

Synthesis and Photocatalytic Properties of a New Heteropolyoxoniobate Compound: $K_{10}[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}] \cdot 12H_2O$

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S Supporting Information

ABSTRACT: The synthesis and photocatalytic properties of a heteropolyoxoniobate, $K_{10}[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}] \cdot 12H_2O$ (**1**), are reported, revealing an important role of Zr^{4+} additives in the crystallization. Compound **1** exhibits overall photocatalytic water splitting activity, and its photocatalytic activity is significantly higher than that of $Na_{10}[Nb_2O_2][SiNb_{12}O_{40}] \cdot xH_2O$ (**2**). Fluorescence lifetime measurements suggest that the enhanced photocatalytic activity of **1** likely results from a larger yield of longer-lived charge trapping states in **1** due to the coordination of one water molecule to the bridging Nb^{5+} , leading to highly unsymmetrical seven-coordinated Nb^{5+} sites.

Generating hydrogen from water with solar energy represents a promising and attractive way to prepare hydrogen as a clean and renewable fuel. During past decades, significant progress has been made as hundreds of photocatalysts have been prepared and tested.¹ Still, it is an ongoing challenge to prepare ideal photocatalytic materials suitable for practical applications, in particular, the overall water splitting to produce H_2 and O_2 .

Most known heterogeneous photocatalysts are based on dense structures such as binary and ternary oxides.¹ Such dense solids (e.g., TiO_2) have been intensively studied. In comparison, other structure types such as polyoxometalates (POMs)² and open-framework materials,³ which usually consist of a higher order of structural building blocks (variously known as clusters, secondary building units, SBUs, etc.), have received much less attention. These materials exhibit diverse compositions and topological features, and some of them also contain open coordination sites (those not occupied by network-forming groups)⁴ and internal cavities, which may allow reactant molecules to access active sites more readily.³ Furthermore, the electronic band structures can be tuned by adjusting both fundamental properties of the structural building blocks and their spatial organizations.

POMs are a large family of early transition metal–oxygen clusters.⁵ While structurally different from common dense solids, POMs have compositions closely related to some dense photocatalysts. The photocatalytic H_2 evolution activity of both iso- and heteropolyoxotungstates has been studied.² Among POMs,

polyoxoniobates are of particular interest for photocatalysis because some dense niobates have been shown to be overall water-splitting photocatalysts.⁶ However, despite the well-developed POM chemistry, photocatalytic water-splitting activity of polyoxoniobates has not been demonstrated.

A number of isopolyoxoniobate compounds with Lindqvist structures, such as $[Nb_6O_{19}]^{8-}$ and $[Nb_{10}O_{28}]^{6-}$, are known.⁷ In comparison, heteropolyoxoniobate compounds are much less common and have proved quite difficult to synthesize. A breakthrough in heteropolyoxoniobate chemistry was achieved by Nyman et al., who synthesized $K_{12}[Ti_2O_2][SiNb_{12}O_{40}] \cdot 16H_2O$ and $Na_{14}[H_2Si_4Nb_{16}O_{56}] \cdot 45.5H_2O$.⁸ These two structures were the only known heteropolyoxoniobates that could form crystals large enough for in-house single-crystal X-ray analysis. Later, the low-yield syntheses of microcrystalline forms of several other dodecaniobate compounds with Keggin structure, such as molecular $Na_{16}[TNb_{12}O_{40}] \cdot 4H_2O$ ($T = Si, Ge$),⁹ and one-dimensional (1-D) $Na_{10}[M_2O_2][TNb_{12}O_{40}] \cdot xH_2O$ ($M = Ti, Nb$; $T = Si, Ge$),¹⁰ were also reported. For 1-D dodecaniobates, Keggin $[TNb_{12}O_{40}]$ clusters are connected by a $[M_2O_2]$ bridging unit. The cations in the $[M_2O_2]$ unit are six-coordinated, and the chains are straight.

