

**Self-assembly and photocatalytic H₂ evolution activity of two
nanoscale polytantalotungstates based on the unprecedented
{Cr₃Ta₆} and {Cr₄Ta₁₂} clusters**

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1. Materials and Methods

All reagents and solvents for the syntheses were purchased from commercial sources and used as received, except for $\text{Cs}_8\text{K}[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{TaO}_2)_3]\cdot 22\text{H}_2\text{O}$,¹ which was synthesized according to the procedures described in the literature, and their purity was characterized by IR spectra, thermogravimetric analyses, and elemental analysis. Elemental analyses (Cs, P, K, Na, Cr, Ta, and W) 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 $\text{K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) 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 \AA molecular sieve column (2 mm \times 2 m) using Ar as carrier gas.

3. Synthesis

Synthesis of 1. The mixture of $\text{Cs}_8\text{K}[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{TaO}_2)_3]\cdot 22\text{H}_2\text{O}$ (50 mg) and $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (10 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 green crystals were separated from the solution and washed with distilled water several times, yielding 78% based on $\text{Cs}_8\text{K}[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{TaO}_2)_3]\cdot 22\text{H}_2\text{O}$. Anal. Calc: P, 1.22; Ta 10.67; W, 54.22; Cr, 1.53; Cs, 6.53; K, 1.54. Found: P, 1.43; Ta 10.28; W, 55.12; Cr, 1.69; Cs, 6.97; K, 1.36.

Synthesis of 2. Compound **2** was prepared following the procedure described for **1**, but by using a larger quantity of $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (20 mg). The resulting products were green block crystals (yield: 72%). Anal. Calc: P, 1.22; Ta 10.70; W, 54.36; Cr, 1.02; Cs, 5.56; Na, 0.22; K, 1.54. Found: P, 1.31; Ta 11.03; W, 53.22; Cr, 1.27; Cs, 5.43; Na, 0.18; K, 1.15.

4. Single-Crystal Studies

Intensity data of **1** and **2** were collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) 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**: H₅₄Cs₅K₄P₄Cr₃Ta₆W₃₀O₁₅₁, $M_r = 10172$, Monoclinic, $c2/m$, $a = 40.806(5)$ Å, $b = 23.313(5)$ Å, $c = 21.672(5)$ Å, $\alpha = 90.000(5)^\circ$, $\beta = 113.690(5)^\circ$, $\gamma = 90.000(5)^\circ$, $V = 18879(6)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 3.560$ g cm⁻³, final $R_1 = 0.0640$ and $wR_2 = 0.2041$ ($R_{\text{int}} = 0.1317$) for 16744 independent reflections ($I > 2\sigma(I)$). **2**: H_{135.5}Cs_{8.5}K₈Na₂P₈Cr₄Ta₁₂W₆₀O₃₁₃, $M_r = 20290$, Triclinic, $P-1$, $a = 23.7129(14)$ Å, $b = 24.0511(14)$ Å, $c = 35.458(2)$ Å, $\alpha = 108.8930(10)^\circ$, $\beta = 93.6940(10)^\circ$, $\gamma = 113.2160(10)^\circ$, $V = 17149.1(17)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 3.903$ g cm⁻³, final $R_1 = 0.0907$ and $wR_2 = 0.2968$ ($R_{\text{int}} = 0.1329$) for 49379 independent reflections ($I > 2\sigma(I)$). CCDC 1058413 (**1**) and 1002179 (**2**), 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** and **2**.

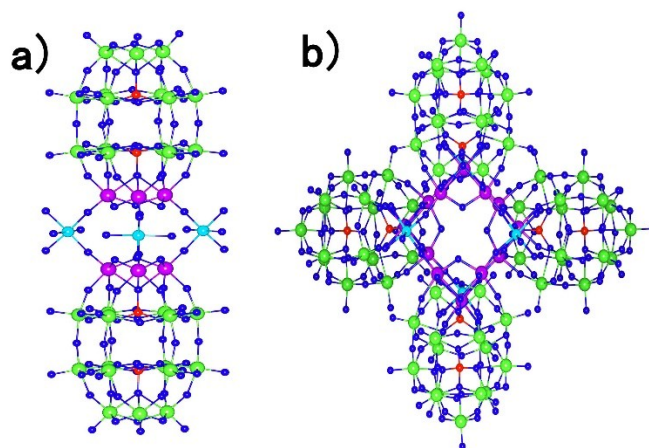


Fig. S1 Ball-and-stick presentations of **1** and **2**, respectively.

