

Supporting Information

**Size-dependent Al-doped SrTiO₃ affecting solar-driven overall
water splitting**

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Materials and methods

Preparation of catalysts

The powdered Al^{3+} -doped SrTiO_3 catalysts were simply prepared by the polymerizable complexation method. Specifically, 3.26 mL of Isopropyl titanate (Shanghai Macklin Biochemical Co., 97%) as titanate sources was dissolved in 25 mL ethylene glycol (Shanghai Macklin Biochemical Co., 98%) under continuous stirring. After hydrolyzing for 30 min, 3.4885g of $\text{Sr}(\text{NO}_3)_2$ (Aladdin Reagents (Shanghai) Co., 99.5%) and a certain amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Shanghai Macklin Biochemical Co., 99.0%) were added, and stirring was continued for 5 hours. This was followed by the addition of citric acid (Shanghai Macklin Biochemical Co., $\geq 99.5\%$) at the molar ratio of (Ti+Sr): citric acid = 1: x (x=0, 0.55, 1.1, 1.65, 2.2, 3.3), and stirring continued until a unique transparent solution formed. The resultant homogeneous solution was steam-dried for 12 hours in an oil bath to accelerate polymerization. After heating and evaporation of the solvent, the reaction mixture condensed into a transparent brown resin. The resulting brown complexation was calcined in air at 623 K for 3 hours with a slow heating rate, followed by 973 K for 4 hours, and then ground to obtain fine nanopowder. Subsequently, the objective nanopowder was mixed with a stoichiometric amount of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (Shanghai Macklin Biochemical Co., 99.5%) using an agate mortar and calcined in a muffle furnace under airflow at 1423 K for 10 hours. Finally, the mixture was centrifuged and washed repeatedly 10 times with deionized water. The obtained Al^{3+} -doped SrTiO_3 nanopowder without citric acid was recorded as Non-CA and the other nanopowder (x=0.55, 1.1, 1.65, 2.2, 3.3) were recorded as 0.55-CA, 1.1-

CA, 1.65-CA, 2.2-CA, 3.3-CA, respectively.

Loading cocatalysts

The SrTiO₃:Al powder was loaded with RhCrO_x (0.1 wt% Rh and 0.05 wt% Cr) and CoOOH (0.05 wt% Co) by Step-by-step Photodeposition. The concentrations of 0.01693 mol/L Na₃RhCl₆·12H₂O (Alfa Aesar (China) Chemical Co., 17.1 wt% as Rh) and 0.04 mol/L K₂CrO₄ (Shanghai Macklin Biochemical Co., 99.5%) were formulated and applied as Rh and Cr sources, respectively. The synthetic SrTiO₃:Al nanopowder (100 mg) was dispersed in a certain amount of deionized water. Secondly, the appropriate amount of Na₃RhCl₆·12H₂O solution was added into the suspension under continuous stirring, and the resulting mixture was exposed to a 300 W xenon lamp ($\lambda > 250$ nm; Profect Light, PLS-SXE300+UV, see Supporting Information, Figure S1) for 2 hours. Since deposition requires a closed environment, it is necessary to remove air from the system to maintain a vacuum each time a cocatalyst is added. Subsequently, the K₂CrO₄ solution was incorporated into the suspension under irradiation for 1 hour, followed by the addition of Co (NO₃)₂ ·6H₂O (Shanghai Macklin Biochemical Co., 99.99%) solution with additional irradiation for 1 hour. Finally, the deposited products were cleaned three times and dehydrated at 338 K, then represented as Non-CA/ RhCrO_x/ CoOOH and x-CA/ RhCrO_x/ CoOOH, respectively.

Photocatalytic activity tests of catalysts

The water-splitting reaction and gas production process occurred in a closed gas circulation system (MC-SPH20-A, Merry Change) under ultraviolet irradiation from a 300 W xenon lamp ($\lambda > 300$ nm, MC-PF300B, Merry Change). The spectrum

distribution data of the xenon lamp and light intensity are recorded in Figure S2 and Table S1, separately. 40 mg of the deposited samples loaded with RhCrO_x and CoOOH cocatalysts were dispersed in 80 mL of deionized water and placed in a photocatalytic quartz reactor to engage in a water-splitting reaction. Before the water splitting test, the air in the system is removed using a vacuum pump (2XZ-4B, Yonghao Vacuum Equipment Co.) to ensure closed. During the reaction, a flow of cooling water maintained the temperature of the reactant solution at 298 K. A gas chromatograph (GC-2014C, Shimadzu Co.) equipped with a molecular sieve and thermal conductivity detector was used to analyze the evolved gases.

