

# {Ta<sub>12</sub>}/{Ta<sub>16</sub>} Cluster-Containing Polytantalotungstates with Remarkable Photocatalytic H<sub>2</sub> Evolution Activity

Shujun Li,<sup>†,†</sup> Shumei Liu,<sup>†,‡,†</sup> Shuxia Liu,<sup>\*,†</sup> Yiwei Liu,<sup>†</sup> Qun Tang,<sup>†</sup> Zhan Shi,<sup>§</sup> Shuxin Ouyang,<sup>||</sup> and Jinhua Ye<sup>||</sup>

<sup>†</sup>Key Laboratory of Polyoxometalate Science of the Ministry of Education, College of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China

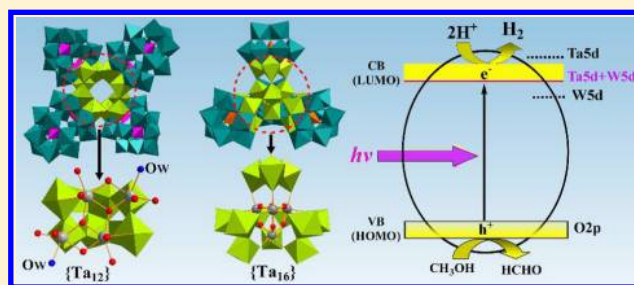
<sup>‡</sup>Department of Materials Science and Engineering, Jilin University, Changchun 130025, China

<sup>§</sup>State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, China

<sup>||</sup>Photocatalytic Materials Center (PCMC), National Institute for Materials Science (NIMS) 1-2-1, Sengen, Tsukuba, Ibaraki, 305-0047, Japan

## Supporting Information

**ABSTRACT:** Four novel polytantalotungstates  $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3] \cdot 17H_2O$  (1),  $K_8Na_8H_4[P_8W_{60}Ta_{12}(H_2O)_4(OH)_8O_{236}] \cdot 42H_2O$  (2),  $Cs_3K_{3.5}H_{0.5}[SiW_9(TaO_2)_3O_{37}] \cdot 9H_2O$  (3), and  $Cs_{10.5}K_4H_{5.5}[Ta_4O_6(SiW_9Ta_3O_{40})_4] \cdot 30H_2O$  (4) were synthesized. Compounds 1 and 3 are tris-(peroxotantalum)-substituted Dawson- and Keggin-type derivatives, whereas 2 and 4 are tetrameric oligomers containing respectively an unprecedented {Ta<sub>12</sub>} and {Ta<sub>16</sub>} cluster core. The photocatalytic activities of 2 and 4 for H<sub>2</sub> evolution from water were evaluated. The significantly enhanced performance against the control  $K_6[P_2W_{18}O_{62}]$  can be attributed to the modulation of the electronic structures of these novel POMs by Ta incorporation. The highest activity observed so far with the use of 2 can be further rationalized by the presence of distorted heptacoordinate Ta atoms in the form of TaO<sub>7</sub> pentagonal bipyramid.



## INTRODUCTION

Since the discovery of the photocatalytic splitting of water on TiO<sub>2</sub> electrodes by Fujishima and Honda in 1972, the photocatalytic H<sub>2</sub> evolution has attracted much attention because of the increasing energy crisis and environmental issues.<sup>1</sup> Over the past decades, great progresses have been made in the discovery of metal oxide semiconductor (MOS, such as TiO<sub>2</sub>, titanates, Ta<sub>2</sub>O<sub>5</sub> and tantalates)-based photocatalysts.<sup>1a,2</sup> As soluble metal oxides, polyoxometalates (POMs) are well-defined metal–oxygen clusters formed by early transition metal of d<sup>0</sup> electronic configuration.<sup>3</sup> Similar to MOSs, POMs are mostly constructed from corner- and edge-shared MO<sub>6</sub> (M = Mo<sup>6+</sup>, W<sup>6+</sup>, Nb<sup>5+</sup>, Ta<sup>5+</sup>) octahedra. The similarities in composition and structure endow POMs and MOSs with similar electronic and light-absorption characteristics.<sup>4</sup> For example, like the valence band (VB) and conduction band (CB) in MOSs, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of POMs are also composed of oxygen 2p and metal d orbitals, respectively.<sup>5</sup> Upon irradiation, electrons in POMs are promoted from HOMO to LUMO as from VB to CB in MOSs inducing oxygen-to-metal charge transfer (OMCT). In addition, the HOMO–LUMO gap of POMs generally approximates the band gap of MOSs. For example,

the HOMO–LUMO gap of Keggin polyoxotungstates is about 2.8 eV, whereas the band gap of TiO<sub>2</sub> is about 3.2 eV.<sup>4,6</sup> A corollary is that POMs exhibit similar photochemical and photocatalytic behaviors to MOS photocatalysts and may be considered as soluble analogues of MOSs.<sup>7</sup>

As green photocatalysts, polyoxotungstates (POTs) have been extensively studied for the degradation of organic pollutants in water.<sup>4,6,8</sup> The H<sub>2</sub> evolution activity of a few POTs has also been investigated,<sup>9</sup> but the performance is not nearly as good as that of MOS photocatalysts, among which Ta oxides<sup>10</sup> and tantalates<sup>11</sup> such as Ta<sub>2</sub>O<sub>5</sub>, MTaO<sub>3</sub> (M = Na, K, Li, Ag), M<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> (M = Ca, Ba), MTa<sub>2</sub>O<sub>6</sub> (M = Mg, Ba, Sr), and La-doped NaTaO<sub>3</sub> are most notable. The high CB levels have been proved to be key to the activity of these Ta-based catalysts.<sup>1a,2</sup> Because the CB level largely depends on the nature of the metal(s) and can be tuned with appropriate combination of metals,<sup>12</sup> it may be feasible in the case of POT to lift their relatively low LUMO energy levels,<sup>4,6</sup> for example, by incorporating Ta atoms in order to achieve mixing or hybridization of Ta5d and W5d orbitals. As such, the

Received: July 30, 2012

Published: November 6, 2012

photocatalytic H<sub>2</sub> evolution activity of the resulting poly-tantalotungstates may be enhanced over pure polytungstates.

