Supporting Information

Boosting Photocatalytic Performance of Inactive Rutile TiO_2 Nanorods under Solar Light Irradiation: Synergistic Effect of Acid Treatment and Metal Oxide Co-catalysts

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Table S1a Band gap, binding energy peak position and corresponding EDAX analysis of TO-NR and ATO-NR samples

Sr.No.	Sample Name	[a]Band gap Energy (eV)	[b]Binding energy (eV) peak position			[c]EDAX analysis of
			O1s (Ti-O)	O1s (OH^-)	O1s (absorbed H_2O)	Na/ Ti (w %) (remaining amount oxygen)
1.	TO-NRs	2.97	529.68	530.60	531.73	0.58/ 68.08
2.	TO-NRs [0.5 M]	2.96	529.73	530.50	531.95	00.16/ 58.03
3.	TO-NRs [1.0 M]	2.99	529.50	530.38	531.70	00.08/ 65.33
4.	TO-NRs [2.0 M]	2.97	529.61	530.59	532.05	00.06/ 56.02

[a]Band gap energy measured by UV-DRS characterization (eV), [b]Binding energy measured by XPS characterization (eV) and X-ray energy dispersive spectrometer (EDAX) FESEM based Na/ Ti (wt %), remained amount given by oxygen.

Table S1b XPS analysis of O 1s OH peak in TO-NR and ATO-NR samples

Sr.No.	Sample Name	O 1s (OH^-) peaks		
		Binding energy (eV)	**FWHM**	**Area under the curve**
1.	TO-NRs	530.60	1.13	6448.40
2.	TO-NRs [0.5 M]	530.50	1.31	7335.01
3.	TO-NRs [1.0 M]	530.38	1.12	8869.03
4.	TO-NRs [2.0 M]	530.59	1.32	7271.20

Table S2 Dye degradation efficiency of TO-NR and ATO-NR samples at 180 and 300 min, respectively.

Sr.No.	Photocatalyst	Degradation efficiency in 180 min (in %)	Degradation efficiency in 300 min (in %)
1.	TO-NRs	04.92	08.42
2.	1.0 M ATO-NRs	56.26	74.17
3.	Cobalt oxide** loaded TO-NRs	81.06	94.22
4.	Cobalt oxide** loaded 1.0 M ATO-NRs	98.73*	-

*Cobalt oxide loaded 1.0 M acid treated sample showed synergistic effect over photocatalytic Orange (II) dye degradation; within 3 hours dye concentration reached its minimum value.

**Cobalt oxide 1 wt % loading

Table S3 Dye degradation efficiency of TO-NR and different concentrations of cobalt oxide loaded ATO-NR samples

Sr.No.	*a Cobalt oxide concentration (in wt %)	Degradation efficiency in 180 min (in %)	Degradation efficiency in 300 min (in %)
1.	*b TO-NRs	04.92	08.42
2.	0.5	89.12	97.28
3.	1.0	98.73*	-
4.	2.0	98.73	-

*a different concentration of cobalt oxide nanoparticles loaded on (1.0 M) ATO-NR.

*b TO-NR is untreated sample.

*Cobalt oxide loaded 1.0 M acid treated sample showed synergistic effect over photocatalytic Orange (II) dye degradation; within 3 hours dye concentration reached its minimum value.

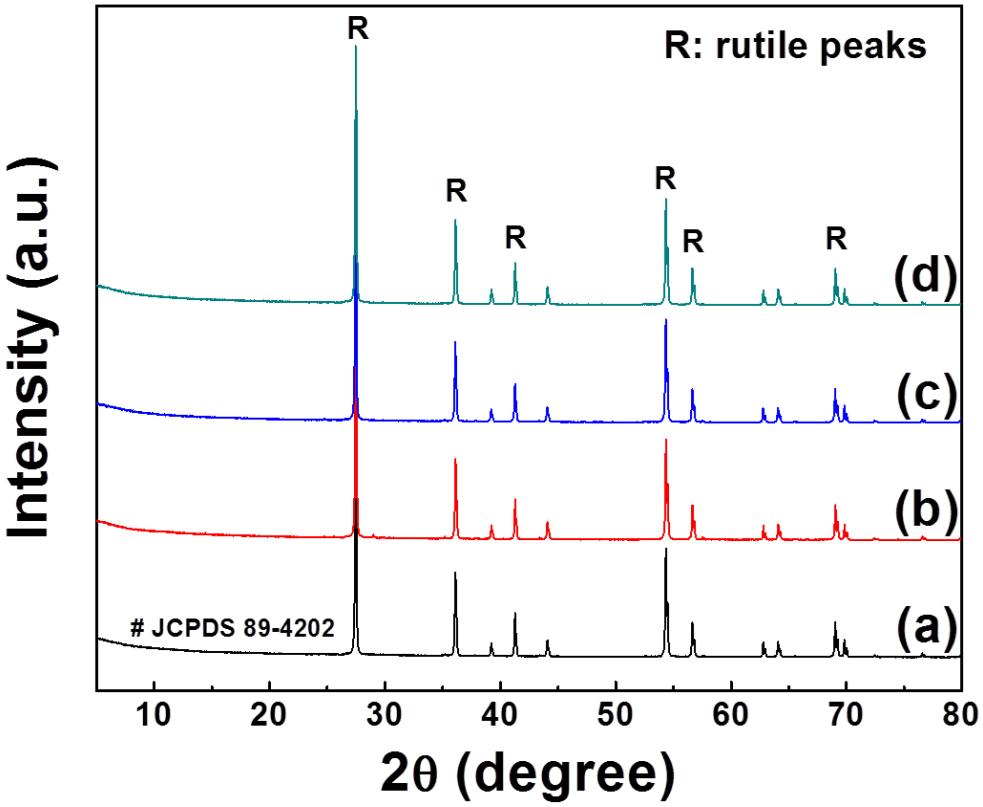

Figure S1 XRD patterns of (a) TO-NRs, (b) ATO-NRs [0.5 M], (c) ATO-NRs [1.0 M] and (d) ATO-NRs [2.0 M].

