Electronic Supplementary Information (ESI)

Biomimetic Structure Design and Construction of Cactus-like $MoS_2/Bi_{19}Cl_3S_{27}$ Photocatalyst for Efficient Hydrogen Evolution

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Experimental

All the chemicals were of analytical grade, purchased from Sino pharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received without further purification.

Materials Preparation

$Bi_{19}Cl_3S_{27}$ nanorods were prepared by the method reported in our previous work.[21]

$MoS_2/Bi_{19}Cl_3S_{27}$ heterostructures (noted as MBH) were synthesized via a facile in situ hydrothermal route assisted by glucose. Typically, 30 mg sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and 60 mg thioacetamide (C_2H_5NS) were dissolved in 40 mL glucose solution (0.03 mol L^{-1}) by ultrasonication for 1 h, then, a certain amount of $Bi_{19}Cl_3S_{27}$ were added (the theoretical weight percent of MoS_2 in the 1D $Bi_{19}Cl_3S_{27}$ nanorods were designed to be 1, 3, 5 and 10 wt%), after agitation for another 1 h, the suspension were been transferred into a 100 mL Teflon-lined stain-less steel autoclave and kept at 180 °C for 24 h, and then naturally cooled to ambient temperature, the black product (labeled as MBH-1, MBH-3, MBH-5 and MBH-10) were rinsed with deionized water and ethanol several times before being dried in an oven.

In the typical synthesis procedure of MoS_2 nanosheets, 30 mg of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and 60 mg of thioacetamide (C_2H_5NS) were dissolved in 40 mL deionized water (H_2O) with the ultrasonication until the solvents were well-distributed and solution was homogeneous, Subsequently, the solution was transferred into a 100 mL Teflon-lined stain-less steel autoclave and kept at 180 °C for 24 h, and then naturally cooled to ambient temperature, the black product was rinsed with deionized water and ethanol several times before being dried in an oven.

MoS_2 nanosheets decorated $Bi_{19}Cl_3S_{27}$ nanorods (signed as MDB) were acquired by the impregnation method. 1 mg, 3 mg, 5 mg and 10 mg MoS_2 nanosheets were well dispersed in 40 mL absolute ethyl alcohol through ultrasonic dissolving for 2 hours and tabbed as solution A_1, A_2, A_3, A_4, respectively. 100 mg $Bi_{19}Cl_3S_{27}$ nanorods were also dissolved in 40 mL absolute ethyl alcohol and marked as solution B. Subsequently, solution B was slowly added into solution A in drops with continuous stirring, and then the mixtures (marked as MDB-1, MDB-3, MDB-5 and MDB-10) were transferred into a rotatory evaporator and held at 60 °C till the solvents volatilize and the black precipitate come out, respectively. The products were put in an oven at 60 °C for 12 h to guarantee the catalysts dried enough for further characterization.

Noble mental Pt doped $Bi_{19}Cl_3S_{27}$ (tabbed as PDB) were got through a photo-deposition route. 100 mg $Bi_{19}Cl_3S_{27}$ was uniformly dispersed in 50 mL ethyl alcohol, 0.1 and 0.5 mL of H_2PtCl_6 (0.01 g mL^{-1}) aqueous solution were added, respectively. After stirring for 3 h in the dark, the above-mentioned suspension was irradiated by a 350 W Xe lamp for 4 h with a circulation condensed water system. The collected samples (theoretical mass ratios of Pt to $Bi_{19}Cl_3S_{27}$ were 1 wt% and 5 wt%, noted as PDB-1 and PDB-5) were washed with deionized water and absolute ethanol for several times, and dried at 60 ˚C for 12 h.

Characterization

The crystalline structure of the catalysts was characterized by powder X-ray diffraction (XRD) (Cu Kα = 1.5404 Å) (Bruker D8 Advance, Germany). The XRD pattern was recorded within 2θ range from 10° to 80° at a scanning rate of 0.05°/s. The morphologies and particle sizes of the samples were observed by SU8010 field-emission scanning electron microscope (FESEM, Hitachi, Japan). Transmission electron micrograph (TEM) and high-resolution transmission electron microscopy (HRTEM) using a JEM-2100F (JEOL, Japan) microscope operated at accelerating voltage of 200 kV, energy dispersive spectrum analysis (EDS) system was connected to the TEM. The sample was prepared by dispersing the powder in ethanol and dropping a drop of very dilute suspension onto a carbon film-coated copper grid. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Multilab 2000 (VG Inc) photoelectron spectrometer using Al Kα radiation as the excitation source under vacuum at 2×10^{-6} Pa. All the binding energy (BE) values were calibrated by the C 1s peak at 284.6 eV of the surface adventitious carbon. UV-vis diffused spectrum (DRS) was measured using the diffuse reflectance method with an Agilent Cary-5000 spectrophotometer (America) using an integrating sphere accessory. $BaSO_4$ was used as a reference material in UV-vis diffuse experiments. Photoluminescence (PL) measurements were carried out at room temperature in a Hitachi F-7000 (Japan) with a 150 W Xe lamp. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the corresponding energy-dispersive X-ray (EDX) mapping analysis were conducted on FEI Titan Themis 200 (America) equipped with Bruker Super-X. The element analysis was tested by varioMICRO (Germany).

Photoelectrochemical measurements

Photoelectrochemical measurements were carried out using a three-electrode quartz cell in the CHI-760E electrochemical workstation. Ag/AgCl was used as the reference electrode, and platinum wire serves as the counter electrode. The working electrodes were MBH-coated, and the electrolyte was the 0.5 M Na_2SO_4 solution.

Photocatalytic hydrogen evolution

Photocatalytic performance of the MoS_2, $Bi_{19}Cl_3S_{27}$, MBH, MDB and PDB samples were calculated through the hydrogen evolution. In each run, 20 mg catalysts, 30 mmol anhydrous sodium sulfate (Na_2SO_3) and 10 mmol sodium sulfide nonahydrate ($Na_2S•9H_2O$) were dispersed in 100 mL deionized water. All experiments were carried out at 27 °C with a circulation condensed water system in a 430 mL of self-designed photo-chemical reactor. A 350 W Xe lamp was employed to provide the simulate visible light. Before the top-irradiation, the mixture was treated by ultrasonic for 10 min and then remove residual gas with nitrogen for 1 hour. A chromatograph containing a thermal-conductivity detector (TCD) was used to detect the formation of H_2 per half an hour. The cycling experiments were conducted to state the reusable ability of the catalysts.

