Supplementary information

Enhanced photocatalytic hydrogen evolution from cation modified single perovskite niobates in the absence of noble metal cocatalysts

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Table S1. Composition and synthesis temperature for $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Sr. No.	Chemical composition	Synthesis condition	Colour
1.	$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	850 °C/12 h; 950 °C/12 h; 1000 °C/24h in air	
2.	$Na_{0.5}Sr_{0.5}Mn_{0.25}Nb_{0.75}O_3$	850 °C/12 h; 950 °C/12 h; 1000 °C/24h in air	
3.	$Na_{0.5}Sr_{0.5}Fe_{0.25}Nb_{0.75}O_3$	850 °C/12 h; 950 °C/12 h; 1000 °C/24h in air	
4.	$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	850 °C/12 h; 950 °C/12 h; 1000 °C/24h in air	

Table S2. Position, thermal and occupancy parameters for $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Wyckoff	Atom	Position	M = Cr	M = Mn	M = Fe	M = Co	Occupancy
4c	Na/Sr	x y z	0 0 0	0 0 0	0 0 0	0 0 0	0.5
		B	0.671(1)	0.607(1)	0.364(1)	0.163(1)	
4b	M/Nb	x y z	0.5 0.5 0.5	0.5 0.5 0.5	0.5 0.5 0.5	0.5 0.5 0.5	0.25/0.75
		B	0.095(2)	0.596(1)	0.038(2)	0.396(1)	
4c	O1	x y z	0 0.5 0.5	0 0.5 0.5	0 0.5 0.5	0.0 0.5 0.5	1
		B	1.109(1)	2.131(1)	1.557(1)	2.577(1)	

Table S3. Refined cell parameters and reliability factors for $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Parameters	**M = Cr**	**M = Mn**	**M = Fe**	**M = Co**
a = b = c (Å)	3.9394(1)	3.9554(1)	3.9502 (1)	3.9721(1)
R_{Bragg} (%)	1.61	3.15	2.22	3.07
R_f (%)	1.52	2.69	1.89	2.59
R_p (%)	4.14	5.32	4.47	3.49
R_{wp} (%)	5.49	7.52	6.27	5.23
χ^2	3.47	6.28	5.49	5.42

Table S4. Bond distances for $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

	Bond distance (Å)			
Type of Bond	**Cr**	**Mn**	**Fe**	**Co**
M/Nb−O1 × 6	1.9697(1)	1.9777(1)	1.9751(2)	1.9860(2)

Table S5. Tolerance factor *t* for $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Compound $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$	**Tolerance factor *t* Low spin**	**Tolerance factor *t* High spin**
M = Cr	0.9789	0.9789
M = Mn	0.9831	0.9753
M = Fe	0.9868	0.9753
M = Co	0.9874	0.9795

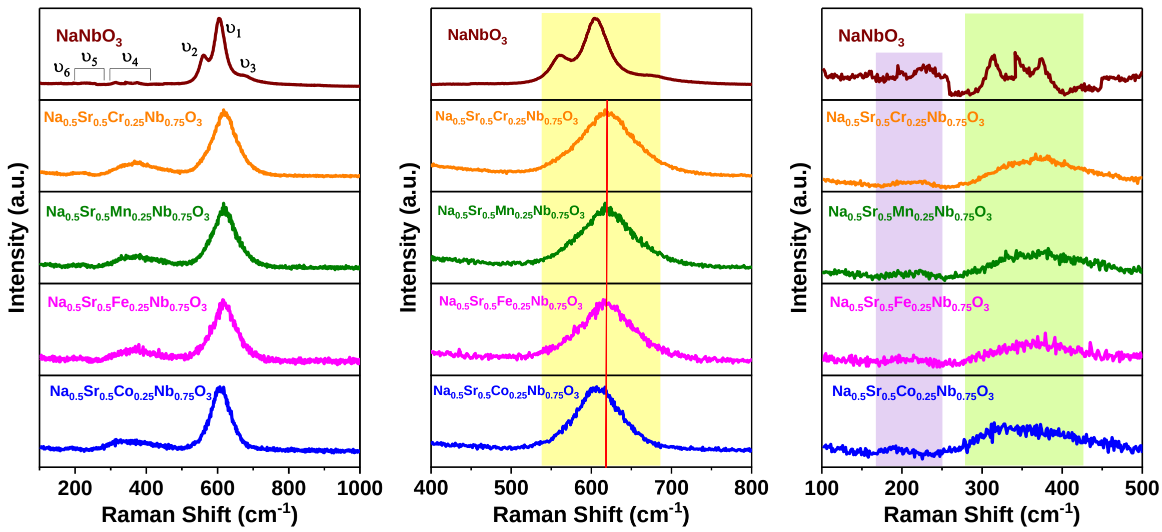

Fig. S1 Raman Spectra of $NaNbO_3$ and $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