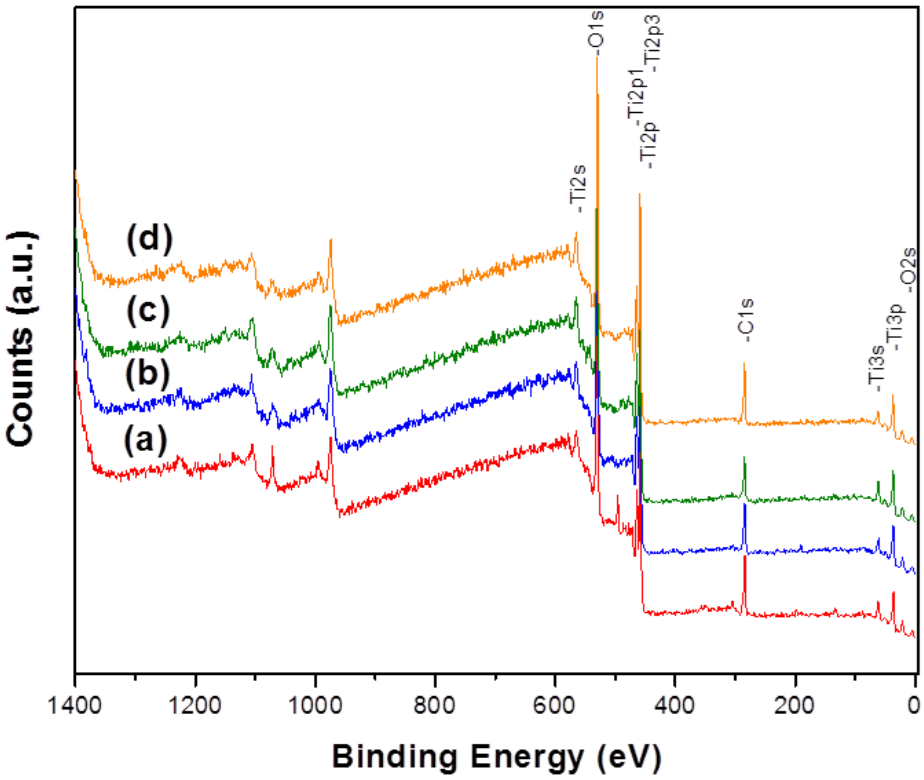

Figure S2A XPS survey scan of (a) as-prepared TO, (b) ATO-0.5 M, (c) ATO-1.0 M and (d) ATO-2.0 M -NRs samples.

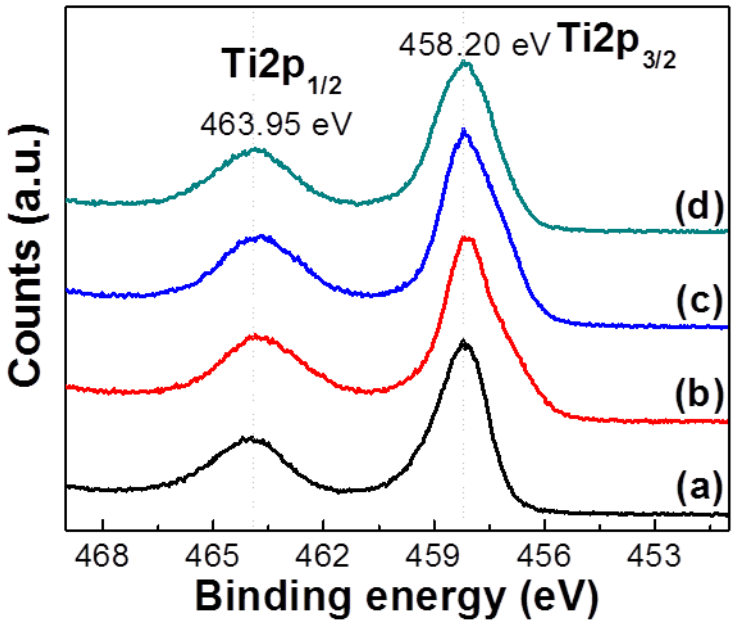

Figure S2B High resolution Ti 2p XPS spectra of (a) as-prepared TO, (b) ATO-0.5 M, (c) ATO-1.0 M and (d) ATO-2.0 M NR samples.

The optical properties of as-prepared TO-NRs and ATO-NRs were investigated by UV-vis spectroscopy (was shown in Fig. 4). The light absorbance edge (λ_g) of as-prepared NRs was around 414.6 nm; due to the broad band gap energy (~3.00 eV) allows only UV-light and similar to the reported rutile TiO_2.[66] [67] No significant red shift was observed for acid treated samples, these results indicated that acid treatment could not give enhancement in light absorbance. The optical properties of as-prepared and acid treated TO-NRs are summarized in Table 1.

