Supporting Information

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Investigation on Regeneration Kinetics at Perovskite/Oxide Interface with Scanning Electrochemical Microscopy

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In this study, we report a comparative investigation of charge transfer kinetics with electrochemical microscopy (SECM) measurement between $MAPbI_3$ and conventional sensitizers. The electrolyte used for the investigation of reduction process is 1-methy-1H-tetrazole-5-thiolate (T^-) for P1/NiO and $MAPbI_3$/NiO. Disulfide dimmer (T_2) is used as for Z907/TiO_2 and $MAPbI_3$/ TiO_2 films.

The experimental approach curves $i_T(z)$ were normalized to $I_T(L)$ and the normalized heterogeneous rate constants have been extracted by fitting them to an analytical approximation suggested by Cornut and Lefrou for a first-order reaction at the sample and infinitely fast reaction at the UME (equation S1).[1-4]

$$I_T(L,k,RG)=I_T^{con}\left(L+\frac{1}{k},RG\right)+\frac{I_T^{ins}(L,RG)-1}{\left(1+2.47RG^{0.31}LK\right)\left(1+L^{0.006RG+0.133}k^{-0.0236RG+0.91}\right)} \quad (S1a)$$

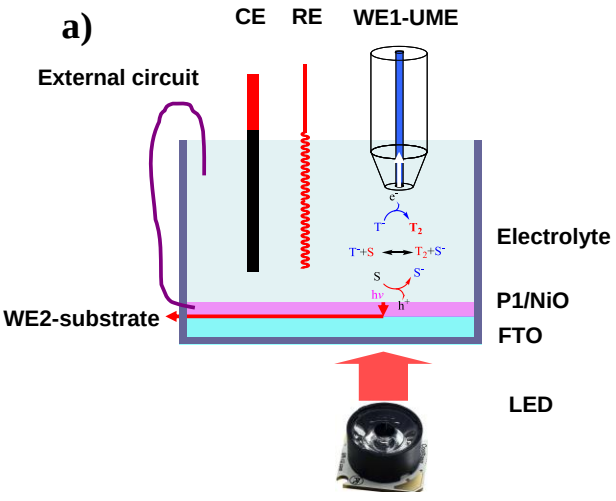
$$I_T^{ins}(L,RG)=\frac{\left(2.08/RG^{0.358}\right)\left(L-(0.145/RG)\right)+1.585}{\left(2.08/RG^{0.358}\right)(L+0.0023RG)+1.57+(\ln RG/L)+(2/\pi RG)\ln(1+(\pi RG/2L))} \quad (S1b)$$

$$I_T^{cond}\left(L+k^{-1},\ RG\right)=\alpha(RG)+\frac{\pi}{4\beta(RG)\arctan\left(L+k^{-1}\right)}+\left(1-\alpha(RG)-\frac{1}{2\beta(RG)}\right)\frac{2}{\pi}\arctan\left(L+k^{-1}\right) \quad (S1c)$$

$$\alpha(RG)=\ln 2+\ln 2\left(1-\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)-\ln 2\left(1-\left(\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)^2\right) \quad (S1d)$$

$$\beta(RG)=1+0.639\left(1-\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)-0.186\left(1-\left(\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)^2\right) \quad (S1e)$$

where I^{ins}_T(L, RG) is the contribution of diffusion of T^- for the NiO electrode and diffusion of T_2 for the TiO_2 electrode from solution to the UME. $I^{cond}_T(L+k^{-1},RG)$ is the current that results from the reaction of $2S^+ + 2T^- \rightarrow 2S + T_2$ for the sensitized n-type semiconductor oxide, $2S^- + T_2 \rightarrow 2S + 2T^-$ for the sensitized p-type semiconductor sample. α(RG) and β(RG) are the constants.



