

## Electronic Supplementary Information

# Design of 3D artificial leaves with spatially separated active sites for H<sub>2</sub> and O<sub>2</sub> generation and their application in water splitting

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## Experimental Section

### 1. Synthesis of 3D CoO<sub>x</sub>/TiO<sub>2</sub>/Pt artificial leaves

The fresh green leaves (*Pritchardia gaudichaudii*) used as biological templates were obtained from the plant plots of Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. Before use, the leaves were washed by water. The water used throughout all experiments was purified through a Millipore system. The fresh leaves were cut into 1 cm × 1 cm pieces and pretreated with 5 % HCl solution for 12 h to remove the K, Ca, Mg, P and other ions. In a typical synthesis, a concentrated ammonia solution (0.3 mL, 28 wt%), absolute ethanol (100 mL), tetrabutyl titanate (0.75 mL, TBOT) were added into a beaker flask. Then, the pretreated leaves were added into the above solution, the reaction was allowed to proceed for 8 h at 45 °C under continuous mechanical stirring. After that, the leaves were taken out and washed with deionized water and ethanol for 3 times, respectively, then were dried at 45 °C overnight. Finally, the obtained leaves were calcined in air at 550 °C for 2 h with a constant heating rate of 1 °C min<sup>-1</sup>.

Loading of CoO<sub>x</sub> and Pt cocatalysts: CoO<sub>x</sub> cocatalyst was loaded onto the inner surface of TiO<sub>2</sub> leaves by an ion exchange method. The Co<sup>2+</sup>-leaves were prepared by stirring pretreated leaves, a given amount of Co(Ac)<sub>2</sub>, ultrapure water (18.2 MΩ, 10 mL) in the dark for 48 h. After filtering and washing with water, the leaves were dried in air overnight. After coating of TiO<sub>2</sub> and calcining in air at 550 °C, the CoO<sub>x</sub> cocatalyst was obtained on the inner surface of TiO<sub>2</sub> leaf. The Pt cocatalyst was loaded onto the outer surface of TiO<sub>2</sub> leaf by a photoreduction method. CoO<sub>x</sub>/TiO<sub>2</sub> leaf was immersed in 20 mL of H<sub>2</sub>PtCl<sub>4</sub> aqueous solution of different concentrations. The suspension was stirred and irradiated by UV light (300 W Xe lamp) for 30 min, the precipitates were collected by centrifugation, then, rinsed with deionized water and ethanol, finally dried at 60 °C in an oven.

### 2. Characterizations

Crystalline phases were examined by X-ray diffraction (XRD) using a Rigaku D/Max-2550 diffractometer with CuK<sub>α</sub> radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at 50 kV and 200 mA in the 2 $\theta$  range 20–80° with a scanning rate of 5° min<sup>-1</sup>. Scanning electron microscopy (SEM) measurements were made by using a XL30 ESEM FEG scanning electron microscope (FEI Company). Transmission electron microscopy (TEM) measurements were made by using a HITACHI H-8100 EM (Hitachi, Tokyo, Japan). The Brunauer–Emmett–Teller (BET) surface areas and porosity of the samples were determined using a Micro-meritics ASAP 2020 nitrogen adsorption apparatus. All the samples were degassed at 180 °C prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05–0.3. Desorption data were used to determine the pore size distribution via the Barret-Joyner-Halender (BJH) method. The volume of adsorbed nitrogen at the relative pressure ( $P/P_0$ ) of 0.969 was used to determine the pore volume and average pore size. The loading contents of Co for all samples were measured by Inductively Coupled Plasma optical emission spectrometer (ICP-OES, Focused Photonics).

