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 [Te₂Mo₄O₁₉]⁶⁻ clusters and decavanadate-type [H₄TeV₉O₂₈]⁻ clusters. 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. Solid niobates have also been studied as water-splitting photocatalysts, along with more effective and well-known titanates and tantalates, as niobium oxides have a bandgap energy of about 3.4 eV and that compares well to ZnO or TiO₂. Photocatalytic H₂ evolution activities of oligomeric polyoxoniobates have been reported recently.

The synthesis of [H₂TeNb5O₁₉]⁵⁻ was carried out by a hydrothermal reaction of a mixture of Te(OH)₅ (telluric acid), hydrosol 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 hexaniobate, TMA₅[H₃Nb₆O₁₉]·20H₂O (2) [Fig. S1, S4 and S5, ESIF]. The peak positions match well with calculated peaks of the TMA salt of Te-monosubstituted hexaniobate [Fig. S1, ESIF].

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 μ₂-O, linking Nb2 and Nb3 on the equatorial plane. Five TMA countercations 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, which is in agreement with the isostructural and isovalent Lindqvist-type cluster.

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† 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 3, 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
cristallized 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 (2.28325(15) Å) is shorter than Nb–µ4–O bonds (2.41480(16) and 2.44065(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 hydrous 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 behavior [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 peroxyhexaniobate, TMA$_2$[H$_3$Nb$_6$O$_{13}$(O$_2$)$O_4$]$9.5H_2$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 peroxohexaniobate ion 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 evolution activity than the original solution [Fig. 3] probably due to the smaller amount of precipitate, suggesting that coexistence of the niobate cluster and metallic Te0 is necessary to maintain the high H2 evolution activity.

These results suggest a mechanism for photocatalytic H2 evolution shown in Scheme 1. Photoexcitation of TeNb5 forms an electron–hole pair and the electron reduces TeVIII to Te0. As a result, TeNb5 is decomposed to Te0 and Nb6, with the hole oxidizing methanol as a sacrificial electron donor, ultimately forming CO2 and H2O. Once TeVIII is fully reduced to Te0, it may further accept electrons to become telluride (Te2−). We speculate that this aqueous telluride will reduce protons to evolve H2, as H2Te has been shown to decompose to metallic tellurium in aqueous solution. Thus we believe that the high H2 evolution activity in this system is due to coexistence of Nb6 and Te0 nanowires or colloids and that the native tellurium metal acts as a H2-evolution cocatalyst. Cobalamine or H2PtCl6 has been commonly used as a cocatalyst in the study of H2 evolution from telluric acid and isotope-exchange kinetics of the TeNb5 molecule, by using 17O and 125Te NMR together, and compare hydrolysis chemistry with that of the unsubstituted Nb6.

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 17O and 125Te NMR together, and compare hydrolysis chemistry with that of the unsubstituted Nb6.

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Notes and references

† Crystal data. (1) CCDC 959006. C25H44N5O39.25TeNb5, M = 1625.15, monoclinic, α = 33.8700(15), β = 8.4954(4) Å, c = 21.9238(10) Å, β = 110.4751(1), U = 5909.8(5) Å3, T = 93 K, space group C2/c (no. 15), Z = 4, 31567 reflections measured, 6782 unique (Rint = 0.0218) which were used in all calculations. The final wR2(F2) was 0.0407 (all data).