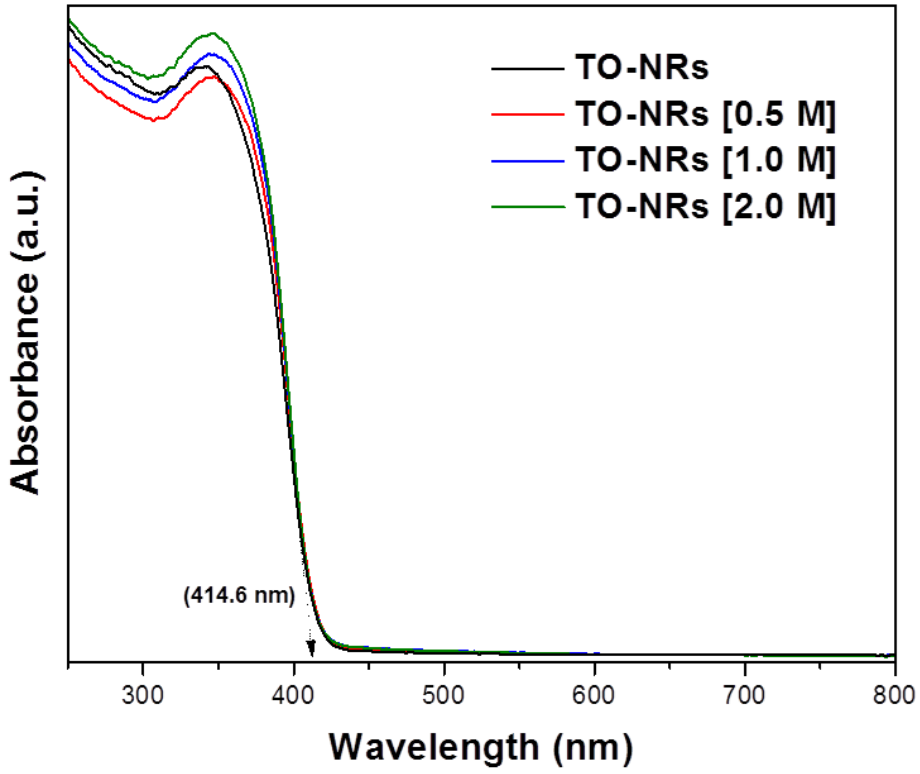

Figure S2C UV-vis spectra of (a) TO, (b) ATO-0.5 M, (c) ATO-1.0 M and (d) ATO- 2.0 M.

