## Supplementary Information

### Experimental Section：

All chemicals are analytically pure and can be used without further purification. Ultrapure water was used in the whole study.

Preparation of $Sb_2MoO_6$: $Sb_2MoO6$ was prepared by a typical hydrothermal method. First,0.19g $SbCl_3$ and 0.1g $Na_2MoO_4 \cdot 2H_2O$ were added to 20 mL of absolute ethanol sonicated 10 min and stirred for 30 min (adjusting pH to 11 with NaOH). Subsequently, the suspension was heated up to 170°C in a polytetrafluoroethylene lined autoclave for 2h to yield green powder. Finally, the products were washed, centrifuged and dried at 60°C to obtain $Sb_2MoO_6$ samples.

Preparation of PCN: The material of PCN was obtained by a high-temperature solid phase method, and urea was used as a raw material, and it was kept at 550 °C for 2 hours in a muffle furnace at a heating rate of 10 °C / min.

Preparation of $Bi_2O_3$: First, 0.49g $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in dilute acetic solution adjusting pH to 7 with $NH_3 \cdot H_2O$ (4.6 mL, 25 wt% NH3). Subsequently, the suspension was hydrothermally treated at 150 °C for 3 h. After cooling down to room temperature, the products were centrifuged, washed and dried at 60 °C for 5 h to get the precursor.
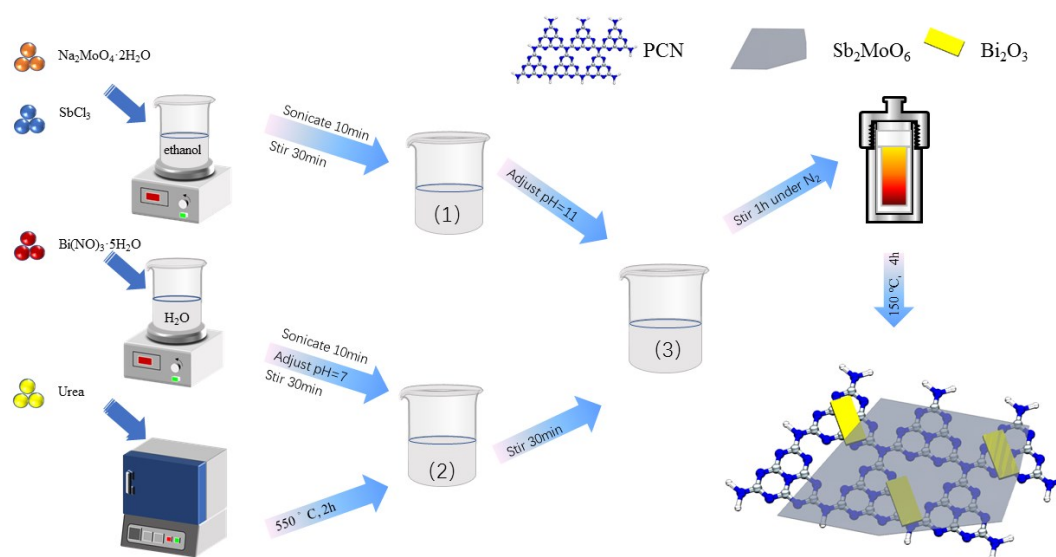


Scheme.S1 Fabrication of SMBC

Preparation of PCN/Bi$_2$O$_3$/Sb$_2$MoO$_6$ (be called SMBC for short): SMBC heterojunction was prepared by a facile hydrothermal method. First 0.09g SbCl$_3$ and 0.05g Na$_2$MoO$_4$•2H$_2$O were added to 20ml of absolute ethanol, sonicate for 10min, stir for 30min, and adjust the pH to 11 with NaOH, then make the solution as number (1) 0.97g Bi(NO$_3$)$_3$•5H$_2$O was added into 10ml water with stirring and ultrasonic, then mix it with 0.3g PCN and adjust the pH to 7 with ammonia water, the solution is number (2). Solution (3) was obtained by mixing solution (1) and (2) under N$_2$ and stir for 1 hour. Then the solution (3) was put into the inner lining of a hydrothermal kettle of PTFE to be heated with water at 150°C for 4 hours. The solution was centrifuged, washed and dried at 60°C to obtain the SMBC composite material. The composite SMBC samples with different Sb$_2$MoO$_6$ weight ratios are labeled as SMBC-x (x = 2.5 wt%, 5 wt%, 7.5 wt%, 10 wt%)，which wererespectively correspond with SMBC1-4.