Here, we report the synthesis, structure, and photocatalytic properties of a new heteropolyoxoniobate, $K_{10}[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}] \cdot xH_2O$ (**1**). The successful synthesis of this phase, in high yield and large single crystals, resulted from our unexpected finding that the addition of $ZrOCl_2/HfOCl_2$ can dramatically affect the synthetic process and final product. One major structural difference between compound **1** and the previously reported compound **2** ($Na_{10}[Nb_2O_2][SiNb_{12}O_{40}] \cdot xH_2O$) is that there is a water molecule directly coordinated to each of the two bridging Nb sites in compound **1**. Thus, compared to the octahedral coordination of Nb^{5+} in compound **2**, the bridging Nb^{5+} site in **1** is seven-coordinated with four O^{2-} anions from the Keggin cluster, two bridging O^{2-} sites shared with another Nb^{5+} , and one water molecule. The seventh coordination affects not only the local coordination geometry of Nb^{5+} but also the 1-D chain configuration and packing of the chains.

Compound **1** was synthesized in 70% yield by the hydrothermal reaction of $ZrOCl_2$, amorphous Nb_2O_5 , tetraethylorthosilicate,

Received: February 22, 2011

Published: April 18, 2011

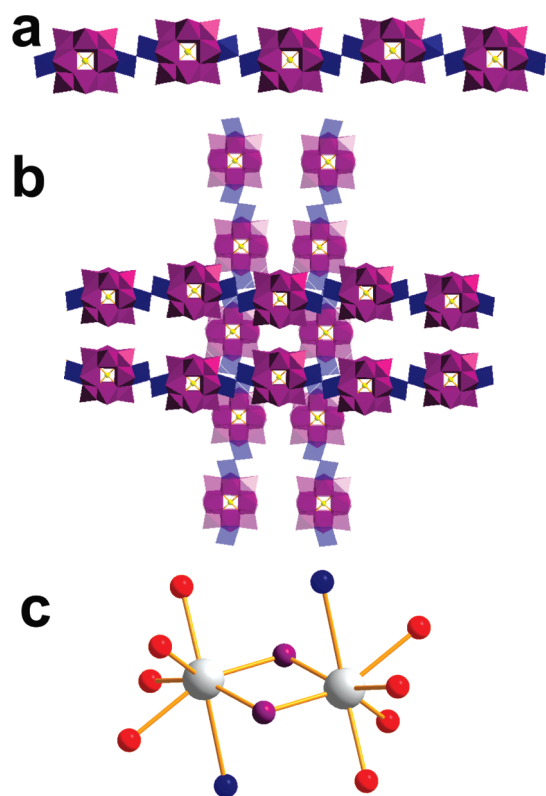


Figure 1. (a) Polyhedral representation of infinite chains formed by $[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2]^{6+}$ (blue) and $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ (purple). (b) View of crossed $\{[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2][\text{SiNb}_{12}\text{O}_{40}]\}^{10-}$ chains at adjacent layers. (c) Ball-and-stick model of the $[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2]^{6+}$ bridging unit. Gray, Nb^{5+} in the bridging unit; red, O^{2-} in the Keggin cluster; purple, bridging O^{2-} ; and blue, O^{2-} in H_2O .

and KOH at 220 °C for 20 h.¹¹ No crystals were obtained when KOH was replaced with NaOH, RbOH, or CsOH. The structure was determined by single-crystal X-ray diffraction¹² and is shown in Figure 1. Contrary to compound 2, which contains straight chains, 1 is composed of anionic zigzag chains formed by $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ α -Keggin clusters linked together via bridging $[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2]^{6+}$ units. These zigzag chains pack in parallel in the *ab* plane, and the chains between two neighboring layers along the *c* axis are perpendicular to each other.

One very interesting discovery is the catalytic role of ZrOCl_2 as an additive in the synthesis. Zr^{4+} is not incorporated into the final product, as confirmed by the bond valence sum (BVS) calculation and EDX elemental analysis (see Supporting Information, Figure S1). Additional experiments were performed to further probe the role of ZrOCl_2 in the synthesis. Several interesting observations were made: (a) without ZrOCl_2 , a clear solution was obtained; (b) 1 can also be prepared by adding $\text{Zr}(\text{OEt})_4$ (zirconium butoxide) or $\text{ZrO}(\text{NO}_3)_2$ as additive; (c) only powders were obtained upon lowering the amount of ZrOCl_2 to one-half or one-quarter of the original amount; (d) amorphous products were obtained by replacing ZrOCl_2 with equal moles of other additives such as $\text{Bi}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, $\text{Al}(\text{NO}_3)_3$, $\text{In}(\text{NO}_3)_3$, $\text{Ga}(\text{NO}_3)_3$, $\text{UO}_2(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2$; and (e) crystals of 1 could also be synthesized by replacing ZrOCl_2 with HfOCl_2 , but with a lower yield (15%).

