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Supporting Information

Surface modified titanium dioxide by transition metals: nickel as a winning transition metal for solar light photocatalysis

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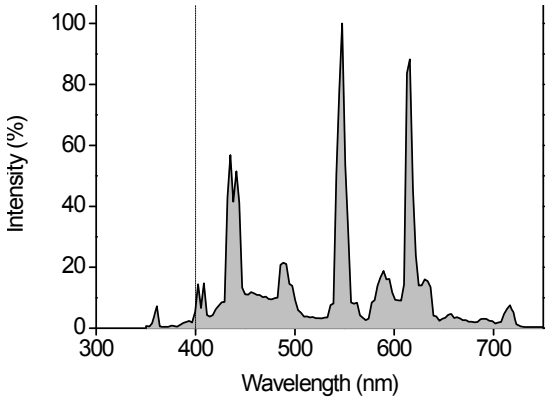

Fig. S1. Spectrum of the solar lamps used in Rz ink and TPA test. The dashed line shows the UV cutoff filter applied in visible-light tests.

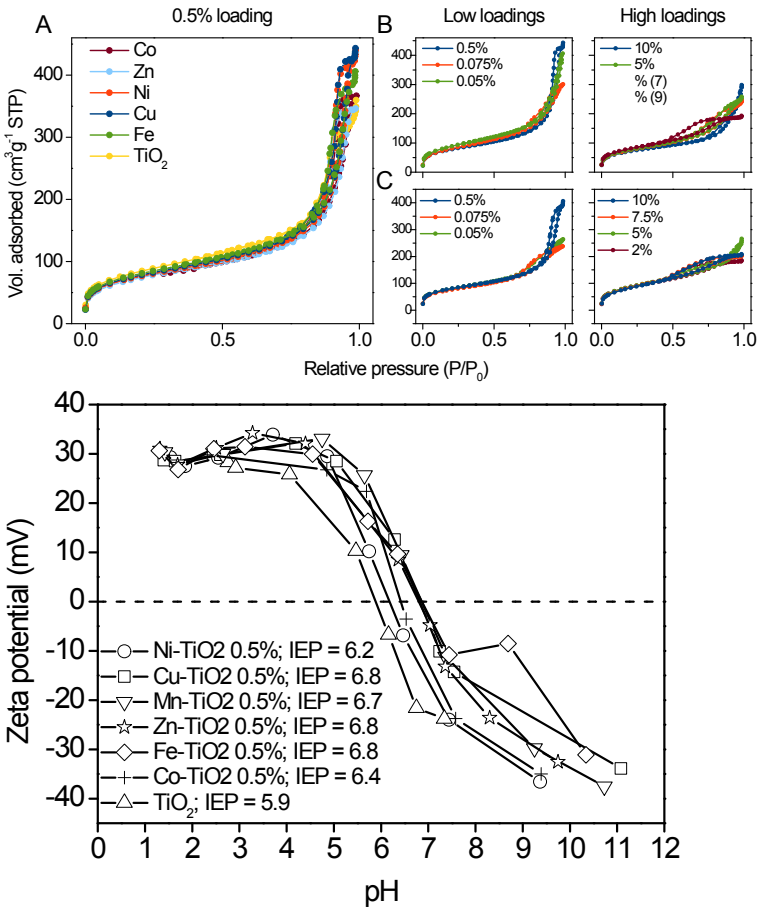

Fig. S2. Top – N_2-sorption isotherms of metal grafted TiO_2 (a). (b) and (c) show isotherms of low and high concentration Cu and Fe-grafted TiO_2, respectively. Bottom – Zeta potential measurements of titania with its surface modified with selected transition metals.

