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Electronic Supplementary Information

Enhancing charge separation on high symmetry SrTiO₃ exposed with anisotropic facets for photocatalytic water splitting

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Figure S1 The XRD pattern of 6-facet and 18-facet SrTiO₃.



Figure S2 The UV-vis diffuse reflectance spectrum of 6-facet and 18-facet SrTiO₃.



Figure S3 XPS of typical samples. a, Pt/SrTiO₃. b, Au/SrTiO₃. c, Ag/SrTiO₃. d, Co/SrTiO₃. e, Mn/SrTiO₃.

XPS of Pt 4f, Au 4f and Ag 3d revealed that the deposited elements were all in the metallic form (Pt, Au and Ag), although a small portion of incompletely reduced PtO species remained. According to the binding energy of Co 2p and Mn 2p in XPS, the species can be ascribed to Co_3O_4 and MnO_x , where x is between 1.5 and 2.0, since the observed binding energy of manganese oxides were between Mn₂O₃ and MnO₂.



Figure S4 The SEM images of cocatalysts deposited on SrTiO₃ nanocrystals by impregnation method. **a**, Pt/18-facet SrTiO₃. **b**, Co₃O₄/18-facet SrTiO₃. **c**, Pt/6-facet SrTiO₃. **d**, Co₃O₄/6-facet SrTiO₃.



Figure S5 a, EDS of Pt-Co/6-facet SrTiO₃. **b**, EDS of Pt-Co/18-facet SrTiO₃. a-b match with Figure 3. **c-d**, HRSEM image of Pt-MnO_x/18-facet SrTiO₃.



Figure S6 a, Overall water splitting performance of $Pt-Co_3O_4/18$ -facet SrTiO₃. **b**, HER of Pt/18-facet SrTiO₃ with CH₃OH as sacrificial reagent.

Table S1 The active sites on the surface of photocatalysts for two kinds of $SrTiO_3$ nanocrystals.

Photocatalyst	Active Metal Surface Area (m ² ·g ⁻¹)	
Pt/6-facet SrTiO ₃	0.34	
Pt/18-facet SrTiO ₃	0.29	

Half Reaction	Sacrificial Agent	Photocatalyst	AQE (365 nm)
Water Oxidation	AgNO ₃	6-facet SrTiO ₃	3.4%
water Oxidation	AgNO ₃	18-facet SrTiO ₃	12.2%
Proton Reduction	CH ₃ OH	Pt/6-facet SrTiO ₃	1.1%
	CH ₃ OH	Pt/18-facet SrTiO ₃	0.8%

Table S2 The apparent quantum efficiency for half reaction.

Reaction time: 0.5 h. AgNO₃ was used as sacrificial reagent for oxidation half reaction (0.002 M), CH₃OH was used as sacrificial reagent for reduction half reaction (20% CH₃OH-H₂O solution). The content of the deposited Pt is 0.1 wt%.

{001} 1			3	4	5
6	7		8	9	Pt Co₃O₄
Entry	Pt Cocatalyst	Co ₃ O ₄ Cocatalyst	H_2 Evolution (µmol·h ⁻¹ ·m ⁻²)	O ₂ Evolution (µmol·h ⁻¹ ·m ⁻²)	H_2/O_2
1	-	-	0	0	-
2	Imp ^a	-	800	406	2.0
3	P.D. ^b	-	787	381	2.1
4	-	Imp	0	0	-
5	-	P.D.	0	0	-
6	Imp	P.D.	838	419	2.0
7	P.D.	Imp	799	406	2.0
8	Imp	Imp	888	407	2.2
9	P.D.	P.D.	660	356	1.9

Table S3 Photocatalytic overall water splitting performance of 6-facet $SrTiO_3$ nanocrystals with cocatalysts deposited.

^a Impregnation method. ^b Photo-deposition method. Reaction time: 1 h. The contents of the deposited Pt and Co_3O_4 are optimized to be 0.1 wt% and 0.01 wt%, respectively. The activities are normalized by the number of Pt active sites.

Entry	Photocatalyst	H ₂ Evolution (μmol·h ⁻¹)	O ₂ Evolution (µmol·h ⁻¹)
1	6-facet SrTiO ₃	0	0
2	Pt/6-facet SrTiO ₃	6.2	3.0
3	Co ₃ O ₄ /6-facet SrTiO ₃	0	0
4	Pt-Co ₃ O ₄ /6-facet SrTiO ₃	5.2	2.8
5	18-facet SrTiO ₃	0	0
6	Pt/18-facet SrTiO ₃	16.4	9.0
7	Co ₃ O ₄ /18-facet SrTiO ₃	0	0
8	Pt-Co ₃ O ₄ /18-facet SrTiO ₃	32.2	16.5

Table S4 Raw data of photocatalytic overall water splitting on $SrTiO_3$ nanocrystals.

Entry	Pt Cocatalyst	Co ₃ O ₄ Cocatalyst	H ₂ Evolution (μmol·h ⁻¹)	O2 Evolution (µmol·h ⁻¹)
1	-	-	0	0
2	Imp	-	8.7	3.9
3	P.D.	-	16.4	9.0
4	-	Imp	0	0
5	-	P.D.	0	0
6	Imp	P.D.	5.9	3.2
7	P.D.	Imp	9.5	4.5
8	Imp	Imp	4.2	2.2
9	P.D.	P.D.	32.2	16.5

Table S5 Raw data of photocatalytic performance of 18-facet $SrTiO_3$ with cocatalystsdeposited.

Scheme S1 In-situ photodeposition.

The photo-reduction and photo-oxidation reactions can be described as follows:

Semiconductor +
$$nhv \rightarrow n (h^+ + e^-)$$

For photo-reduction deposition,

$$M^{n+} + ne^- \to M^0 \tag{1}$$

$$\frac{n}{6}CH_{3}OH + nh^{+} + \frac{n}{6}H_{2}O \rightarrow \frac{n}{6}CO_{2} + nH^{+}$$
(2)

For photo-oxidation deposition,

$$M'^{m+} + \frac{(n+m)}{2}H_20 + nh^+ \rightarrow M'_20 - \frac{n+m}{2} + (n+m)H^+$$
(3)

$$nH^{+} + \frac{n}{6}IO_{3}^{-} + ne^{-} \rightarrow \frac{n}{6}I^{-} + \frac{n}{2}H_{2}O$$
(4)

Where,

M is the noble metal for reduction, such as Pt, Au, Ag...

M' is the metal for oxidation, such as Mn, Co, Pb...

CH₃OH and IO₃⁻ are used as sacrificial reagents.

For a simultaneous photo-reduction and photo-oxidation deposition, the whole reaction can be divided into two half reactions, (1) and (3), sacrificial reagents are not used.