The apparent quantum yield (AQY) has brought more accurate and rigorous references for photocatalyst activity evaluation. The AQY values were identified under irradiation from a xenon lamp installed with a 365 nm monochromatic filter in Figure S3 and the specific test method and procedure were consistent with previous reports. Moreover, the AQY is determined by the following equations¹⁻⁵.

$$\begin{aligned} \text{AQY} &= [\text{number of reacted electrons} / \text{number of incident photons}] \times 100\% \\ &= [2 \times \text{number of H}_2 \text{ molecules evolved in 1 h} / \text{number of incident photons} \\ &\quad \text{in 1 h}] \times 100\% \end{aligned}$$

Electrochemical measurements

With as-prepared catalysts, a mixed suspension of deionized water, anhydrous ethanol (Sinopharm Chemical Reagent Co.) (volume ratio 1:2) containing 10 mg target catalyst and 50 μ L Nafion solution (Shanghai Macklin Biochemical Co.) was prepared. After temporary ultrasonic treatment, the mixed suspension was uniformly dispersed

on the FTO with an effective area of 2.25 cm² using the spray method, to obtain prepared electrode sheets. This coating process should be dried at 473 K on a constant temperature heating station (Weitek Electronics Co.). Moreover, the prepared electrode sheets were annealed at 673 k for 2 hours. The electrochemical evaluation is performed by using an electrochemical workstation (CHI 760, Chenhua Instrument Co.) equipped with a three-electrode quartz cell with Ag/AgCl as the reference electrode, Pt sheet as the counter electrode and FTO coated with the target catalyst as the working electrode. The Mott-Schottky were measured at a frequency of 1000 Hz. The electrochemical measurements were performed in phosphate buffer and 1.0 M K₂SO₄ aqueous solution (pH = 7). Besides, based on the following equation, the electrochemical potential was converted to a reversible hydrogen electrode potential¹⁻³.

$$E_{\text{RHE}} = E(\text{Ag/AgCl}) + 0.197 \text{ V} + 0.059 \times \text{PH.}$$

Transient current-time (*i-t*) curves were conducted on a light turn-on/off system with an applied potential of 0 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was measured under light irradiation with 5 mV amplitude and a frequency range from 10 kHz to 0.01 Hz at a potential of 0 V vs. Ag/AgCl.

Photocatalysts' characterizations

The multifunctional X-ray diffractometer (XRD) patterns were recorded on a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source. The field emission scanning electron microscopy (FE-SEM) images were demonstrated with a Gemini SEM 300 scanning electron microscope. The transmission electron microscopy (TEM) high-resolution TEM (HRTEM) images were conducted on a JOEL JEM-2100F

electron microscope. And again, the selected area electron diffraction (SAED), the energy-dispersive X-ray (EDX) spectroscopy, and the scanning TEM-EDX element mapping were obtained from the JOEL JEM-2100F electron microscope. Valence band X-ray photoelectron spectroscopy (VB-XPS) measurements were implemented on a Thermo Scientific K-Alpha with an Al K α radiation source. The UV-visible diffuse reflectance spectra (UV-vis DRS) of the catalysts were detected by a UV-vis spectrophotometer (Shimadzu UV-2600) over the range of 200-800 nm. The photoluminescence spectra (PL) and the time-resolved fluorescence spectroscopy of the catalysts with an excitation wavelength of 375 nm were performed on an FLS1000 spectrometer.

