Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Use of Surface Photovoltage Spectroscopy to Probe Energy Levels and Charge Carrier Dynamics in Transition Metal (Ni, Cu, Fe, Mn, Rh) Doped $SrTiO_3$ Photocatalysts for H_2 Evolution from Water

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Electronic Supplementary Information

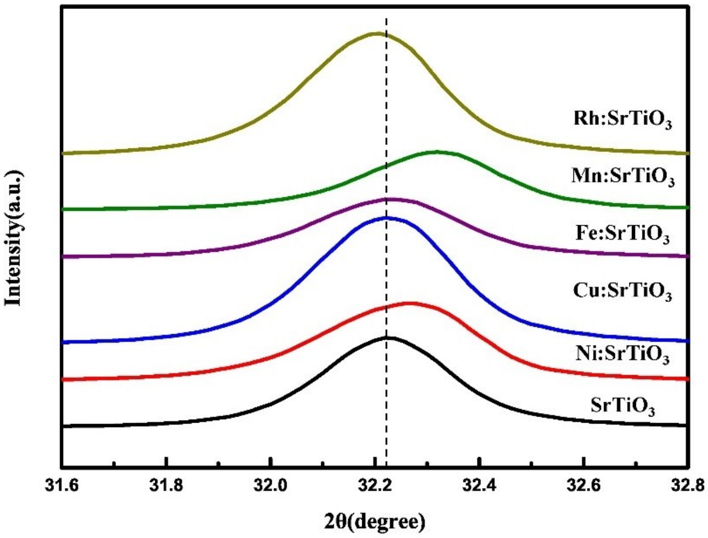

Figure S1. (110) XRD diffraction peaks of as-prepared $SrTiO_3$ and TM (Ni, Cu, Fe, Mn, Rh) doped $SrTiO_3$ nanoparticles.