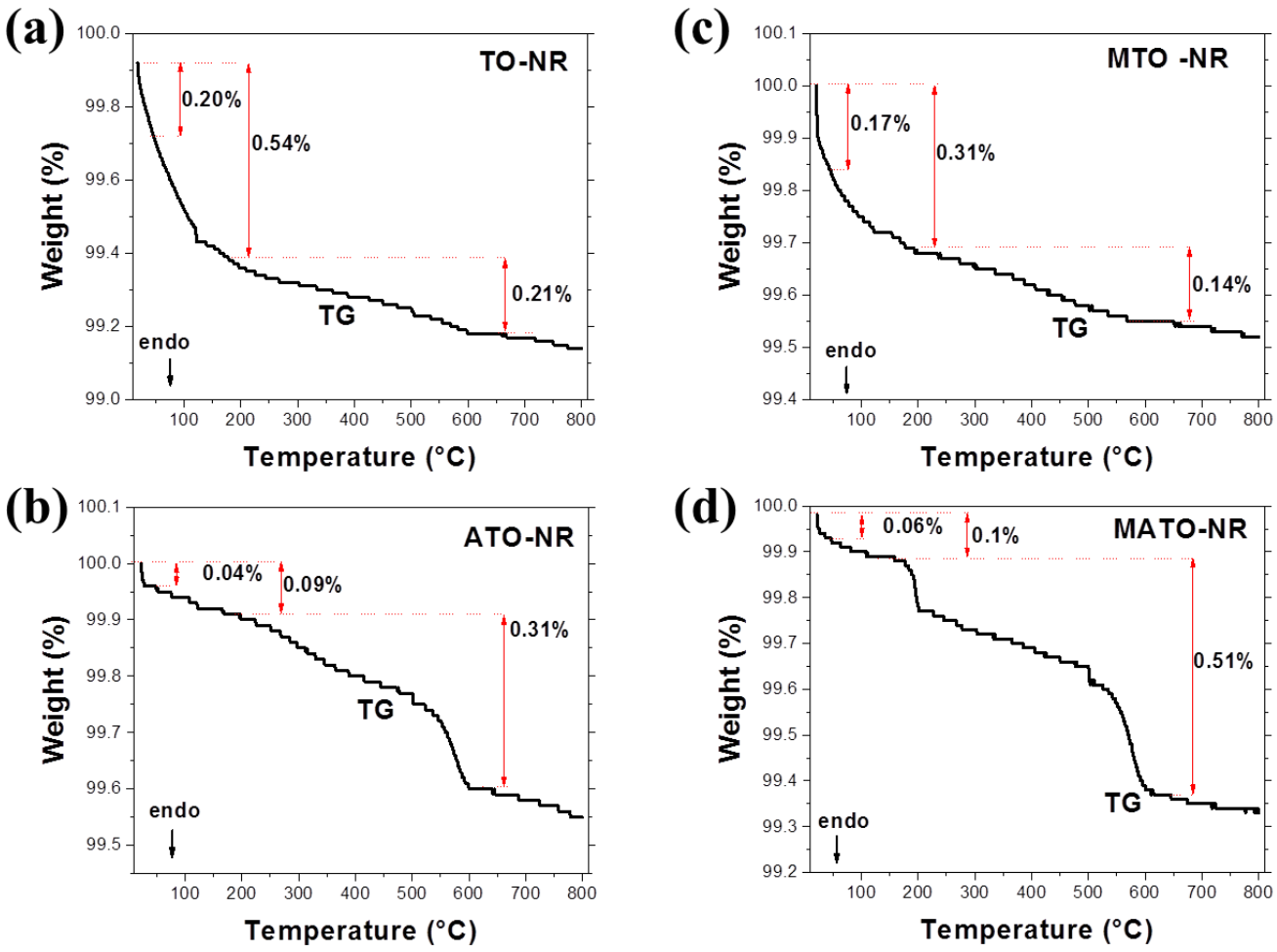

Figure S3 TGA analysis of (a) TO-NR, (b) ATO [1.0 M]-NRs, (c) Co/TO-NR (MTO-NR) and (d) Co/ATO-NR (MATO-NR) samples.

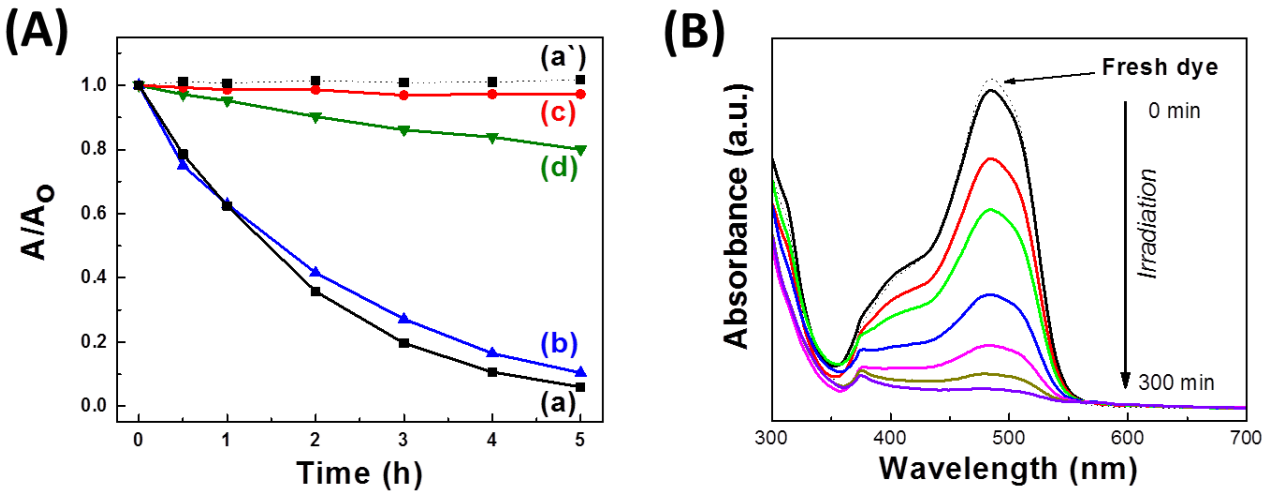

Figure S4 (A) Effect of different 1 wt % metal oxide loading over TO-NRs (MTO-NRs) samples for photocatalytic Orange (II) dye degradation under solar light (a) Co/TO-NRs, (b) Cu/TO-NRs, (c) Mn/TO-NRs, and (d) Ni/TO-NRs and **(B)** Orange (II) dye degradation by 1 wt % Co/TO-NRs photocatalyst. (where "M = metal oxide" abbreviated by element identity; e.g. M = Co/ or Cu/ or Mn/ or Ni/)