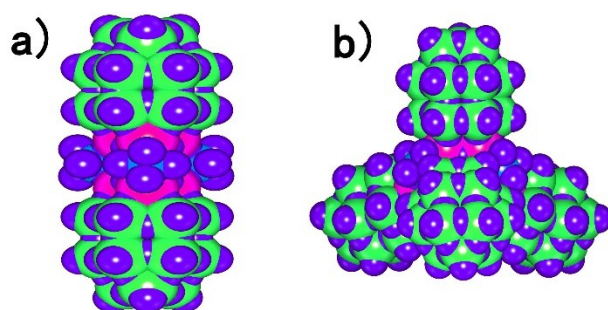


Fig. S2 Space-filling presentations of **1** and **2**, respectively.

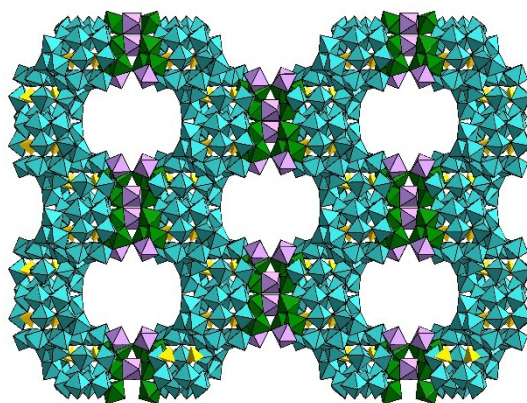


Fig. S3 The 3D architecture with 1D channels built by $\{\text{Cr}_3[\text{Ta}_3\text{P}_2\text{W}_{15}\text{O}_{62}]_2(\text{H}_2\text{O})_{12}\}^{9-}$ units, K and Cs cations for **1** (H atom, and water molecules are omitted for clarity). Color scheme: NbO_6 (green), WO_6 (aqua), PO_4 (yellow), CrO_6 (lavender).

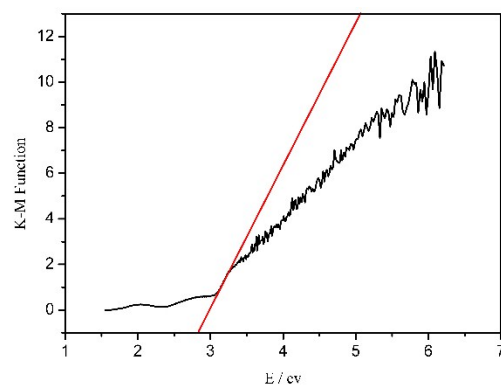


Fig. S4 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **1**.

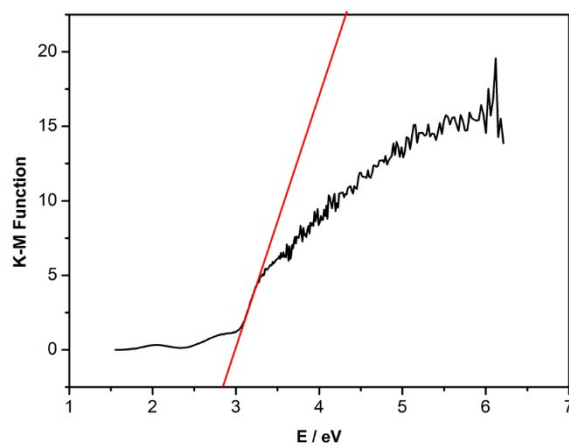


Fig. S5 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **2**.