The above results imply that the Zr-containing additive plays an important role in the synthesis of compound 1 in high yield. It

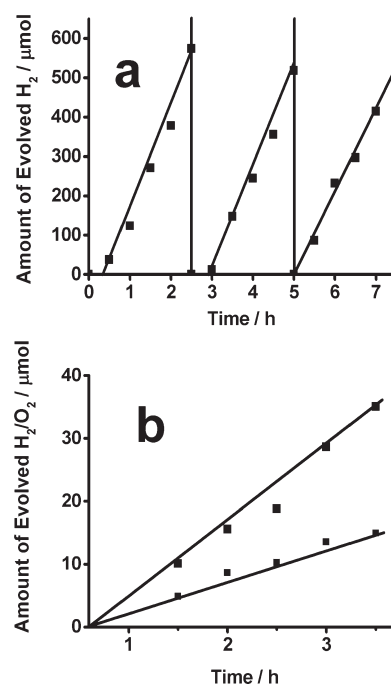


Figure 2. (a) Time course of H_2 evolution from 100 mg of 0.5% Pt-loaded photocatalyst 1 under UV irradiation in 270 mL of 20% methanol aqueous solution. (b) Time course of overall water splitting from 50 mg of 0.5% Ni-loaded photocatalyst 1 under UV irradiation in 270 mL of pure water.

should be noted that only the group 4 compounds with d^0 configuration have been observed to promote the crystallization of compound 1. It appears that the bridging unit tends to form from metal ions with high charge density. Among the group 4 cations, the charge density of Ti^{4+} is the closest to that of Nb^{5+} . Thus, the addition of Ti^{4+} precursor could induce the formation of $[\text{Ti}_2\text{O}_2]^{4+}$ instead of $[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2]^{6+}$ as the bridging unit. The charge densities of Zr^{4+} and Hf^{4+} are lower than that of Nb^{5+} ; therefore, in the presence of Zr^{4+} or Hf^{4+} , $[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2]^{6+}$ serves as the bridging unit.

The pure sample of compound 1 was obtained via ultrasonic isolation of the raw product in deionized water. Phase purity was confirmed by powder X-ray diffraction and optical microscopy (Figures S2 and S3). The amount of water in 1 was determined by thermogravimetric analysis (TGA). As shown in Figure S4, there was a continuous weight loss from 50 to 400 °C, with a total loss of 9.5%, corresponding to about 14 H_2O . The BET surface area of compound 1 was 9.5 m^2/g based on N_2 adsorption analysis (see Figure S5). The UV/vis diffuse reflectance spectrum of 1 reveals that the band gap of 1 is about 3.8 eV (Figure S6). It has been reported that all niobate photocatalysts with overall water splitting activity show photoluminescence (PL) at 77 K.^{6a,b} The PL of compound 1, as shown in Figure S7, showed a broad green emission at a maximum of 510 nm. The onset of the excitation spectrum agreed with that of the absorption spectrum.

To explore the photocatalytic H_2 evolution activity of 1, 100 mg of 0.5% Pt-loaded 1 was suspended in 270 mL of a 20% methanol solution in a quartz cell. The catalyst suspension was irradiated under a 300 W Xe lamp. As shown in Figure 2a, H_2 continuously evolved in 7.5 h at a rate of about 2100 $\mu\text{mol h}^{-1}$ g^{-1} . The total H_2 evolved over 7.5 h was 1616 μmol , with a turnover number of 44. For comparison, we also measured the

photocatalytic H₂ evolution activity of Pt-loaded **2** under the same condition. As shown in Figure S8, the H₂ evolution rate for compound **2** is about 1205 $\mu\text{mol h}^{-1} \text{g}^{-1}$. Considering that the band gap and the BET surface area (13.5 m²/g for **2**) of **2** were comparable to those of **1** and the particle size of **2** was about tens to hundreds of nanometers, which was smaller than that of **1**, as shown in Figure S10, the higher activity of **1** likely originates from its unique structure.