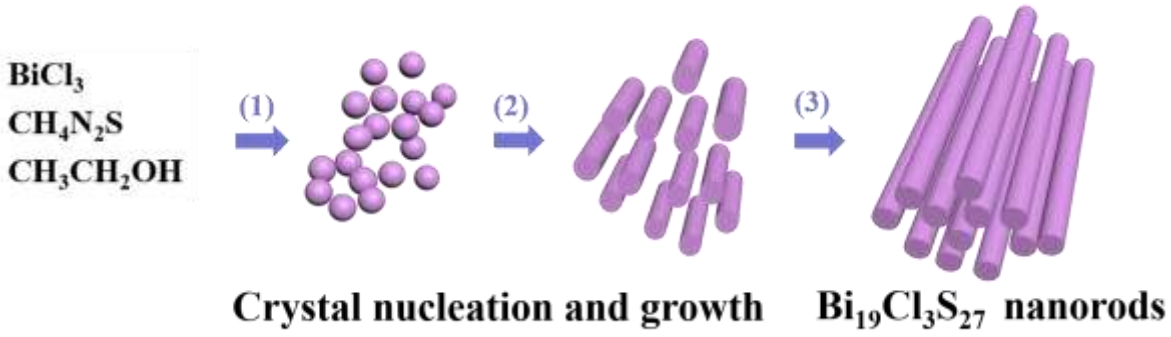

Fig. S1 Schematic illustration of the synthetic process of MBH.

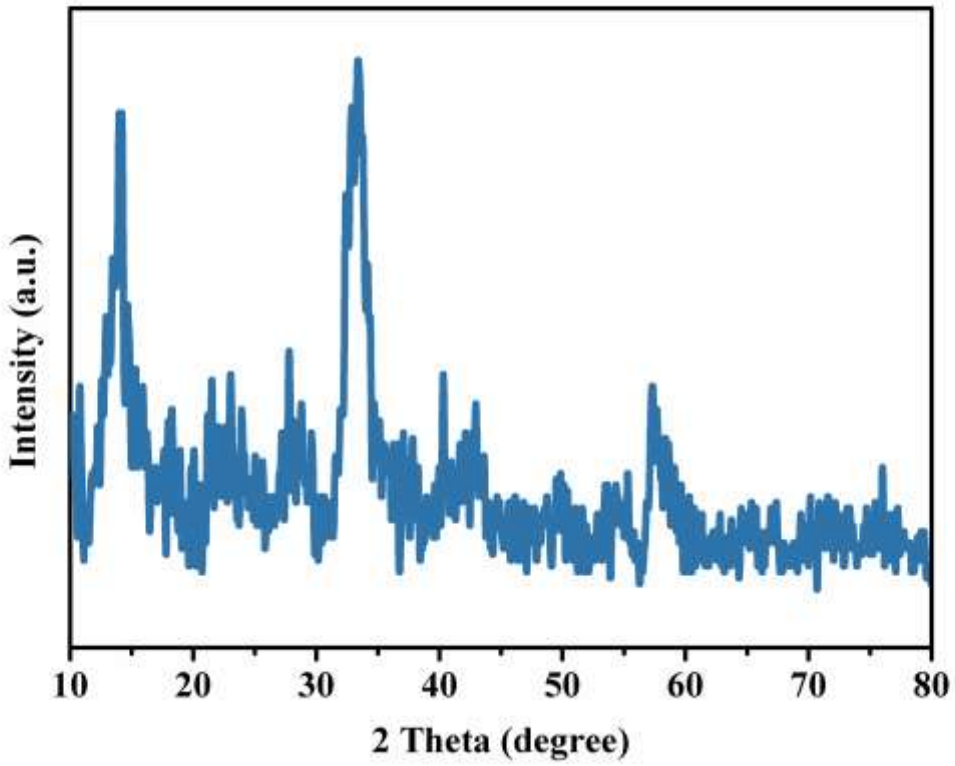

Fig. S2 XRD pattern of MoS_2 nanosheets.

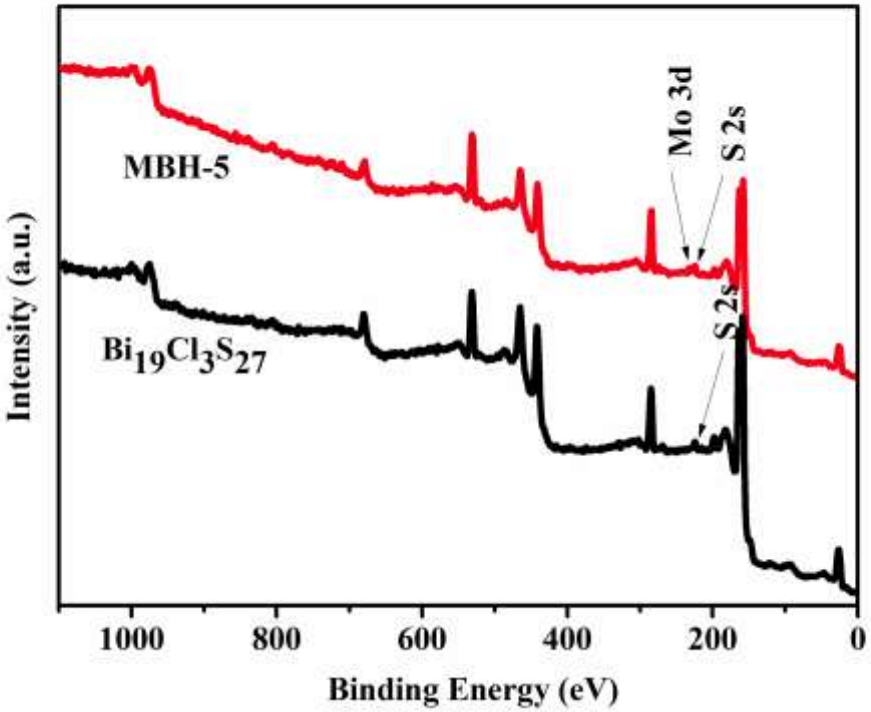

Fig. S3 XPS spectra of $Bi_{19}Cl_3S_{27}$ and MBH-5.