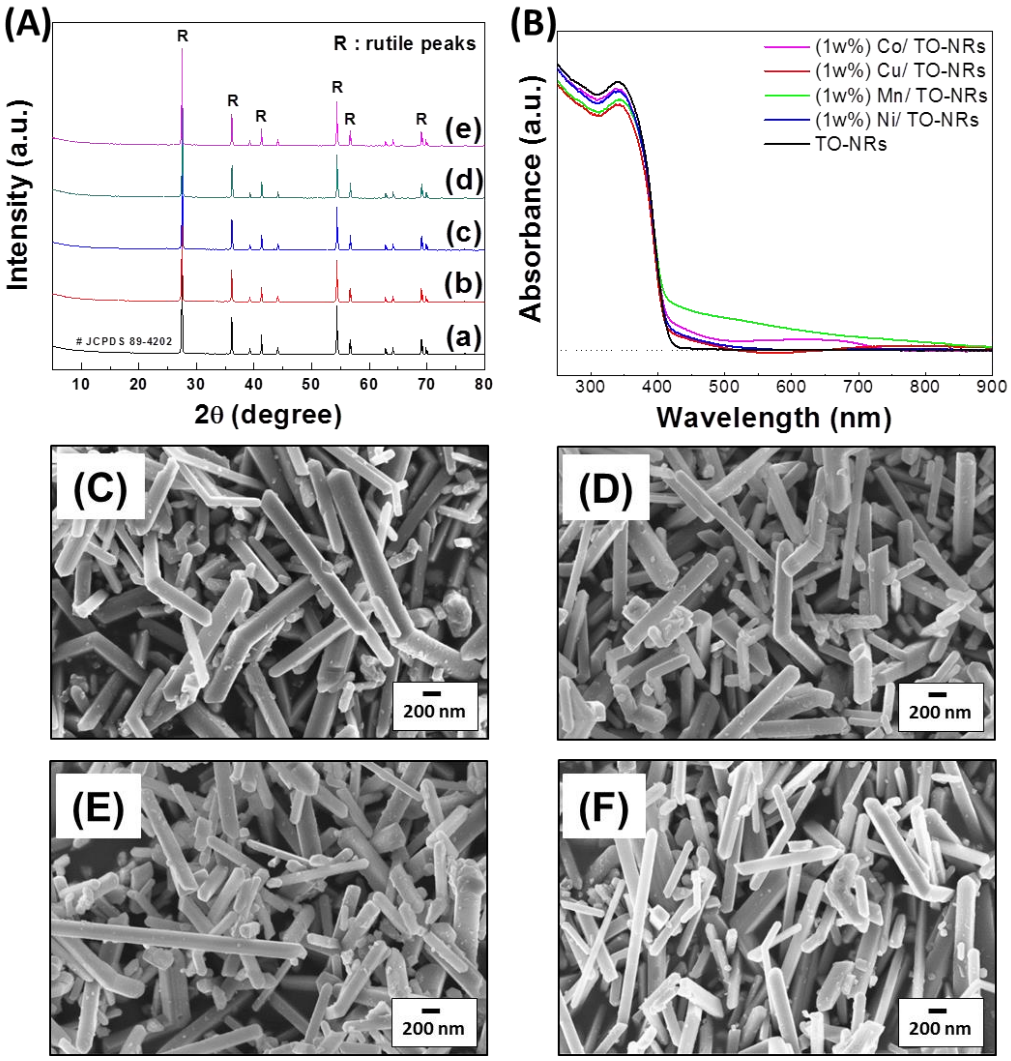

Figure S5 (A) XRD images of (a) as-prepared TO-NRs, and 1 wt % metal loaded samples as, (b) Co/TO-NRs, (c) Cu/TO-NRs, (d) Mn/TO-NRs, and (e) Ni/TO-NRs; **(B)** UV-vis spectra of as-prepared and metal oxide loaded (untreated) TO-NRs; FE-SEM images of MTO samples as (1 wt %) metal loading on TO-NRs- **(C)** Co/TO-NRs, **(D)** Cu/TO-NRs, **(E)** Mn/TO-NRs and **(F)** Ni/TO-NRs. (where "M = metal oxide" abbreviated by element identity; e.g. M = Co/ or Cu/ or Mn/ or Ni/)

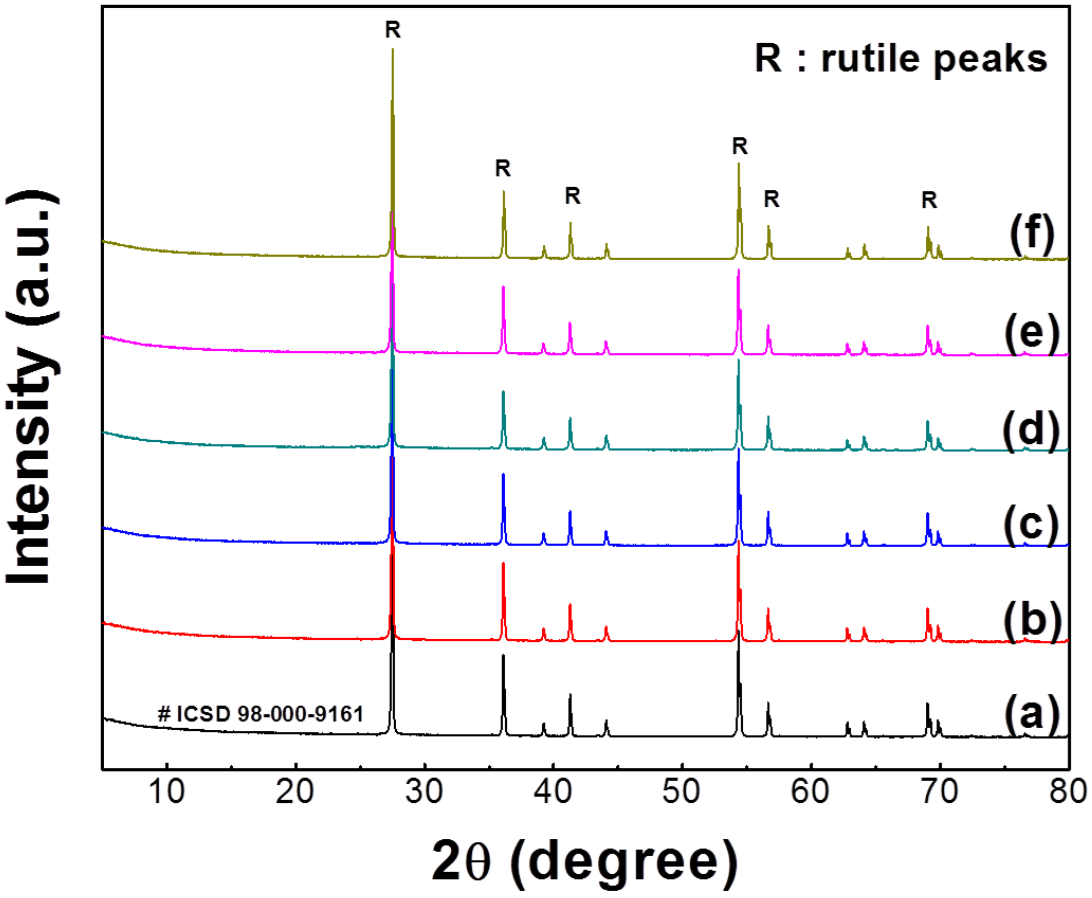

Figure S6 XRD patterns of (a) as-prepared TO-NRs (untreated), and (b) TO-NRs, (c) (0.5 wt %), (d) (1.0 wt %), (e) (1.5 wt %), (f) (2.0 wt %) of cobalt oxide loaded on [1.0 M] acid treated NRs.

