

A novel Ta/W mixed-addendum polyoxometalate with photocatalytic properties

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1. Materials and Methods

Precursors $\text{Cs}_3\text{K}_{3.5}\text{H}_{0.5}[\text{SiW}_9(\text{TaO}_2)_3\text{O}_{37}] \cdot 9\text{H}_2\text{O}$,¹ was synthesized according to the procedures described in the literature, and their purity was characterized by IR spectra, thermogravimetric analyses, and elemental analysis. All other reagents were readily available from commercial sources and were used as received without further purification. Elemental analyses (Cs, K, W, and Ta) were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded on Alpha Centaur FT/IR spectrophotometer (KBr pellets) over the region of 400–4000 cm^{-1} . PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation in the range 3–50°. UV–vis absorption spectroscopy was obtained on a U-3010 spectrophotometer (Hitachi, Japan). Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 7 analyzer heated from room temperature to 800 °C under a nitrogen gas atmosphere with a heating rate of 10 °C min^{-1} .

2. Photocatalytic Measurements.

Photocatalytic reactions were carried out in a Pyrex inner-irradiation-type reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using Ar several times to ensure complete air removal and then irradiated by using a 500 W Xe lamp. The produced H_2 was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 m) using Ar as carrier gas.

3. Synthesis

Synthesis of 1. The mixture of $\text{Cs}_3\text{K}_{3.5}\text{H}_{0.5}[\text{SiW}_9(\text{TaO}_2)_3\text{O}_{37}] \cdot 9\text{H}_2\text{O}$ (50 mg) and TiO_2 (20 mg) were put in a 5-cm high vial, which was then transferred and sealed in a Teflon-lined autoclave with 3 mL HCl (aq. 1.0 M) and heated at 120 °C for 3 days followed by slow cooling to room temperature. The resulting products were colorless crystals (yield: 62%). Anal. Calc: Si, 0.80; Ta 15.61; W, 48.92; Cs, 11.94; K, 1.26. Found: Si, 0.84; Ta 15.97; W, 49.01; Cs, 11.13; K, 1.39. IR (KBr disks): 505, 686, 784, 924, 970 cm^{-1} (Fig. S6).

4. Single-Crystal Studies

Intensity data of **1** was collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Absorption corrections were applied using multiscan techniques. Their structures were solved by direct methods of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.² Anisotropic thermal parameters

were used to refine all non-hydrogen atoms, with the exception of some oxygen atoms. Hydrogen atoms attached to lattice water molecules were not located. Crystallization water molecules were estimated by thermogravimetry, and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. **1**: $\text{H}_{51}\text{Cs}_{12.5}\text{K}_{4.5}\text{Si}_4\text{Ta}_{12}\text{W}_{37}\text{O}_{183}$, $M_r = 13902$, Triclinic, $P-1$, $a = 19.827(5) \text{ \AA}$, $b = 22.503(5) \text{ \AA}$, $c = 23.791(5) \text{ \AA}$, $\alpha = 69.253(5)^\circ$, $\beta = 72.150(5)^\circ$, $\gamma = 85.897(5) (10)^\circ$, $V = 9440(4) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 4.873 \text{ g cm}^{-3}$, final $R_1 = 0.0728$ and $wR_2 = 0.2247$ ($R_{\text{int}} = 0.0723$) for 33391 independent reflections ($I > 2\sigma(I)$). CCDC 1058415 (**1**), contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif for **1**.

5. UV-Vis Diffuse Reflectance Spectra of **1**

For the sake of studying the conductivity of **1**, the UV-vis diffuse reflectance spectra of the powder sample was measured to achieve their band gaps (E_g), which was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka-Munk function F against E .³ As shown in Figures S1, the corresponding well-defined optical absorption associated with E_g can be assessed at 3.3 eV for compound **1**, which reveals the presence of an optical band gap and the nature of semiconductivity.

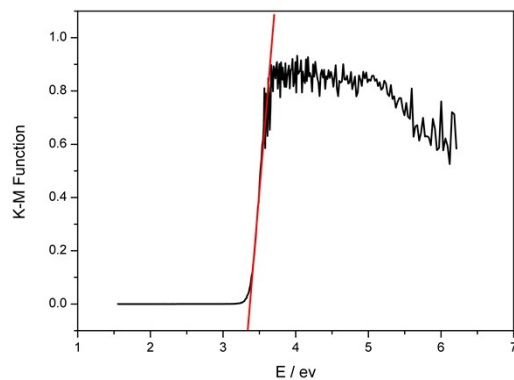


Fig. S1 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **1**.

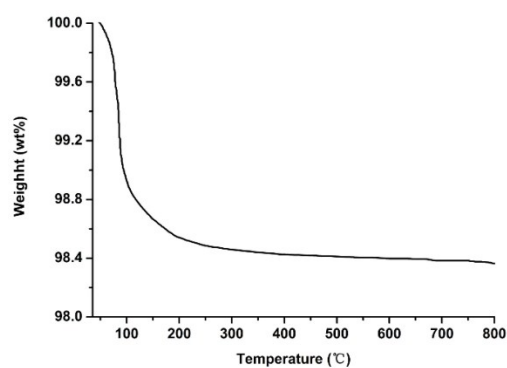


Fig. S2 TGA curve of **1**.