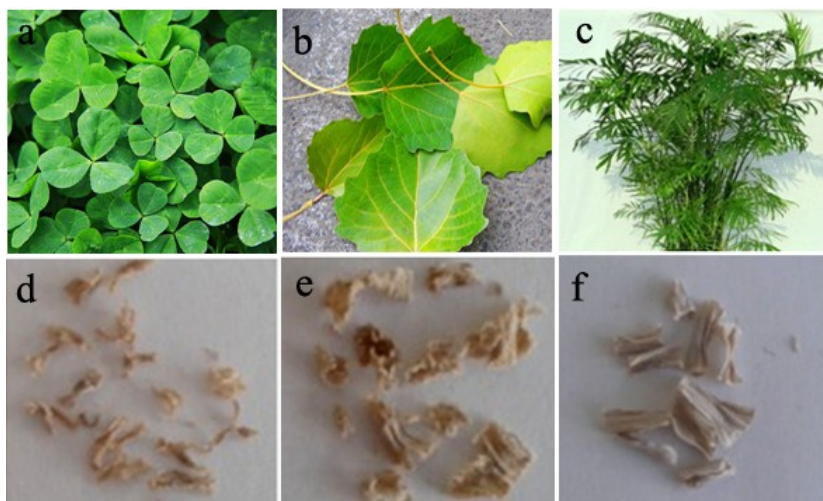
### 3. Photocatalytic H<sub>2</sub> evolution

The photocatalytic reaction was carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system (Fig. S9). A 300 W Xe lamp equipped with a 365 nm band-pass filter was used as the light source. The reaction was performed in distilled water containing 40 mg of the sample. Before irradiation, the suspension was dispersed by ultrasonication and bubbled with nitrogen to remove the dissolved oxygen. The evolved gases were measured by on-line gas chromatography (CLARUS 580 GC, PerkinElmer) with a thermal conductivity detector and nitrogen carrier gas. The photoreduction of water to H<sub>2</sub> was performed in 50 mL aqueous solution containing 10 mL of 20 vol % CH<sub>3</sub>OH. CH<sub>3</sub>OH was used as a sacrificing electron donor, and reacted with the photoinduced hole of valance band, which would inhibit the recombination of photoinduced electron-hole pairs. Photooxidation of water to O<sub>2</sub> was performed using an aqueous AgNO<sub>3</sub> solution (0.02 M, 50 mL), AgNO<sub>3</sub> was used as a sacrificing electron acceptor, reacted with the photoinduced electron of conduction band, thus would inhibit the recombination of photoinduced electron-hole pairs. The comparison experiments were prepared with the same quality of the photocatalysts.

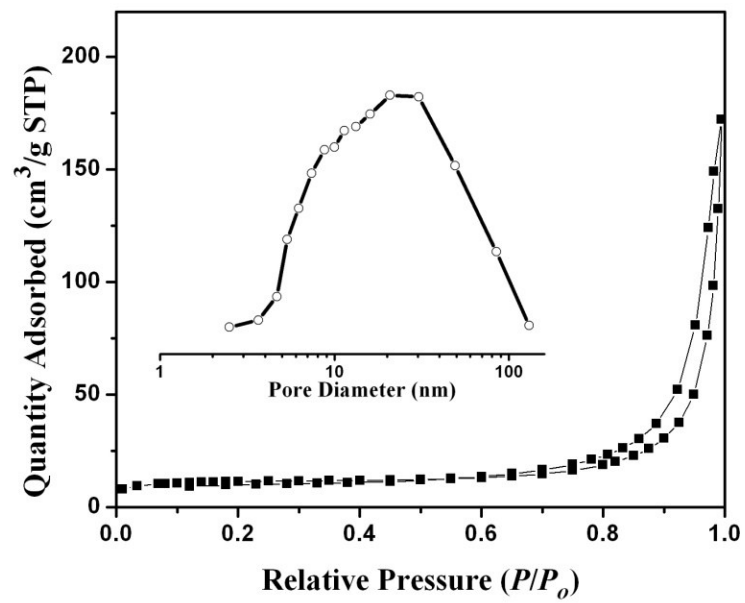
The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction conditions and it was calculated according to the following equation:

$$\begin{aligned}
 \text{QE } [\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident electrons}} \times 100 \\
 &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \quad (i)
 \end{aligned}$$