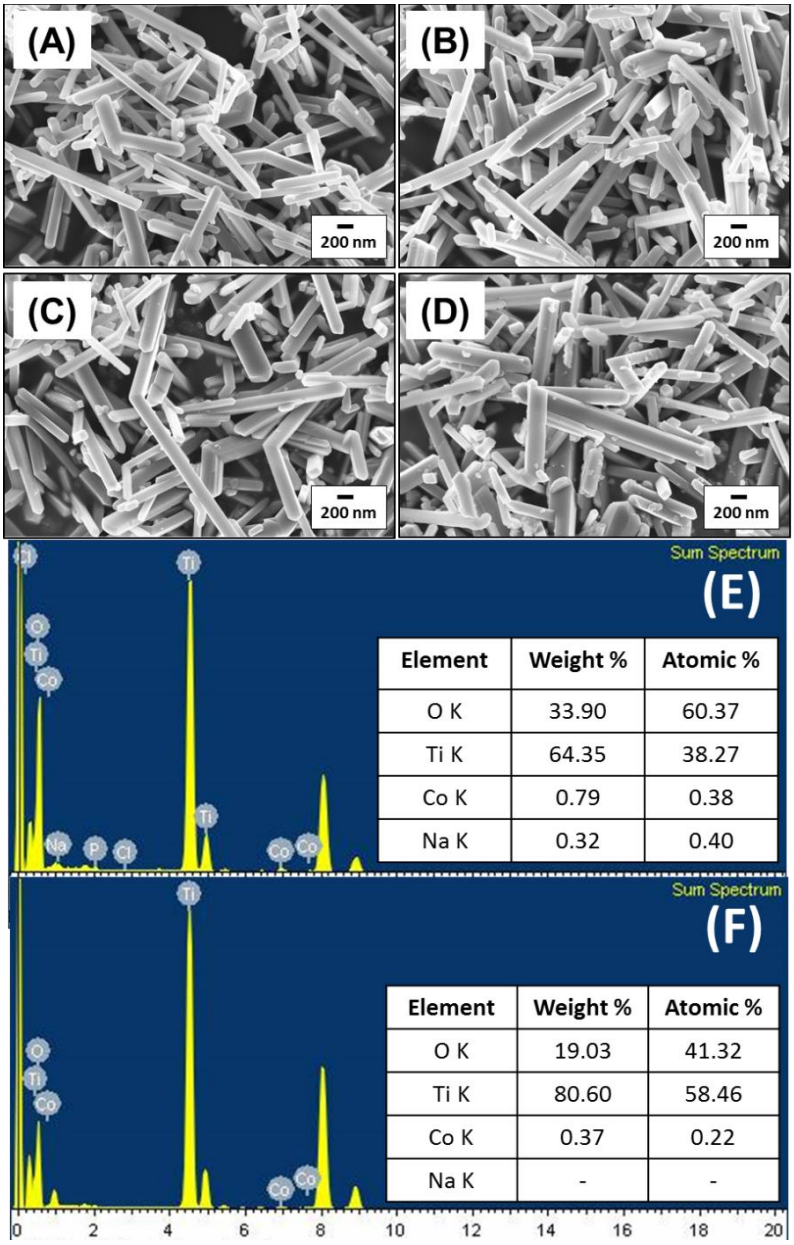

Figure S7 FE-SEM image of MATO samples as (1 wt %) metal loading on (1.0 M) acid treated NRs- **(A)** Co/ATO-NRs, **(B)** Cu/ATO-NRs, **(C)** Mn/ATO-NRs and **(D)** Ni/ATO-NRs; TEM/ EDAX images of MTO-NRs **(E)** and MATO-NRs **(F).** (where "M = metal oxide" abbreviated by element identity; e.g. M = Co/ or Cu/ or Mn/ or Ni/)