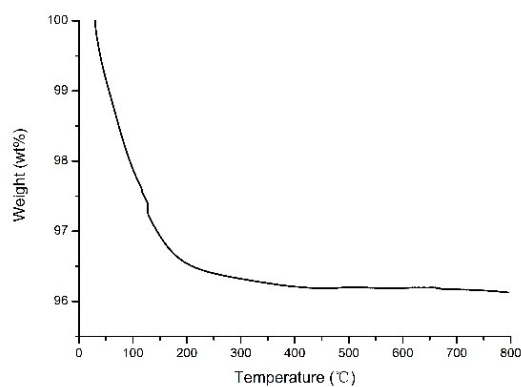


Fig. S6 TGA curve of **1**.

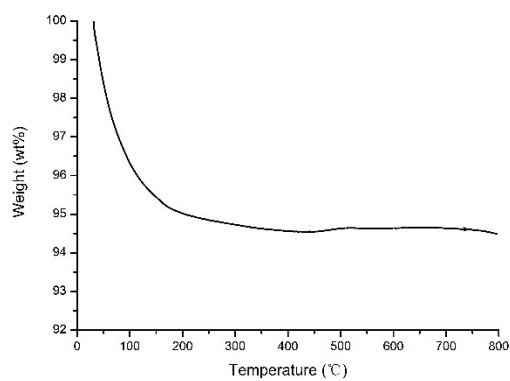


Fig. S7 TGA curve of **2**.

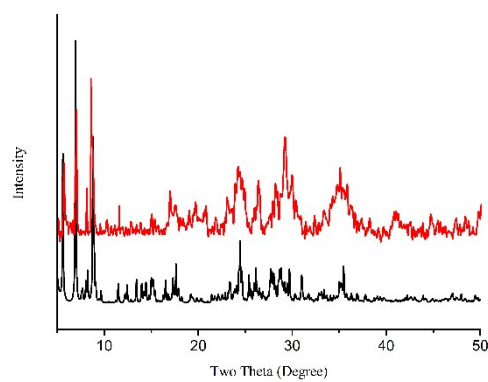


Fig. S8 The XRPD patterns for as-synthesized (top) and simulated (bottom) **1**.

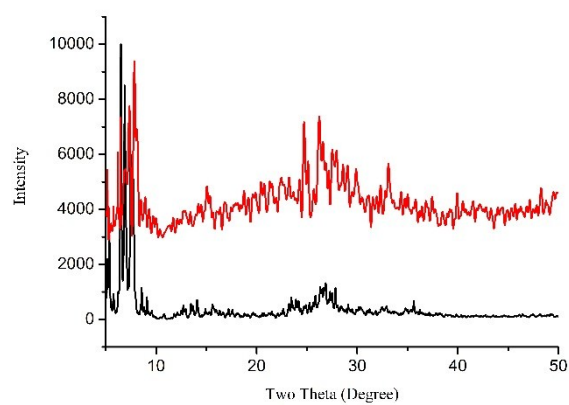


Fig. S9 The XRPD patterns for as-synthesized (top) and simulated (bottom) **2**.

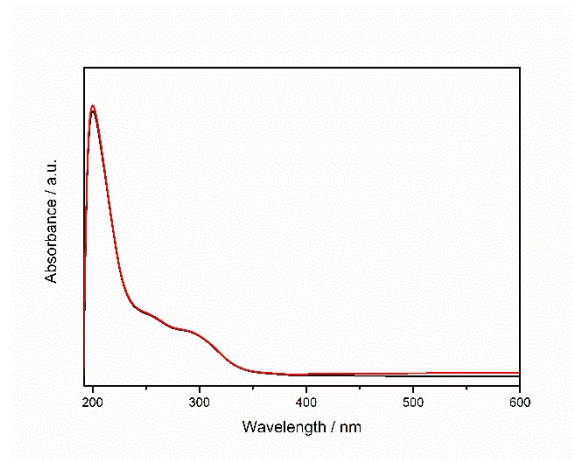


Fig. S10 UV-Vis spectra of compound **1** before (black) and after (red) the photocatalytic reactions.