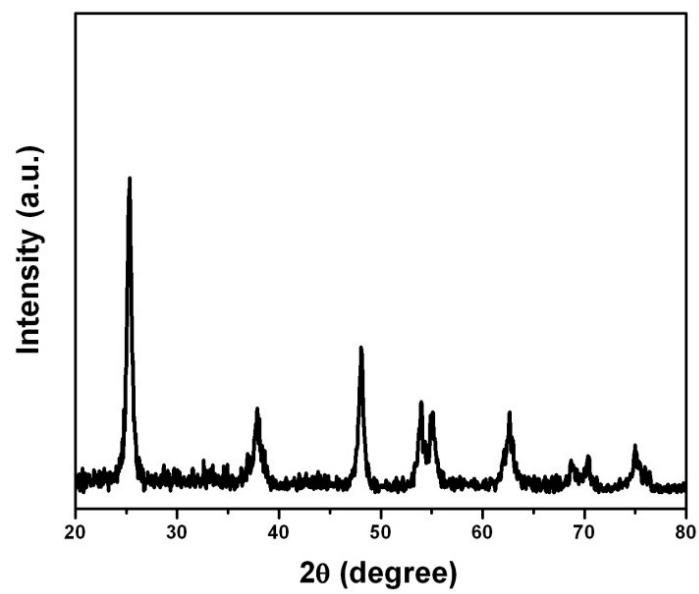
The number of incident photons was  $1.48 \times 10^{17}$  photons/s which was measured by using a calibrated Si photodiode.



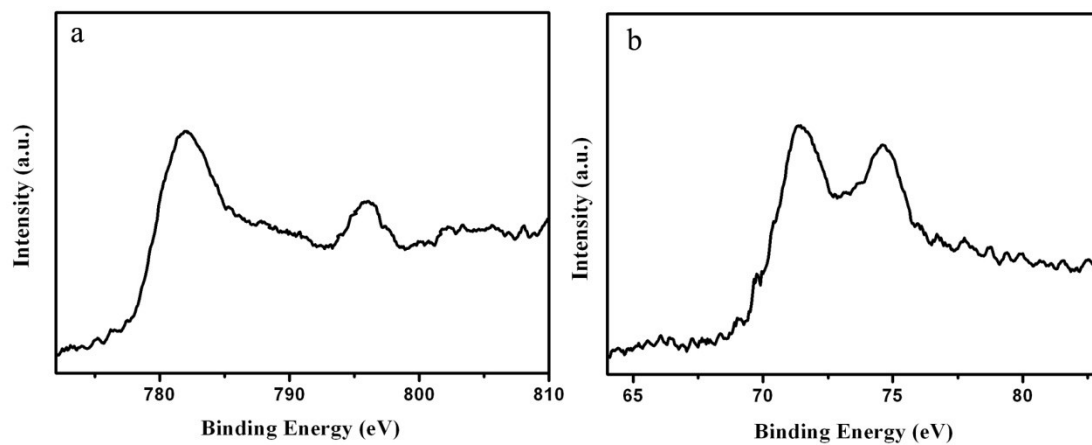
**Fig. S1** The photograph of the as-prepared artificial leaves using different biotemplates, (a,d) *Trifolium repens L.* leaves, (b,e) aspen leaves and (c,f) *Pritchardia gaudichaudii* leaves.