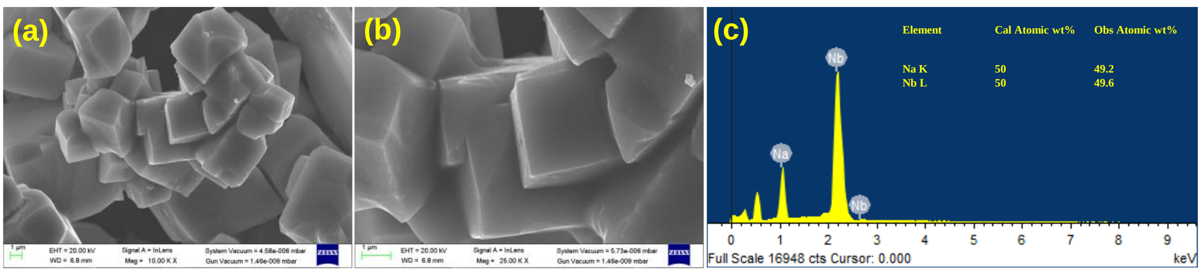

Fig. S2 (a-b) FE-SEM and (c) EDX data for $NaNbO_3$.

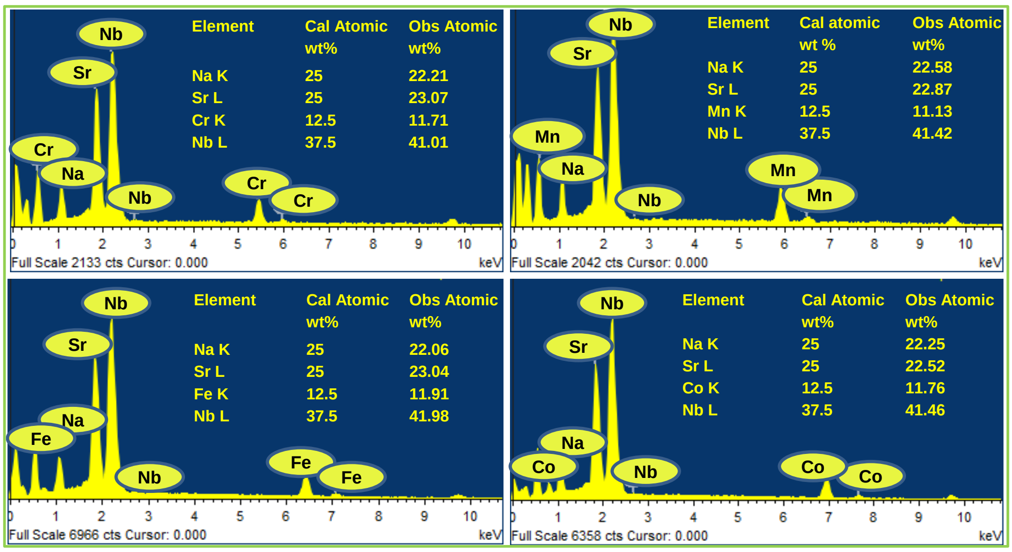

Fig. S3 EDX analysis of the $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Table S6. Compositions of the $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co) determined by ICP-MS.