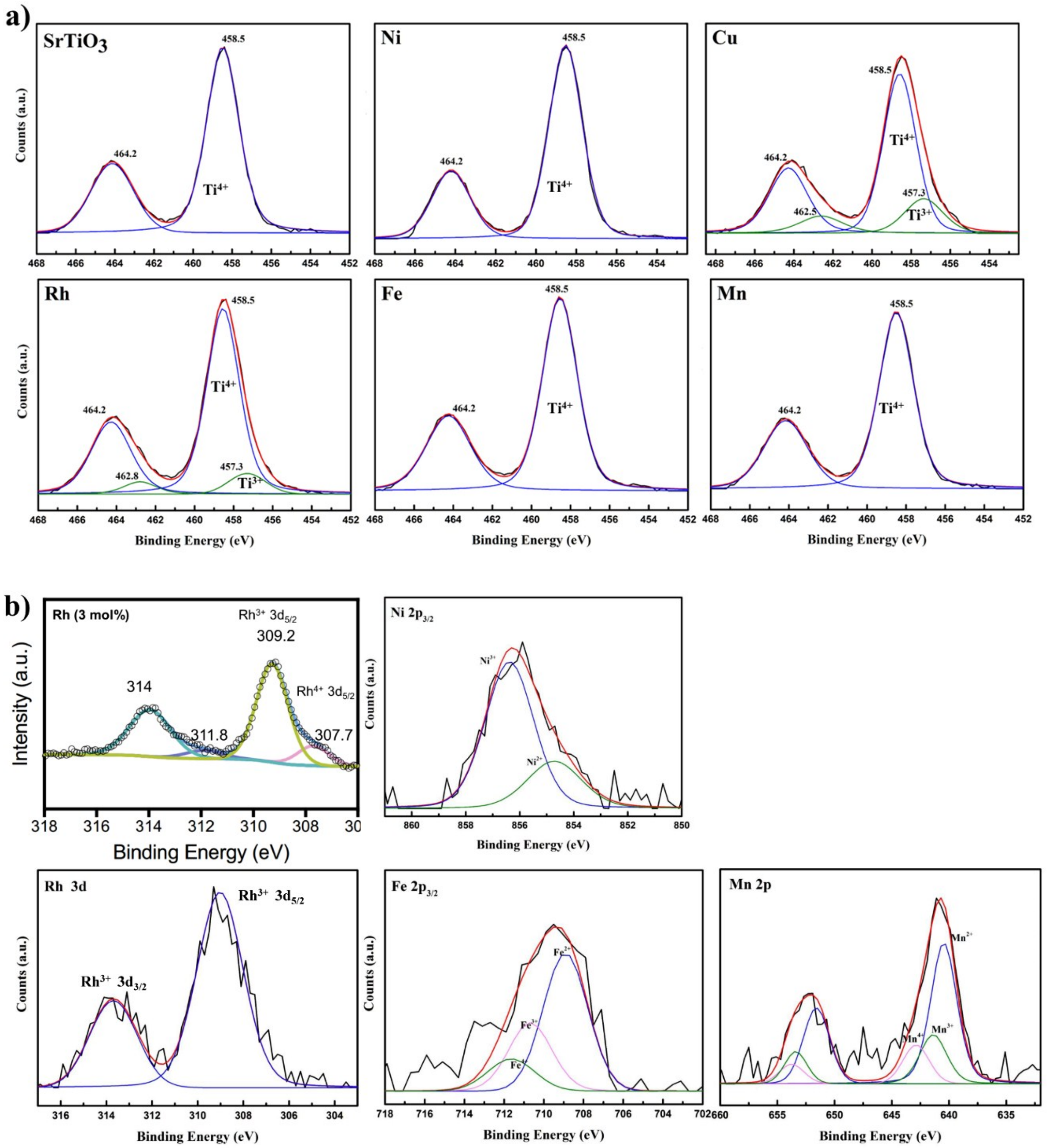

Figure S2. XPS spectra of the $SrTiO_3$ nanocrystals. a) Ti energy region and b) at variable energy. To observe transition metal states, samples were doped in the presence of 6 mol% transition metal reagent. For Rh:$SrTiO_3$, an additional XPS spectrum for the 3 mol% doped sample is shown also.

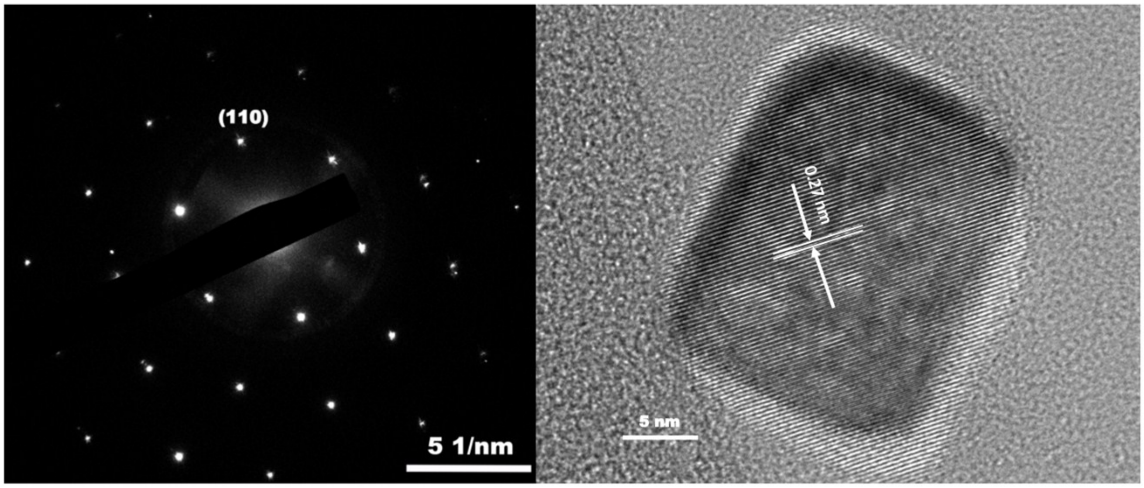

Figure S3. SAED and HRTEM images of a single Ni-doped $SrTiO_3$ nanoparticle. The SAED diffraction pattern is that of the perovskite crystal structure viewed along the [111] zone axis. [1] A second, weaker set of diffraction spots indicates a small amount of a secondary lattice domain (twinning). The HRTEM shows a single set of 110 planes with spacing of 0.27 nm in the direction of the cube diagonal with no evidence for amorphous phases or twining.