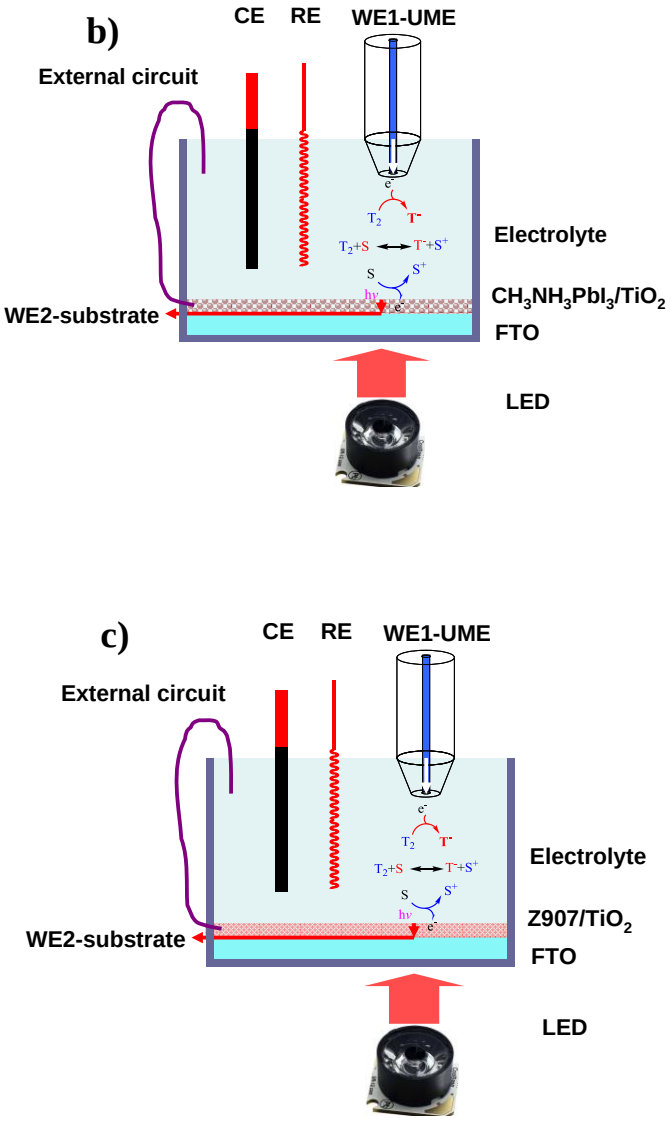


Figure S1. Basic arrangements for the SECM investigation of heterogeneous reaction at a) P1/NiO, b) $MAPbI_3/TiO_2$, and c) $Z907/TiO_2$ films with feedback mode under short-circuit condition with illumination.

A 25 μm diameter Pt wire (Good fellow, Cambridge, UK) was sealed into a 5 cm glass capillary prepared by a Vertical pull pin instrument (PC-10, Japan) (Figure S2a). The ultra-microelectrode (UME) was polished by a grinding instrument (EG-400, Japan) and micro-polishing cloth with 1.0, 0.3 and 0.05 μm alumina powder (Figure S2b). Then the UME was sharpened conically to a RG of 10, where RG is the ratio between the diameters of the glass sheath and the Pt disk. Figure S2c and Figure S2d compare the cyclic voltammeter of a Pt electrode (d=3 mm) and a Pt UME (d=25 um) in the 0.5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ with a scan rate of 50 mV s^{-1}. One can get the electrode size by using the formula of $i_\infty = 4nFDCr_T$, where r_T is the radius of the microelectrode, D is the diffusion coefficient of the redox couple.