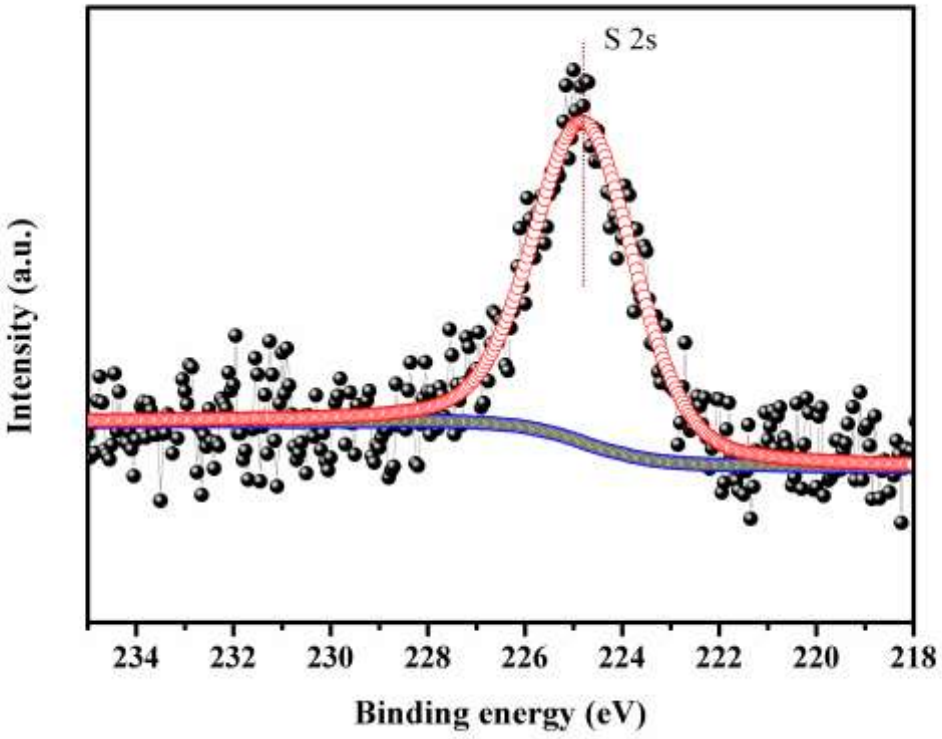

Fig. S4 High-resolution XPS signal spectrum of the S 2s in $Bi_{19}Cl_3S_{27}$.

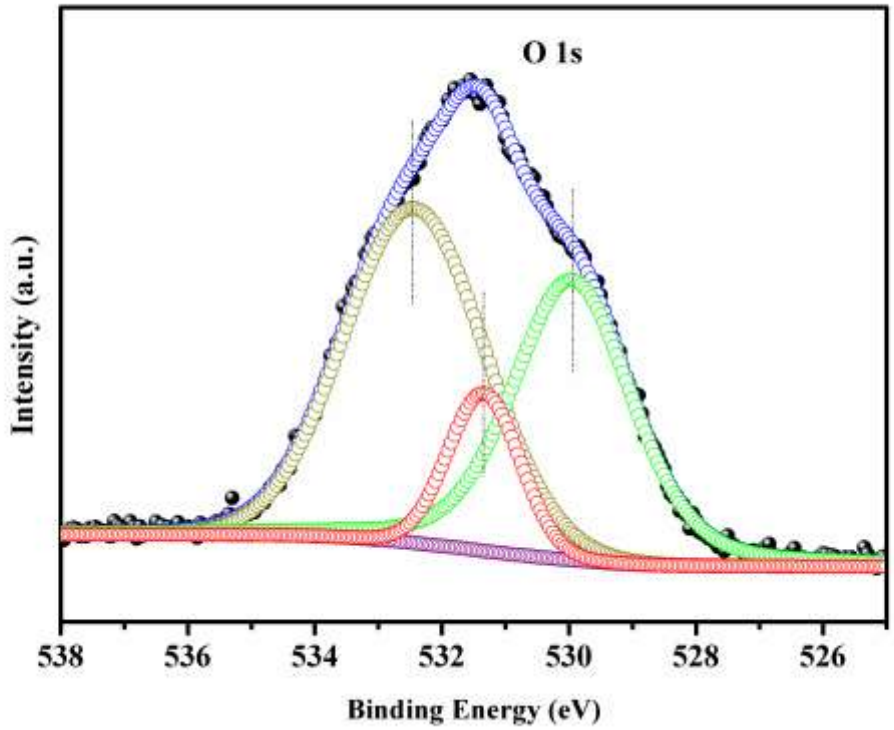

Fig. S5 High-resolution XPS signal spectrum of the O 1s in MBH-5.

