## Surface Photovoltage Spectroscopy Observes Photochemical Charge Transfer in Nanoscale Hydrogen Evolving Photocatalyst

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## **Electronic Supplementary Information (3 pages)**



Figure S1. Powder X-Ray diffraction of  $SrRh_{0.03}Ti_{0.97}O_3$  (the pattern of  $SrTiO_3$  are from ICDD PDF Card 00-002-1454). The sizes of the particles were calculated by Scherrer Equation to be  $35.1\pm1.3$  nm. This is close to the TEM diameter (20-75 nm), suggesting the presence of single crystals.



Figure S2. Spectra of SPS light source (Grating 2 was used for all the measurements)



Figure S3. SPS configuration and example spectra showing the generation of a photovoltage as a result of photochemical charge transfer in the sample film. <sup>1</sup> Reprinted with permission from Ref. 1. Copyright 2014, American Chemical Society.



Figure S4. Visible light driven hydrogen evolution from Rh(3mol%):SrTiO<sub>3</sub>-Pt(2%) in water under 380 mW/cm<sup>2</sup> illumination from a 300 W Xe lamp with filter (>400 nm).



Figure S5. UV/Vis absorbance spectra of 0.05 M potassium ferrocyanide (green), 0.05 M potassium ferricyanide (red) and the solution after visible light hydrogen evolution reaction with 50 mL 0.05 M potassium ferrocyanide as the sacrificial agent (reaction shown in Figure 3D). A quartz cell of 1 cm path length was used and pure water was used as reference. The photocatalyst is particularly sensitive to the light intensity change in the 400-500 nm. Also, from  $T=10^{-A}$ , a 0.2 absorbance (at 450 nm, solution after reaction, blue line) means that 37% of the light is lost by passing through merely 1 cm of the solution.

Table S1. Calculation of the electron and hole diffusion lengths for SrTiO<sub>3</sub>

Parameter	electron	hole	Reference
Diffusion Length L [m] = SQRT(D t) for Fe-doped SrTiO <sub>3</sub>		1.51E-07	
Diffusion Length L [m] = SQRT(D t) for SrTiO <sub>3</sub> single crystals	4.09E-06	3.26E-06	
Lifetime [s] at 298 K for SrTiO <sub>3</sub> single crystal	5.88E-08	5.88E-08	
Recombination coefficient A $[s^{-1}]$ at 298 K for SrTiO <sub>3</sub> single crystal	1.70E+07	1.70E+07	2
Diffusion Coefficient $D[m^2 s^{-1}] = m kT/e$ for Fe-doped SrTiO <sub>3</sub>		3.88E-07	Einstein Relation
Diffusion Coefficient $D[m^2 s^{-1}] = m kT/e$ for SrTiO <sub>3</sub> single crystals	2.85E-04	1.81E-04	Einstein Relation
Mobility [m <sup>2</sup> s <sup>-1</sup> V <sup>-1</sup> ] at 800 K for Fe-doped SrTiO <sub>3</sub>		1.50E-05	3
Mobility [m <sup>2</sup> s <sup>-1</sup> V <sup>-1</sup> ] at 4 K for SrTiO <sub>3</sub> single crystals	1.10E-02	7.00E-03	4
Boltzmann Constant k [J K-1]	1.38E-23	1.38E-23	
Temperature T [K]	300	300	
electron charge e [As]	1.60E-19	1.60E-19	

## References

- 1. F. E. Osterloh, M. A. Holmes, J. Zhao, L. Chang, S. Kawula, J. D. Roehling and A. J. Moulé, *J. Phys. Chem. C*, 2014, **118**, 14723-14731.
- 2. Y. Yamada, H. Yasuda, T. Tayagaki and Y. Kanemitsu, *Appl. Phys. Lett.*, 2009, **95**, 121112.
- 3. M. Fleischer, H. Meixner and C. Tragut, *J. Am. Ceram. Soc.*, 1992, **75**, 1666-1668.
- 4. C. Itoh, M. Sasabe, H. Kida and K.-i. Kan'no, *J. Lumin.*, 2005, **112**, 263-266.