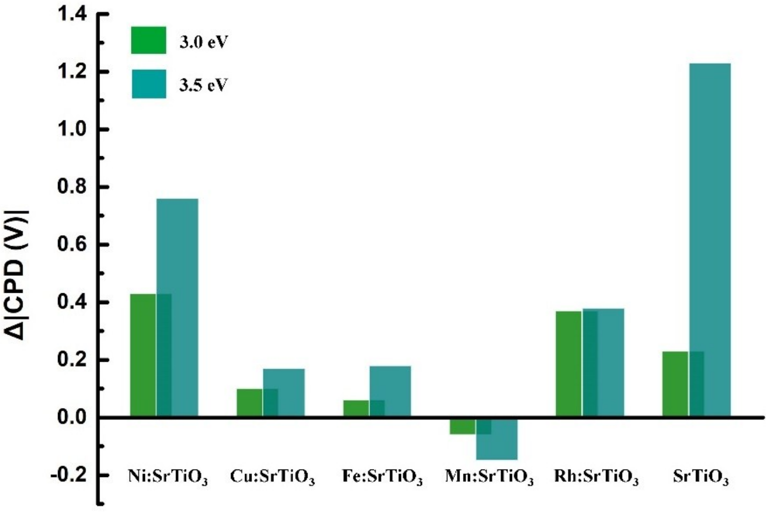

Figure S4. The CPD change by surface methanol addition on each sample film at different excitation energy.