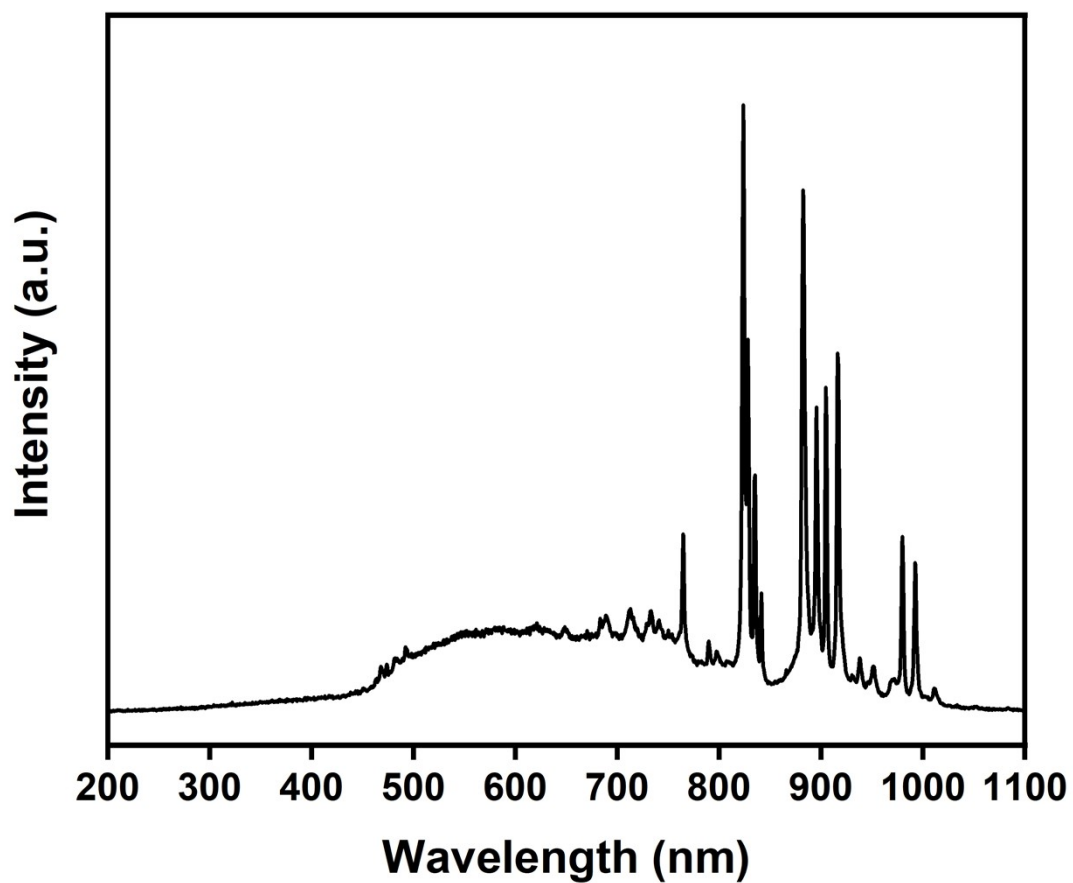


Figure S1. The spectrum of the 300 W Xenon lamp for the stepwise photo-deposition procedure.

