

## **Supporting Information**

Figure S1: Schematic illustration of the general synthesis concept including designation of the samples.

Table S1: Crystallite sizes (nm) of the MC series.

phase	M0h	MC0.5h	MC1h	MC2h	MC5h	MC10h	MC20h	MC24h	MC144h(5M)
TiO <sub>2</sub>	20	21	20	21	20	21	21	19	18
$SrTiO_3$	-	-	-	15	21	21	22	20	21

Table S2: Crystallite sizes (nm) of the NC series.

phase	N0h	NC0.5h	NC1h	NC2h	NC5h	NC10h	NC20h	NC24h	NC144h(5M)
TiO <sub>2</sub>	18	18	19	18	19	18	19	19	-
$SrTiO_3$	-	-	-	19	30	28	33	29	34



Figure S2: Kubelka-Munk plots of the MC and NC series.

	Table S3: Averaged	EDX results	(at%) of	f selected	samples
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sample	Sr	Ti	0	С	N	Na	Cl
MC1h	0.1	25.6	56.5	12.0	5.7	0.0	0.1
MC5h	3.7	26.3	58.2	7.2	4.5	0.0	0.1
MC20h	3.2	24.1	55.7	14.0	2.9	0.0	0.1
MC144h(5M)	5.3	21.8	60.9	6.2	4.6	1.1	0.0
NC144h(5M)	12.4	14.3	50.1	15.2	2.0	0.7	0.0



Figure S3: SEM images of the nanoparticulate  $TiO_2$  starting material (N0h) and the converted sample NC144h(5M) (top). EDX mapping of NC144h(5M) is shown in the middle and a comparison of  $SrTiO_3$  structures of MC144h(5M) and NC144h(5M) is depicted on the bottom.



Figure S4: TEM images of the samples M0h, MC144h(5M), N0h, and NC144h(5M).

sample	C 1s	Sr 3 <i>d</i>	Ti 2 <i>p</i>	0 1 <i>s</i>	Na 1 <i>s</i>	Cl 2 <i>p</i>
M0h	8.34	-	26.34	65.32	-	-
MC0.5h	14.66	0.23	25.42	59.09	-	0.60
MC1h	15.48	0.58	24.22	58.77	-	0.95
MC2h	23.76	8.42	17.58	50.25	-	-
MC5h	14.59	17.62	15.05	52.29	-	0.44
MC10h	14.73	17.59	15.31	51.41	-	0.96
MC20h	13.77	17.59	14.77	53.86	-	-
MC24h	14.95	15.86	14.34	52.53	-	2.33
MC144h(5M)	11.49	17.72	14.41	54.75	1.64	-

Table S4: Atomic percentages (at%) of the MC series obtained from XP survey spectra.



Figure S5: XP survey spectra of the NC series.

sample	C 1 <i>s</i>	Sr 3 <i>d</i>	Ti 2 <i>p</i>	O 1 <i>s</i>	Na 1 <i>s</i>	Cl 2 <i>p</i>
N0h	12.94	-	24.43	62.64	-	-
NC0.5h	7.44	-	27.92	63.73	-	0.91
NC1h	12.25	1.47	24.44	59.62	-	2.22
NC2h	4.30	2.27	29.27	63.99	-	0.18
NC5h	11.4	6.98	22.49	57.00	-	2.13
NC10h	4.10	7.30	22.85	64.75	-	1.01
NC20h	12.07	6.46	22.06	58.03	-	1.37
NC24h	16.00	8.15	20.71	55.13	-	-
NC144h(5M)	9.30	17.67	16.54	56.49	-	-

Table S5: Atomic percentages (at%) of the NC series obtained from XP survey spectra.



Figure S6: High-resolution XP spectra of the MC series (top left: O 1s; top right: Ti 2p; bottom left: C 1s; bottom right: Sr 3d).



Figure S7: High-resolution XP spectra of the NC series (top left: O 1s; top right: Ti 2p; bottom left: C 1s; bottom right: Sr 3d).



Figure S8: XRD patterns of the ME and NE series.

Table S6: Crystallite sizes (nm) of the ME series.

phase	ME0.5h	ME1h	ME2h	ME5h	ME10h	ME20h
TiO <sub>2</sub>	20	20	19	20	20	20

Table S7: Crystallite sizes (nm) of the NE series.





