCl. However, with $[Co(t\text{-}bu_2bpy)_3]^{3+/2}$ the dark current increases by ~ 2 orders of magnitude when the NP TiO_2 film is added to the blocking layer, seen clearly in figure S1b. The increase in the current density behavior is understood to result strictly from the increased surface area of the nanoparticles. The expected increase in surface area is between 2-3 orders in magnitude, slightly higher than the observed change. This is a result of mass transport limitations at higher current for the nanoparticle film electrode which can be seen as a deviation from the linearity of the log plot for the nanoparticle film.



a)



b)

Figure S1: Log(-*J*) vs. *E* curves for electrolyte containing: a) $[Ru(bpy)_2(MeIm)_2]^{3+/2+}$ and b) $[Co(t\text{-}bu_2bpy)_3]^{3+/2+}$ in contact with flat TiO_2 (red solid) and a nanoparticle film on flat TiO_2 (black dashed).

CVs using TiO_2 resulting in multiple features have been reported previously as discussed by Bisquert *et al*. in a recent review.[1] These previous results, measuring the capacitive current only, did not use a redox shuttle. In order to clearly demonstrate that our results are faradaic currents and not influenced by capacitive currents, we have measured the capacitive current using a blocking electrolyte (0.1 M $LiClO_4$ in acetonitrile). Figure S2 shows the comparative currents on a log scale, clearly indicating that in the potential region of interest (-0.1 to 0.2 V vs. AgCl) the capacitive current is 2 to 3 orders of magnitude lower than our measured CVs.

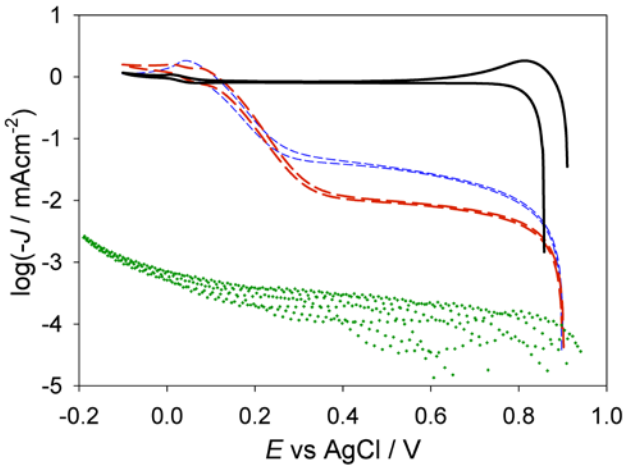


Figure S2: The log(-J) of cyclic voltammograms of $[Ru(bpy)_2(MeIm)_2]^{3+/2+}$ using three different working electrodes: nanoparticle TiO_2 on FTO (black solid), flat TiO_2 (blue short dash), and nanoparticle TiO_2 film on flat TiO_2 (red long dash). Also shown for reference is the capacitive CV of a nanoparticle electrode in contact with blocking electrolyte (green dot).

References:

(1) Bisquert, J.; Fabregat-Santiago, F.; Mora-Sero, I.; Garcia-Belmonte, G.; Barea, E. M.; Palomares, E. *Inorg. Chem. Acta* **2008**, *361*, 684.