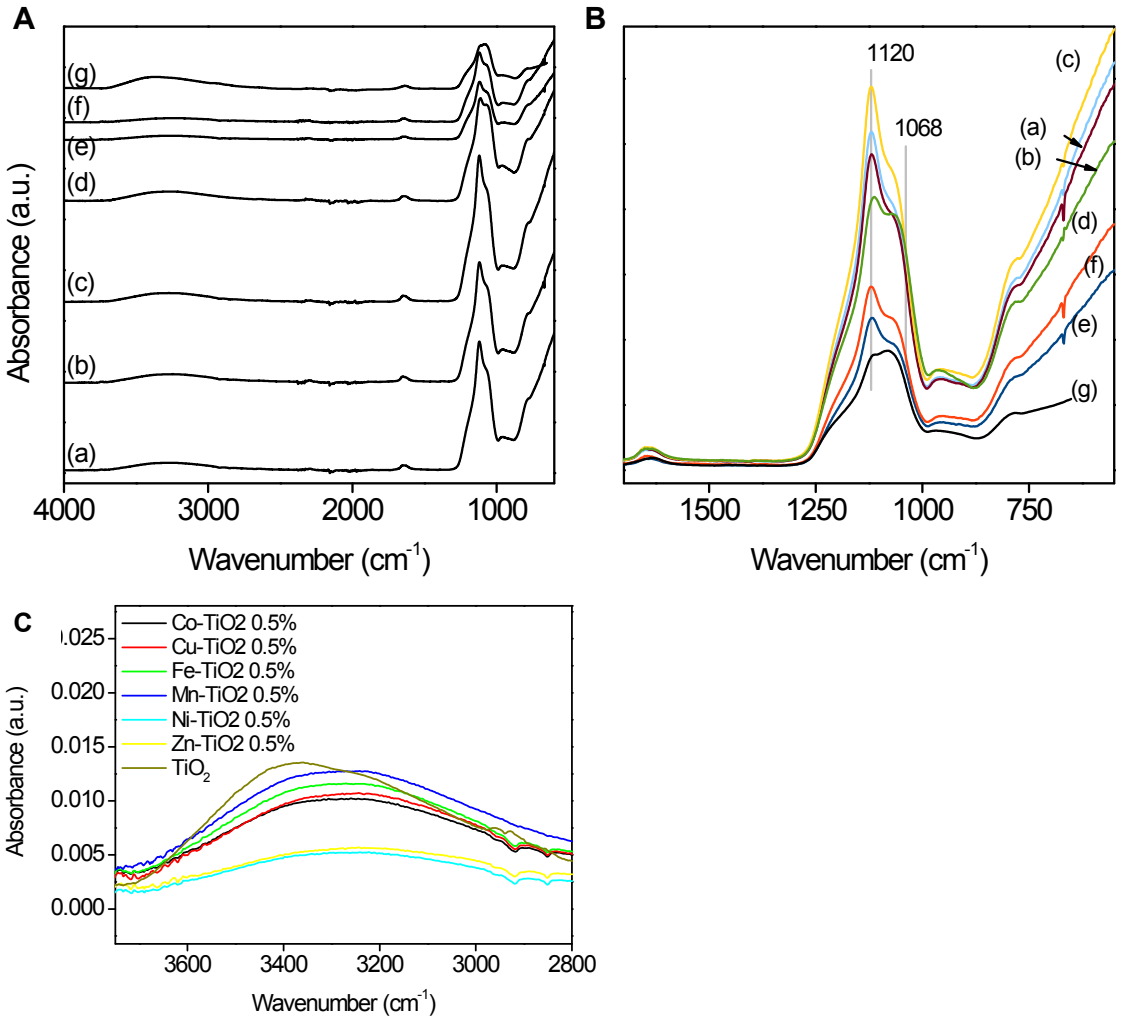

Fig. S3. ATR FT-IR spectra of TiO_2-SiO_2 films (A) near IR range and (B) 1600–600 cm^{-1} range. Asymmetric Si–O–Si stretching is labeled at 1120 cm^{-1}. Samples are labelled (a) Co-TiO2 0.5%, (b) Cu-TiO2 0.5%, (c) Fe-TiO2 0.5%, (d) Mn-TiO2 0.5%, (e) Ni-TiO2 0.5%, (f) Zn-TiO2 0.5%, (g) unmodified TiO_2. In plot (C) a closer view in the 3700–2800 cm^{-1} range is shown. Note the lower intensity of the 3350 cm^{-1} band in Ni- and Zn-modified samples.

XANES spectra were taken to elucidate the oxidation states of nanoclusters on the TiO_2 surface.