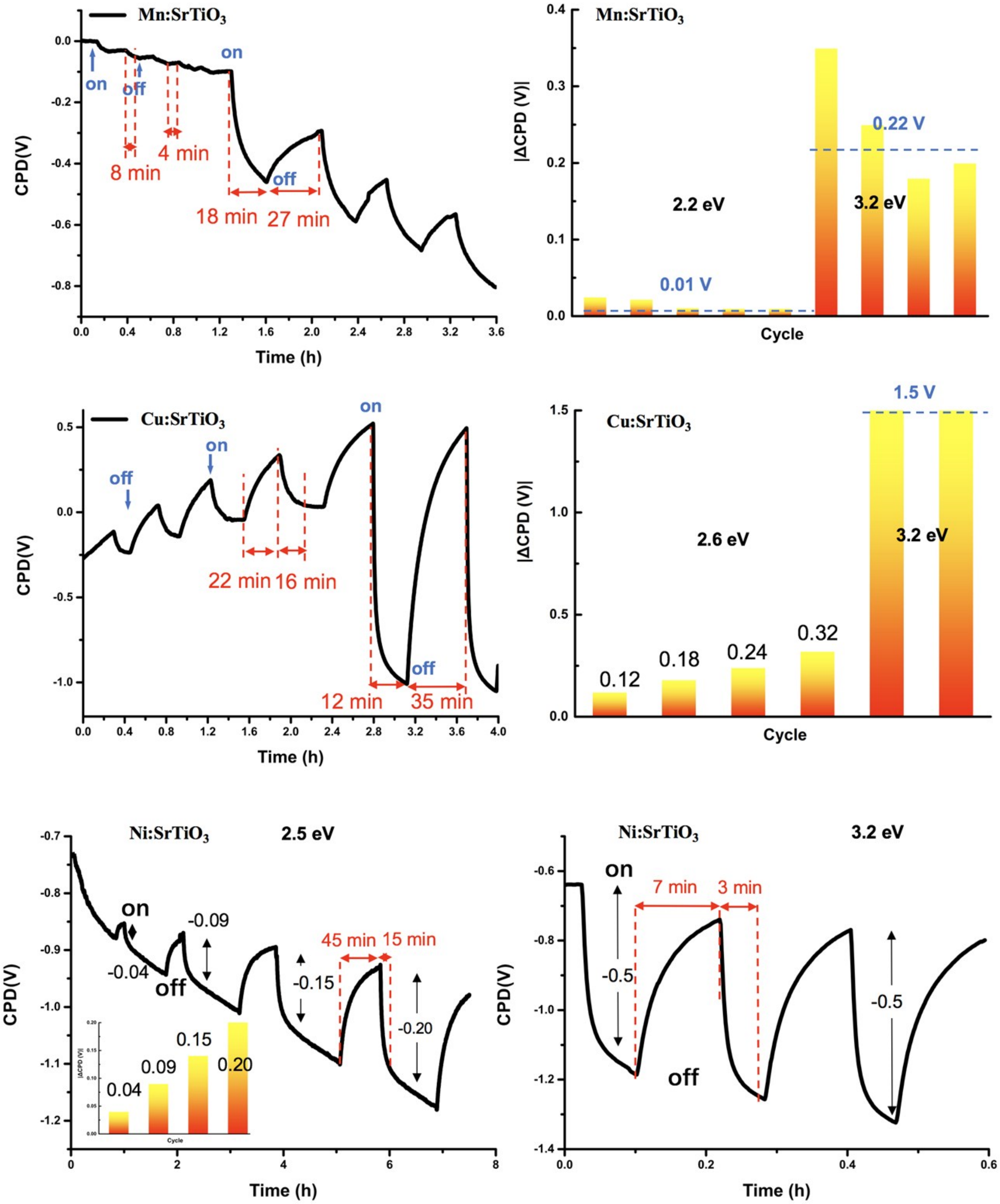

Figure S5. Time-dependent surface photovoltage spectra of Mn, Cu, and Ni-doped SrTiO$_3$ on FTO substrate measured under intermittent light illumination with specific monochromatic excitation energy and histogram plot of ΔCPD after each excitation.

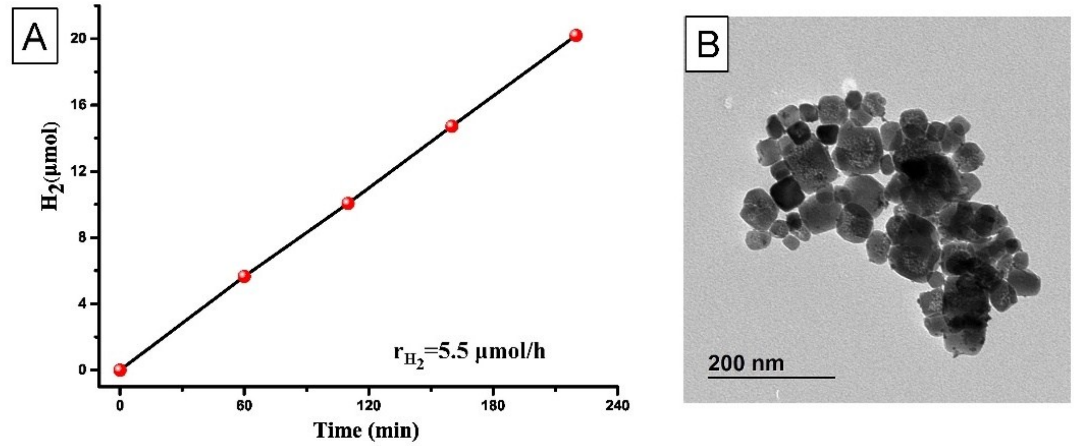

Figure S6. Time-resolved hydrogen evolution plot for Ni (6.0%): $SrTiO_3$ -Pt (2wt%) under LED irradiation (λ = 432 nm) (A); TEM image of Pt loaded Ni (6.0%): $SrTiO_3$ photocatalyst (B).

Table S1. Atomic percentage (at %) of elements in undoped and TM doped $SrTiO_3$ by XRF.

Sample	Sr	Ti	TM
$SrTiO_3$	51.47	48.53	0
Ni: $SrTiO_3$	50.38	49.18	0.44
Cu: $SrTiO_3$	49.99	48.77	1.24
Fe: $SrTiO_3$	49.18	49.12	1.7
Mn: $SrTiO_3$	49.83	48.44	1.73
Rh: $SrTiO_3$	49.8	49.15	1.05

Table S2. Electronic and optical properties of doped and non-doped $SrTiO_3$ samples derived from SPS and UV-vis data.