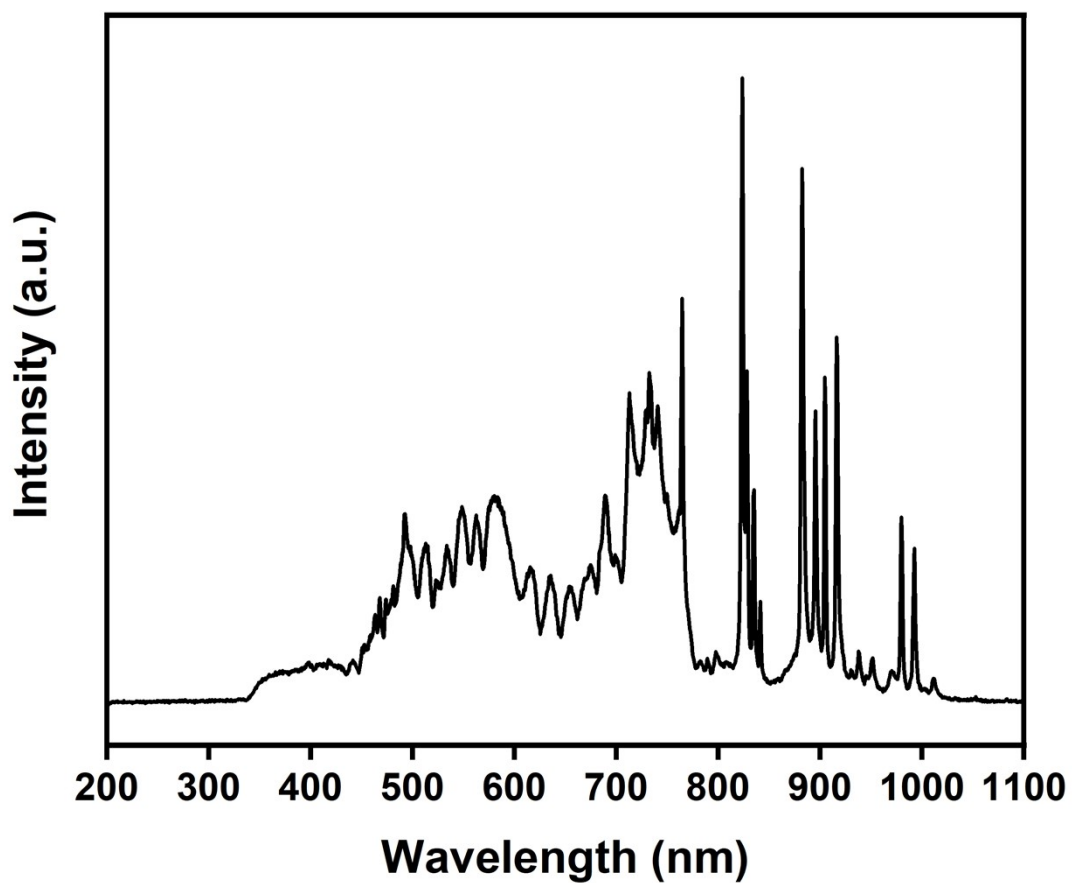


Figure S2. The spectrum of the 300 W Xenon lamp for overall water splitting activity testing procedure.

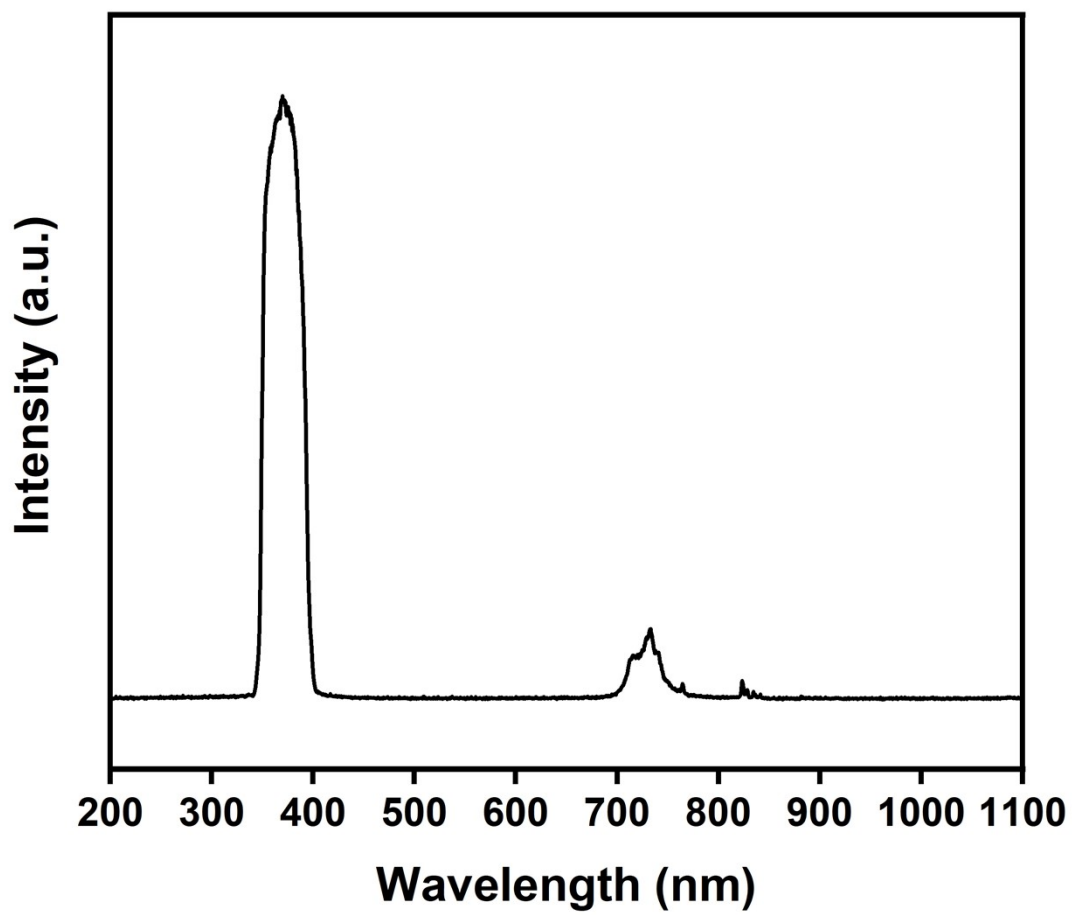


Figure S3. The spectrum of the 300 W Xenon lamp with a 365 nm monochromatic filter for the AQE test procedure.