## Characterization:

Photoelectrochemical measurements: Photoelectrochemical properties of as-prepared samples are collected by the electrochemical workstation (CS 310, Wuhan Corrtest Instrument Co. Ltd.) in a conventional three-electrode system with different photocatalyst coated FTO as working electrodes, a platinum foil counter electrode and an Ag/AgCl (saturated KCl) electrode as a reference electrode. All electrodes are immersed in the Na$_2$SO$_4$ electrolyte solution (0.1 mol L$^{-1}$).Moreover, EIS tests are carried out over the frequency range of 0.01 Hz to 100k Hz with the sinusoidal ac perturbation of 10 mV.

Photocatalytic degradation test: The photodegradation of RhB under various light irradiation is carried out at ambient temperature. In a typical photodegradation procedure, 50 mg photocatalysts are suspended in the RhB solution (10 mg/L, 100 mL) and stirred for 30 min in dark to establish the adsorption–desorption equilibrium. Then, a facility equipped with a LED lamp (50 w) with Vis light source（410nm - 760nm） to start the photocatalysis reactions. A series of certain volume of suspension are taken out at given time interval and centrifugated to remove photocatalyst particles. Finally, the concentration of the RhB at different time are detected via a UV–vis spectrophotometer (PE Lambda 950).

Photocatalytic water splitting test: The photocatalytic O$_2$ evolution experiments are performed

in an automatic gas circulation system (CEL-SPH2N-D9). In a typical photocatalytic $O_2$ evolution process, 50mg photocatalysts are dispersed in 50mL distilled water with a stationary temperature at 6 ºC. The suspension is then thoroughly degassed and irradiated under different light using a 300W Xe lamp equipped with UVIRCUT filter for Vis light (420–780 nm). Finally, the amount of liberated $O_2$ is obtained by the gas chromatography (GC7920, TCD, Ar as a carrier gas).

Sample Characterization: Powder crystalline structures of the samples are characterized through the Bruker D2 PHASER X-ray di□ractometer (XRD) with graphite monochromator using Cu Kα radiation (λ= 1.54184 Å). The surface properties are detected by X-ray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics) under a monochromated Al Ka irradiation. The morphologies of the prepared samples and the energy dispersive X-ray spectroscopy (EDX) spectrum are detected by field emission scanning electron microscopy (FESEM, Hitachi, 30 S-4800N). Moreover, the transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM). The absorption spectra are obtained by a UV–Vis-NIR spectrophotometer (PE Lambda 950) with $BaSO_4$ as a reference with wavelengths in the 200–2500 nm range.
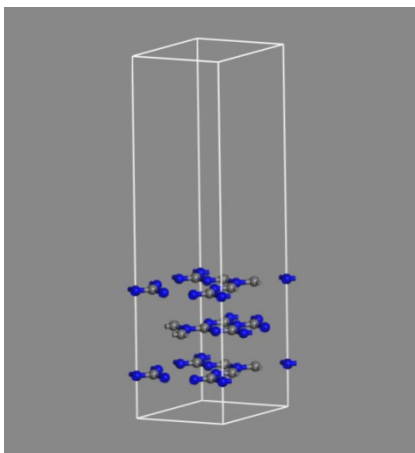
Computational Methods:



Fig.S1 The molecular model of carbon nitride

DFT (Density Functional Theory) calculations were carried out using the VASP (Vienna Ab Initio Simulation Package), the molecular model of carbon nitride for DFT calculation is shown in Fig.S1.The exchange-correlation interactions were treated within the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional. The

electron wave functions were expanded using plane waves with a cutoff energy of 400 eV, and the convergence criteria for the residual force and energy on each atom during structure relaxation were set to 0.005 eV/Å and $10^{-5}$ eV, respectively. Hybrid functionals based on the Heyd-Scuseria-Ernzerhof (HSE06) method were adopted to get the exact band structures of the g-C3N4, $Bi_2O_3$ and $Sb_2MoO_6$ catalysts.