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A tellurium-substituted Lindqvist-type polyoxoniobate showing high H₂ evolution catalyzed by tellurium nanowires from photodecomposition

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5 Synthesis

1.38 g of telluric acid was mixed with 5 g of hydrous niobium oxide and 6.5 g of tetramethylammonium hydroxide pentahydrate (TMAOH·5H₂O) in a PTFE-lined autoclave with 23 mL capacity and reacted at 110 °C for 5 days. The resultant clear solution was washed with isopropanol in a plasic centrifuge tube (50 mL) a few times until the product became sticky. The remaining sticky product ¹⁰ was extracted with ethanol. The ethanolic extract solution was evaporated to form colorless oil, which formed crystalline material after a few weeks or months. The solid product was quickly washed with ethanol on a frit and dried in vacuo. More crystalline product was recovered from the ethanol wash solution after evaporation. Combined yield= 6.9 g (71 %). Elemental analysis Found: C 16.05, H 6.21, N 4.26, Nb 27.30, Te 7.31. Calcd for $C_{20}H_{102}N_5Nb_5O_{39}Te$: C 14.73, H 6.31, N 4.30, Nb 28.52, Te 7.84.

15 Analytical Details

ESI-MS spectrometry was carried out using an Agilent G1956b 1100 series LC/MSD single-quadrupole mass spectrometer with ESI/APCI source using a cone voltage of -20 V and at an injection rate of 0.1 mL/min with a syringe pump for direct source injection. The ESI-MS titration experiments were performed with 31 mM sample concentration solution. 2 mL of the solution was titrated with

- 20 2.75 M TMAOH solution or TMAOH·5H₂O for basic direction and 6 M HCl solution for acidic direction to minimize volume change. Aliquots of 5 μL solution in different pH were diluted with 1 mL of water and injected for ESI-MS. Each spectrum in the figures is averaged signal during the data acquisition for 1 min. A Varian Cary 300 UV-visible spectrometer was used to obtain the UV-Vis absorption spectra. 2 mL of starting solutions were 0.03 mM concentration sample solution with 0.1 M of TMACl as background salt. Background correction was applied with a blank 0.1 M TMACl solution. Dilute TMAOH or HCl solutions were used to adjust the pH to
- ²⁵ a basic or acidic direction, respectively. Infrared spectra were collected on a Bruker Tensor 27 FT-IR spectrometer with a KBr pellet dispersed with sample. Elemental analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN). Solid-state ¹²⁵Te MAS NMR spectrum was collected on a Bruker Avance 500 spectrometer equipped with an 11.74 Tesla widebore Bruker magnet. The powdered sample was loaded in a Bruker 4 mm MAS probe and spun at 8 kHz. The ¹²⁵Te resonance frequency is 157.9 MHz. Direct polarization pulse sequence was used, the pulse length was 1µs, corresponding to 60 degree tip angle, and the relaxation delay was 30 seconds. A
- ³⁰ total of 11553 scans were averaged and 20 Hz of line broadening was used for signal processing. The chemical shift was externally referenced to crystalline ZnTe at -888 ppm.

Photocatalytic Hydrogen Evolution

³⁵ Irradiation tests were performed from solution of 0.2 g of **1-3** in 25 mL of methanol/water (20 % v/v) in a quartz flask. The flask was purged with argon and the solution was irradiated with a 300 W xenon arc lamp with or without a 400 nm long pass filter (Edmund Optics) (380 mW·cm⁻² with 400 nm filter at the flask surface as measured by an International Light IL1400BL photometer equipped with a GaAsP detector for 280 to 660 nm sensitivity range). The airtight irradiation system was connected to a Varian 3800 gas chromatograph (with a 60/80 Å molecular-sieve column and thermal conductivity detector) to identify the gas and measure the amount of ⁴⁰ gas evolved.

X-Ray crystallography

A colorless single crystal of **1** was attached on a glass fiber with Paratone oil and mounted on a goniometer. A Bruker APEX II single ⁴⁵ crystal X-ray diffractometer equipped with monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and a CCD detector was used for data collection. Cold nitrogen stream from liquid nitrogen was flown on the mounted crystal during the data collection to fix the crystal and to maintain the data collection temperature at 86 K. After data collection, data reduction was performed by using SAINT software.¹ Multiscan absorption correction was applied with SADABS program.² The crystal structure was solved with SHELXS software³ by using direct method, which found metal, oxygen and some TMA groups. Subsequent refinement cycles using SHELXL program found other ⁵⁰ atoms in the electron density map. Hydrogen atoms on the TMA group were refined using the riding model.

¹ Bruker (**2007**). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

² Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

³ G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.



Figure S1 ESI-MS data of 1



Figure S2 View of the unit cell of 1 (Te: purple, Nb: gray, O: red, N: blue, C: yellow, H: pink) along the *a*-axis (top) and *b*-axis (bottom). Onedimensional chains of the hydrogen bonded clusters are formed along the *b*-axis (top, gray dash). The structure of 1 comprises layers of clusters in *bc*plane. The intercluster distances measured between central μ_6 -O along the *c*-axis (10.96 Å) and *b*-axis (8.50 Å) are much shorter than that between the cluster layers along the *a*-axis (17.46 Å). The layer of the clusters in *bc*-plane contains one TMA and two water molecules per cluster, which are linking the clusters by hydrogen bond along the *c*-axis. Tel/Nb1 site is oriented toward the interlayer space in the solid state where most of TMA and crystallization waters are located.



Figure S3 FT-IR spectra of (a) 1, (b) 2 and (c) 3 (TMA salt of peroxohexaniobate, $TMA5[H3Nb6O13(O^{(1)}2)6]$ -9.5H2O).⁴ Spectra of 1 and 2 are similar, but differences are noticed in the additional bands in the spectrum of 1, such as 710, 560 and 440 cm⁻¹, due to the lower symmetry of $TeNb_5$ in 1 compared to hexaniobate in 2. In the spectrum of 3, Nb–Ot vibrations shift to lower energy, due to the longer terminal Nb–peroxide bond. Nb–O–Nb vibration bands are broader and are in the higher frequency region compared to that of 1 and 2.

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⁴ C. A. Ohlin, E. M. Villa, J. C. Fettinger, W. H. Casey Angew. Chem. Int. Ed. 2008, 47, 8251 –8254.



Figure S4 Variation of ESI-MS of 31 mM solution of 1 as a function of solution pH



Figure S5 Variation of ESI-MS of 31 mM solution of 2 depending on pH



Figure S6 Normalized abundance of representative ESI-MS peaks of 1 and 2 as a function of pH, based on Fig. S4 and Fig. S5.



Figure S7 UV-Vis titration of 0.03 mM solution of 1 in 0.1 M TMACl solution with dilute TMAOH solution (top) and dilute HCl solution (bottom)

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Figure S8 UV-Vis titration of 0.03 mM solution of 2 in 0.1 M TMACI solution with dilute TMAOH solution (top) and dilute HCl solution (bottom)



Figure S9 SEM image of black-gray precipitate formed after irradiation of 1 in methanol/water solution (20% v/v) with 300 W Xe lamp for 8h.



Figure S10 Powder XRD pattern (black) of black-gray precipitate formed after irradiation of methanol/water solution (20% v/v) of 1with Xe lamp for 8h. 5 Red lines are diffractions listed in JCPDS file 01-0727 (elemental tellurium).