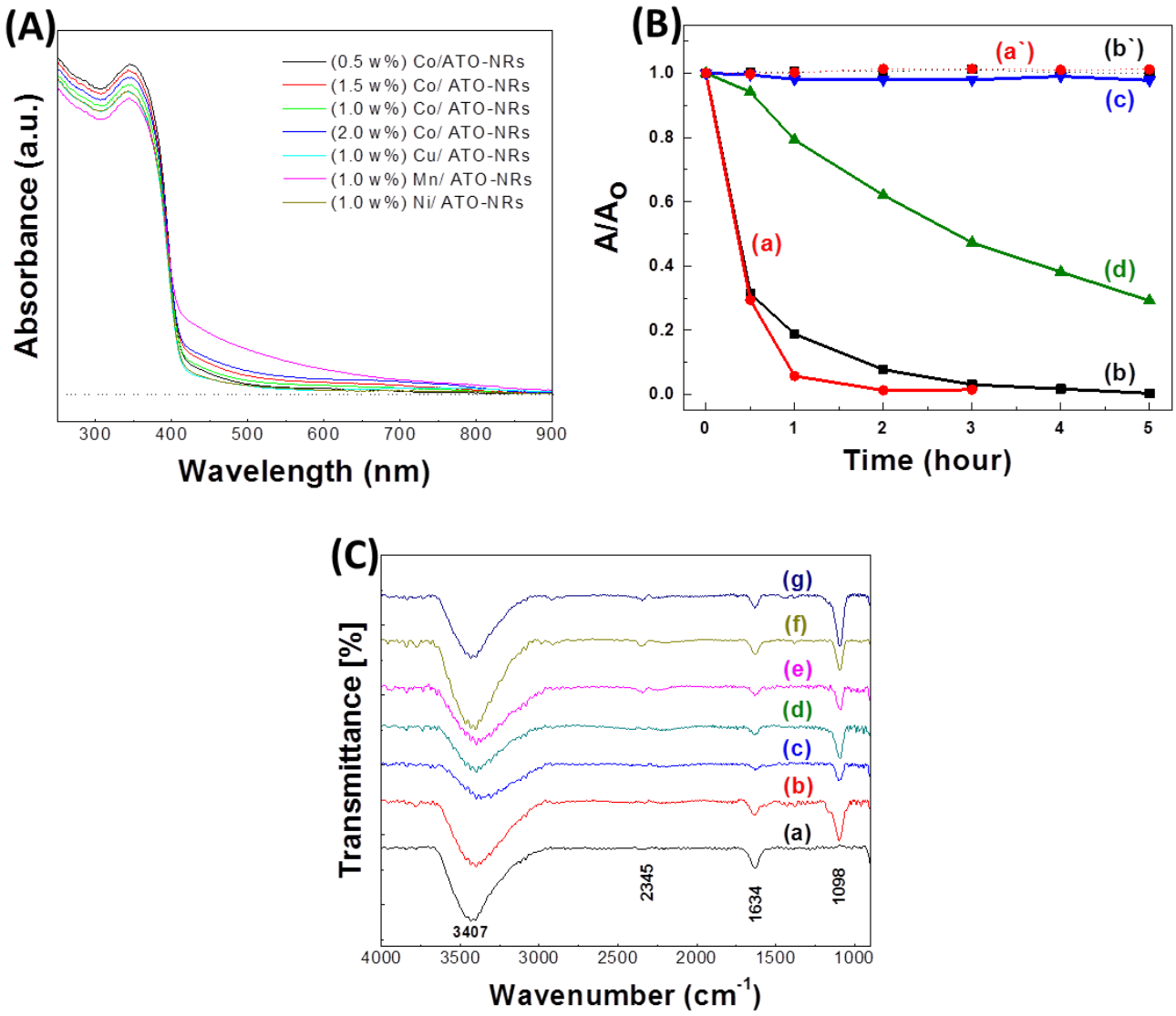

Figure S8 (A) UV-vis spectra of MATO-NRs **(B)** Effect of different 1 wt % metal loaded ATO-NRs photocatalyst samples over photocatalytic Orange (II) dye degradation under solar light (a) Co/ATO-NRs, (b) Cu/ATO-NRs, (c) Mn/ATO-NRs, and (d) Ni/ATO-NRs and **(C)** FT-IR spectra of (a) ATO-NRs [1.0 M], (b) (1 wt %) Co/TO-NRs, (c) (0.5 wt %) Co/ATO-NRs [1.0 M], (d) (1.0 wt %) Co/ATO-NRs [1.0 M], (e) (1.5 wt %) Co/ATO-NRs [1.0 M], (f) (2.0 wt %) Co/ATO-NRs [1.0 M], and (g) (1 wt %) Cu/ATO-NRs [1.0 M]. (where 'M = metal oxide' we abbreviated by element identity; e.g. M = Co/ or Cu/ or Mn/ or Ni/)

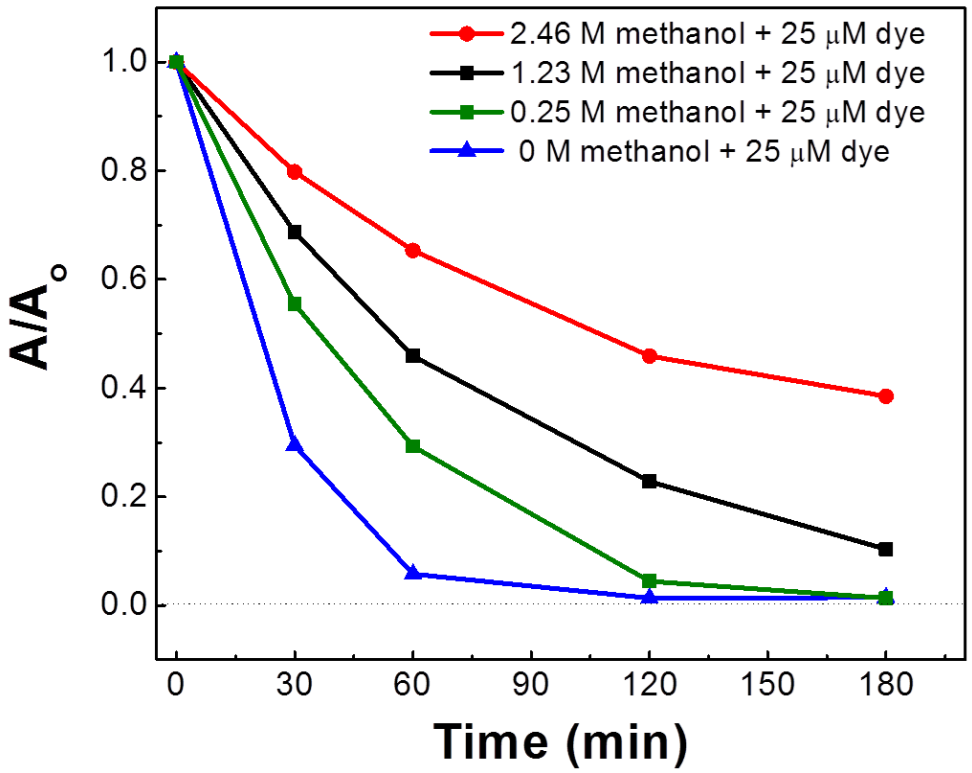

Figure S9 Photocatalytic performance of Co/ATO-NRs photocatalyst over different concentrations of methanol and fixed concentration of Orange (II) dye solution.