Compound	Na	Sr	M	Nb
$NaNbO_3$	1	---	---	0.99
$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	0.49	0.48	0.23	0.73
$Na_{0.5}Sr_{0.5}Mn_{0.25}Nb_{0.75}O_3$	0.49	0.48	0.23	0.74
$Na_{0.5}Sr_{0.5}Fe_{0.25}Nb_{0.75}O_3$	0.48	0.49	0.24	0.73
$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	0.48	0.49	0.23	0.73

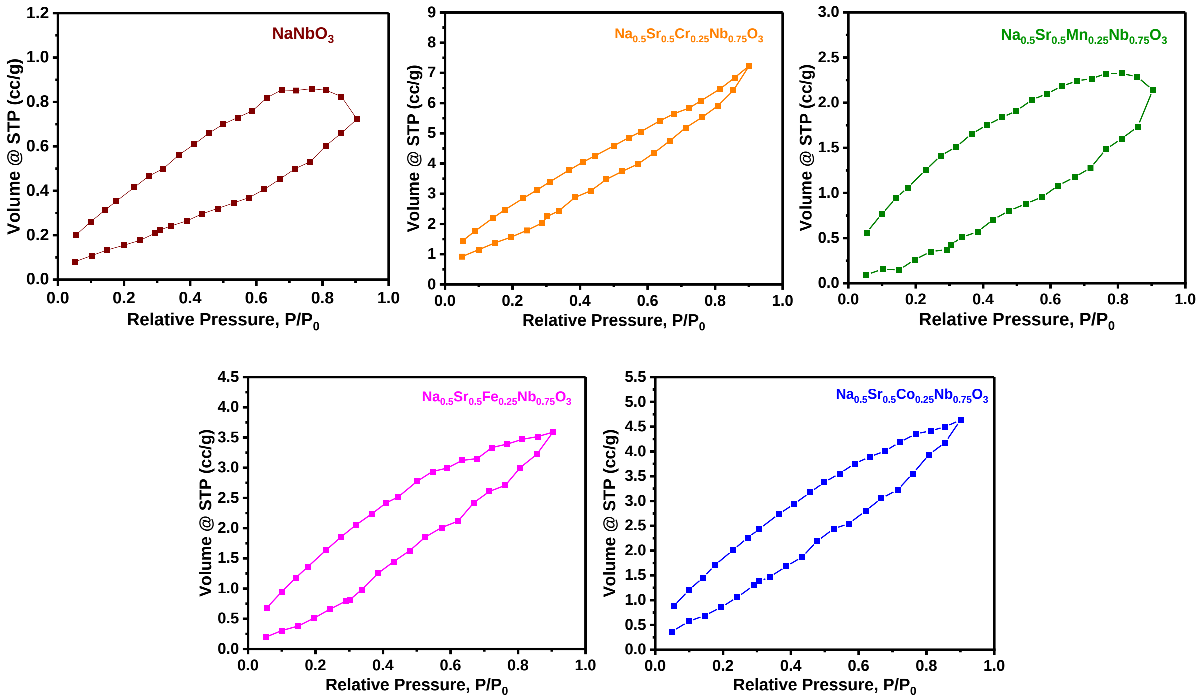

Fig. S4. BET adsorption isotherm for $NaNbO_3$ and $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Table S7. The specific surface area of $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Compound	Specific surface area (m^2/g)
$NaNbO_3$	0.73
$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	6.60
$Na_{0.5}Sr_{0.5}Mn_{0.25}Nb_{0.75}O_3$	1.70
$Na_{0.5}Sr_{0.5}Fe_{0.25}Nb_{0.75}O_3$	3.10
$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	5.37

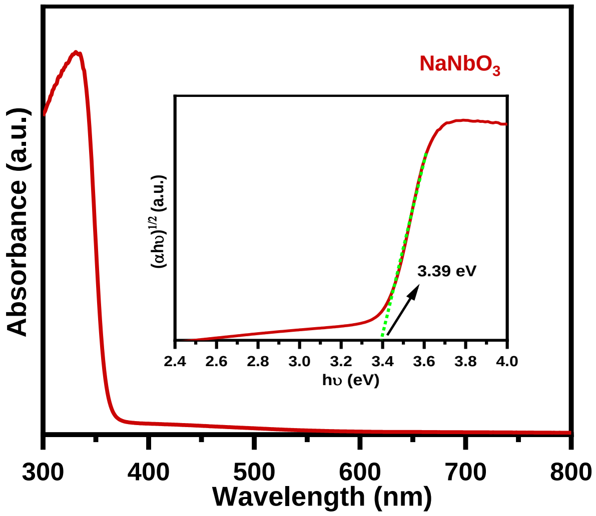

Fig. S5 UV-Vis DRS absorption spectra and the corresponding Tauc plot (inset) of $NaNbO_3$.