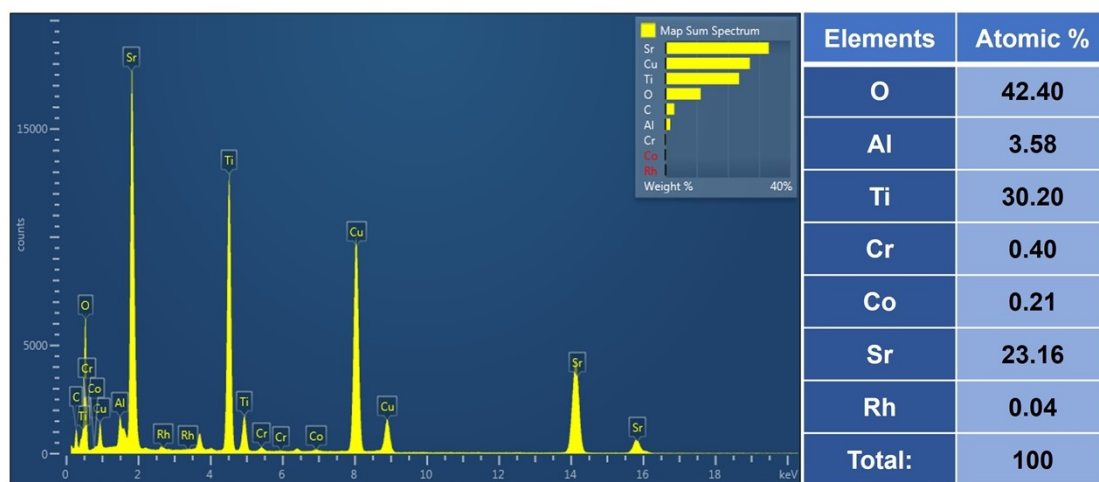


Figure S4. EDS spectrum of 1.1-CA loading Rh (0.1% wt%) / Cr (0.05 wt%) / Co (0.05 wt%).

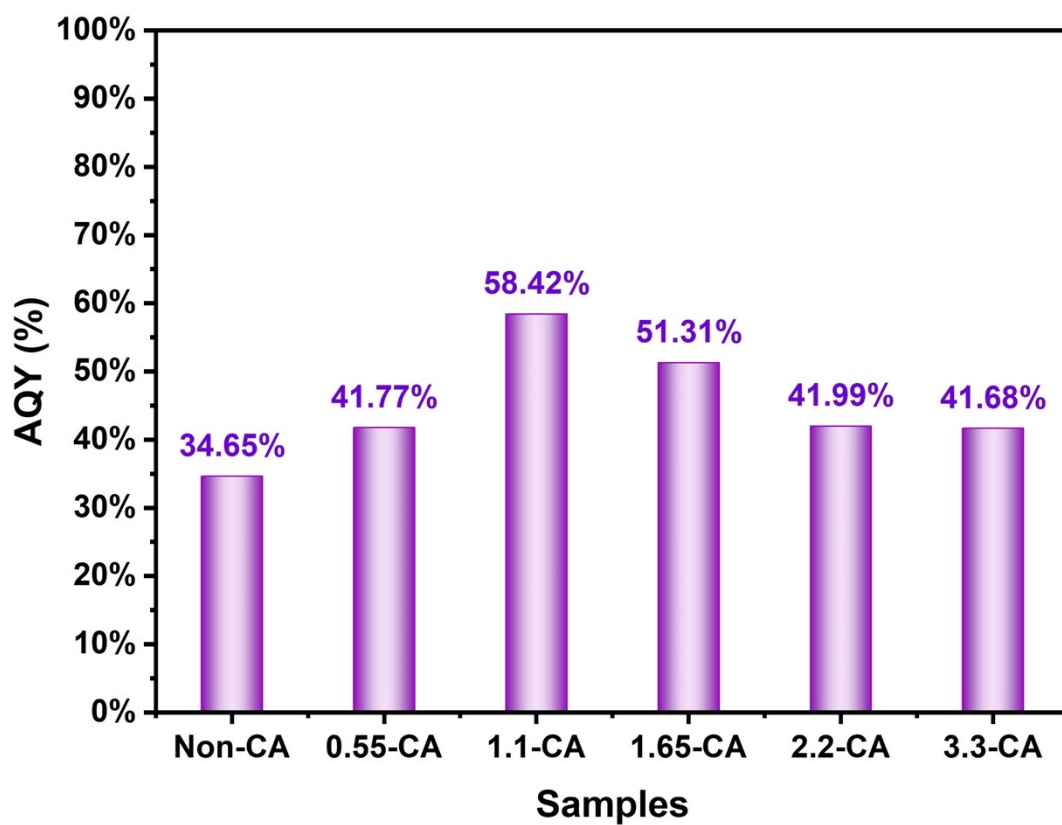


Figure S5. The apparent quantum yield (AQY) measurements of samples.