Figure S9: Kubelka-Munk plots of the ME and NE series.



Figure S10: Tauc plots of the ME and NE series.



Figure S11: DRIFT spectra of the ME and NE series.



Figure S12: Raman spectra of the ME and NE series.



Figure S13: SEM images (top) and TEM images (bottom) of ME20h (left) and NE20h (right).



Figure 14: XP survey spectra of selected samples from the ME and NE series.

sample	C 1 <i>s</i>	Sr 3 <i>d</i>	Ti 2 <i>p</i>	0 1 <i>s</i>	Na 1 <i>s</i>	Cl 2 <i>p</i>
ME1h	14.08	-	24.31	60.54	-	1.07
ME5h	12.75	-	25.05	61.17	-	1.03
ME20h	12.51	-	24.24	62.04	-	1.20
NE1h	13.29	-	24.54	61.60	-	0.57
NE5h	11.84	-	25.37	61.79	-	1.00
NE20h	20.87	-	22.10	56.49	-	0.54

Table S8: Atomic percentages (at%) of selected samples from the ME and NE series obtained from XP survey spectra.



Figure S15: High-resolution XP spectra of selected samples from the ME and NE series (top left: O 1s; top right: Ti 2p; bottom: C 1s).



Figure S16: Overlaid O 1s spectra of selected samples from the ME series.



Figure S17:  $N_2$  physisorption isotherms (top) and cumulative pore volumes (bottom) of the MC series (left) and ME series (right). Isotherms are shifted by 25 cm<sup>3</sup> g<sup>-1</sup>, respectively.

Table S9: BET	surface areas and	cumulative	pore volumes	of the MC an	d ME series.
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sample	M0h	MC0.5h	MC1h	MC2h	MC5h	MC10h	MC20h	MC24h	MC144h(5M)
BET									
surface	54.2	42.7	48.0	42.0	5.8	9.1	4.1	9.1	5.3
area	(average)				0.0	0.1		0.1	
[m²/g]									
cumu-									
lative									
pore	0.072	0.061	0.071	0.037	0.007	0.012	0.007	0.013	0.012
volume									
[cm <sup>3</sup> /g]									
sample	-	ME0.5h	ME1h	ME2h	ME5h	ME10h	ME20h	-	-
BET									
surface	_	13 1	173	11 1	17.8	10.7	56.4	_	_
area	_	43.4	47.5	44.1	47.0	40.7	50.4	_	_
[m²/g]									
cumu-									
lative									
pore	-	0.060	0.068	0.056	0.055	0.049	0.067	-	-
volume									
[cm <sup>3</sup> /g]									



Figure S18: N<sub>2</sub> physisorption isotherms (top), pore size distributions (middle), and cumulative pore volumes (bottom) of the NC series (left) and NE series (right). Isotherms are shifted by 50 cm<sup>3</sup> g<sup>-1</sup> (NC series) and 70 cm<sup>3</sup> g<sup>-1</sup> (NE series), respectively. Pore size distributions are shifted by 0.04 cm<sup>3</sup> nm<sup>-1</sup> g<sup>-1</sup>, respectively.

sample	N0h	NC0.5h	NC1h	NC2h	NC5h	NC10h	NC20h	NC24h	NC144h(5M)
BET surface area [m²/g]	97.4	94.2	92.5	84.2	60.9	50.0	53.8	48.7	33.0
cumu- lative pore volume [cm <sup>3</sup> /g]	0.161	0.261	0.255	0.229	0.156	0.137	0.161	0.133	0.128
sample	-	NE0.5h	NE1h	NE2h	NE5h	NE10h	NE20h	-	-
BET surface area [m <sup>2</sup> /g]	-	97.1	98.7	95.0	80.0	69.8	63.7	-	-
cumu- lative pore volume [cm <sup>3</sup> /g]	-	0.280	0.289	0.264	0.243	0.230	0.225	-	-

Table S10: BET surface areas and cumulative pore volumes of the NC and NE series.



Figure S19: N<sub>2</sub> physisorption isotherms (left), pore size distributions (right), and cumulative pore volumes (bottom) of mesoporous and nanoparticulate control samples (H<sub>2</sub>O work-up, HCl work-up, and H<sub>2</sub>O treatment). Isotherms are shifted by  $30 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Pore size distributions are shifted by  $0.04 \text{ cm}^3 \text{ nm}^{-1} \text{ g}^{-1}$ , respectively.