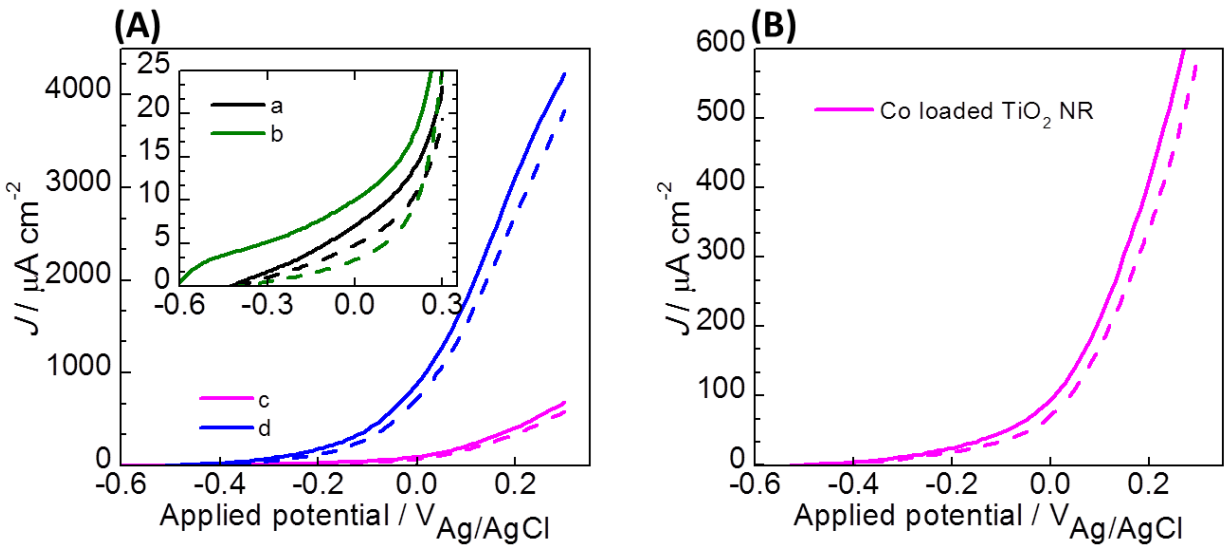

Figure S10 (A) *J*–*V* curves under white-light illumination. Note: The solid lines indicate *J*-*V* under light illumination and dash-dotted line indicates the dark current; **(B)** *J*–*V* curves under solar light illumination for Co loaded TiO_2 NRs.

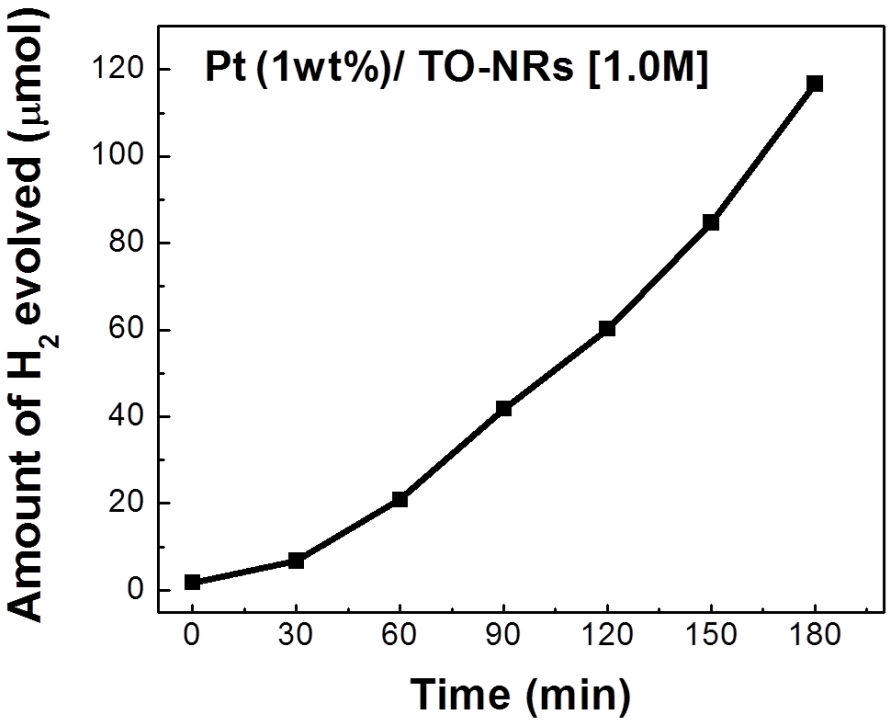

Figure S11 Photocatalytic hydrogen production over Pt/ATO-NRs photocatalysts platinize by wet impregnation method and calcined inside tubular furnace at 400˚C to reduce Pt into Pt^0 under continuous hydrogen gas flow. (Catalyst = 0.11 g loaded with 1 wt % Pt, electrolyte: methanol + water mixed 40 mL volume, under solar light irradiation.)