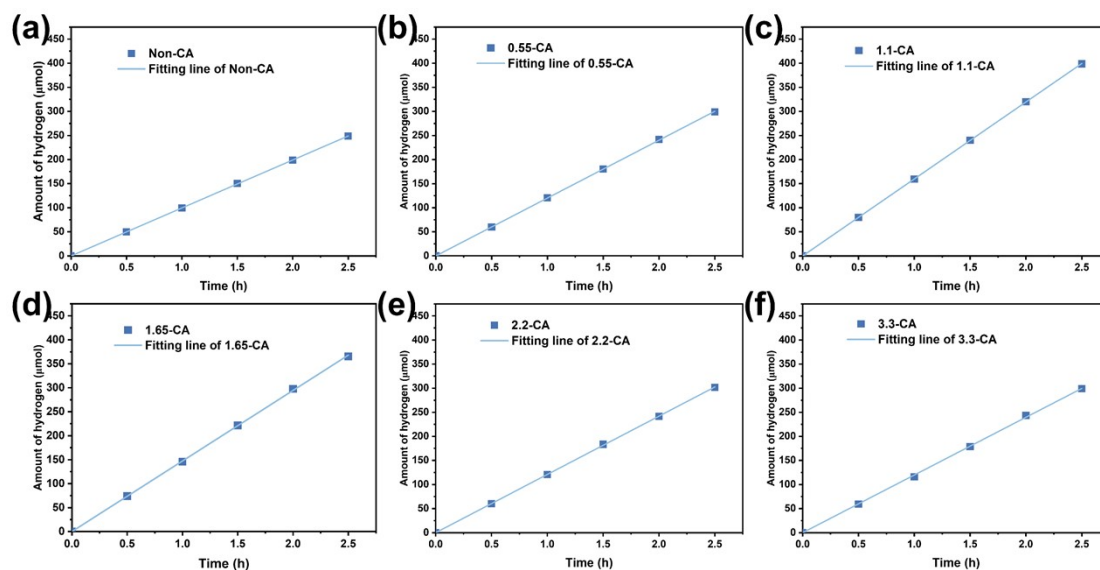


Figure S6. The apparent quantum efficiency (AQE) measurement result of all samples loaded with Rh (0.1% wt%) / Cr (0.05 wt%) / Co (0.05 wt%) during photocatalytic water splitting. The evolution rate shown in the fitting result is $99.55 \mu\text{mol}\cdot\text{h}^{-1}$, $120.19\mu\text{mol}\cdot\text{h}^{-1}$, $159.78 \mu\text{mol}\cdot\text{h}^{-1}$, $147.24 \mu\text{mol}\cdot\text{h}^{-1}$, $120.82 \mu\text{mol}\cdot\text{h}^{-1}$, and $119.93 \mu\text{mol}\cdot\text{h}^{-1}$, respectively.

The apparent quantum efficiency (AQE) value (the ratio of the number of electrons involved in the reaction to the number of incident photons) measurement was inferred according to the following equations:

$$\begin{aligned} \text{AQE (\%)} &= \frac{N_{e^-}}{N_P} \times 100\% \\ &= \frac{N_{(\text{H}_2)} \times 2}{N_P} \times 100\% \\ &= \frac{\mu\text{mol} \times N_A \times 10^{-6} \times 2}{\frac{I \times A \times t}{E_g \times J}} \times 100\% \end{aligned}$$

where N_{e^-} , N_P and N_{H_2} refer to the number of electrons involved in the water splitting reaction, the number of incident photons in contact with the suspension and number of

hydrogen molecules generated, respectively. $N_A = 6.02 \cdot 10^{23}$, t (time) = 3600 s, $E_g =$
 $1240/\lambda$, ($\lambda=365$ nm), A (area) = 7.0686 cm², $J = 1.6 \cdot 10^{-19}$ j.