Table S8. Band gap data of $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Compounds	**Band gap (eV)**	
	E_g(1)	**E_g(2)**
$NaNbO_3$	3.39	
$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	2.17	----
$Na_{0.5}Sr_{0.5}Mn_{0.25}Nb_{0.75}O_3$	1.75	2.15
$Na_{0.5}Sr_{0.5}Fe_{0.25}Nb_{0.75}O_3$	2.07	2.45
$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	2.0	----

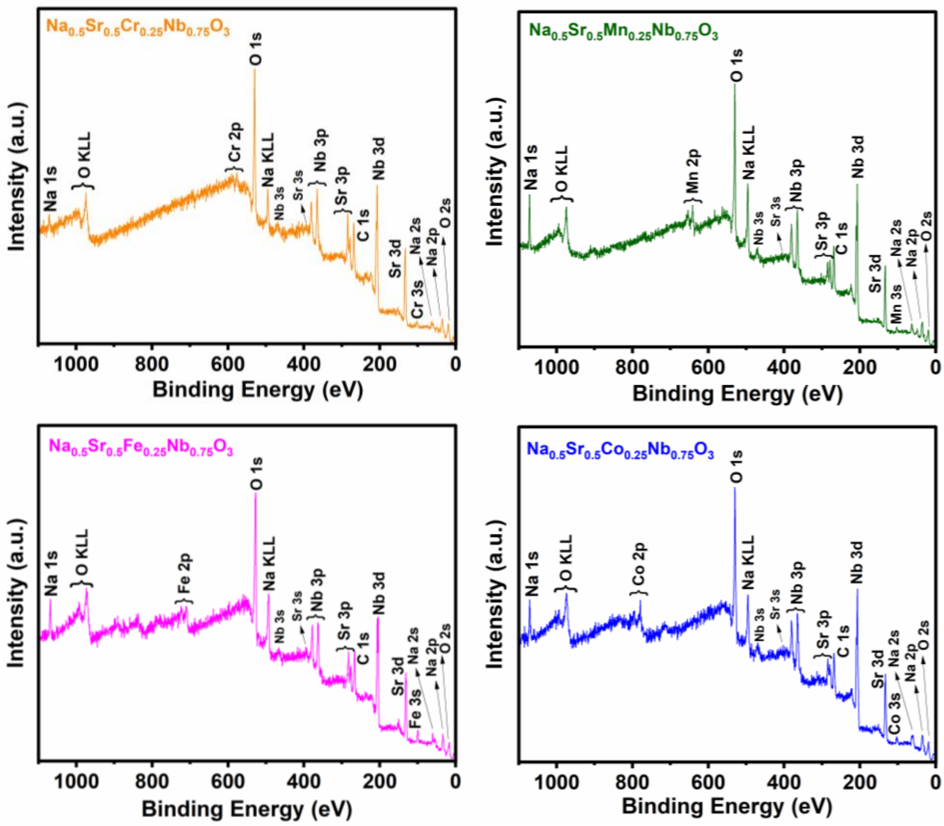

Fig. S6 XPS Survey spectra of $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

Table S9. XPS binding energies (in eV) of Na 1s, Sr 2p, M 2p and Nb 3d for $Na_{0.5}Ca_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co).

	Na 1s	**Sr 2p** **$2p_{3/2}$**	 **$2p_{1/2}$**	**M 2p** **$2p_{3/2}$**	 **$2p_{1/2}$**	**Nb 3d** **$3d_{5/2}$**	 **$3d_{3/2}$**
$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	1070.8	132.3	134.0	575.9	585.8	206.2	208.9
$Na_{0.5}Sr_{0.5}Mn_{0.25}Nb_{0.75}O_3$	1070.8	132.2	134.0	640.3	652.3	206.2	208.9
$Na_{0.5}Sr_{0.5}Fe_{0.25}Nb_{0.75}O_3$	1071.5	132.8	134.6	711.3	724.9	206.5	209.2
$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	1071.5	132.9	134.8	780 777.5	796.5 794.2	206.7	209.4

Table S10. EIS circuit fitting parameters.