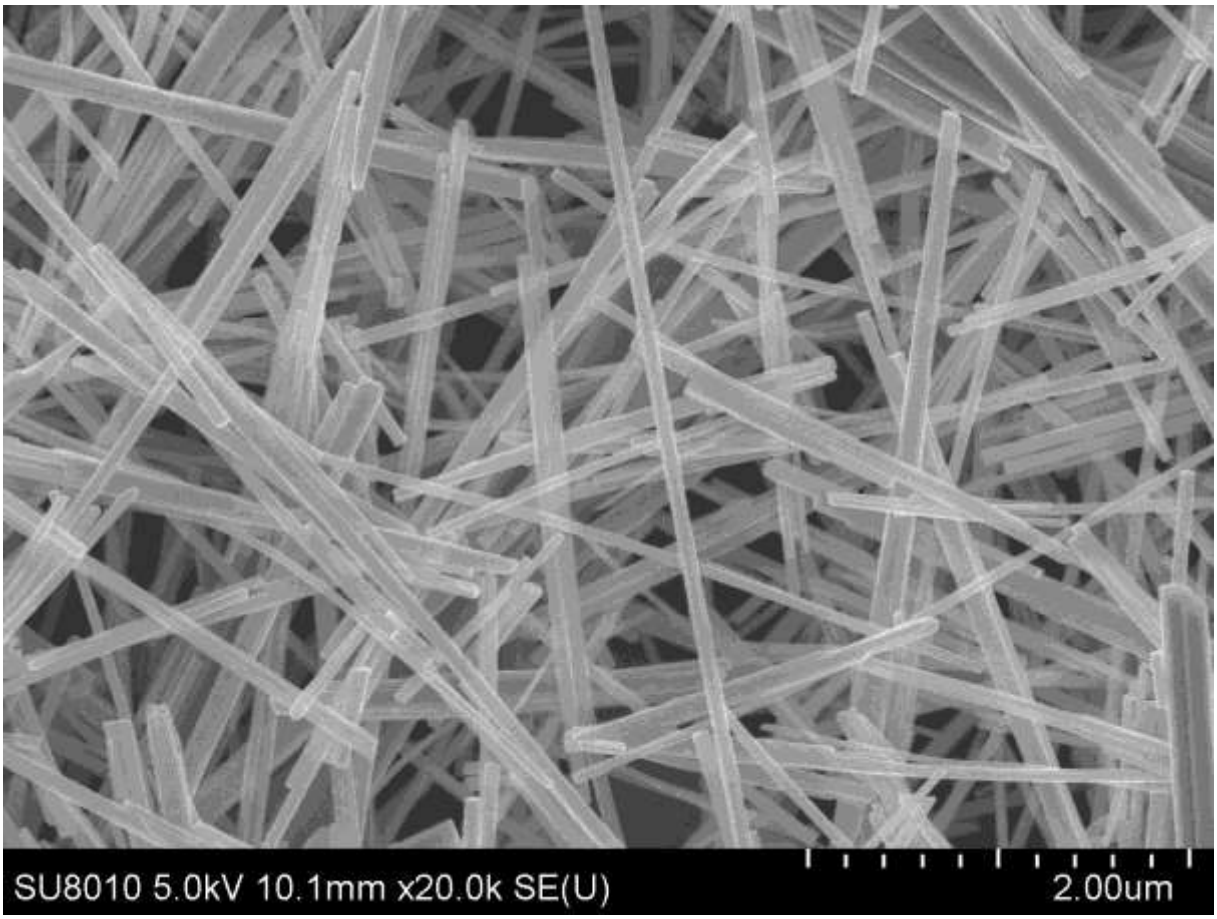

Fig. S6 FESEM image of bare $Bi_{19}Cl_3S_{27}$.

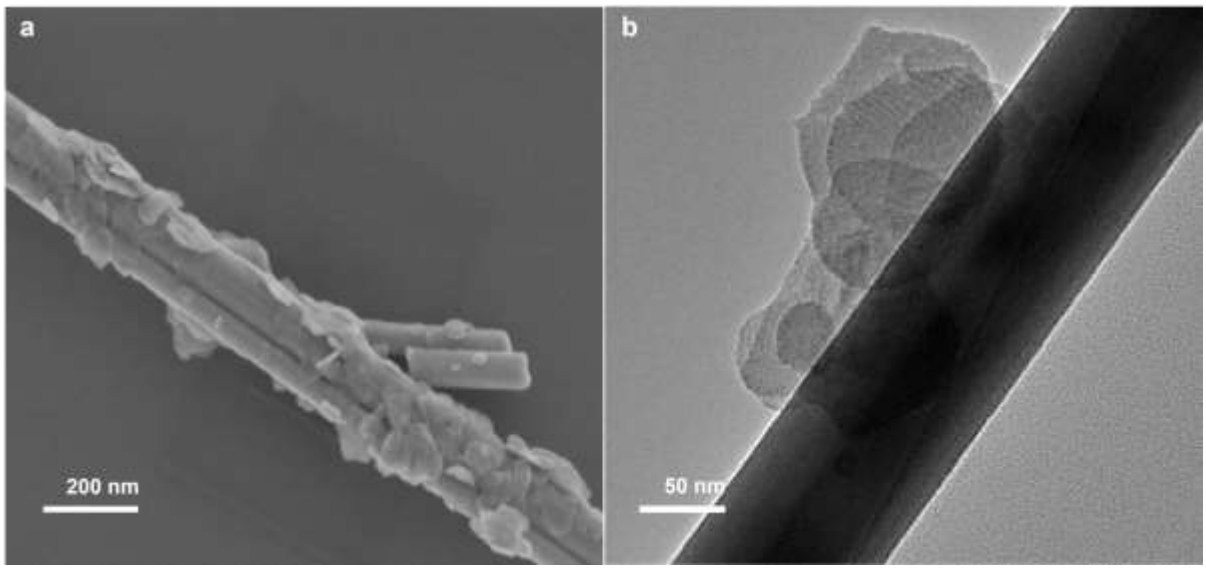

Fig. S7 a) FESEM and b) TEM images of sample MDB-5 (MoS_2 decorated $Bi_{19}Cl_3S_{27}$ with a theoretical loading of 5 wt% by an impregnation method). MoS_2 stands on the $Bi_{19}Cl_3S_{27}$ nanorods by stacking.