Along this line of thinking, we have succeeded in making four novel polytantalotungstates with the use of trivacant [P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> and [SiW<sub>9</sub>O<sub>34</sub>]<sup>10-</sup> as ligands: K<sub>5</sub>Na<sub>4</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>(TaO<sub>2</sub>)<sub>3</sub>]<sub>3</sub>·17H<sub>2</sub>O (**1**), K<sub>8</sub>Na<sub>8</sub>H<sub>4</sub>[P<sub>8</sub>W<sub>60</sub>Ta<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>8</sub>O<sub>236</sub>]<sub>4</sub>·42H<sub>2</sub>O (**2**), Cs<sub>3</sub>K<sub>3.5</sub>H<sub>0.5</sub>[SiW<sub>9</sub>(TaO<sub>2</sub>)<sub>3</sub>O<sub>37</sub>]<sub>9</sub>·9H<sub>2</sub>O (**3**), and Cs<sub>10.5</sub>K<sub>4</sub>H<sub>5.5</sub>[Ta<sub>4</sub>O<sub>6</sub>(SiW<sub>9</sub>Ta<sub>3</sub>O<sub>40</sub>)<sub>4</sub>]<sub>3</sub>·30H<sub>2</sub>O (**4**). Compounds **1** and **3** are tris-(peroxotantalum)-substituted Dawson- and Keggin-type derivatives, respectively. Compounds **2** and **4** are tetrameric oligomers, containing respectively an unprecedented {Ta<sub>12</sub>O<sub>56</sub>} (abbreviated as {Ta<sub>12</sub>}) and {Ta<sub>16</sub>O<sub>66</sub>} (abbreviated as {Ta<sub>16</sub>}) cluster core. The photocatalytic H<sub>2</sub> evolution activities of **2** and **4**, with respect to K<sub>6</sub>[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sub>3</sub>·14H<sub>2</sub>O (abbreviated as P<sub>2</sub>W<sub>18</sub>), have been evaluated. The H<sub>2</sub> evolution rate of **2** reaches 1250 μmol g<sup>-1</sup> h<sup>-1</sup>, which is, to the best of our knowledge, highest among all POT photocatalysts reported thus far.

## RESULTS AND DISCUSSION

**Synthesis.** The synthesis of Ta-containing POMs is challenging largely due to the strong tendency of soluble Ta precursors (e.g., [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> or TaCl<sub>5</sub>) to form intractable gel-like materials in aqueous solution or Ta<sub>2</sub>O<sub>5</sub> precipitate. The chemistry of polyoxotantalate (POTa) has been dominated by that of the Lindqvist anion [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup>, which is under alkaline conditions only.<sup>13</sup> As a result, there exist only a small number of derivatives of [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> in the literature.<sup>14</sup> However, although cluster compounds featuring {Ta<sub>7</sub>} and {Ta<sub>8</sub>} cores stabilized with organic ligands<sup>15</sup> are known, they are prone to oxidation and hydrolysis reactions leading to decomposition in aqueous solutions.

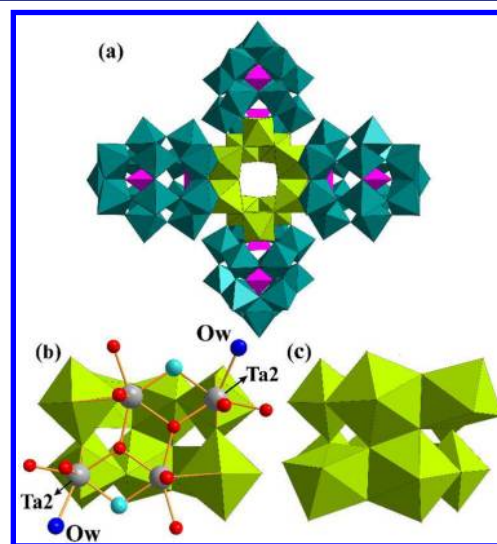
In this article, we demonstrate that it is feasible to access high-nuclearity Ta clusters under acidic conditions with the use of trivacant Dawson- or Keggin-type POTs as supporting and protecting ligands. By reacting [α-P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> and [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> in aqueous H<sub>2</sub>O<sub>2</sub> solution, compound **1**, formulated as K<sub>5</sub>Na<sub>4</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>59</sub>(TaO<sub>2</sub>)<sub>3</sub>]<sub>3</sub>·17H<sub>2</sub>O based on evidence from <sup>31</sup>P and <sup>183</sup>W NMR, IR, thermogravimetric analysis (Figure S3 of the Supporting Information), and elemental analyses (K, Na, P, Ta, W), was obtained; despite our painstaking efforts, single crystals suitable for X-ray diffraction still eluded us. Crucial to the isolation of **1** is the use of excess H<sub>2</sub>O<sub>2</sub> to prevent the formation of insoluble Ta<sub>2</sub>O<sub>5</sub>. Even so, it has been found that [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> decomposes if left in strongly acid solution for an extended period of time. Therefore, the other two reactants, namely hydrochloric acid and Na<sub>12</sub>[α-P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> should be added swiftly to the [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup>/H<sub>2</sub>O<sub>2</sub> solution, after which the pH value of the mixed solution was raised up to about pH 6.2 and the reaction went smoothly. The product yield was maximized if the reaction was carried out at 45 °C for at least one hour.

Compound **2** was obtained facilely and in good yield by refluxing **1** in an acid solution, during which course the peroxo groups of **1** are eliminated. It is of note that one-pot synthesis without isolation of **1** only produced a complex product mixture that is hard to purify. The complication may be caused by the presence of various species present in the solution and at equilibrium prior to the crystallization of **1**; these species, by going through disparate reaction pathways under reflux and in an acidic solution, may lead to the formation of various products present in the product mixture.