Table S11: BET surface areas and cumulative pore volumes of mesoporous and nanoparticulate samples ( $H_2O$  work-up, HCl work-up, and  $H_2O$  treatment).

sample	M0hH₂O	M0hHCl	M0.5hH₂O	M20hH₂O
BET surface area [m²/g]	39.9	40.7	45.3	55.9
cumulative pore volume [cm <sup>3</sup> /g]	0.048	0.050	0.058	0.059
sample	N0hH <sub>2</sub> O	N0hHCl	N0.5hH₂O	N20hH <sub>2</sub> O
BET surface area [m²/g]	97.4	96.1	96.7	86.7
cumulative pore volume [cm <sup>3</sup> /g]	0.254	0.273	0.260	0.264



Figure S20: Number weighted particle size distributions (left) and volume weighted particle size distributions (right) of hydrothermally converted nanoparticles (NC series, top), hydrothermally etched nanoparticles (NE series, middle), and nanoparticulate control samples (bottom) determined by DLS.

Table S12: Maxima of number and volume weighted size distributions of nanoparticulate samples determined by DLS.

sample	maxima	maxima	sample	maxima	maxima	sample	maxima	maxima
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	number	volume		number	number		number	volume
	weighted	weighted		weighted	weighted		weighted	weighted
	size	size		size	size		size	size
	distribution	distribution		distribution	distribution		distribution	distribution
	[nm]	[nm]		[nm]	[nm]		[nm]	[nm]
N0h	44	48/ 1216	-	-	-	N0hH₂O	71	77/ 811
NC0.5h	66	71/ 954	NE0.5h	56	71/ 690	N0hHCl	71	77/ 1319
NC1h	77	84/ 1216	NE1h	52	56/ 1319	N0.5hH₂O	66	1319
NC2h	84	1318	NE2h	66	66/ 954	N20hH₂O	66	71/ 1216
NC5h	77	2144	NE5h	77	84/ 1216	-	-	-
NC10h	148/ 2144	2521	NE10h	71	77/ 1121	-	-	-
NC20h	2144	2325	NE20h	77	84/ 880	-	-	-



Figure S21: XRD patterns (a), Kubelka-Munk plots (b), Tauc plots (c), DRIFT spectra (d), and Raman spectra (e) of mesoporous and nanoparticulate control samples (H<sub>2</sub>O work-up, HCl work-up, and H<sub>2</sub>O treatment).

Table S13: Crystallite sizes (nm) of mesoporous and nanoparticulate control samples ( $H_2O$  work-up, HCl work-up, and  $H_2O$  treatment).

phase	M0hH₂O	M0hHCl	M0.5hH <sub>2</sub> O	M20hH <sub>2</sub> O	N0hH₂O	N0hHCl	N0.5hH₂O	N20hH₂O
TiO <sub>2</sub>	17	17	17	17	18	18	19	19



Figure S22: XP survey spectra of mesoporous and nanoparticulate control samples ( $H_2O$  work-up, HCl work-up, and  $H_2O$  treatment).

Table S14: Atomic percentages (at%) of mesoporous and nanoparticulate control samples ( $H_2O$  work-up, HCl work-up, and  $H_2O$  treatment) obtained from XP survey spectra.

sample	C 1 <i>s</i>	Sr 3 <i>d</i>	Ti 2 <i>p</i>	O 1 <i>s</i>	Na 1 <i>s</i>	Cl 2 <i>p</i>
M0hH <sub>2</sub> O	15.30	-	24.02	60.68	-	-
M0hHCl	15.31	-	24.21	60.22	-	0.26
$M0.5hH_2O$	15.47	-	24.02	59.93	-	0.59
M20hH <sub>2</sub> O	16.97	-	23.88	58.49	-	0.66
N0hH <sub>2</sub> O	15.49	-	25.45	59.06	-	-
N0hHCl	10.49	-	25.38	63.24	-	0.56
N0.5hH₂O	16.54	-	24.83	58.15	-	0.48
N20hH₂O	16.88	-	23.83	58.56	-	0.72



Figure S23: High-resolution XP spectra of mesoporous and nanoparticulate control samples (top left: O 1s; top right: Ti 2p; bottom: C 1s).