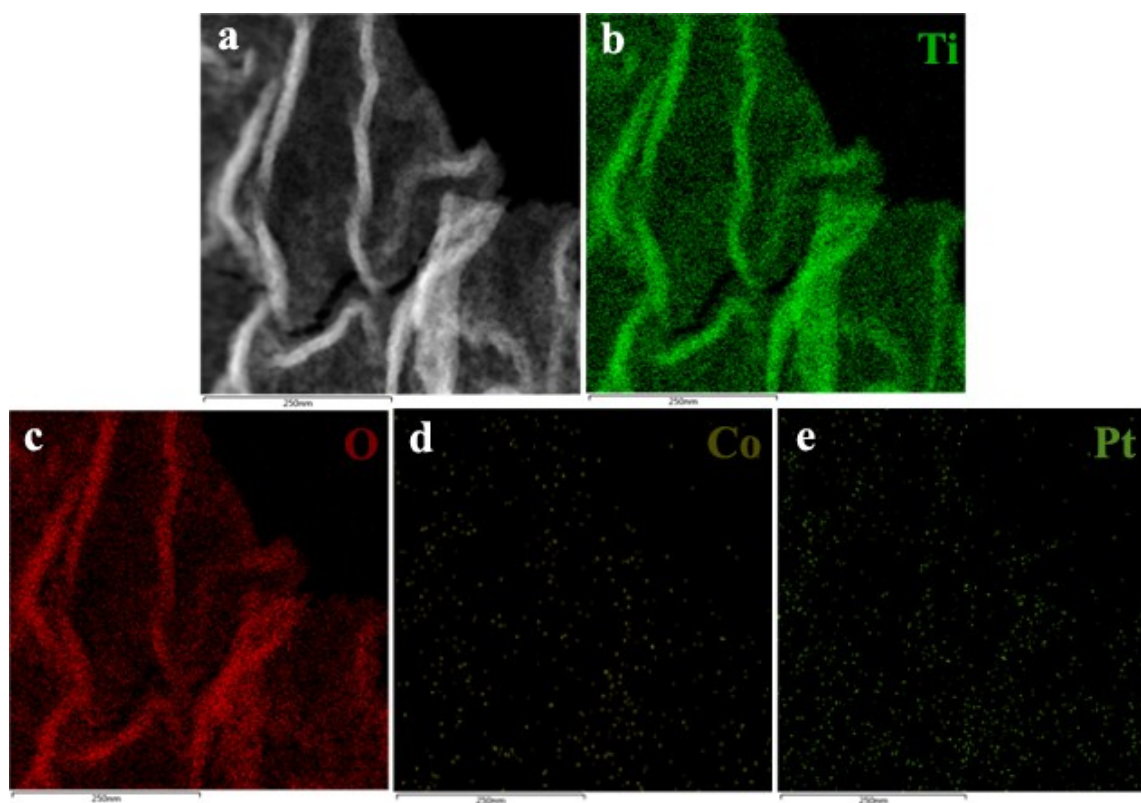
**Fig. S2** N<sub>2</sub> adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of the 3D TiO<sub>2</sub> artificial leaves.



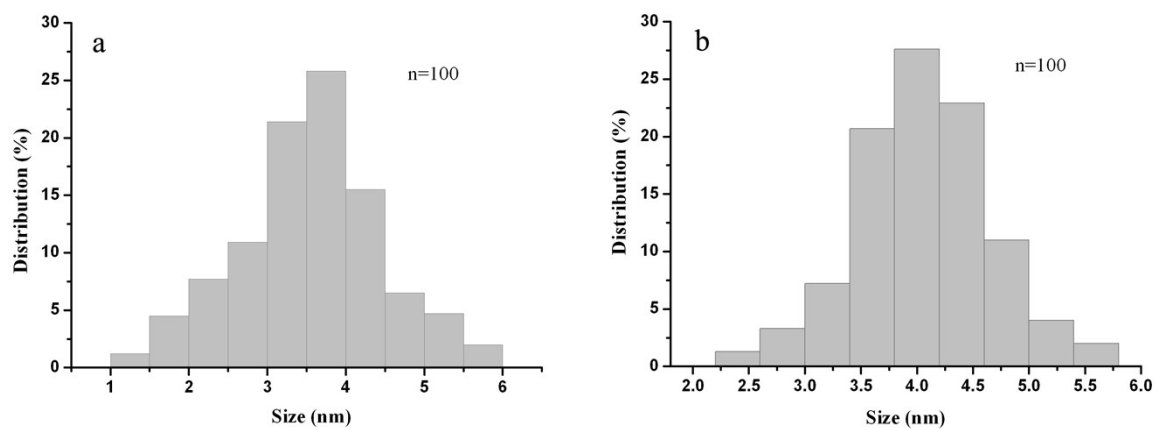
**Fig. S3** XRD pattern of the 3D 0.144 wt% CoO<sub>x</sub>/TiO<sub>2</sub>/3 wt% Pt artificial leaves.



**Fig. S4** XPS spectra of (a) Co 2p and (b) Pt 4f for the 0.144 wt% CoO<sub>x</sub>/TiO<sub>2</sub>/3wt% Pt artificial leaves.