The syntheses of Keggin derivatives **3** and **4** are similar to those of **1** and **2**, respectively. Compound **3** was synthesized by reacting [SiW<sub>9</sub>O<sub>34</sub>]<sup>10-</sup> with [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> in an H<sub>2</sub>O<sub>2</sub> solution but can only be precipitated out as mixed Cs/K salt by the addition of solid CsCl. Reflux of **3** in an acid solution afforded compound **4** in moderate yield.

We also attempted the synthesis of the tris-tantalum substituted monomeric species {P<sub>2</sub>W<sub>15</sub>Ta<sub>3</sub>O<sub>62</sub>} and {SiW<sub>9</sub>Ta<sub>3</sub>O<sub>40</sub>} respectively with classical Dawson or Keggin structures, but failed. They, as controls, would be valuable in investigating the effects of incorporating Ta into the POT frameworks on the photocatalytic properties. We did not succeed, however, possibly because the monomeric species are unstable with a strong tendency to oligomerize under acidic conditions with the formation of M-O-M bonding motifs. Analogous chemistry has previously been demonstrated in Ti- and Nb-containing POMs.<sup>16</sup>

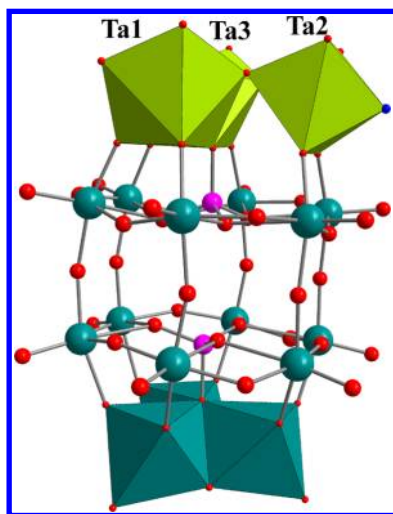
**Structure Description.** As shown in part a of Figure 1 and Figure S1 of the Supporting Information, the polyanion of **2**



**Figure 1.** (a) Polyhedral representation of polyanion **2a**. (b) and (c) Combined polyhedral/ball-and-stick representations of the {Ta<sub>12</sub>} cluster in **2a**. Color scheme for polyhedra: WO<sub>6</sub> (teal), PO<sub>4</sub> (pink), TaO<sub>7</sub> (lime); for spheres: Ta (gray), O (oxo, red; H<sub>2</sub>O, blue; OH, cyan).

(**2a**) consists of four tetrahedrally disposed lacunary Wells-Dawson {P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>} segments linked by a central {Ta<sub>12</sub>} cluster. Each Ta atom is heptacoordinate with O atoms, forming a distorted pentagonal bipyramid of TaO<sub>7</sub> (parts b and c of Figure 1). Three corner- and edge-shared TaO<sub>7</sub> units form a secondary building unit {Ta<sub>3</sub>}; four such units are further assembled to give the {Ta<sub>12</sub>} core. It is tempting to consider this Ta-oxo motif as a potential building block for the assembly of polyoxotantalates and Ta-containing heterometallic POMs characterized by gigantic cluster structures similar to the well-known Mo-, W-, and Nb-based POMs.<sup>17</sup> We also note that several tetrapod-Dawson POMs have been reported,<sup>16a-d,18-20</sup> but they are all regular tetrahedra with ideal or approximate *Td* symmetry. However, the unique configuration of the present {Ta<sub>12</sub>} cluster leads to a markedly different C<sub>2v</sub> symmetry of **2a** (Figure S2 of the Supporting Information).

As shown in Figure 2, in the {Ta<sub>3</sub>} unit, Ta1 and Ta3 atoms are edge-shared, each coordinated by an O(P) atom with a Ta–



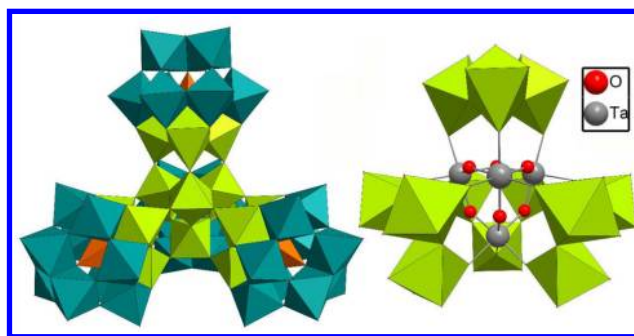
**Figure 2.** Mixed polyhedral/ball-and-stick representation of the quarter motif of polyanion **2a**. Color scheme for polyhedra:  $\text{WO}_6$  (teal),  $\text{TaO}_7$  (lime); for spheres: W (teal), P (purple), O (red and blue).

O(P) distance of 1.53 Å. Ta2 is uniquely corner-shared with Ta1 and Ta3, but not directly bonded to the O(P) atom as indicated by the long Ta $\cdots$ O(P) separation of 3.90 Å. It is however coordinated by an aqua ligand with a normal Ta–O(aqua) bond length of 2.17 Å. The nature of these and other O atoms in **2a** is determined by the bond valence sums (BVS)<sup>21</sup> (Figure S3 of the Supporting Information): there are four terminal  $\text{H}_2\text{O}$  (0.50) and 8  $\mu_2$ -OH (1.39–1.48) with the rest being either  $\mu_2$ -O (2.01–2.06) or  $\mu_3$ -O atoms (2.15–2.21). The BVS results for the other atoms in **2a** are consistent with the assignments of P(V) (4.63–5.12), Ta(V) (4.98–5.21), and W(VI) (5.71–6.11).