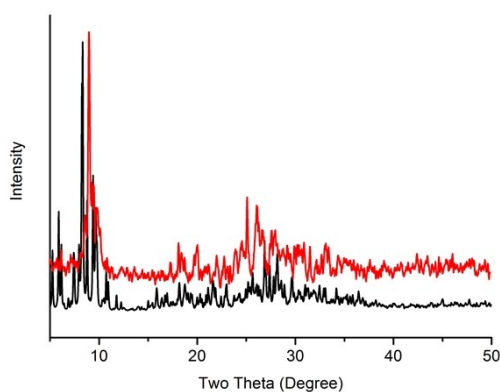


Fig. S3 The XRPD patterns for as-synthesized (top) and simulated (bottom) **1**.

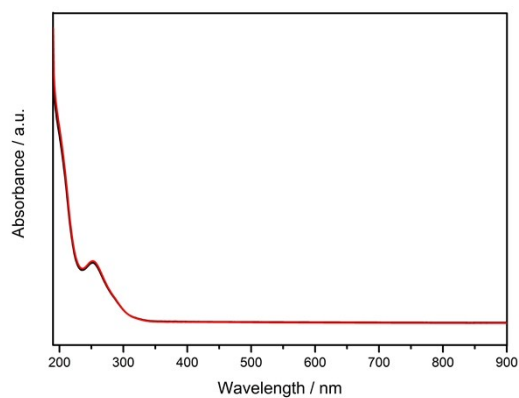


Fig. S4 UV-Vis spectra of compound **1** before (black) and after (red) three runs of the photocatalytic reactions.

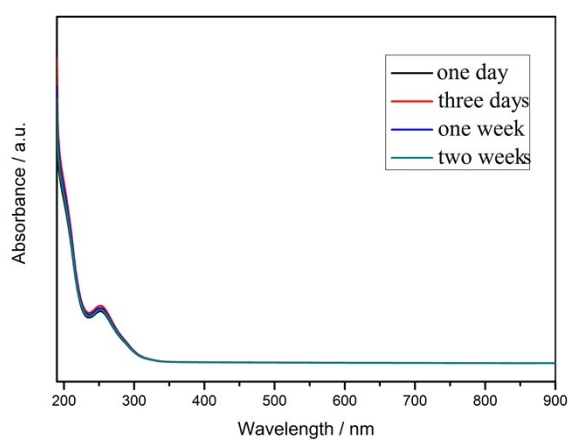


Fig. S5 UV-Vis spectra of compound **1** kept at room temperature.

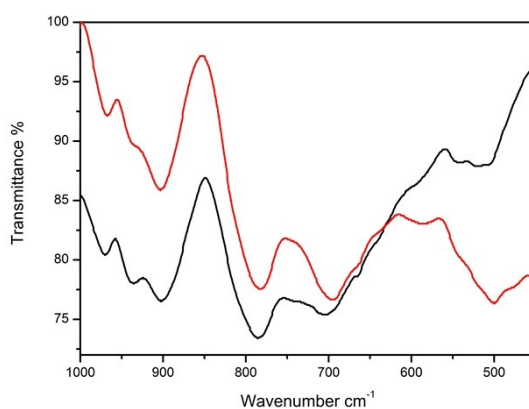


Fig. S6 IR spectra of **1**(black) and the samples recycled from photocatalytic reactions (red).

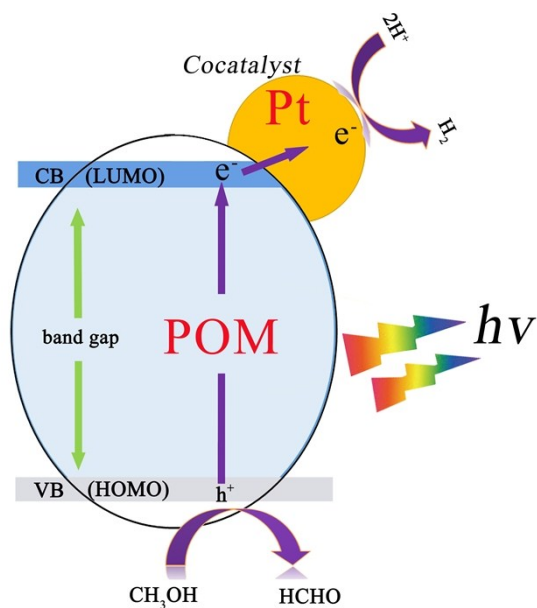


Fig. S7 The proposed mechanism of photocatalytic H_2 production of **1**.

References

1. S. J. Li, S. M. Liu, S. X. Liu, Y. W. Liu, Q. Tang, Z. Shi, S. X. Ouyang, and J. H. Ye, *J. Am. Chem. Soc.*, 2012, **134**, 19716.
2. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure*; University of Göttingen: Germany, 1997.
3. J. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1971, 34.