Compound	**Circuit Elements Value**				
	R_s (Ω)	**R_{ct} (Ω)**	**CPE_1**	**R_1 (Ω)**	**CPE_2**
$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	0.05	1850	5.1935E-05	51.508	7.1423E-08
$Na_{0.5}Sr_{0.5}Mn_{0.25}Nb_{0.75}O_3$	2.65	4148	6.6297E-05	50.781	1.8460E-07
$Na_{0.5}Sr_{0.5}Fe_{0.25}$ $Nb_{0.75}O_3$	0.10	2401	2.0850E-04	47.125	3.7394E-07
$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	2.54	2198	4.2144E-05	56.277	1.0311E-07

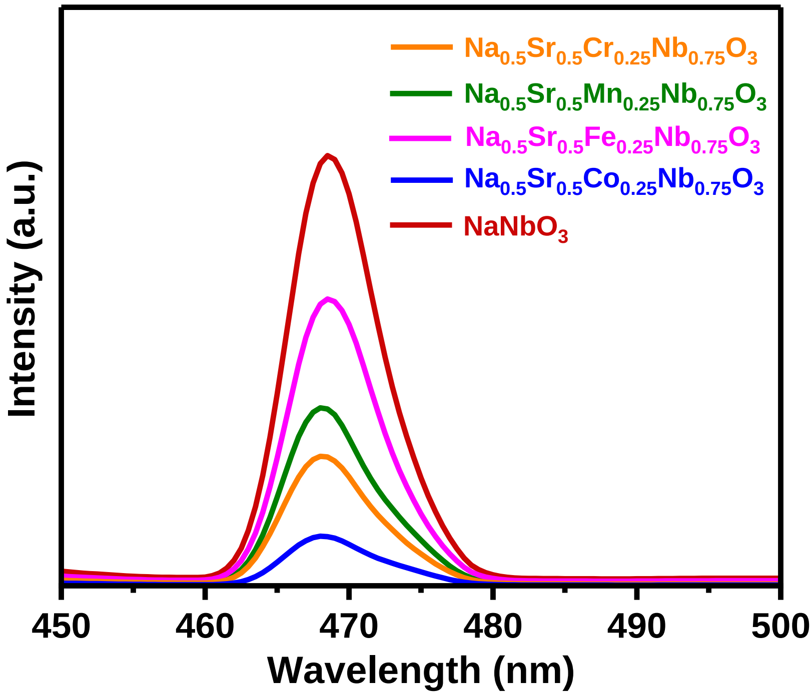

Fig. S7 Steady-state photoluminescence spectra of $NaNbO_3$ and $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Mn, Fe, and Co)

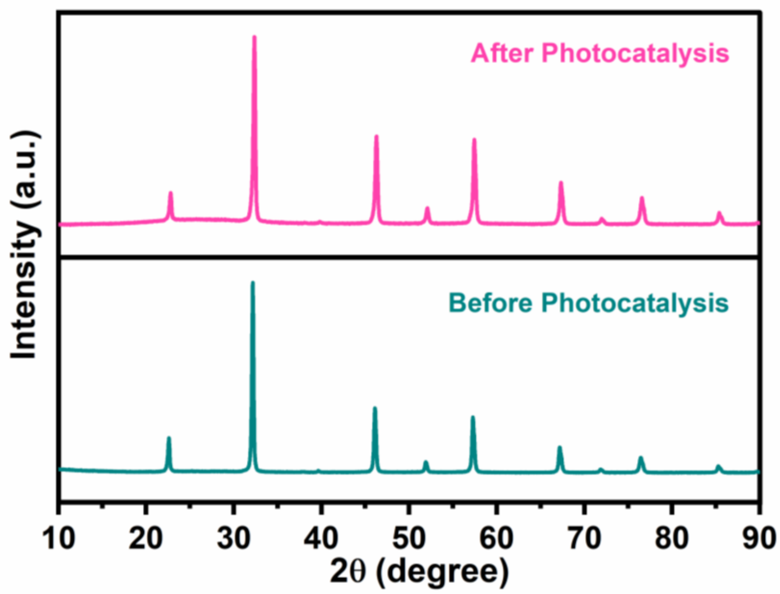

Fig. S8 PXRD data of $Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$ before and after photocatalysis.