Of particular note in the crystal structure of **3a**, the polyanion of compound **3**, is that every Ta atom is coordinated by 5 O atoms and one terminal  $\eta^2$ -peroxy group (Figures S4 and S5 of the Supporting Information). To our best knowledge, the latter is the very first structurally proven Ta-peroxy motif providing a valuable addition to the family of peroxy-containing POMs.<sup>16f,22</sup> The average O–O distance in the peroxy groups of **3a** is 1.50 Å, which is close to the values found in the crystal structures of hydrogen peroxide (1.49 Å)<sup>23</sup> and the aforementioned peroxy-containing POMs.<sup>16f,22</sup>

The crystal structure of **4a**, the polyanion of compound **4**, consists of a  $\{\text{Ta}_{16}\}$  cluster core surrounded by four  $\{\text{SiW}_9\text{O}_{34}\}$  units (Figure 3); the  $\{\text{Ta}_{16}\}$  core contains four tritantalum groups from the Keggin units linked together by a central  $\text{Ta}_4\text{O}_6$  motif (Figures 3 and Figure S6 of the Supporting Information). Unlike the heptacoordinate Ta atoms of  $\text{TaO}_7$  in the structure of **2a**, the Ta atoms in **4a** are each hexacoordinate with O, forming an octahedron of  $\text{TaO}_6$ . On the basis of the bond lengths found in the structures of **3** and **4**, BVS analyses yield the following results: W(VI), Ta(V), Si(IV), peroxy O of **3** (monovalent, 0.869–0.925), and other O atoms (divalent, 1.573–2.044).

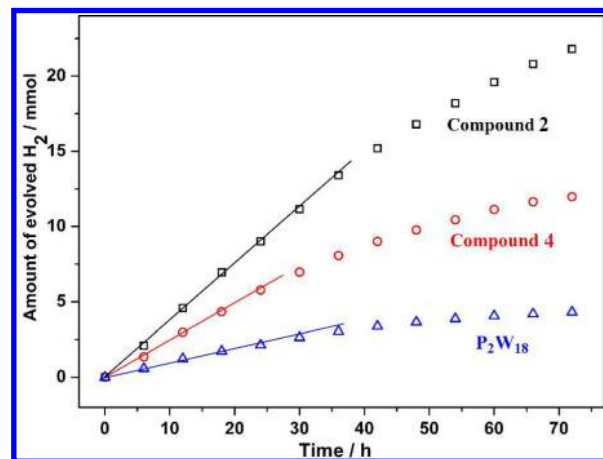
**Photocatalytic Activity.** To demonstrate the potential use of compounds **2** and **4** as photocatalysts and in hopes of demonstrating the effects of Ta incorporation into POTs on the enhancement of catalytic activity, the rate of  $\text{H}_2$  evolution from water under photolytic conditions was measured using the Ta-free  $\text{P}_2\text{W}_{18}$  as control.



**Figure 3.** Polyhedral representation of the polyanion **4a** (left), and the mixed polyhedral/ball-and-stick representation of the  $\{\text{Ta}_{16}\}$  cluster (right). Color scheme:  $\text{WO}_6$  (teal),  $\text{SiO}_4$  (orange),  $\text{TaO}_6$  (lime).

The photocatalysis of all three compounds was first characterized by the color change of the reaction mixture from colorless to deep blue, an indication of the reduction of W(VI). The color remained if the system was protected from oxygen. However, reoxidation of W(V) to W(VI) occurred within hours of air or oxygen exposure with decoloration of the deep-blue solution.

With the use of **2** and in the presence of Pt cocatalyst formed by the reduction of  $\text{H}_2\text{PtCl}_6$  at the beginning of the photoreaction,  $\text{H}_2$  evolved steadily at a rate of 375  $\mu\text{mol h}^{-1}$  after irradiation for 45 min, highest among all known POT photocatalysts. The total amount of  $\text{H}_2$  evolved over 12 h is 101 mL (4.5 mmol), and the corresponding turnover number [(moles of  $\text{H}_2$  formed)/(moles of **2**)] is 247. No obvious decline in the  $\text{H}_2$  evolution rate was observed within 36 h (Figure 4 and Figure S19 of the Supporting Information). In



**Figure 4.** Dependence of  $\text{H}_2$  production on irradiation time with the use of **2** (black), **4** (red), and  $\text{P}_2\text{W}_{18}$  (blue) as photocatalysts. The experiments were performed in 270 mL of solution containing 50 mL  $\text{CH}_3\text{OH}$ , 220 mL 0.5 M HCl, 0.2 mL  $\text{H}_2\text{PtCl}_6$  solution (1.48 mg Pt), and 0.3 g catalysts.

comparison, the use of **4** and  $\text{P}_2\text{W}_{18}$  (control) under otherwise exactly the same reaction conditions led to the production of  $\text{H}_2$  at rates of 241 and 89  $\mu\text{mol h}^{-1}$ , respectively (Figure 4). The  $\text{H}_2$  evolution rate of **2**, **4** and  $\text{P}_2\text{W}_{18}$  were respectively 1250, 803, 297, if using  $\mu\text{mol g}^{-1} \text{h}^{-1}$  as unit.

These results merit further discussion. *First of all*, the significantly higher rates with the use of **2** and **4** versus the  $\text{P}_2\text{W}_{18}$  control clearly indicate the positive effects of Ta incorporation on the photocatalytic activity, possibly due to the