Figure S24: Photocatalytic  $H_2$  evolution under simulated solar light irradiation of all samples (up to 20 h reaction time). Cocatalyst photodeposition (0.1 wt% Pt) was performed after 2 h.



Figure S25: Nyquist plots of photoelectrodes under simulated solar light irradiation.





Figure S26: XRD patterns of the MC series (top left), NC series (top right), ME series (middle left), NE series (middle right), and control experiments (bottom) after photocatalytic H<sub>2</sub> evolution experiments.



Figure S27: Kubelka-Munk plots of converted (top), etched (middle), and control samples (bottom) after photocatalytic H<sub>2</sub> evolution experiments.



Figure S28: Tauc plots of converted (top), etched (middle), and control samples (bottom) after photocatalytic H<sub>2</sub> evolution experiments. Steeper tangents of the background are the result of broad absorption of the Pt co-catalyst.



Figure S29: DRIFT spectra of converted (top), etched (middle), and control samples (bottom) after photocatalytic H<sub>2</sub> evolution experiments.



Figure S30: Raman spectra of converted (top), etched (middle), and control samples (bottom) after photocatalytic  $H_2$  evolution experiments.





Figure S31:  $H_2O$  physisorption isotherms of converted mesoporous samples (top) and etched mesoporous TiO<sub>2</sub> (bottom). Isotherms normalized by  $N_2$  BET surface area are shown on the left and were derived from full isotherms depicted on the right.

sample	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> m <sup>-2</sup> <sub>BET</sub> ]	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	sample	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> m <sup>-2</sup> <sub>BET</sub> ]	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> ]
M0h	0.17	9.37	-	-	-
MC0.5h	0.35	14.82	ME0.5h	0.36	15.58
MC1h	0.37	17.68	ME1h	0.34	15.87
MC2h	0.49	20.39	ME2h	0.30	13.24
MC5h	2.07	12.09	ME5h	0.35	16.55
MC10h	1.70	15.51	ME10h	0.40	16.11
MC20h	2.65	10.87	ME20h	0.38	21.31



Figure S32:  $H_2O$  physisorption isotherms of converted nanoparticles (top) and etched TiO<sub>2</sub> nanoparticles (bottom). Isotherms normalized by  $N_2$  BET surface area are shown on the left and were derived from full isotherms depicted on the right.

sample	$V_{ads}$ [cm <sup>3</sup> g <sup>-1</sup> m <sup>-2</sup> act]	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	sample	$V_{ads}$ [cm <sup>3</sup> g <sup>-1</sup> m <sup>-2</sup> act]	$V_{ads}$
N0h	0.20	19 29	-		-
NC0.5h	0.23	21.62	NE0.5h	0.22	21.27
NC1h	0.24	21.75	NE1h	0.21	21.20
NC2h	0.31	25.88	NE2h	0.24	23.20
NC5h	0.29	17.94	NE5h	0.24	19.36
NC10h	0.32	16.13	NE10h	0.20	14.15
NC20h	0.29	15.50	NE20h	0.19	12.31

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Table S16: Normalized and measured adsorbed volumes of the NC and NE series at  $p/p_0 = 0.3$ .



Figure S33:  $H_2O$  physisorption isotherms of mesoporous and nanoparticulate control samples. Isotherms normalized by  $N_2$  BET surface area are shown on the left and were derived from full isotherms depicted on the right.

sample	$V_{ads}$ [cm <sup>3</sup> g <sup>-1</sup> m <sup>-2</sup> <sub>BET</sub> ]	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	sample	$V_{ads}$ [cm <sup>3</sup> g <sup>-1</sup> m <sup>-2</sup> <sub>BET</sub> ]	V <sub>ads</sub> [cm <sup>3</sup> g <sup>-1</sup> ]
M0hH <sub>2</sub> O	0.23	9.20	N0hH <sub>2</sub> O	0.24	23.31
M0hHCl	0.23	9.46	N0hHCl	0.26	24.56
M0.5hH₂O	0.27	12.15	N0.5hH₂O	0.25	24.26
M20hH <sub>2</sub> O	0.28	15.40	N20hH₂O	0.26	22.77

Table S17: Normalized and measured adsorbed volumes of mesoporous and nanoparticulate control samples at  $p/p_0 = 0.3$ .