Graphic report	
Weight [mg]	C [%]
2.038	1.17%

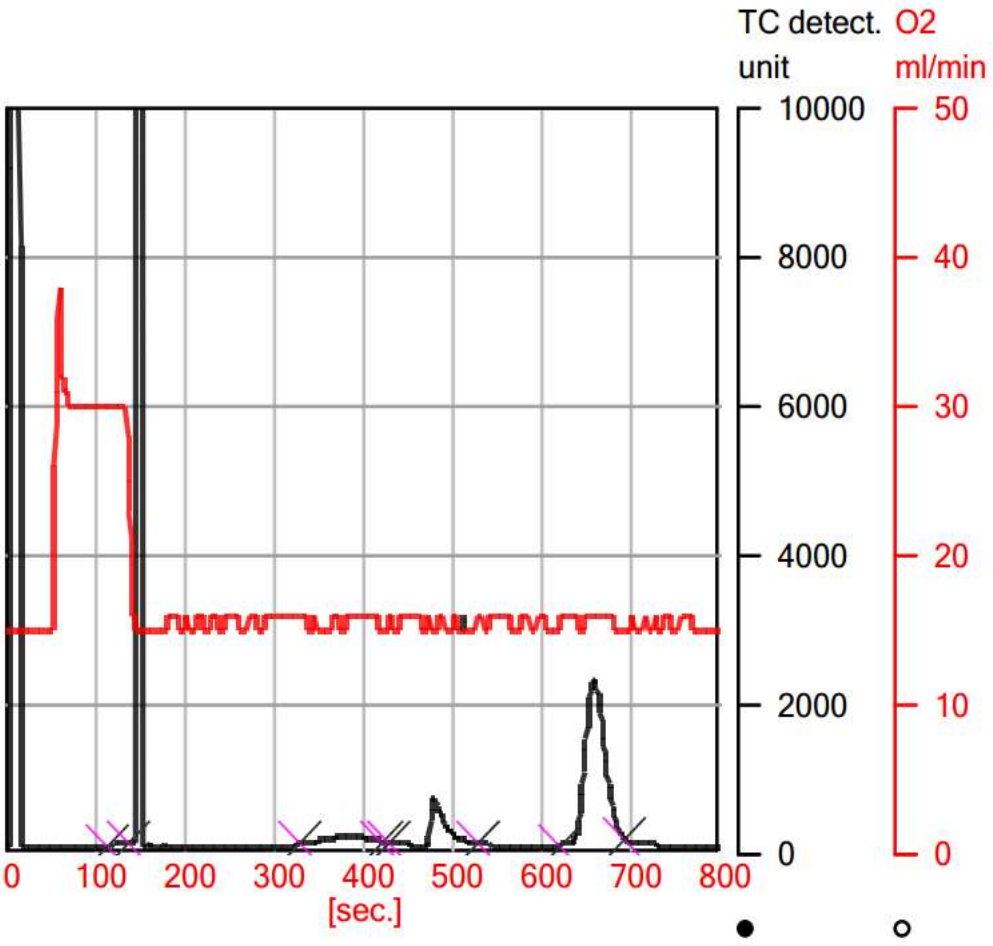

Fig. S8 The element analysis of carbon.

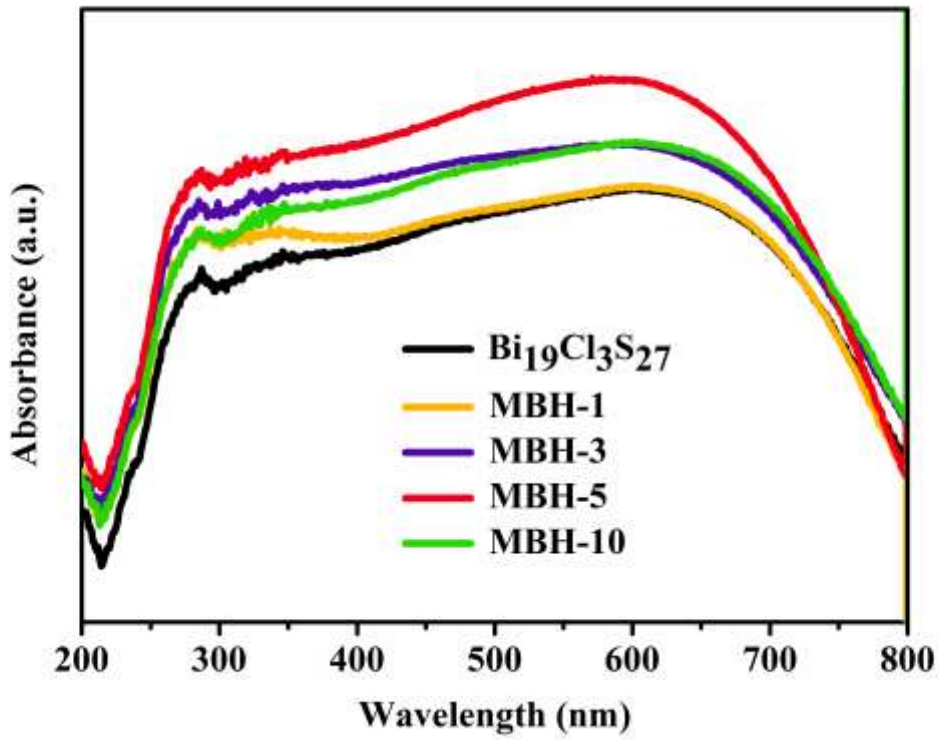

Fig. S9 UV–visible diffuse reflectance spectra of $Bi_{19}Cl_3S_{27}$ and MBH samples.