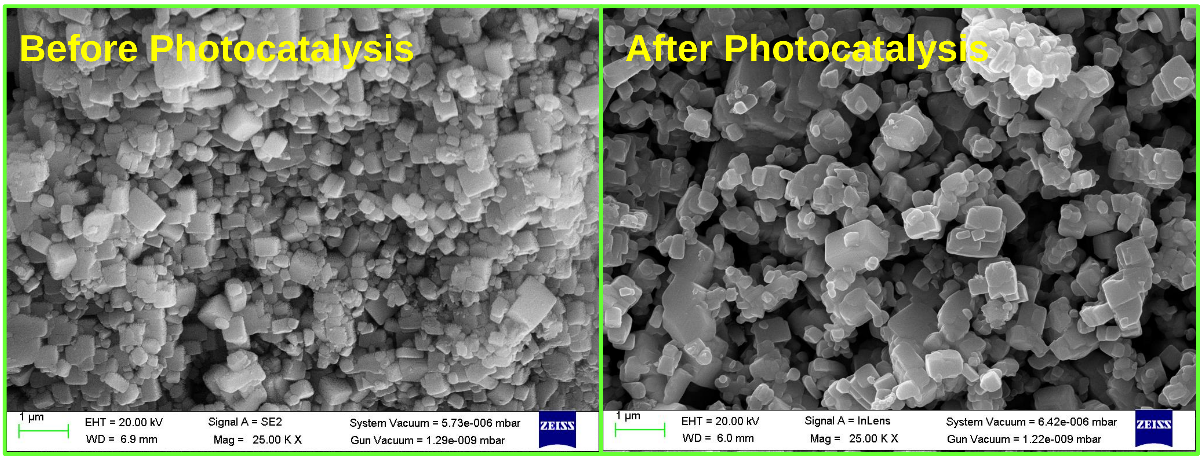

Fig. S9 FE-SEM images of $Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$ before and after photocatalysis.

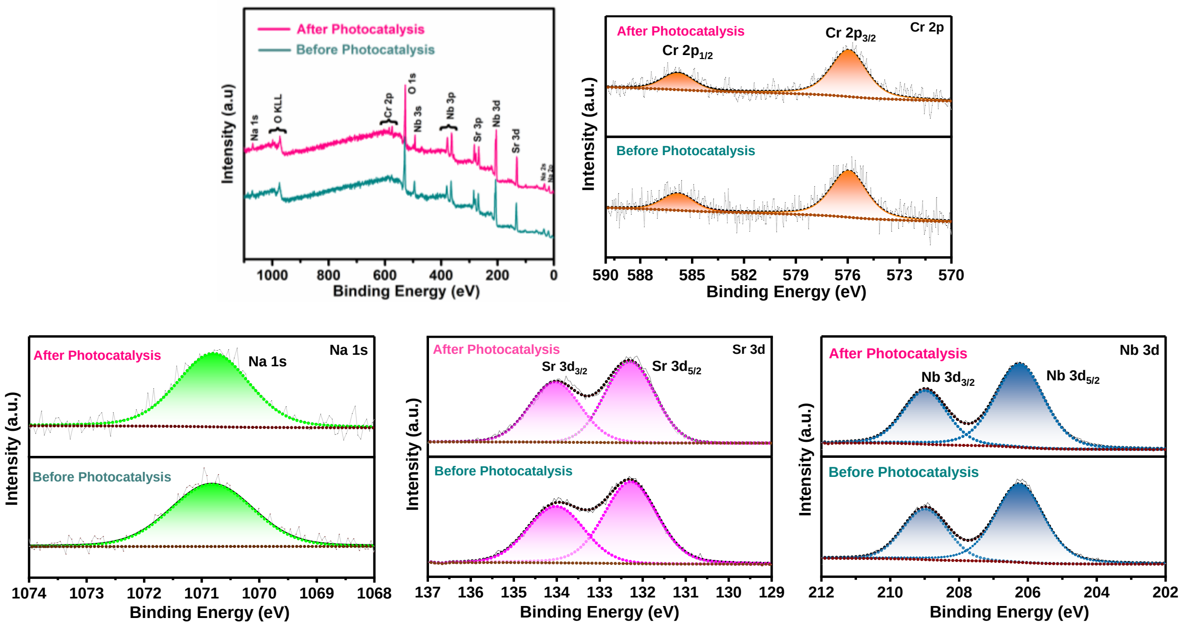

Fig. S10 Binding energy of the $Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$ for Cr 2p, Na 1s, Sr 3d and Nb 3d before and after photocatalysis.

