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

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Tellurium substitution has been previously achieved in other polyoxometalate systems including Anderson-type [TeMo6O19]6− clusters, trans-disubstituted Lindqvist-type [Te3Mo5O19]6− clusters and decavanadate-type [H3TeV9O28]4− clusters.4,5 A mixed oxide of molybdenum, vanadium, tellurium and niobium has been shown to be a good catalyst for conversion of hydrocarbons; thus the tellurium-substituted niobate ion has potential to act as a catalytically active oxide precursor.4,6 Solid niobates have also been studied as water-splitting photocatalysts, along with more effective and well-known titanates and tantalates,6 as niobium oxides have a bandgap energy of about 3.4 eV and that compares well to ZnO or TiO2.7 Photocatalytic H₂ evolution activities of oligomeric polyoxoniobates have been reported recently.8

The synthesis of 1 was carried out by a hydrothermal reaction of a mixture of Te(OH)6 (telluric acid), hydrous niobium oxide and TMAOH. Electrospray-ionization mass spectrometry (ESI-MS) of the solution after reaction suggested the formation of a new Te-substituted cluster, as proven by the complex fingerprint of each peak due to the naturally occurring Te isotopes and higher m/z values compared to the TMA salt of hexaniobiate, TMA5[H2TeNb5O19]20H2O (2) [Fig. S1, S4 and S5, ESI†]. The peak positions match well with calculated peaks of the TMA salt of Te-monosubstituted hexaniobiate [Fig. S1, ESI†].

The structure of [H2TeNb5O19]5− (TeNb5) in 1 was determined by X-ray single crystallography [Fig. 1].‡ The tellurium substitution is obvious from the high electron density in one (Te1/Nb1 site) of the three crystallographically independent metal sites. Tellurium is disordered between the two opposite metal sites in the Lindqvist ion due to its centrosymmetry. Refinement with the partial occupancy model at the Te1/Nb1 site showed that the sum of tellurium occupancy in these two sites is 0.95, which is in good agreement with the suggested TeNb5 stoichiometry. Two protons are bound on the two opposite μ-2-O, linking Nb2 and Nb3 on the equatorial plane. Five TMA counterions are found in the structure refinement, and the formula is expressed as TMA5[H2TeNb5O19]20H2O. The cell constants are very similar to those of the previously reported 2,9 which is in agreement with the isostructural and isovalent Lindqvist-type cluster.

† Electronic supplementary information (ESI) available: Synthesis details, instrumental analysis conditions, ESI-MS spectrum of 1, crystal packing diagram, FT-IR spectra of 1, 2 and 4, pH dependent ESI-MS and UV-Vis spectra of 1 and 2, SEM and XRD of tellurium precipitate. CCDC 959006. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc47001f

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crystallized with the same number of TMA counterions and crystallization water. As a result of the substitution, the terminal Te/Nb–O bond (1.8082(12) Å) is longer than the unsubstituted terminal Nb–O bond in the periphery (1.7505(11) and 1.7727(11) Å). And the Te/Nb–μ4-O bond (2.2832(15) Å) is shorter than Nb–μ4-O bonds (2.4148(16) and 2.4406(15) Å). Because of the mixed metal occupancy, thermal ellipsoids of Te1/Nb1 and μ4-O are elongated in the axial direction [Fig. 1].

Solid-state $^{125}$Te NMR experiment was performed to characterize the Te$^{VI}$ in the cluster. The single substitution in TeNb$_5$ suggests one peak. As predicted, solid-state $^{125}$Te NMR spectrum shows one isotropic peak at 754 ppm accompanied with spinning sidebands [Fig. 2]. We note that the spinning sidebands are not symmetric about the central isotropic peak because Te is in an asymmetric structural environment. The Te is located at one metal site of the Lindqvist cluster, which is intrinsically asymmetric, and faces the center of the cluster on one side, while the other side is coordinated with the terminal oxygen atom and is closer to TMA ions and crystallization waters [Fig. 1, Fig. S2, ESI†].