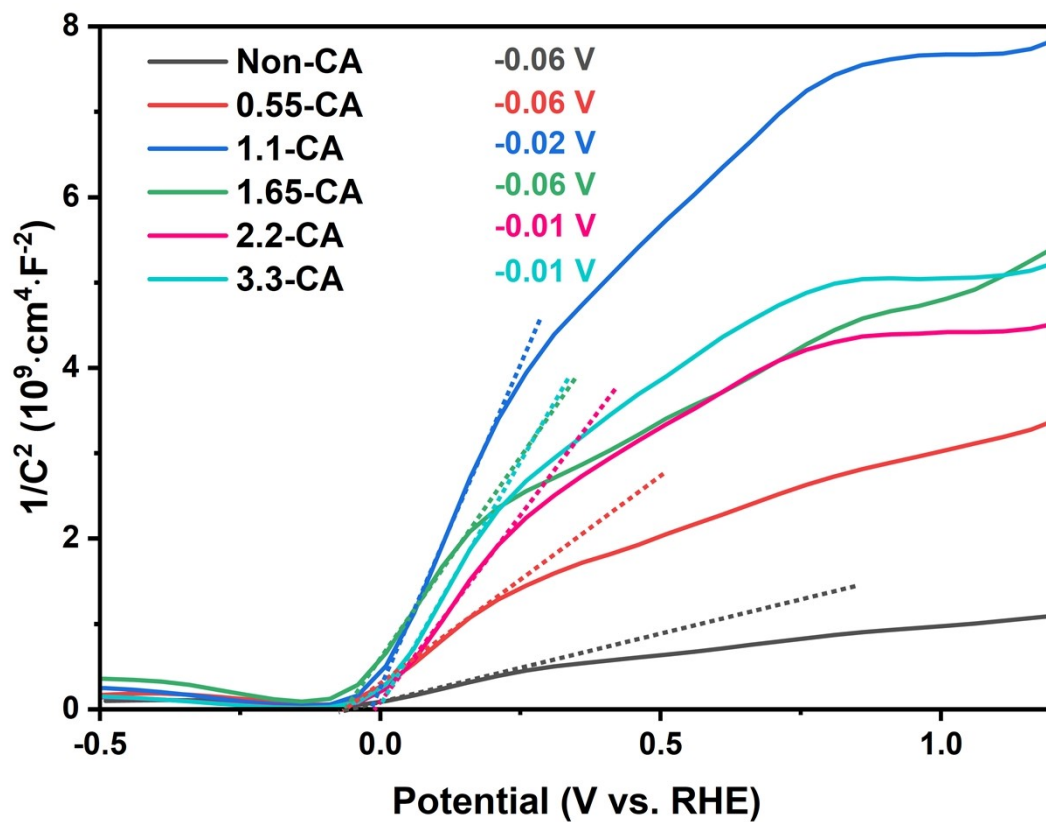


Figure S7. The Mott-Schottky curves of all samples.