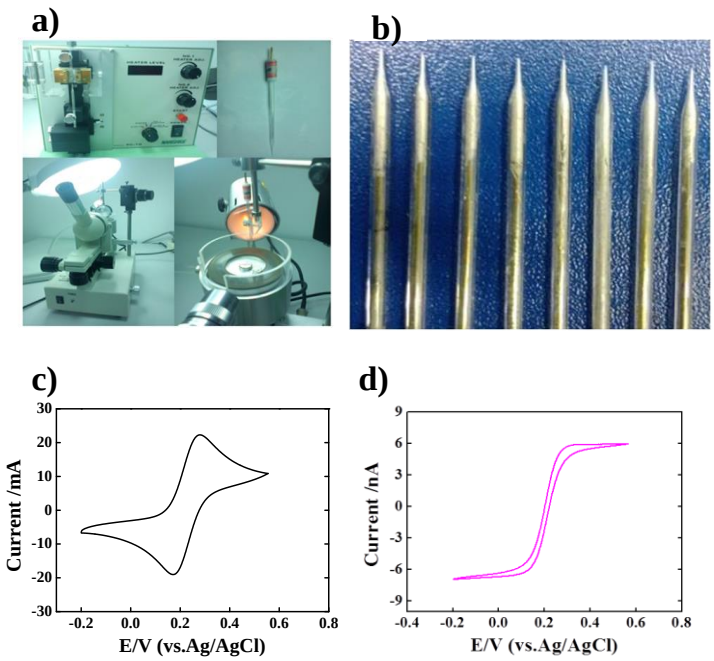


Figure S2. Optical images of (a) a grinding instrument (EG-400, Japan), (b) several ultra-microelectrodes (UME) with 25 μm diameter Pt wire (Good fellow, Cambridge, UK) sealed into a 5 cm glass capillary. Cyclic voltammetry of (c) Pt electrode (d= 3 mm) and (d) Pt UME (d=25 um) in 0.5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ with a scan rate of 50 mV s^{-1}.

Figure S3 shows cyclic voltammogram of a Pt UME in 1 mM T^- electrolyte.

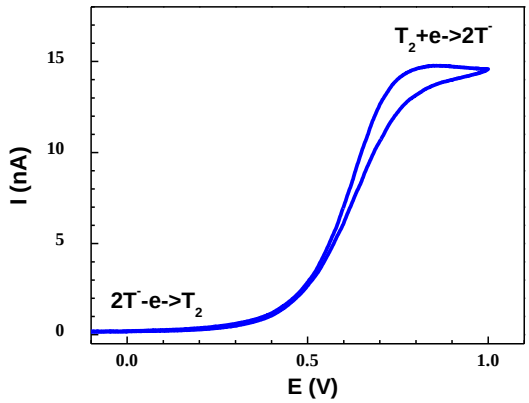


Figure S3. Cyclic voltammogram of a Pt UME in 1 mM T^- (isoperponal/alcohol solution) at a scan rate of 0.05 V s^{-1}.