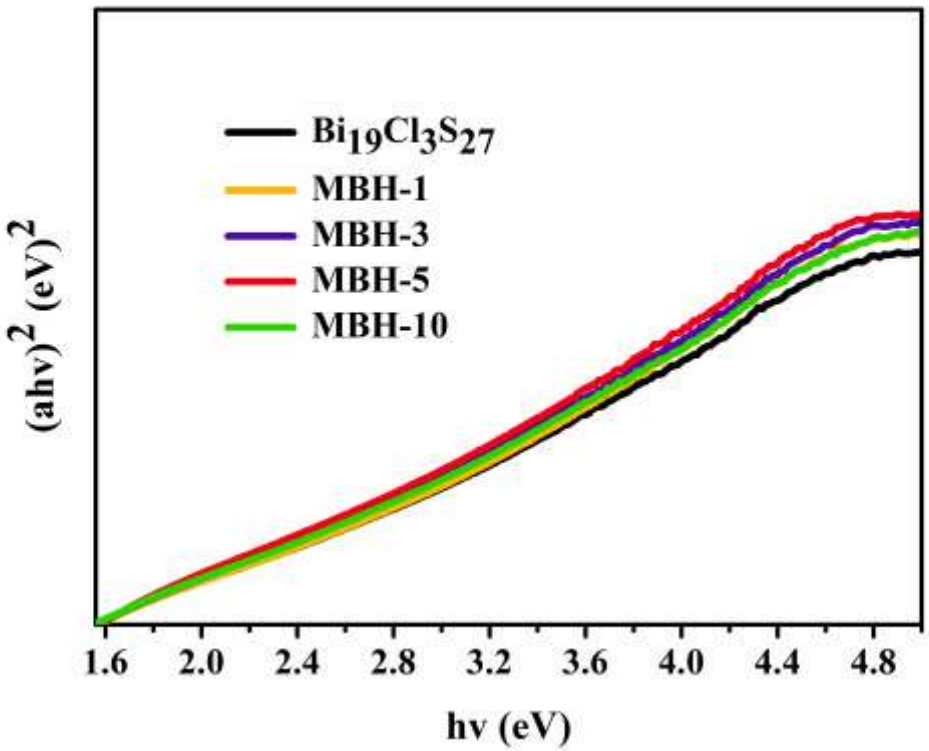

Fig. S10 Transformed Kubelka-Munk function versus light energy spectra of $Bi_{19}Cl_3S_{27}$ and MBH samples.

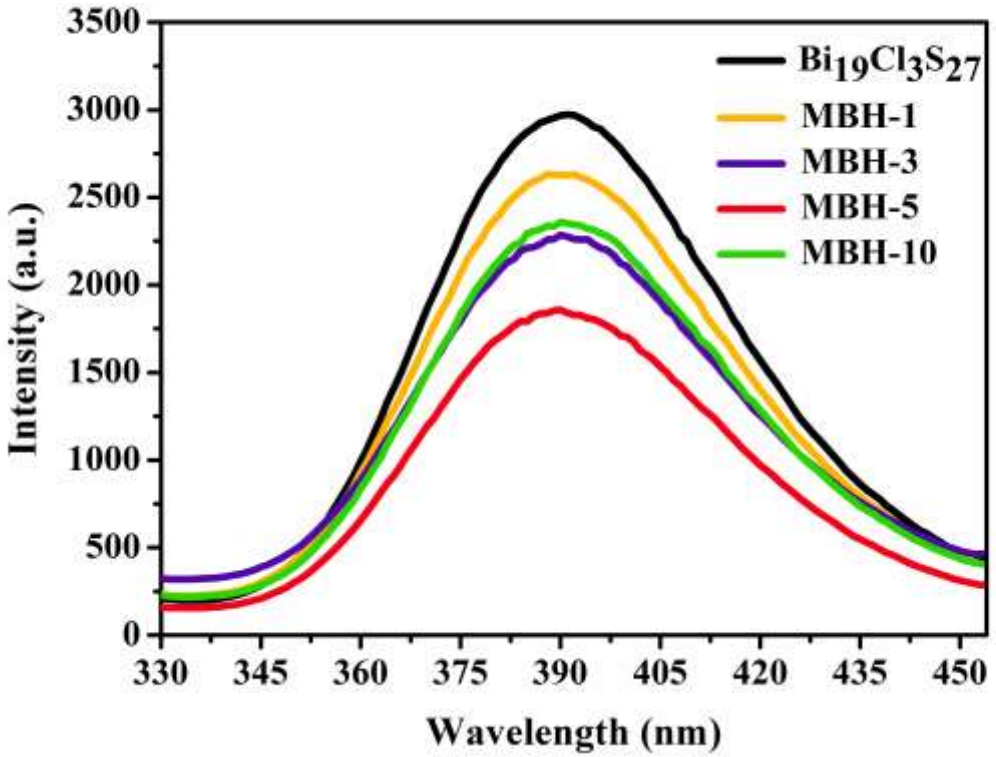

Fig. S11 PL spectra of $Bi_{19}Cl_3S_{27}$ and MBH samples.

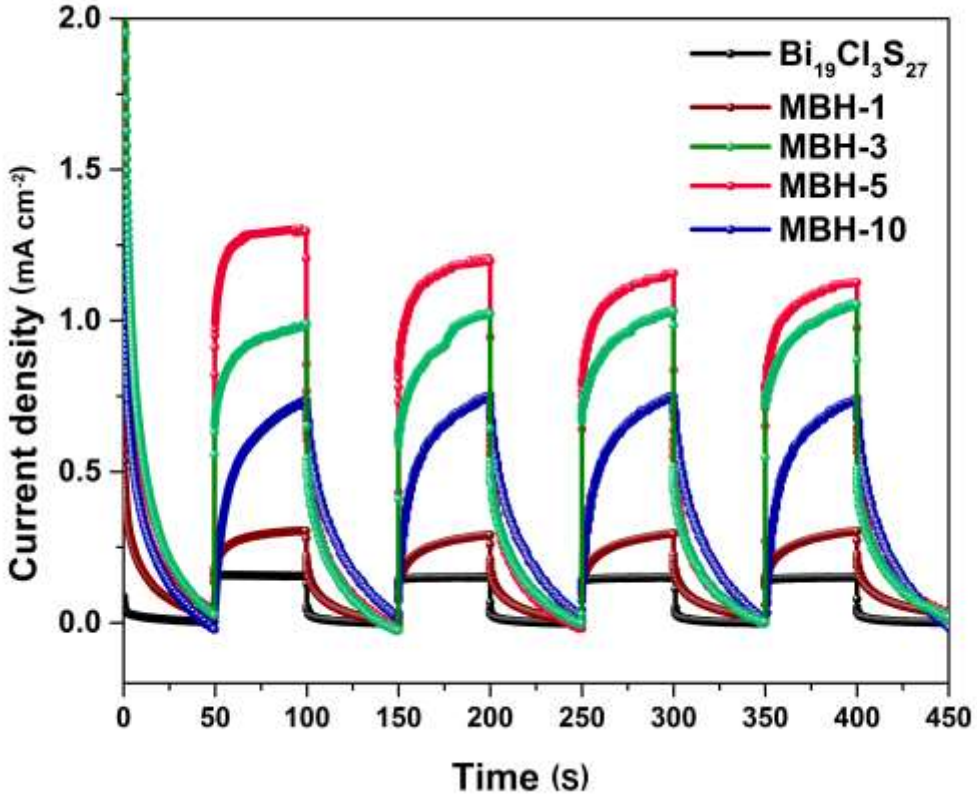

Fig. S12 Transient photocurrent density of $Bi_{19}Cl_3S_{27}$ and MBH samples.