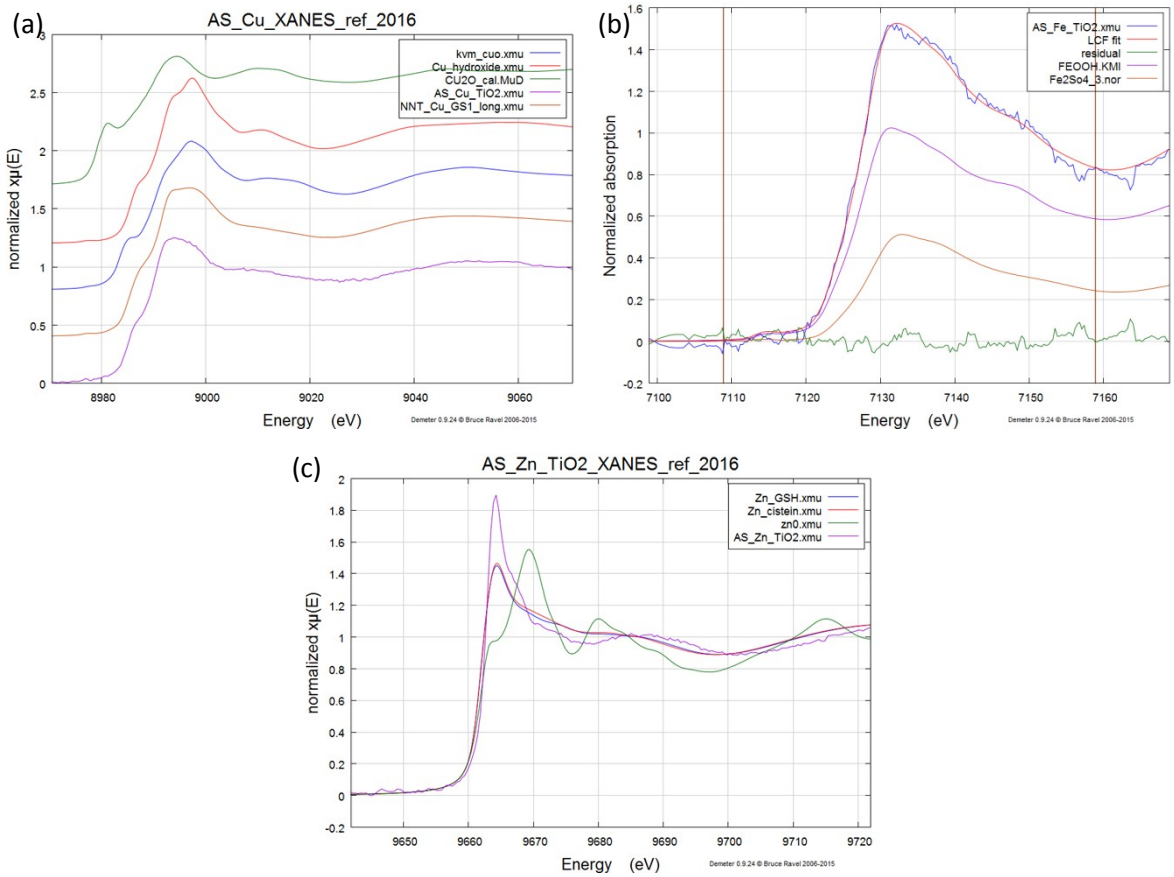

Fig. S4. XANES spectra of (a) Cu-TiO2 0.5%, (b) Fe-TiO2 0.5% and (c) Zn-TiO2 0.5% samples.

Table S1. Most common oxidation states of 3d ions.

Ox. #	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+1							x	x	
+2	x	x	x	x	x	x	x	x	x
+3	x	x	x	x	x	x	x	x	
+4	x	x		x	x	x			
+5		x	x	x					
+6			x	x	x				
+7				x					

