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Supporting Information

Experimental details

1. Materials and measurements

All reagents were purchased commercially and used without further purification. Diffraction data sufficient for unit cell determination for compound **1** was determined on a Bruker Apex CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The structure was solved by direct methods using the olex2.solve program and the refinement was performed against F² using Olex2. Anisotropic thermal parameters were used to refine all nonhydrogen atoms. All hydrogen atoms were located by ideal geometry and refined by a fixed isotropic displacement parameters. The CCDC data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC number 1866189 for **1**. XRD was performed on a Philips X'Pert-MPD instrument with Cu Kα radiation ($\lambda = 1.54056$ Å) in the range 2 $\theta = 5-50^{\circ}$ at 293 K. IR spectra were obtained with an Alpha Centaurt FT/IR spectrometer with KBr pellets in the range 400–4000 cm⁻¹. The UV-vis spectra were recorded with a 756 CRT spectrophotometer (Shanghai Optical Instrument Company, China). Quartz cuvettes with an optical path of 1.00 cm were used. Diffuse reflectance UV-vis spectra were measured from 200 to 800 nm on a Varian Cary 500 UV-vis NIR spectrometer equipped with a 110 mm diameter integrating sphere at room temperature. A barium sulfate (BaSO₄) pellet was used as the standard with 100% reflectance.

2.Ba-1 modified electrode

The modified electrode was prepared as follow: we reacted barium chloride with **1** to obtain the precipitation of Ba-**1**. The films were prepared with 0.2g of the Ba-**1** in ethanol (3 mL), and terpineol (1.0 g) in a porcelain mortar and the mixture was ground until it was about 2 mL. The paste was coated over fluorine-doped tinoxide (FTO) glass by doctor blade technique. After air drying, the prepared films were annealed at 573K for 6 hours.

3.Photocurrent measurement

In order to study the charge separation efficiency, we planed to measure the photocurrent response of Ba-1 at 0.3 v voltage. A 150 W high-pressure xenon lamp was used as the full-wavelength light source. The electrochemical experiments were performed by using a CHI 660 Electrochemical Workstation in a three-electrode system, with Ba-1/FTO as the working electrode with an effective area of 1 cm² (Φ = 0.7 cm), a saturated calomel electrode as reference electrode (SCE), and a Pt wire as counter electrode. All the photocurrent experiments were carried out at a constant bias of 0.3 V in a 0.50 mol·L⁻¹ Na₂SO₄ electrolyte solution under illumination (AM1.5, 100mW·cm⁻²) upon on–off cycling irradiation with xenon light (intervals of 25 s).

2. Synthesis

Compound $K_9[Ti_3O_4(O_2)_3 (C_7H_3O_4N)_3(OH_2)_2]Cl·4H_2O 1$ was synthesized by a conventional reaction method. 3.00 g (18 mmol) of 2,6-dipicolinic acid was dissolved in 75 ml of deionized water with stirring and an aqueous solution of titanium(IV) tetrachloride (15 mL, 15 mmol, 1.0 M solution) was slowly added

to the reaction mixture, and the mixture was left stirring for 30 min. In a second step, 30 mL of 30% H_2O_2 was dropwise introduced into the reaction mixture cooled in an ice bath. The solution underwent a color change from colorless to dark red under stirring. Next, an additional amount of 5.0 M KOH solution was added to adjust the pH value, followed by a color change to light yellow at pH values around 8.0-9.0. Slow evaporation of the solution afforded Light-yellow rhomboid crystal after approx. 7 d. Yied: 2.22g, 11% based on Ti. IR (2% KBr pellet, v/cm⁻¹): 1636(s), 1596(w), 1432(s), 1363(s), 1276(w), 1182(s), 1144(m), 1075(s), 1034(s), 923(m), 865(m), 758(w), 715(w), 674(w), 577(vw), 524(vw).

3. Ba-1 modified electrode

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Fig. S1 The PXRD pattern and simulated pattern of 1.



Fig. S2 IR spectra of compound **1** and Ba-1.



Fig. S3 Influence of the pH values on the stability of **1**.



Fig. S4 The PXRD of compound **1** recrystalized from pH=8 and pH=10.



Fig. S5 Mott-Schottky plots for the Ba-1 film.



Fig. S6 SEM of cross section of the Ba-1/FTO film. The thickness of the Ba-1/FTO film was about 18 μ m.



Fig. S7 Comparative of dark current-time responses of the Ba-1/FTO film and FTO in a 0.5 M Na_2SO_4 electrolyte.