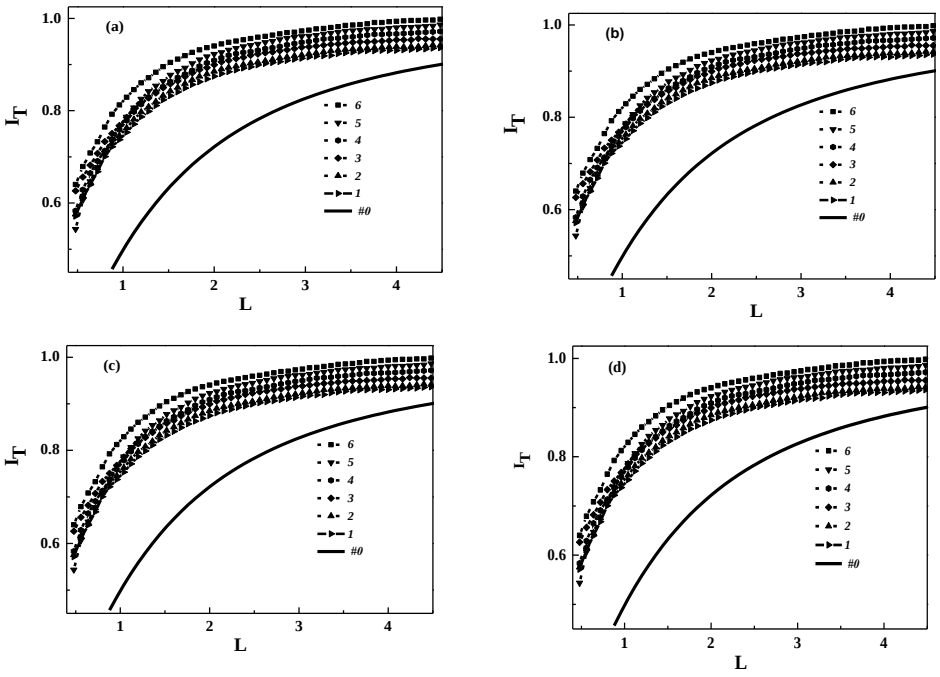


Figure S4. (a) The normalized SECM feedback approach curves for the approach of a Pt disk UME towards P1/NiO film in the dark (curve #0) and under illumination by a blue LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1}: (1) 2.2, (2) 6.1, (3)11.8, (4) 13.9, (5) 19.8, and (6) 22.4; scanning rate 0.05 V s^{-1} E_T= 0.7 V with electrolyte [T^-]=1 mM. Curves (#1-6) are calculated curves for an approach of an UME towards an inert insulating surface (curve 0), and to samples with the first order kinetics rate constant κ: (1) 0.0229, (2) 0.0481, (3) 0.0577, (4) 0.0737, (5) 0.0781, and (6) 0.0815; the effective rate constant k_{eff} $\times 10^{-3}$cm s^{-1}: (1) 2.48, (2) 5.19, (3) 6.24, (4) 7.96, (5) 8.43, (6) 8.81. (b) P1/NiO film under illumination by a red LED Photon flux in 10^{-9} mol cm^{-2} s^{-1}: (1) 4.19, (2) 6.81, (3)9.44.8, (4) 12.06, (5) 13.11, and (6) 14.68. The first order kinetics rate constant *k* is: (1) 0.0353, (2) 0.0538, (3) 0.0626 (4) 0.0692, (5) 0.0712, and (6) 0.0742, and k_{eff}

($\times 10^{-3}$ cm s^{-1}): (1) 3.81, (2) 5.82, (3) 6.76, (4) 7.47, (5) 7.69, and (6) 8.01. (c) The normalized SECM feedback approach curves for the approach of a Pt disk UME towards $MAPbI_3$/NiO film in the dark (curve#0) and under illumination by blue LED Photon flux density in 10^{-9} mol cm^{-2} s^{-1}: (1) 2.2, (2) 6.1, (3)11.8, (4) 13.9, (5) 19.8, and (6) 22.4; electrolyte [T_2]=1 mM, the first order kinetics normalized rate constants κ: (1) 0.0497, (2) 0.0525, (3) 0.0671, (4) 0.0711, (5) 0.0791, (6) 0.0829, and k_{eff} $\times 10^{-3}$ cm s^{-1}: (1) 3.02, (2) 5.68, (3) 7.24 (4) 7.67, (5) 8.54, and (6) 8.96. (d) $MAPbI_3$/NiO film under illumination by a red LED Photon flux density in 10^{-9} mol cm^{-2} s^{-1}: (1) 4.19, (2) 6.81, (3)9.44.8, (4) 12.06, (5) 13.11, and (6) 14.68. The first order kinetics rate constant κ: (1) 0.0539, (2) 0.0731, (3) 0.112, (4) 0.123, (5) 0.127, and (6) 0.132, k_{eff} $\times 10^{-3}$ cm s^{-1}: (1) 7.90, (2) 10.41, (3) 12.12 (4) 13.38, (5) 13.79, (6) 14.33.