Dopant	Ions (radii) [2] Å	Optical E_g (eV)	Effective E_g (photoonset) (eV)	Color	Light Absorption feature
none	Sr^{2+} (1.44) Ti^{4+} (0.61)	3.2	3.1	white	band edge
Ni	[3] Ni^{2+} Ni^{3+} (0.69) (0.56)	3.1 + 2.4	2.75	pink	abs shoulder + abs peak
Cu	[4] Cu^{2+} Cu^{+} (0.73) (0.77)	3.1	2.7	light green	abs shoulder
Fe	[5] Fe^{2+} Fe^{3+} Fe^{4+} (0.61) (0.55) (0.585)	2.8	2.8	light yellow	abs shoulder + tail
Mn	[6] Mn^{4+} Mn^{3+} Mn^{2+} (0.53) (0.58) (0.83)	2.0	2.45	yellowish brown	abs shoulder + tail
Rh	[7] Rh^{3+} Rh^{4+} (0.67) (0.60)	2.3	2.3	yellow	abs shoulder + tail

Table S3. |CPD| of TM doped and undoped $SrTiO_3$ at 3.0 eV and at 3.5 eV before and after methanol addition.

|CPD| (V) / Sample	3.0 eV		3.5 eV	
	before	after	before	after
$SrTiO_3$	0.02	0.25	0.52	1.75
Ni: $SrTiO_3$	0.19	0.62	0.44	1.20
Cu: $SrTiO_3$	0.10	0.20	0.20	0.37
Fe: $SrTiO_3$	0.04	0.10	0.14	0.32
Mn: $SrTiO_3$	0.16	0.10	0.30	0.15
Rh: $SrTiO_3$	0.17	0.54	0.15	0.53

Table S4. Visible light driven H_2 evolution rate (μmol/h) of Pt (2.0 wt%) modified metal doped and undoped $SrTiO_3$ catalysts from 20 vol.% aqueous methanol.

Doping molar ratio / Catalyst with Pt	3.0%	6.0%
$SrTiO_3^a$	0.89	
Ni: $SrTiO_3^a$	0.73	1.51
Cu: $SrTiO_3^a$	0.82	1.25
Fe: $SrTiO_3^a$	1.12	1.00
Mn: $SrTiO_3^a$	0.81	0.73
Rh: $SrTiO_3^{b[7]}$	5.00 (PH 3.5) at 112 mW cm^{-2}	

Catalyst: 0.05 g; [a] Reactant solution: 50 mL; Light source: 300 W Xe lamp with cutoff filter ($\lambda > 400$

nm); Intensity: 600 mW cm^{-2}. [b]Reactant solution: 50 mL at pH 3.5 (adjusted with H_2SO_4); Light source: 300 W Xe lamp with cutoff filter ($\lambda > 400$ nm); Intensity: 112 mW cm^{-2}

References

1. L. Miranda, K. Boulahya, D. C. Sinclair, M. Hernando, A. Varela, J. M. Gonzalez-Calbet and M. Parras, J. Mater. Chem., 2012, 22, 15092-15103.
2. W. M. Haynes, *CRC handbook of chemistry and physics*, CRC press, 2014.
3. R. Niishiro, H. Kato and A. Kudo, *Phys. Chem. Chem. Phys.*, 2005, 7, 2241.
4. S. Shen, L. Zhao, Z. Zhou and L. Guo, *J. Phys. Chem. C*, 2008, 112, 16148-16155.
5. T.-H. Xie, X. Sun and J. Lin, *J. Phys. Chem. C*, 2008, 112, 9753-9759.
6. P. Moretti and F. Michel-Calendini, *Phys. Rev. B*, 1987, 36, 3522.
7. J. Wang, J. Zhao and F. E. Osterloh, *Energy Environ. Sci.*, 2015, 8, 2970-2976.