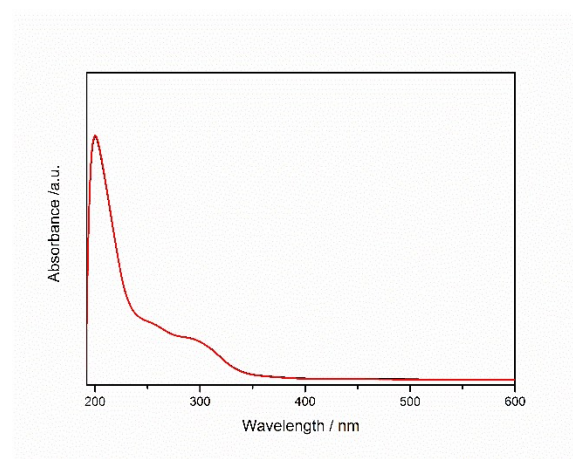


Fig. S11 UV-Vis spectra of compound **2** before (black) and after (red) three runs of the photocatalytic reactions.

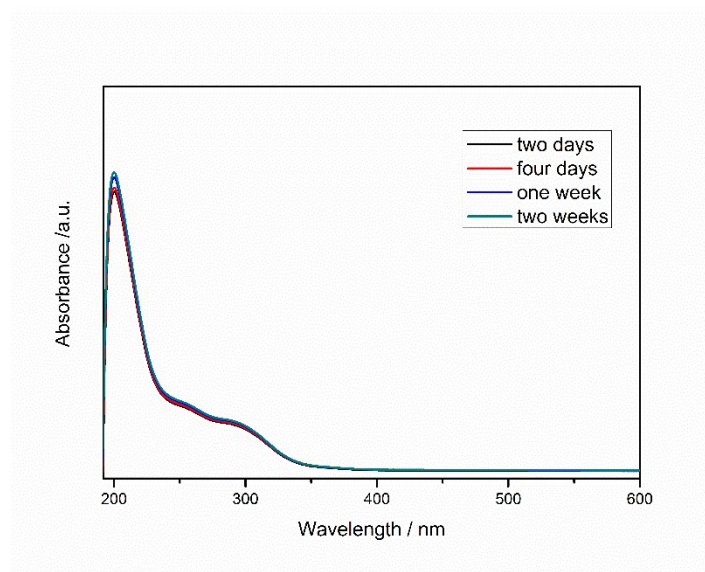


Fig. S12 UV-Vis spectra of compound **1** kept at room temperature.

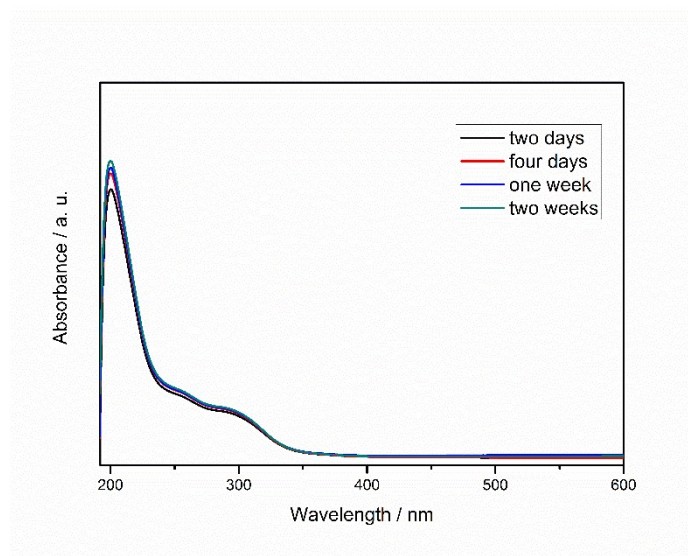


Fig. S13 UV-Vis spectra of compound **2** kept at room temperature.