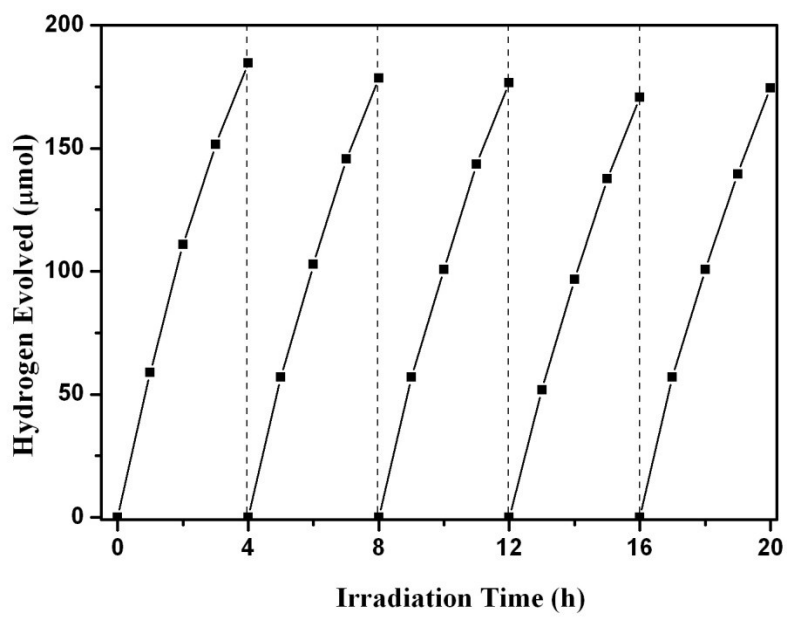


**Fig. S5** EDS mapping images of Ti, O, Co, Pt elements for the 0.144 wt%  $\text{CoO}_x/\text{TiO}_2/3$  wt% Pt artificial leaves.

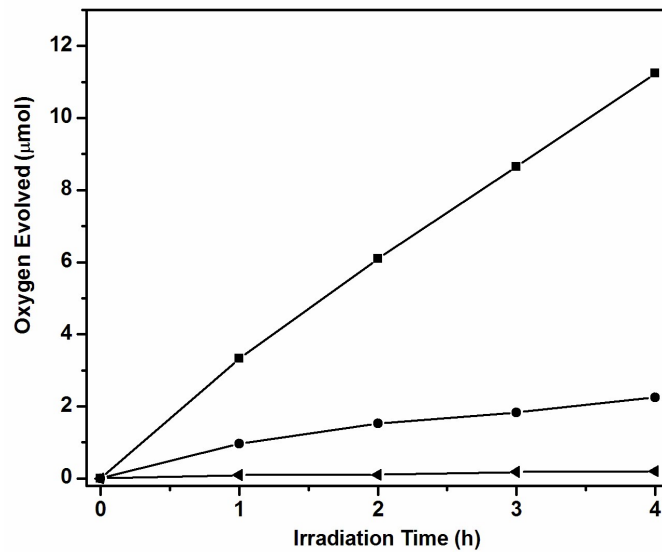


**Fig. S6** The size distribution histograms of (a) CoO<sub>x</sub> and (b) Pt nanoparticles.





**Fig. S7** Cycling performance of the 0.144 wt% CoO<sub>x</sub>/TiO<sub>2</sub>/3 wt% Pt artificial leaves.



**Fig. S8** Time courses of photocatalytic O<sub>2</sub> evolution on the (■) 0.144 wt% CoO<sub>x</sub>/TiO<sub>2</sub>/3 wt% Pt artificial leaf, (●) both 0.144 wt% CoO<sub>x</sub> and 3 wt% Pt loaded on the outer surface of TiO<sub>2</sub> artificial leaf with AgNO<sub>3</sub> as a sacrificing agent. (◄) 0.144 wt% CoO<sub>x</sub>/TiO<sub>2</sub>/3 wt% Pt artificial leaf without adding AgNO<sub>3</sub> a sacrificing agent.



**Fig. S9** The photograph of the experimental setup of the photocatalytic H<sub>2</sub> production.

The photocatalytic on-line analysis system mainly includes the following sections: a Pyrex reaction cell, a closed gas circulation and evacuation system, Xe lamp, gas chromatography, and computer.