The pH-dependent stabilities of 1 and 2 were examined by performing ESI-MS and UV-Vis titration experiments. ESI-MS spectra of 31 mM solution (pH = 8.1) of each compound were recorded after the addition of acid or base to modify the solution pH. The peaks of 1 only slightly decreased up to pH ~ 13 when titrated with base, indicating that the TeNb$_5$ cluster is stable under strongly basic conditions [Fig. S4, ESI†]. When titrated with acid, the solution became cloudy, and increasingly so, upon addition of each aliquot below pH 7, which was probably due to formation of hydroxides niobium–oxide colloids. However, most of the clusters in solution had converted to colloidal particles at pH ~ 5 and below. ESI-MS titration of 2 showed similar behaviour [Fig. S5, ESI†]; Nb$_6$ was stable between 7 < pH < 12 but less stable under extreme pH conditions, as suggested by normalized abundance of representative peaks in ESI-MS depending on pH [Fig. S6, ESI†]. In the UV-Vis titration experiment using a more dilute solution (0.03 mM), the electronic spectra of 1 which show LMCT bands at 240 nm and small shoulder at 265 nm did not change significantly up to pH 12.5, which agrees with the stability of TeNb$_5$ under the basic conditions [Fig. S7, ESI†]. During the titration with acid, the overall absorption increased up to pH ~ 4, which is indicative of decomposition. A solution of 2 showed a similar trend in the UV-Vis titration [Fig. S8, ESI†].

We examined photochemical H$_2$ evolution from each 0.2 g of 1 and 2 in a water–methanol solution (25 mL, 80 : 20 v/v) under UV and visible light from a 300 W Xe lamp. Hydrogen evolution activity of TMA salt of peroxohexametaniobate, TMA$_2$[H$_2$TeNb$_5$O$_{19}$]$_6$(O$_2$)$_3$.H$_2$O (3), was also measured. Methanol was used as a sacrificial electron donor and H$_2$ was monitored by gas chromatography. Visible light (~400 nm) did not produce H$_2$; however, under full Xe spectrum illumination a solution of 1 evolved H$_2$ at a rate of 776 µmol h$^{-1}$ g$^{-1}$, which is 70 times higher than that of 2 (11 µmol h$^{-1}$ g$^{-1}$) [Fig. 3]. Upon irradiation, the solution of 2 remained colorless while the solution of 1 became gradually darker and about 10 mg of a black precipitate formed after 8 hours, which was identified as metallic tellurium in mostly nanowire morphology mixed with some microcrystals, on the basis of SEM and XRD data (Fig. S9 and S10, ESI†). The formation of metallic tellurium indicates reduction of the Te$^{VI}$ in 1 to Te$^0$ as the cluster decomposed. The apparent chemical conversion of the niobate cluster is also reflected in the nonlinear H$_2$ evolution plot, which shows an abrupt increase of activity after 2 h. The main product of the photo-assisted
conversion of 1–3 in the solution phase after irradiation was the Nb₆ ion, as detected by ESI-MS. The peroxyxanionate ion 3 showed lowest H₂ evolution activity (1 μmol h⁻¹ g⁻¹) when compared to 1 and 2, but evolved small amounts of O₂ during irradiation, likely due to the photo-induced removal of the peroxy ligand.

The supernatant and precipitate were separated after irradiation of solution of 1 for 8 h to evaluate the H₂-evolution activity of each photo-decomposition product separately. Te⁰ wires alone showed very low H₂ evolution activity when mixed with water—methanol [Fig. 3]. The separated supernatant continued to form more Te⁰ upon irradiation due to the small amount of tellurate present in the supernatant. This supernatant showed a similar H₂ evolution curve but lower H₂ amount of tellurate present in the supernatant. This super-

natant showed a similar H₂ evolution curve but lower H₂ activity in the solution of Nb₆, but higher than that produced from the

H₂Te has been shown to decompose to metallic tellurium in the solution of Nb₆ from the photogenerated electron–hole pairs, in such a way that formation of metallic tellurium in the solution of 1 is faster than in the simple solution mixture of telluric acid and 2. This explains the high H₂ evolution rate in the early stage of irradiation of 1 compared to the control experiment. The total surface area of the particles in the solution of 1 might also be higher than that in the mixture of telluric acid and 2 because of the faster formation of particles, which might have resulted in the high H₂-evolution activity.

In conclusion, the TMA salt of the TeNb₅ molecule reported herein exhibits a similar pH stability window and solid-state structure compared to Nb₆, but demonstrates much higher H₂-evolution activity via a photo-decomposition route to Nb₆ and Te⁰ nanowires. Future studies shall focus on the hydrolysis and isotope-exchange kinetics of the TeNb₅ molecule, by using ^1⁰O and ^12⁵Te NMR together, and compare hydrolysis chemistry with that of the unsubstituted Nb₆.

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**Notes and references**


**Scheme 1** Proposed photocatalytic reaction mechanism.