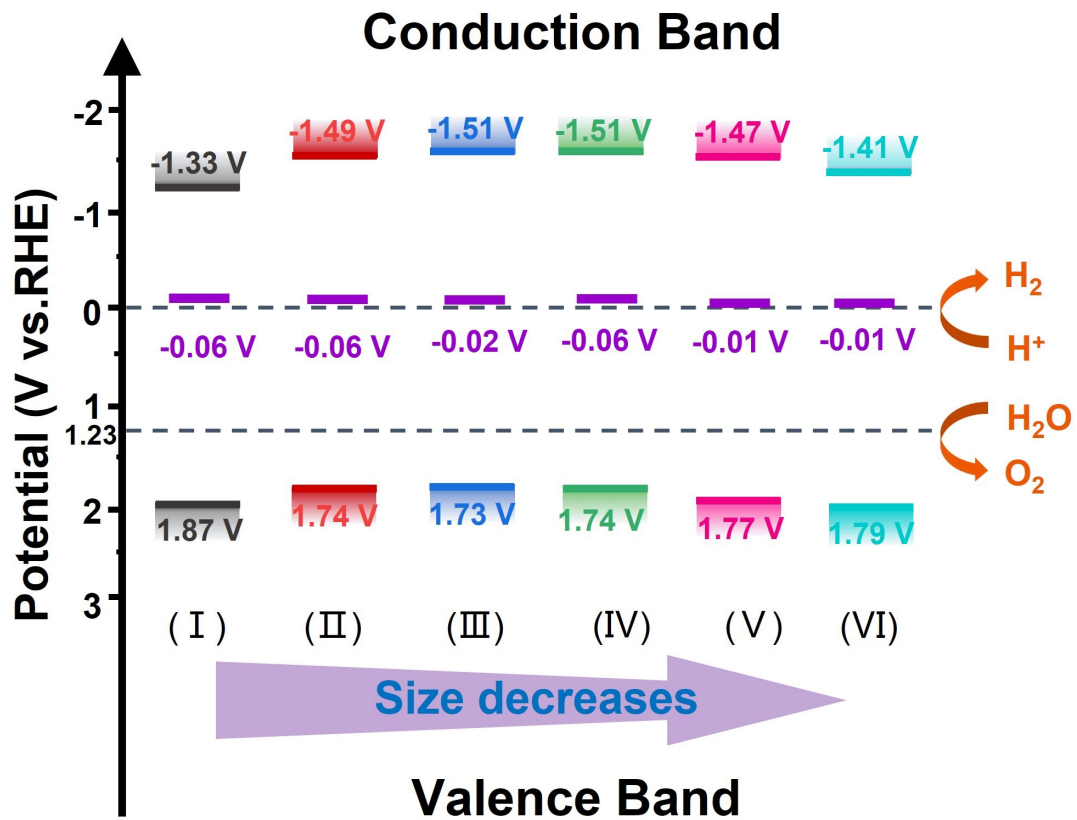


Figure S8. The band structure diagram of samples.

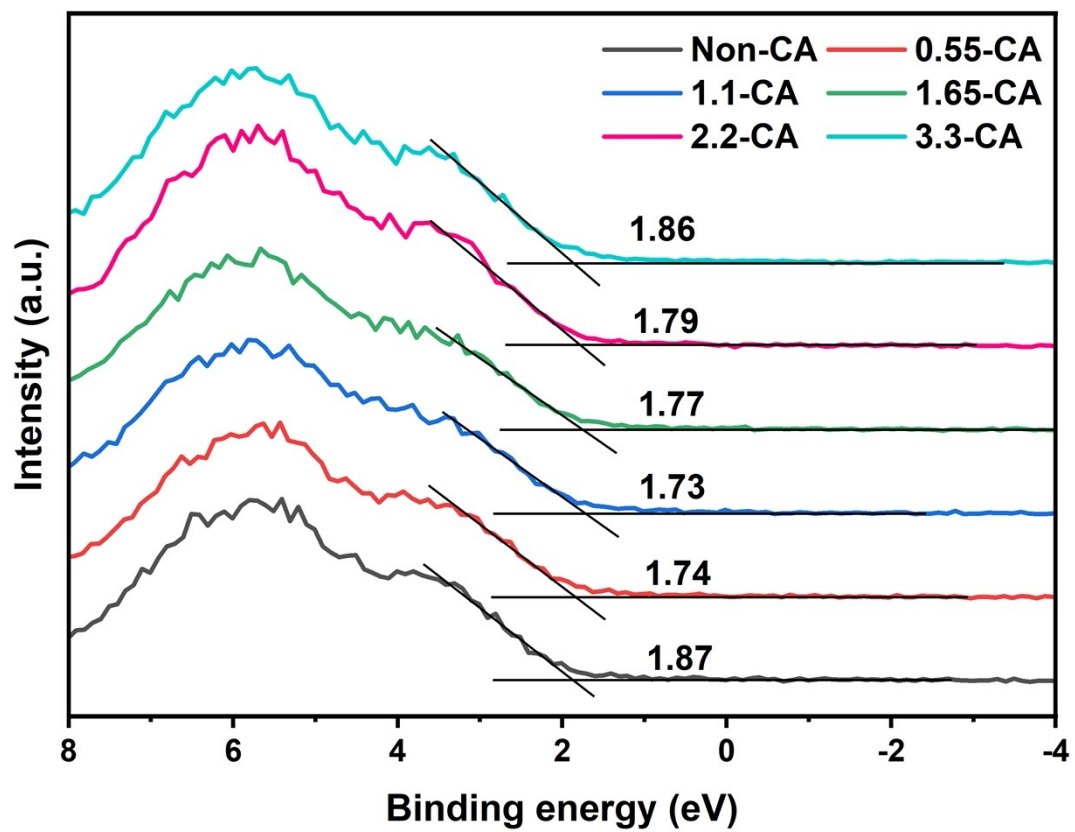


Figure S9. Valence band X-ray photoelectron spectroscopy (VB-XPS) spectra of samples.

Table S1 The irradiation intensity data were collected under a 365 nm monochromatic filter for the quantum yield test and full spectrum for the activity test.

Spot position	Irradiation intensity (mW/cm ²)	
	Natural sunlight	365 nm
(1)	1049	8.5
(2)	839	8.3
(3)	1150	6.5
(4)	885	4.5
(5)	906	5.4
(6)	1060	6.0
(7)	1158	8.5
(8)	1620	9.8
(9)	1290	9.7
Average	1106	7.5

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