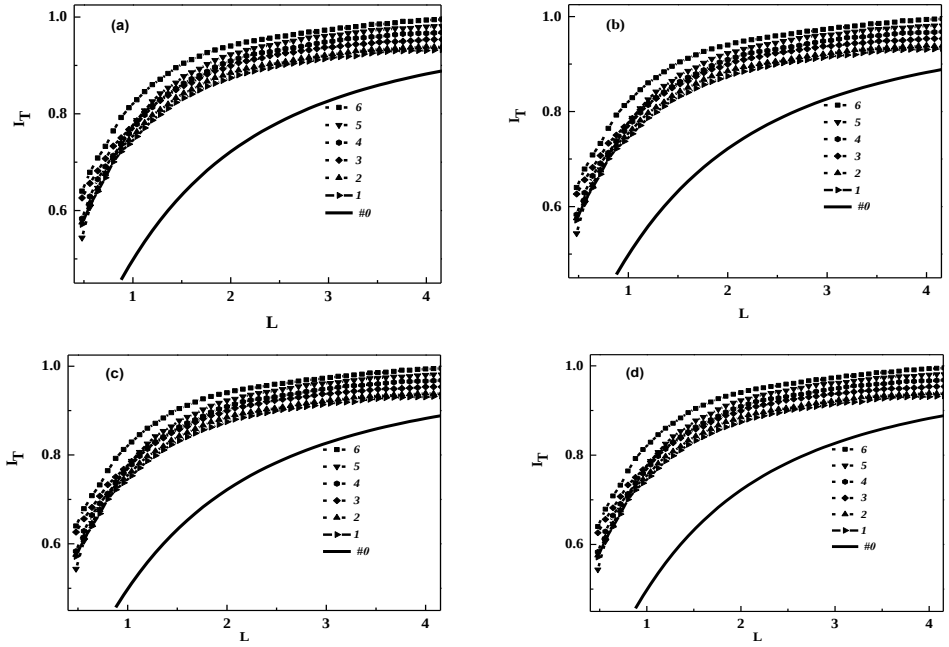


Figure S5. (a) The normalized SECM feedback approach curves for the approach of a Pt disk UME towards Z907-sensitized TiO_2 film in the dark (curve #0) and under illumination by a blue LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1}: (1) 2.2, (2) 6.1, (3)11.8, (4) 13.9, (5) 19.8 (6) 22.4; scanning rate 0.05Vs^{-1}, E_T=0.7 V, [T^-]=1 mM. Curves (#1-6) are calculated curves for an approach of an UME towards an inert insulating surface (curve # 0), and to samples with the first order kinetics rate constant κ: (1) 0.065, (2) 0.069, (3) 0.087 (4) 0.092, (5) 0.102, (6) 0.106; the effective rate constant k_{eff} $\times 10^{-3}$cm s^{-1}: (1) 1.15, (2) 1.22, (3) 1.55 (4) 1.64, (5) 1.82, (6) 1.89. (b) Z907-sensitized TiO_2 film under illumination by a red LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1}: (1) 4.19, (2) 6.81, (3) 9.44.8, (4) 12.06, (5) 13.11, (6) 14.68 Lines (1-6) are calculated curves for an approach of an UME towards an inert insulating surface (curve# 0), samples with first order kinetics *k* (1) 0.017 (2) 0.035, (3) 0.044, (4) 0.047, (5) 0.052, (6) 0.055 k_{eff} $\times 10^{-3}$ cms^{-1} (1) 3.01 (2) 6.23, (3) 7.95 (4) 8.43, (5) 9.37 (6) 9.67 (c) $MAPbI_3$-sensitized TiO_2 film in the dark (curve #0) and under illumination by a blue LED. Photon flux density of LED in 10^{-9} mol cm^{-2} s^{-1}(1) 2.2, (2) 6.1, (3)11.8, (4) 13.9, (5) 19.8, and (6) 22.4; ET= 0.7 V [T^-] = 1mM. Lines (1-6) samples with first order kinetics *k* (1) 0.238, (2) 0.251, (3) 0. 321, (4) 0.341, (5) 0.373, (6) 0.391 k_{eff} $\times 10^{-3}$ cms^{-1} (1) 4.21, (2) 4.45, (3) 5.67 (4) 6.02, (5) 6.61 (6) 6.91 (d) Under

illumination by a red LED Photon flux density of 10^{-9} mol cm^{-2} s^{-1}(1) 4.19, (2) 6.81, (3)9.44.8, (4) 12.06, (5) 13.11 (6) 14.68 .4;, ET= 0.7 V [T^-]=1mM.Lines (1-6) (1) 0.034, (2) 0.0437 (3) 0.051, (4) 0.056 (5) 0.058,(6) 0.061 and k_{eff} $\times 10^{-3}$ cms^{-1} (1) 5.99, (2) 7.74, (3) 9.01 (4) 9.95, (5) 10.26 (6) 10.66.

References

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