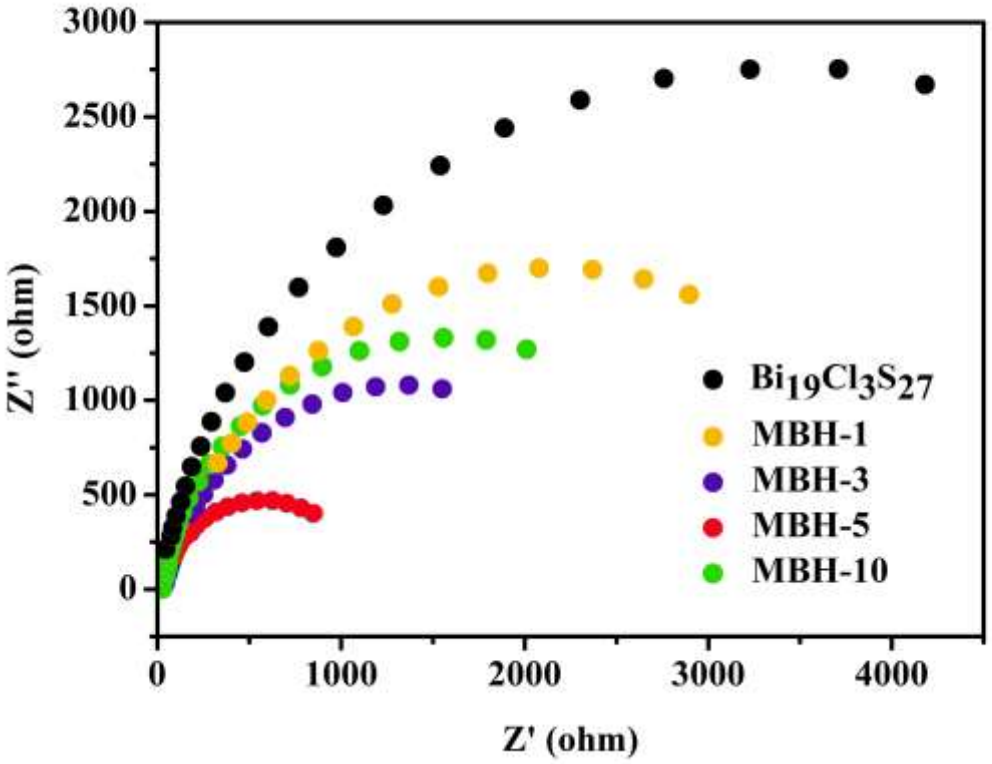

Fig. S13 EIS Nyquist plots of $Bi_{19}Cl_3S_{27}$ and MBH samples.

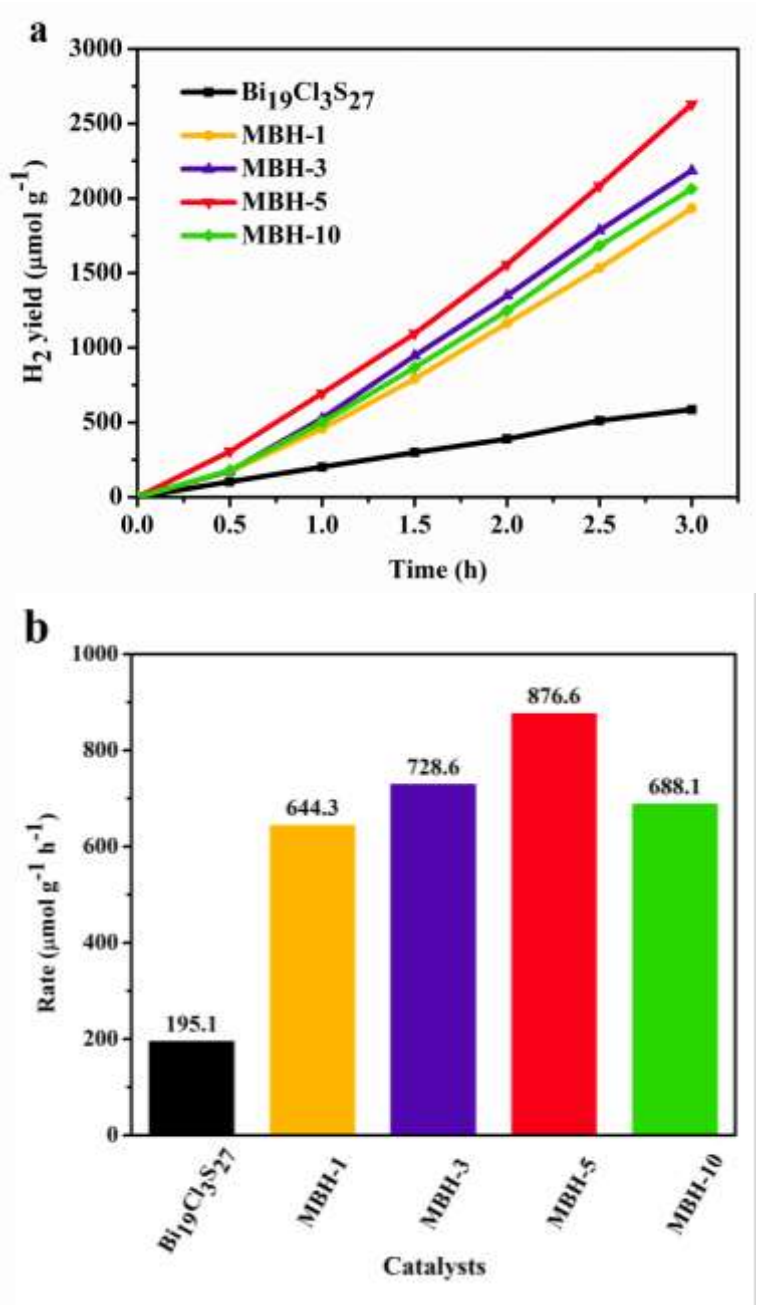

Fig. S14 The hydrogen evolution yield and rate of $Bi_{19}Cl_3S_{27}$ and MBH samples.