modulation of the electronic structure by way of mixing the W5d and Ta5d orbitals and specifically raising the LUMO level of the polytantalotungstates with respect to Ta-free POTs. *Second*, the noticeably higher rate of H<sub>2</sub> evolution in the case of 2 versus 4 may be rationalized in terms of its unique structure. On the one hand, the TaO<sub>7</sub> pentagonal bipyramids in 2 are severely distorted as reflected by the Ta–O bond lengths between 1.92 Å and 2.18 Å and the O–Ta–O bond angles between 67.0° to 156.9°. It is commonly believed that the dipole moment originated from the distortion of M–O polyhedra is important for charge separation in the photolytic process and consequently the resulting catalytic activities of POMs.<sup>12a,24</sup> On the other hand, the formation of protonated intermediates in titania and homogeneous organometallic complex systems has been shown to play important roles in the photocatalytic production of H<sub>2</sub>.<sup>25</sup> In 2, 4 aqua ligands and 8 μ<sub>2</sub>–OH are bonded directly to Ta atoms in the {Ta<sub>12</sub>} cluster, providing effective pathway(s) for electron transfer and the subsequent reduction of proton to H/H<sub>2</sub>. *Third*, compound 2 can be regenerated and recovered (Figure S18 of the Supporting Information) when the deep-blue reaction mixture was reoxidized by exposure to air or oxygen. The robustness of 2 and its catalytically active equivalents under the acidic catalytic conditions is collectively supported by the following evidence: (1) No change took place in the <sup>31</sup>P NMR spectrum of 2 after its storage in acid solution for four months (part B of Figure S21 of the Supporting Information); (2) Compound 2 can be recrystallized repeatedly in nearly quantitative yields from acidic solutions (aq. HCl, HNO<sub>3</sub>, or H<sub>2</sub>SO<sub>4</sub>; 0.1–1.0 M [H<sup>+</sup>]); (3) The cyclic voltammograms of 2 in 1.0 M H<sub>2</sub>SO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> are reproducible in multiple scans (Figure S16 of the Supporting Information) suggesting that 2 is stable during the reversible redox process leading to the photocatalysis; (4) the IR and <sup>31</sup>P NMR spectra of the recovered sample after photocatalytic experiments (Figure S20 and part C of Figure S21 of the Supporting Information) are the same as those produced from the as-prepared 2.

Analogous photocatalytic studies were not done for compounds 1 and 3 because neither can maintain their structural and compositional integrity during the photocatalytic reactions because of the presence of the easily reduced Ta-peroxo moieties. A gamut of reduction products including 2, 4, and some unknown species was produced; the species possibly responsible for catalysis cannot be unambiguously identified.

## SUMMARY

In summary, two tris-(peroxotantalum)-substituted polytantalotungstates (1 and 3) and two high-nuclearity Ta cluster-containing polytantalotungstates (2 and 4) were obtained by facile aqueous routes in which two different trivacant polytungstates were used to control the assembly of the unprecedented and highest-nuclearity Ta cluster cores. Significant photocatalytic activities of 2 and 4 for H<sub>2</sub> production from water were demonstrated with respect to the use of K<sub>6</sub>[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]·14H<sub>2</sub>O, a structurally closely related and Ta-free polyoxotungstate, clearly suggesting the importance of modulating the electronic structure of these novel POMs by way of Ta incorporation. Compound 2 is characterized by uniquely structured pentagonal bipyramids of TaO<sub>7</sub>. This severely distorted building unit is presumably responsible for the observed photocatalytic effects of 2 because of its enhanced ability to promote charge separation and to prevent electron–hole recombination during the photolytic process. Further-

more, the presence of Ta-bonded aqua and hydroxo ligands is believed to offer the pathways for facile electron transfer for the reduction of proton to H<sub>2</sub>. Thus, the present work not only adds four novel members to a new all-important family of POMs but also offers a new approach to the development of effective photocatalysts for the production of H<sub>2</sub>, a much sought-after clean energy source. Our future work will be extended to the Ta/W, Ta/Nb, and Ta/Mo mixed-metal POMs systems.

## EXPERIMENTAL SECTION

**Materials and Instruments.** K<sub>6</sub>[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]·14H<sub>2</sub>O was synthesized according to a published procedure.<sup>26</sup> The IR spectra in KBr pellets were recorded in the range 400–4000 cm<sup>-1</sup> with an Alpha Centaur FT/IR spectrophotometer. Elemental analyses for Cs, Na, P, K, Si, Ta, and W were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Thermogravimetric analyses were carried out by using a PerkinElmer TGA7 instrument, with a heating rate of 10 °C/min, under a nitrogen atmosphere. UV–vis absorption spectra were obtained by using a 752 PC UV–Vis spectrophotometer. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku D/MAX-3 instrument with Cu–Kα radiation in the angular range 2θ = 3–60° at 293 K. UV–vis diffuse reflectance spectra (UV–vis/DRS) were recorded on a Cary 500 UV–vis-NIR spectrometer. The <sup>183</sup>W NMR spectra and <sup>31</sup>P NMR spectra were measured on Avance-400 Bruker NMR spectrometers. Electrochemical measurements were performed with a CHI660B electrochemical workstation (Chenhua Instruments Co., Shanghai, China). Three-electrode system was employed in this study. The glass carbon electrode (*d* = 3 mm) was used as a working electrode, the Ag/AgCl electrode as a reference electrode, and Pt coil as a counter electrode. All potentials were measured and reported versus the Ag/AgCl. All of the experiments were conducted at ambient temperature (25–30 °C). The H<sub>2</sub> evolution reaction was performed in an inner-irradiation-type quartz reactor. The reaction solution was irradiated with the UV light emitted by a 250 W high-pressure Hg lamp (CEL-LAM 250). The amounts of H<sub>2</sub> evolved were determined using a gas chromatograph (Agilent 6890N).

**Synthesis of 1.** K<sub>8</sub>[Ta<sub>6</sub>O<sub>19</sub>]·17H<sub>2</sub>O<sup>27</sup> (2.20 g, 1.10 mmol) was dissolved in an H<sub>2</sub>O<sub>2</sub> solution (12 mL of 30% aqueous H<sub>2</sub>O<sub>2</sub> in 160 mL of water). With vigorous stirring, HCl (aq. 1.0 M) was added in one aliquot (14 mL), followed by the immediate addition of Na<sub>12</sub>[α-P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]·18H<sub>2</sub>O<sup>28</sup> (9.50 g, 2.20 mmol). The resulting mixture was stirred with heating at 45 °C for 1 h, cooled to room temperature, and then filtered to remove some white precipitate. To the filtrate was added solid KCl (7.0 g). The mixture was stirred for 40 min and filtered to remove the small amount of white precipitate formed. To the yellow filtrate was again added KCl (25 g), and the mixture was stirred for another 40 min and then filtered to collect the yellow precipitate formed. The precipitate was washed first with ethanol (12 mL) and then diethyl ether (12 mL), and dried in air to give the product as a yellow powder (5.9 g, 53% yield based on Ta precursor). Anal. Calcd (%) for K<sub>5</sub>Na<sub>4</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>59</sub>(TaO<sub>2</sub>)<sub>3</sub>]·17H<sub>2</sub>O: Na 1.84, P 1.24, K 3.91, Ta 10.87, W 55.20; found Na 1.80, P 1.28, K 3.83, Ta 10.96, W 54.88. IR (KBr disks): 1089(s), 952(s), 916(sh), 854(sh), 772(vs), 559(vw), 526(w). <sup>31</sup>P NMR (ppm) –10.5, –14.5. <sup>183</sup>W NMR (ppm) –150.2, –187.0, –216.4.