Long-term photocatalytic H<sub>2</sub> evolution measurement, literature comparison, and comparison of band edge positions



Figure S34: Long-term photocatalytic  $H_2$  evolution of ME20h under simulated solar light irradiation. Co-catalyst photodeposition (0.1 wt% Pt) was performed after 2 h. The highest activity of 107.6 µmol h<sup>-1</sup> was measured approximately 1 h after the photodeposition.

Table S18: Comparison of photocatalytic H<sub>2</sub> evolution rates discussed in this work with literature results of different SrTiO<sub>3</sub>/TiO<sub>2</sub> samples obtained by hydrothermal conversion of a TiO<sub>2</sub> starting materials. Stated H<sub>2</sub> evolution rates might deviate from values in the respective publications due back calculations from  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> to  $\mu$ mol h<sup>-1</sup>.

photo- catalyst	experimental conditions	co-catalyst	H <sub>2</sub> evolution [µmol h <sup>-1</sup> ]	percentage increase compared to TiO <sub>2</sub> starting material	Ref.
etched meso-TiO₂ (ME20h)	150 W Xe lamp, air mass 1.5G filter, 50 mg photocatalyst, 150 mL 10 vol% methanol aqueous solution	0.1 wt% Pt	106.7	102%	This work
short conversion time of meso-TiO₂ (MC0.5h)	150 W Xe lamp, air mass 1.5G filter, 50 mg photocatalyst, 150 mL 10 vol% methanol aqueous solution	0.1 wt% Pt	71.5	35%	This work
SrTiO₃/TiO₂	300 W Xe lamp, no filter, 50 mg photocatalyst, 100 mL 10 vol% methanol aqueous solution	1 wt% Pt	650.3	cannot be determined	[1]
SrTiO <sub>3</sub> /TiO <sub>2</sub>	300 W Xe lamp, 200- 2500 nm, 100 mg photocatalyst, 100 mL 6 M methanol aqueous solution	no co- catalyst	90.3 (averaged from 8 h experiment)	138%	[2]
SrTiO₃/TiO₂	300 W Xe lamp, no filter, 100 mg photocatalyst, 100 mL 20 vol% methanol aqueous solution	0.3 wt% Pt	664	cannot be determined precisely	[3]
SrTiO <sub>3</sub> /TiO <sub>2</sub>	300 W Xe lamp, no filter, 10 mg photocatalyst, 40 mL 10 vol% methanol aqueous solution	5 wt% HAuCl₄·H₂O	3.3	924%	[4]
SrTiO₃/TiO₂	250 W Hg lamp, no filter, 10 mg photocatalyst, 35 mL 25 vol% methanol aqueous solution	3.5 wt% Pt	1112.6	152%	[5]
SrTiO₃/TiO₂	300 W Xe lamp, no filter, 50 mg photocatalyst, 99 mL 20 vol% triethanolamine aqueous solution	1 wt% Pt	18.7	154%	[6]
SrTiO₃/TiO₂	400 W Hg lamp, no filter, 0.5 g/L photocatalyst methanol aqueous solution	no co- catalyst	approx. 750	cannot be determined precisely	[7]



Figure S35: Band edge positions and fermi levels (dotted line) of TiO<sub>2</sub> (anatase) and SrTiO<sub>3</sub> relative to the normal hydrogen electrode (NHE). Values are based on experimental data from references [8–12].

Overall water splitting (OWS)



Figure S36: Photocatalytic OWS of the starting materials M0h and N0h and the converted samples MC24h, NC24h, and MC144h(5M).

## Post photocatalysis (OWS):



Figure S37: XRD patterns after photocatalytic OWS experiments.



Figure S38: Kubelka-Munk plots after photocatalytic OWS experiments.



Figure S39: Tauc plots after photocatalytic OWS experiments. High amounts of co-catalyst lead to steeper background fits.



Figure S40: DRIFT spectra after photocatalytic OWS experiments.



Figure S41: Raman spectra after photocatalytic OWS experiments. Photodeposited co-catalysts lead to broad intensities, which shift signals of the samples compared to spectra before photocatalysis.

## References

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