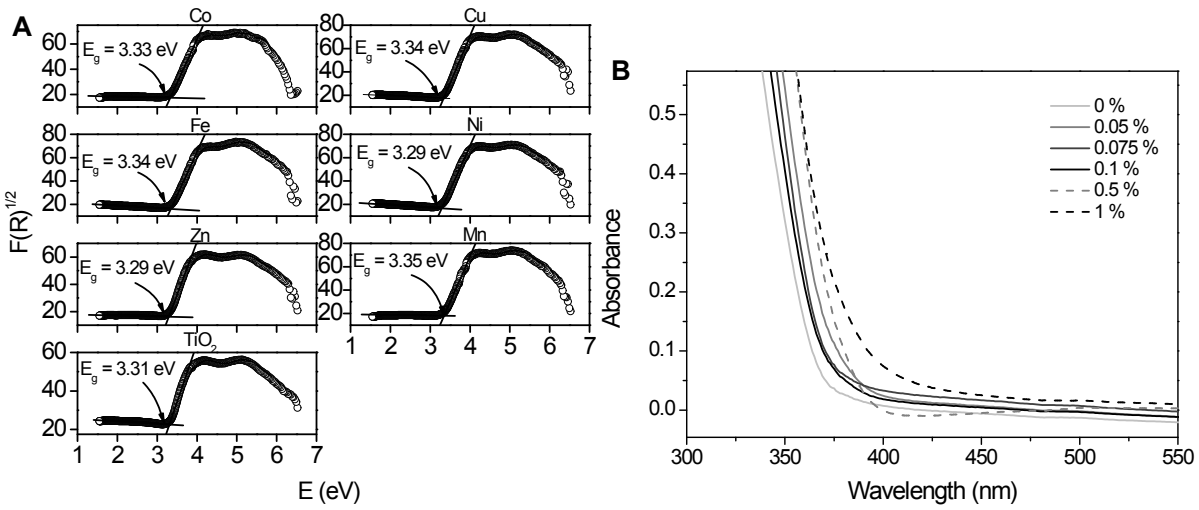

Fig. S5. Diffuse reflectance data of the films; (a) Tauc plots of the films and (b) true absorbance for nickel modified sample series in the concentration range 0 to 1 wt.%. Note the non-linear red-shift of the absorption in (b) suggesting that Ni-ions were not included in the TiO_2 lattice.

Table S2. Values of indirect band gap for concentration series of Fe^{3+}– and Cu^{2+}–modified titania films. The values were obtained by plotting the Kubelka-Munk-transformed reflectance spectra of the films. Then the onsets in the K-M-transformed plots were taken as the E_g values.

Sample (x–TiO_2)	Indirect band gap (eV)
0.05% Fe^{3+}	3.05
0.075% Fe^{3+}	3.18
0.1% Fe^{3+}	3.29
0.5% Fe^{3+}	3.34
2% Fe^{3+}	3.00
5% Fe^{3+}	3.06
7.5% Fe^{3+}	3.08
10% Fe^{3+}	2.90
0.05% Cu^{2+}	3.35
0.075% Cu^{2+}	3.28
0.1% Cu^{2+}	3.31
0.5% Cu^{2+}	3.34
2% Cu^{2+}	3.22
5% Cu^{2+}	3.33
7.5% Cu^{2+}	3.34
10% Cu^{2+}	3.40

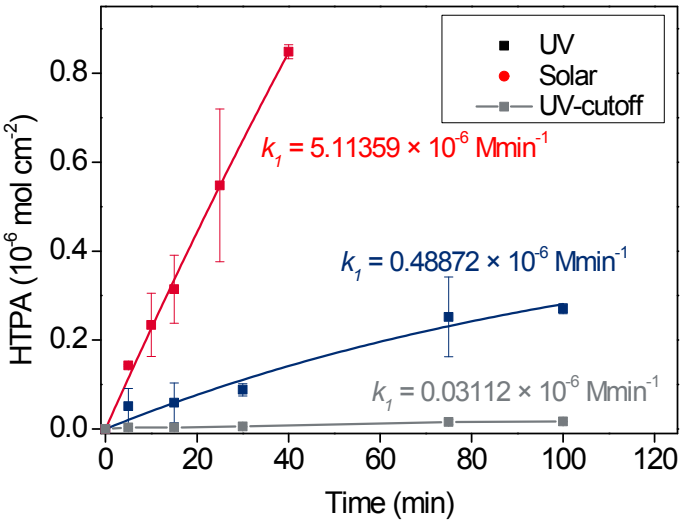

Fig. S6. Formation of HTPA from TPA for TiO_2 modified with 2 wt.% Fe under visible (grey), solar (blue) and UVA (red) irradiation.

Table S3. HTPA formation rate constants under solar and under visible light illumination.