**Synthesis of 2.** A yellow solution of 1 (1.0 g) in 20 mL of HCl (0.5 M) was refluxed for 5 h to produce a colorless solution. It was cooled to room temperature and filtered. The filtrate was allowed to evaporate at room temperature, affording single crystals suitable for X-ray crystallography (yield 76% based on 1). Anal. Calcd (%) for K<sub>8</sub>Na<sub>8</sub>H<sub>4</sub>[P<sub>8</sub>W<sub>60</sub>Ta<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>8</sub>O<sub>236</sub>]·42H<sub>2</sub>O: Na 0.98, P 1.33, K 1.67, Ta 11.62, W 59.01; found Na 1.05, P 1.27, K 1.74, Ta 11.24, W 58.67. IR (KBr disks): 1092(s), 960(s), 919(sh), 768(s), 557(vw), 523(w). <sup>31</sup>P NMR (ppm) –11.4, –14.4.

Compound 2 can also be obtained by refluxing 1.0 g of 1 in 20 mL of HNO<sub>3</sub> (0.5 M) or H<sub>2</sub>SO<sub>4</sub> (0.25 M) for 5 h till the yellow solution

was decolorized. Upon cooling and standing of the filtrate, the product was obtained as well-faceted crystals (yield: 71% in HNO<sub>3</sub> and 72% in H<sub>2</sub>SO<sub>4</sub>). If necessary, 2 can be recrystallized from an acidic solution (0.1–1.0 M [H<sup>+</sup>] for HCl, HNO<sub>3</sub>, or H<sub>2</sub>SO<sub>4</sub>) in nearly quantitative yield.

**Synthesis of 3.** To a solution containing K<sub>8</sub>[Ta<sub>6</sub>O<sub>19</sub>]·17H<sub>2</sub>O (3.15 g, 1.57 mmol), H<sub>2</sub>O<sub>2</sub> (30 mL, 30% aqueous H<sub>2</sub>O<sub>2</sub>), and water (190 mL) was added with vigorous stirring 24 mL of HCl solution (aq. 1.0 M) in one aliquot. Finely powdered A-α-Na<sub>10</sub>SiW<sub>9</sub>O<sub>34</sub>·18H<sub>2</sub>O<sup>29</sup> (8.73 g, 3.14 mmol) was added immediately after. The resulting mixture was stirred at 45 °C for 30 min to produce a yellow solution to which solid CsCl (30 g, 179 mmol) was added (Note: The use of less expensive KCl did not lead to the precipitation of the product.). This mixture was stirred for 30 min and then filtered. The yellow precipitate collected was washed with two 15-mL aliquots of diethyl ether and then dried in air (yield 40%, based on Ta precursor). Yellow single crystals suitable for X-ray crystallography were obtained by recrystallization from a dilute H<sub>2</sub>O<sub>2</sub> solution in 82% yield. Anal. Calcd for Cs<sub>3</sub>K<sub>3.5</sub>H<sub>0.5</sub>[SiW<sub>9</sub>(TaO<sub>2</sub>)<sub>3</sub>O<sub>37</sub>]·9H<sub>2</sub>O: Si, 0.78; K, 3.79; Cs, 11.04; Ta, 15.03; W, 45.81. Found: Si, 0.82; K, 3.90; Cs, 11.25; Ta, 14.78; W, 45.43. IR (KBr disks): 998 (sh), 962 (w), 916 (s), 848 (sh), 790 (vs), 668 (w), 616 (w), 577 (vw), 535(w), 492(w).

**Synthesis of 4.** The yellow solution prepared by dissolving 3 (0.80 g, 0.22 mmol) in 30 mL of HCl solution (aq. 0.5 M) was decolorized after reflux for 2 h. It was cooled to room temperature, and then filtered to remove the white precipitate. The filtrate was allowed to evaporate at room temperature, from which colorless crystals suitable for X-ray diffraction were obtained in one week (yield: 34% based on 3). Anal. Calcd for Cs<sub>10.5</sub>K<sub>4</sub>H<sub>5.5</sub>[Ta<sub>4</sub>O<sub>6</sub>(SiW<sub>9</sub>Ta<sub>3</sub>O<sub>40</sub>)<sub>4</sub>]·30H<sub>2</sub>O: Si, 0.77; K, 1.08; Cs, 10.53; Ta, 19.95; W, 45.61. Found: Si, 0.83; K, 1.24; Cs, 10.77; Ta, 19.56; W, 46.04. IR (KBr disks): 1062 (w), 987 (w), 915(s), 782(s), 688(vs), 521(w).

**Photocatalytic Studies.** To an aqueous methanol solution containing 50 mL CH<sub>3</sub>OH and 220 mL 0.5 M HCl was added the catalyst (2, 4, or P<sub>2</sub>W<sub>18</sub>, 0.3 g) and 0.2 mL H<sub>2</sub>PtCl<sub>6</sub> solution (0.038 M, containing 1.48 mg Pt).<sup>30</sup> The resulting solution was irradiated with a 250 W high-pressure Hg lamp.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

X-ray crystallography, additional figures, characterization, and properties of 1–4. This material is available free of charge via the Internet at <http://pubs.acs.org>. For instructions on what should be included in the Supporting Information as well as how to prepare this material for publication, check the Instructions for Authors at (<http://pubs.acs.org/page/jacsat/submission/authors.html>).