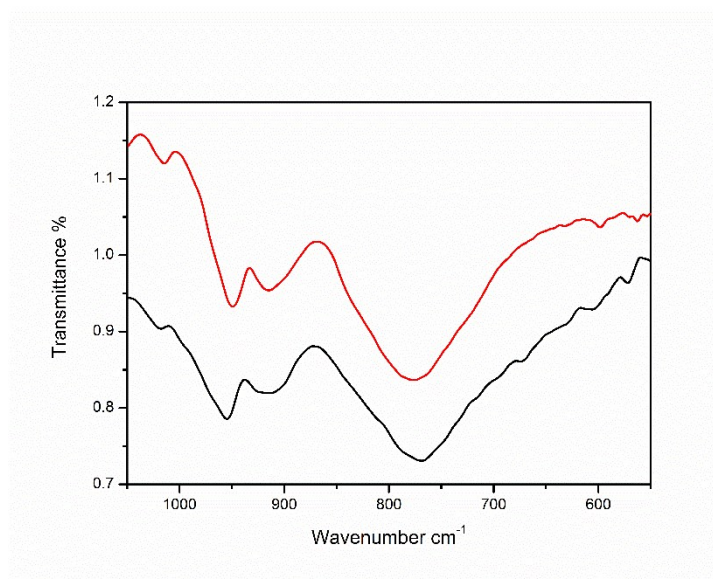


Fig. S14 IR spectra of **1** (black) and the samples recycled from photocatalytic reactions (red).

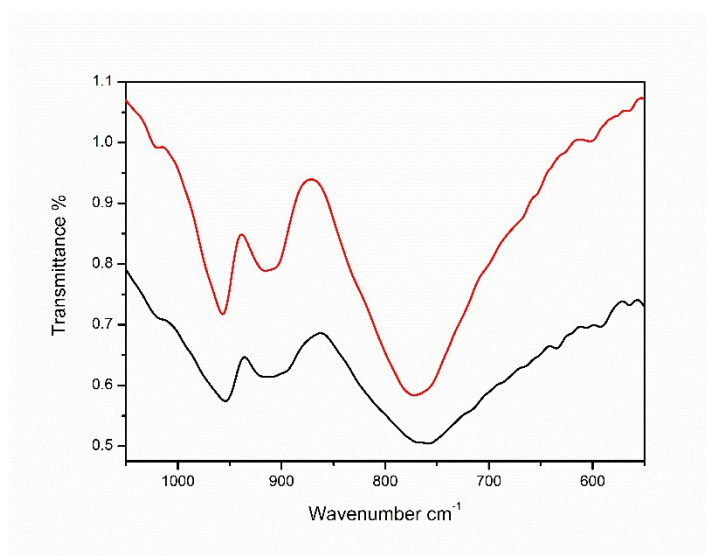


Fig. S15 IR spectra of **2** (black) and the samples recycled from photocatalytic reactions (red).

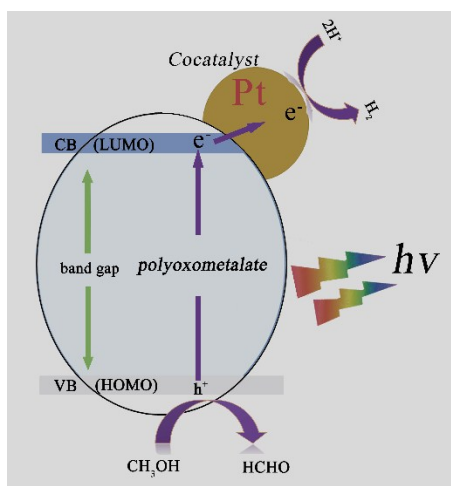


Fig. S16 The proposed mechanism of photocatalytic H₂ production of **1** and **2**.

References

1. P. Huang, C. Qin, Y. Zhou, Y. M. Hong, X. L. Wang and Z. M. Su, *Chem. Commun.*, 2016, **52**, 13787.
2. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure*; University of Göttingen, Göttingen, Germany, 1997.