	HTPA formation ($\times 10^{-9}$ M/min)	
Sample (x-TiO_2)	Solar	Visible
Mn	7.16	0.45
Fe	39.94	2.56
Co	20.98	1.33
Ni	68.13	4.57
Cu	18.43	1.08
Zn	92.80	6.44

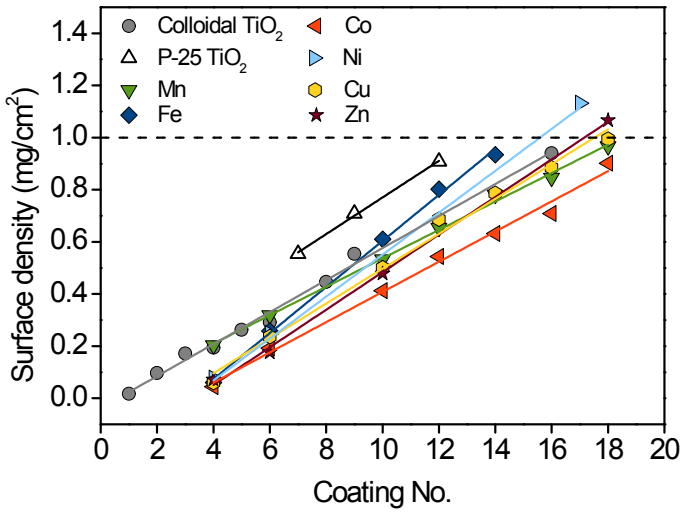

Fig. S7. Surface density of TiO_2 laid on glass substrate as a function of number of coatings. The dashed line represents 1 mg/cm^2 benchmark, where the activity reaches the plateau, i.e. further increasing of mass does not increase the photoactivity. TiO_2 samples were modified with 0.5 wt.% of transition metal chosen.

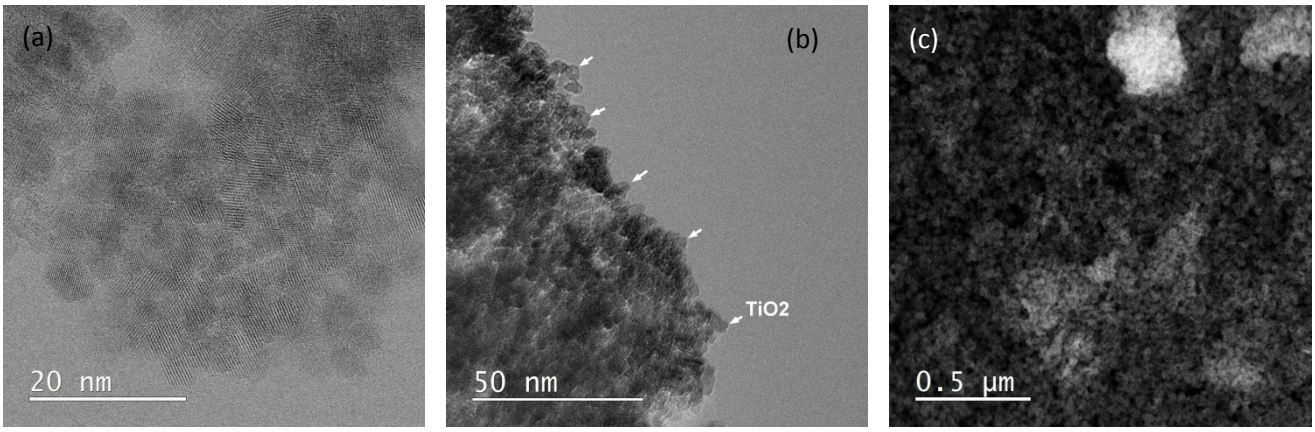

Fig. S8. TEM micrographs of Cu-modified sample. (a) and (b) bright-field micrographs and (c) dark-field.

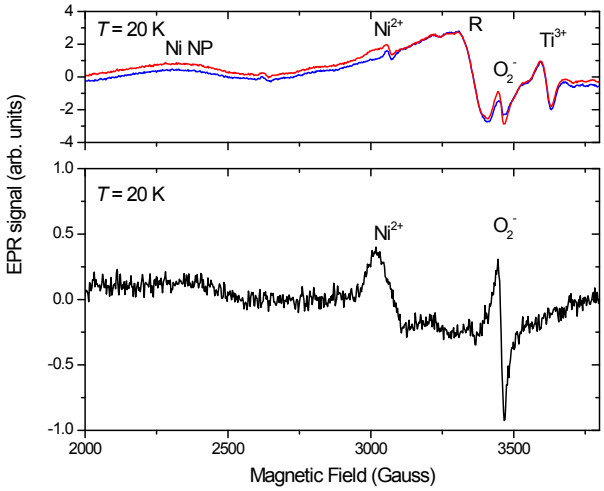

Fig. S9. EPR spectra of Ni-TiO_2 1% at 20 K; blue and red colours in the upper plot represent spectra with the light on and off, respectively; the lower plot denotes the difference between the two.