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: liusx@nenu.edu.cn.

### Author Contributions

†These authors contributed equally to this work.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the NSFC (Grants 20973035, 21171032, and 21231002), Fundamental Research Funds for the Central Universities (Grants 09ZDQD0015 and 10SSXT136), and the Open Research Fund of the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (Jilin University, Grant 2012–10).

## ■ REFERENCES

- (1) (a) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. *Chem. Rev.* **2010**, *110*, 6503–6570. (b) Porob, D. G.; Maggard, P. A. *J. Solid State Chem.* **2006**, *179*, 1727–1732. (c) Kudo, A.; Kato, H. *Chem. Phys. Lett.* **2000**, *331*, 373–377.
- (2) (a) Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253–278. (b) Zou, Z.; Ye, J.; Sayama, K.; Arakawa, H. *Nature* **2001**, *414*, 625–627.
- (3) (a) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, Netherlands, 2001. (b) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239–271. (c) Long, D.-L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105–121. (d) Kortz, U.; Müller, A.; van Slageren, J.; Schnack, J.; Dalal, N. S.; Dressel, M. *Coord. Chem. Rev.* **2009**, *253*, 2315–2327. (e) Nyman, M.; Bonhomme, F.; Alam, T. M.; Rodriguez, M. A.; Cherry, B. R.; Krumhansl, J. L.; Nenoff, T. M.; Sattler, A. M. *Science* **2002**, *297*, 996–998. (f) Hill, C. L.; Prosser-McCarthy, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407–455. (g) Yin, P.; Wu, P.; Xiao, Z.; Li, D.; Bitterlich, E.; Zhang, J.; Cheng, P.; Vezenov, D. V.; Liu, T.; Wei, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 2521–2525. (h) Zhang, Z.; Lin, Q.; Kurunthu, D.; Wu, T.; Zuo, F.; Zheng, S.-T.; Bardeen, C. J.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2011**, *133*, 6934–6937.
- (4) (a) Hiskia, A.; Mylonas, A.; Papaconstantinou, E. *Chem. Soc. Rev.* **2001**, *30*, 62–69. (b) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1–31.
- (5) (a) Yamase, T. *Chem. Rev.* **1998**, *98*, 307–325. (b) Biboum, R. N.; Njiki, C. P. N.; Zhang, G.; Kortz, U.; Mialane, P.; Dolbecq, A.; Mbomekalle, I. M.; Nadjou, L.; Keita, B. *J. Mater. Chem.* **2011**, *21*, 645–650.
- (6) (a) Yamase, T. *Catal. Surv. Asia* **2003**, *7*, 203–217. (b) Yang, H.; Liu, T.; Cao, M.; Li, H.; Gao, S.; Cao, R. *Chem. Commun.* **2010**, *46*, 2429–2431. (c) Guo, Y.; Hu, C. *J. Mol. Catal. A: Chem.* **2007**, *262*, 136–148.
- (7) (a) Maldotti, A.; Amadelli, R.; Varani, C.; Tollari, S.; Porta, F. *Inorg. Chem.* **1994**, *33*, 2968–2973. (b) Crano, N. J.; Chambers, R. C.; Lynch, V. M.; Fox, M. A. *J. Mol. Catal. A: Chem.* **1996**, *114*, 65–75.
- (8) (a) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148–5157. (b) Ioannidis, A.; Papaconstantinou, E. *Inorg. Chem.* **1985**, *24*, 439–441. (c) Streb, C. *Dalton Trans.* **2012**, *41*, 1651–1659. (d) Crano, N. J.; Chambers, R. C.; Lynch, V. M.; Fox, M. A. *J. Mol. Catal. A: Chem.* **1996**, *114*, 65–75.
- (9) (a) Yamase, T.; Cao, X. O.; Yazaki, S. *J. Mol. Catal. A: Chem.* **2007**, *262*, 119–127. (b) Darwent, J. R. *J. Chem. Soc., Chem. Commun.* **1982**, *14*, 798–799. (c) Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, *5*, 793–799. (d) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, *2*, 395–399. (e) Yamase, T.; Watanabe, R. *J. Chem. Soc., Dalton Trans.* **1986**, *8*, 1669–1673. (f) Hori, H.; Koike, K. *Energy Fuels* **2005**, *19*, 2209–2213. (g) Zhang, Z.; Lin, Q.; Zheng, S.-T.; Bu, X.; Feng, P. *Chem. Commun.* **2011**, *47*, 3918–3920.
- (10) (a) Huang, J.; Ma, R.; Ebina, Y.; Fukuda, K.; Takada, K.; Sasaki, T. *Chem. Mater.* **2010**, *22*, 2582–2587. (b) Kudo, A. *Pure Appl. Chem.* **2007**, *79*, 1917–1927.
- (11) (a) Ikeda, S.; Fubuki, M.; Takahara, Y. K.; Matsumura, M. *Appl. Catal., A* **2006**, *300*, 186–190. (b) Kato, H.; Asakura, K.; Kudo, A. *J. Am. Chem. Soc.* **2003**, *125*, 3082–3089. (c) Shimizu, K. I.; Itoh, S.; Hatamachi, T.; Kodama, T.; Sato, M.; Toda, K. *Chem. Mater.* **2005**, *17*, 5161–5166. (d) Husin, H.; Su, W.-N.; Chen, H.-M.; Pan, C.-J.; Chang, S.-H.; Rick, J.; Chuang, W.-T.; Sheu, H.-S.; Hwang, B.-J. *Green Chem.* **2011**, *13*, 1745–1754.
- (12) (a) Kato, H.; Kudo, A. *J. Photochem. Photobiol. A: Chem.* **2001**, *145*, 129–133. (b) Kato, H.; Kobayashi, H.; Kudo, A. *J. Phys. Chem. B* **2002**, *106*, 12441–12447.
- (13) (a) Nelson, W. H.; Toblas, R. S. *Inorg. Chem.* **1963**, *5*, 985–992. (b) Anderson, T. M.; Rodriguez, M. A.; Bonhomme, F.; Bixler, J. N.; Alam, T. M.; Nyman, M. *Dalton Trans.* **2007**, 4517–4522.
- (14) (a) Hartl, H.; Pickhard, F.; Emmerling, F.; Röhr, C. Z. *Anorg. Allg. Chem.* **2001**, *627*, 2630–2638. (b) Nyman, M.; Anderson, T. M.;