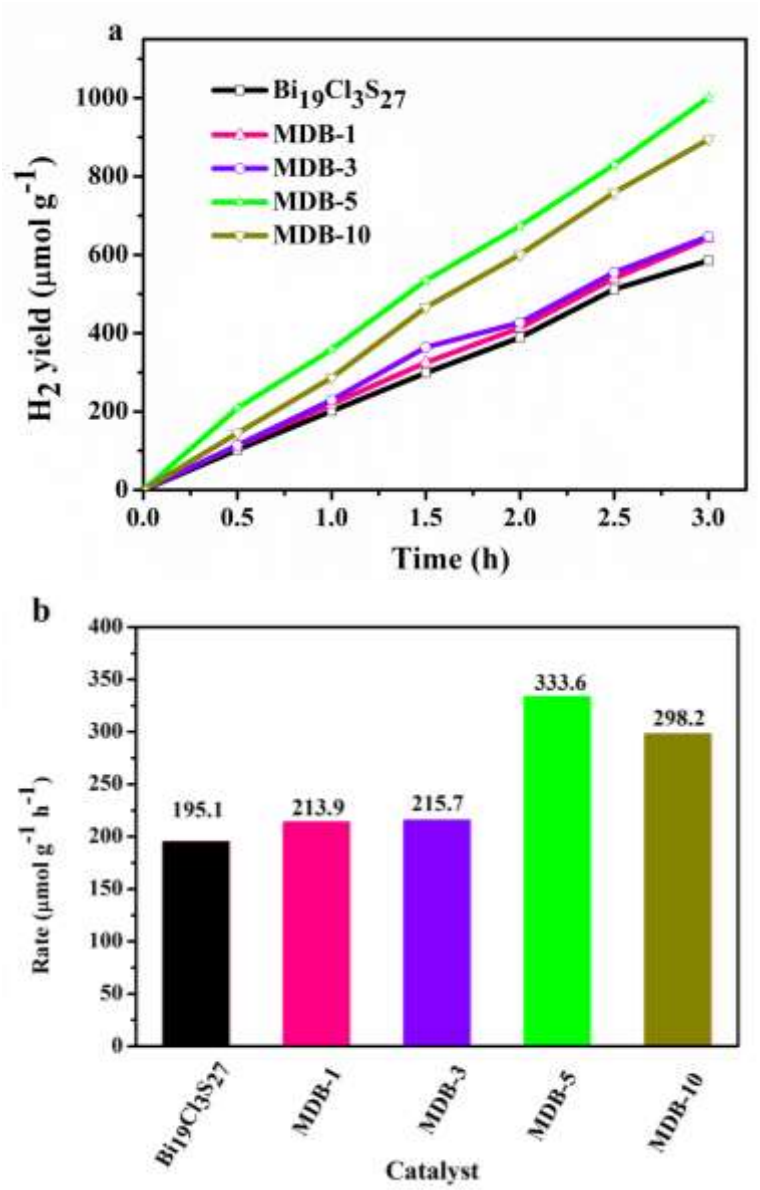

Fig. S15 The hydrogen evolution yield and rate of $Bi_{19}Cl_3S_{27}$ and MDB samples.

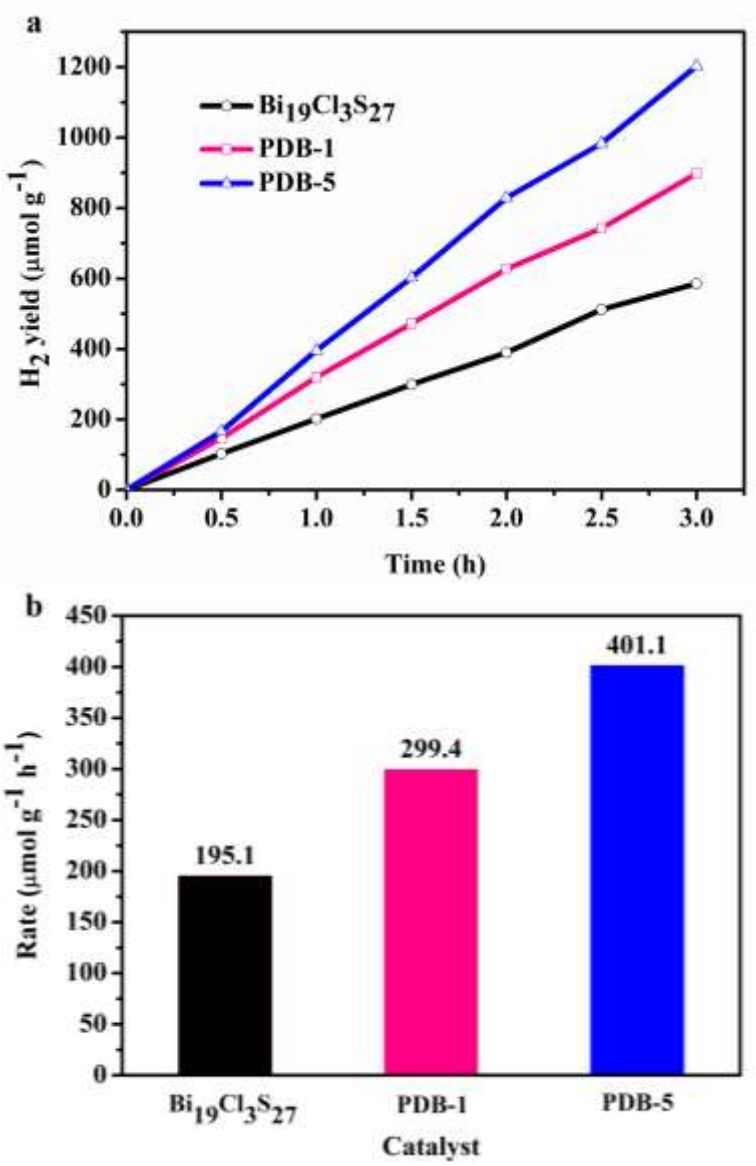

Fig. S16 The hydrogen evolution yield and rate of $Bi_{19}Cl_3S_{27}$ and PDB samples.