During photocatalytic reaction, an electron is excited from valence band (O2p) to conduction band (mainly composed of the empty orbitals from the metal cation). The electron then transfers from metal to H₂O to produce H₂. The H₂O molecules bonded directly to Nb in compound **1** might be the reason for the higher activity of **1**. As shown in homogeneous H₂ production reactions, the photoinduced unsaturated sites allow the substrate to coordinate to metal cations, and the intermediate states of substrate–organometallic catalytic complexes play a key role in the molecular photocatalytic H₂ production reactions.¹³ Another structural factor that may contribute to the high photocatalytic activity is the distorted coordination configuration of Nb. It has been indicated that distortion of the MO₆ octahedra was essential for the efficient water-splitting reaction due to the large dipole moment in the materials that could facilitate the electron–hole charge separation.^{6d,14} In **1**, seven O²⁻ atoms are around Nb⁵⁺ in the bridging unit, and this unusual geometry gives rise to an extreme angular distortion of the bridging [Nb₂O₂(H₂O)₂]⁶⁺ dimer (O–Nb–O bond angles ranging from ~73° to 122°). This distorted NbO₇ unit in the bridging unit of **1** might provide a better charge separation effect than that of the NbO₆ octahedron in **2**. Fluorescence lifetime measurements (Figure S9) indicated that there was a higher yield of longer-lived trapped charges in **1**, which might be due to stabilization of the surface charges by the bound H₂O, the more distorted NbO₇ unit, or the deactivation of a nonradiative recombination mechanism due to the occupation of a surface site by the H₂O. In any case, the net result would be a larger yield of longer-lived charge trapping states. These states may play a role in the surface reactions that give rise to the enhanced photocatalytic activity of compound **1**.

With NiO as the co-catalyst, the overall photocatalytic water-splitting property of **1** was studied. NiO was loaded to 50 mg of compound **1** in pure water. As shown in Figure 2b, both H₂ and O₂ evolved under UV irradiation at rates of 222 and 97 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively. The stoichiometric ratio of H₂ to O₂ is 2.3:1. The total H₂ evolved over 3.5 h was 35 μmol , about twice the amount of the photocatalyst, proving the photocatalytic nature of the water-splitting reaction.

Dye cation exchange has been shown to be an effective way to sensitize 2-D layered niobates or nanoscrolls¹⁵ as visible-light-active photocatalysts. The same strategy could be applied to sensitize compound **1** for visible light photocatalytic activity. After immersion of compound **1** in Ru(bpy)₃²⁺ for 1 h, H₂ evolution was observed at a rate of about 3 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under visible light irradiation (Figure S11).

In conclusion, a new heteropolyoxoniobate, **1**, was synthesized and structurally characterized. A unique structural characteristic of **1** is seven-coordinated Nb⁵⁺ bound directly by a H₂O. Comparison of the photocatalytic H₂ evolution activity of **1** and **2** implies that the creation of an open metal site might be a new effective strategy to achieve more efficient photocatalysts. Moreover, the feasibility of using POM compounds for photocatalytic overall water-splitting reactions has been demonstrated here. POMs are a large family of compounds with diverse

structures and compositions, which should provide many new opportunities for developing novel and highly efficient photocatalysts. Our discovery of an overall water-splitting photocatalyst based on POM should provide impetus for further development of photocatalysts from diverse types of materials, such as POMs and open-framework compounds.

■ ASSOCIATED CONTENT

Supporting Information. TGA diagram and CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This work was supported by NSF (P.F., DMR-0907175; X.B., DMR-0846958). C.J.B. acknowledges support by the U.S. Department of Energy, Basic Energy Sciences, Grant DOE-FG02-09ER16096.

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(11) In a 23 mL autoclave, 0.36 g of KOH, 0.35 g of amorphous Nb₂O₅, 0.18 g of tetraethylorthosilicate, and 0.08 g of ZrOCl₂ were dissolved in 8 g of H₂O. After the mixture was stirred at room temperature for 30 min, the autoclave was sealed and heated in a 220 °C oven for 24 h. The white crystalline product was purified by ultrasonic separation in deionized water.

(12) Crystal data: tetragonal, P4₂/mnm, $a = b = 16.5765(4)$ Å, $c = 19.2519(10)$ Å, $V = 5290.3(3)$ Å³, $Z = 2$, $D_c = 3.365$ g cm⁻³, $T = 150$ K, 19 720 measured reflections, $R_1 = 0.0723$ for 2161 reflections ($I > 2\sigma(I)$), GooF = 1.048. The structure was solved by direct methods, and the structure refinements were based on $|F^2|$.

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