Electronic Supplementary Material (ESI) for Faraday Discussions.
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Stochastic Electrochemistry and Photoelectrochemistry of Colloidal Dye-Sensitized Anatase Nanoparticles at a Pt Ultramicroelectrode

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Supporting information

Section 1. Control Experiments

We performed control experiments in the dark and under illumination shown in Figure S1. We used 1.5 µM N719 (dye) in methanol with no TBAP as control and 0.1M TBAP in methanol as the blank of our control experiments. The dye concentration used in the control experiments corresponds to the dye concentration in 2.5 nM DSNPs. *I-t* curve obtained for both solutions did not show current steps in dark or during illumination. The background current oscillation observed in both measurements are < 1 pA.

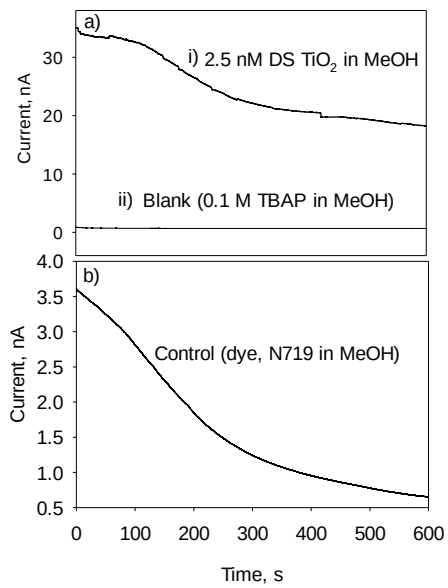

Figure S1. *I-t* curve obtained for different solutions during illumination a) Overlay plot for blank and sample i) 2.5nM DSNP in methanol ii) 0.1 M TBAP in methanol

Section 2. Digital Simulations

We simulated the cyclic voltammetry experiment for 1 mM N719 in 0.1 M TBAP in acetonitrile at 1 V/s in the dark condition. We took the third and 4th segments at 1 V/s because these segments did not show an adsorption peak. We simulated the electrochemical process followed by an irreversible chemical reaction with DigiElch (ElchSoft). From the simulation, we obtained diffusion coefficient of dye is 4.4×10^{-7} cm^2/s. E^0 = 0.93 V vs NHE and k^0 = 0.0009 cm/s.

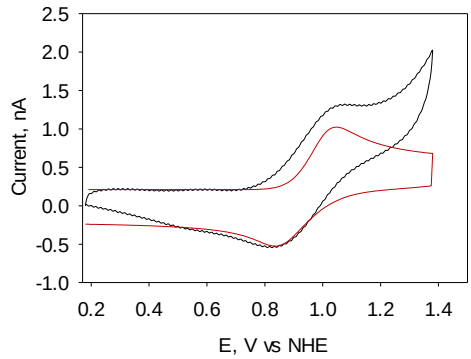

Figure S2. Cyclic voltamogram obtained for 1 mM N719 (dye), 0.1 M TBAP in acetonitrile at the scan rate of 1 V/s in the dark. The background corrected experimental data (––, black) and the simulation results (—, red) are shown for comparison.

Simulation parameters:

Mechanism: ErCi

$D^+ + e \rightarrow D$

$D + S \rightarrow P$

$E^0 = 0.93V$ vs. NHE

$\alpha = 0.5$

Diffusion coefficients:

$D^+ = D = P = 4.4 \times 10^{-7}$

$S = 3.18 \times 10^{-5}$

Analytical (initial) concentrations:

$D^+ = 0$ M

D= 0.001M

P= 0M

S= 19.147M

Radius of microelectrode: 0.00125cm

Uncompensated resistance (Ru) = 30 kΩ

Double layer capacitance= 2.1×10^{-10} F