Table S11. Comparative assessment of the photocatalytic activity of $Na_{0.5}Sr_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Cr, Fe and Co) with other catalysts reported in literature.

S. No.	Photocatalyst	Co-catalyst	Light source	Sacrificial agent	H_2 evolved ($\mu mol\ h^{-1}\ g^{-1}$)	Ref.
1.	$Na_{0.5}Sr_{0.5}Cr_{0.25}Nb_{0.75}O_3$	None	250W Medium Pressure Hg-vapor lamp	Methanol (20 vol %)	188	This work
2.	$Na_{0.5}Sr_{0.5}Co_{0.25}Nb_{0.75}O_3$	None	250W Medium Pressure Hg-vapor lamp	Methanol (20 vol %)	62	This work
3.	$Na_{0.5}Sr_{0.5}Fe_{0.25}Nb_{0.75}O_3$	None	250W Medium Pressure Hg-vapor lamp	Methanol (20 vol %)	54.6	This work
4.	$CaTiO_3$: Rh	Pt	300-W Xe lamp ($\lambda > 420$ nm)	Methanol	28.3	[1]
5.	Mo-doped $BaTiO_3$	Pt	300 W Xe lamp	Aqueous methyl alcohol solution	63	[2]
6.	CdSe QDs/$BaTiO_3$	None	300 W Xe lamp ($\lambda > 420$ nm)	Na_2SO_3 and Na_2S	53.4	[3]
7.	Cu doped- $PbTiO_3$	None	125 W, medium pressure Hg lamp	Methanol (10 vol %)	90	[4]
8.	$PbTiO_3/LaCrO_3$	None	150W Xe lamp, $\lambda \geq 400$ nm	Methanol (10 vol %)	171.7	[5]
9.	$SrTiO_3$:Rh	Pt	300-W Xe lamp ($\lambda > 440$ nm)	Methanol	390	[6]
10.	$SrTiO_3$: Ir	Pt	300-W Xe lamp ($\lambda > 440$ nm)	Methanol	28.7	[6]
11.	$SrTiO_3$: Ni/Ta	None	Xe lamp	Methanol	2.4	[7]
12.	$SrTiO_3$: Cr/Sb	None	Xe lamp	Methanol	78	[8]
13.	Cr, Ta co-doped $SrTiO_3$	Pt	300 W Xe lamp ($\lambda > 420$ nm)	Methanol (10 vol %)	122.6	[9]
14.	$La_2Ti_2O_7$: Cr	Pt	500-W Hg lamp ($\lambda >420$ nm)	Methanol	30	[10]
15.	$La_2Ti_2O_7$: Fe	Pt	500-W Hg lamp ($\lambda >420$ nm)	Methanol	20	[10]
16.	Ag-$NaTaO_3$	None	300 W Xe lamp	Methanol (25 vol %)	3.54	[11]
17.	Ag-$KTaO_3$	None	300 W Xe lamp	Methanol (25 vol %)	185.60	[11]
18.	$NaTaO_3$: La/Cr	Pt	300 W Xe lamp (λ >420 nm)	Methanol (20 vol%)	4.4	[12]
19.	g-$C_3N_4/SrTa_2O_6$	Pt	300 W Xe lamp ($\lambda > 420$ nm)	TEOA (5 vol %)	37.2	[13]
20.	CdS/Ni/$KNbO_3$	None	500 W lamp	Methanol (50 vol %)	23.5	[14]
21.	$SnNb_2O_6$ nanosheets	Pt	300 W Hg-arc lamp ($\lambda \geq 420$ nm)	Lactic acid (20 vol%)	264	[15]
22.	$LaFeO_3$/g-C_3N_4	NiS	300 W Xe lamp	Ethanol	121.0	[16]
23.	$Sr_{0.85}Bi_{0.15}Ti_{0.85}Cr_{0.15}O_3$	Pt	300 W Xe lamp ($\lambda > 420$ nm)	Methanol (10 vol %)	3.7	[17]
24.	$Sr_2Ti_{0.9}Cr_{0.1}O_{4-\delta}$	Pt	500 W high-pressure Hg lamp	Na_2SO_3	17.0	[18]

25.	$Sr_2Ti_{0.95}Cr_{0.05}O_{4-\delta}$	Pt	500 W high-pressure Hg lamp	Na_2SO_3	97.7	[18]

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