Provencio, P. P. *Cryst. Growth Des.* **2009**, *9*, 1036–1040. (c) Pickhard, F.; Hartl, H. Z. *Anorg. Allg. Chem.* **1997**, *623*, 1311–1316. (d) Besserguenev, A. V.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2001**, *40*, 2582–2586. (e) Guo, G.-L.; Xu, Y.-Q.; Chen, B.-K.; Lin, Z.-G.; Hu, C.-W. *Inorg. Chem. Commun.* **2011**, *14*, 1448–1451. (f) Shen, L.; Xu, Y. Q.; Gao, Y. Z.; Cui, F. Y.; Hu, C. W. *J. Mol. Struct.* **2009**, *934*, 37–43.

(15) (a) Hegetschweiler, K.; Raber, T.; Reiss, G. J.; Frank, W.; Worle, M.; Currao, A.; Nesper, R.; Kradolfer, T. *Angew. Chem., Int. Ed.* **1997**, *36*, 1964–1966. (b) Arimondo, P. B.; Calderazzo, F.; Hiemeyer, R.; Maichle-Mössmer, C.; Marchetti, F.; Pampaloni, G.; Strähle, J. *Inorg. Chem.* **1998**, *37*, 5507–5511.

(16) (a) McGlone, T.; Vila-Nadal, L.; Miras, H. N.; Long, D.-L.; Poblet, J. M.; Cronin, L. *Dalton Tran.* **2010**, *39*, 11599–11604. (b) Kortz, U.; Hamzeh, S. S.; Nasser, N. A. *Chem.–Eur. J.* **2003**, *9*, 2945–2952. (c) Sakai, Y.; Yoza, K.; Kato, C. N.; Nomiya, K. *Chem.–Eur. J.* **2003**, *9*, 4077–4083. (d) Sakai, Y.; Ohta, S.; Shintoyo, Y.; Yoshida, S.; Taguchi, Y.; Matsuki, Y.; Matsunaga, S.; Nomiya, K. *Inorg. Chem.* **2011**, *50*, 6575–6583. (e) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274–7277. (f) Kim, G.-S.; Zeng, H.; Neiwert, W. A.; Cowan, J. J.; VanDerveer, D.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2003**, *42*, 5537–5544. (g) Li, S.-J.; Liu, S.-X.; Li, C.-C.; Ma, F.-J.; Liang, D.-D.; Zhang, W.; Tan, R.-K.; Zhang, Y.-Y.; Xu, L. *Chem.–Eur. J.* **2010**, *16*, 13435–13442.

(17) (a) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtman, M.; Peters, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3359–3363. (b) Schäffer, C.; Merca, A.; Bögge, H.; Todea, A. M.; Kistler, M. L.; Liu, T.; Thouvenot, R.; Gouzerh, P.; Müller, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 149–153. (c) Tsunashima, R.; Long, D.-L.; Miras, H. N.; Gabb, D.; Pradeep, C. P.; Cronin, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 113–116.

(18) Gaunt, A. J.; May, I.; Collison, D.; Travis Holman, K.; Pope, M. T. *J. Mol. Struct.* **2003**, *656*, 101–106.

(19) Pradeep, C. P.; Long, D.-L.; Kögerler, P.; Cronin, L. *Chem. Commun.* **2007**, *41*, 4254–4256.

(20) Lydon, C.; Sabi, M. M.; Symes, M. D.; Long, D.-L.; Murrie, M.; Yoshii, S.; Nojiri, H.; Cronin, L. *Chem. Commun.* **2012**, *48*, 9819–9821.

(21) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247.

(22) (a) Judd, D. A.; Chen, Q.; Campana, C. F.; Hill, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 5461–5462. (b) Kim, G.-S.; Zeng, H.; Neiwert, W. A.; Cowan, J. J.; VanDerveer, D.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2003**, *42*, 5537–5544. (c) Mal, S. S.; Dickman, M. H.; Kortz, U. *Chem.–Eur. J.* **2008**, *14*, 9851–9855. (d) Sakai, Y.; Kitakoga, Y.; Hayashi, K.; Yoza, K.; Nomiya, K. *Eur. J. Inorg. Chem.* **2004**, 4646–4652. (e) Bassil, B. S.; Mal, S. S.; Dickman, M. H.; Kortz, U.; Oelrich, H.; Walder, L. *J. Am. Chem. Soc.* **2008**, *130*, 6696–6697. (f) Mal, S. S.; Nsouli, N. H.; Carraro, M.; Sartorel, A.; Scorrano, G.; Oelrich, H.; Walder, L.; Bonchio, M.; Kortz, U. *Inorg. Chem.* **2010**, *49*, 7–9.

(23) Abrahams, S. C.; Collin, R. L.; Lipscomb, W. N. *Acta Crystallogr.* **1951**, *4*, 15–20.

(24) (a) Sato, J.; Kobayashi, H.; Inoue, Y. *J. Phys. Chem. B* **2003**, *107*, 7970–7975. (b) Ogura, S.; Kohno, M.; Sato, K.; Inoue, Y. *Appl. Surf. Sci.* **1997**, *121/122*, 521–524. (c) Kohno, M.; Ogura, S.; Sato, K.; Inoue, Y. *Chem. Phys. Lett.* **1997**, *267*, 72–76.

(25) (a) Zheng, Z.; Huang, B.; Lu, J.; Wang, Z.; Qin, X.; Zhang, X.; Dai, Y.; Whangbo, M.-H. *Chem. Commun.* **2012**, *48*, 5733–5735. (b) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238–7266. (c) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022–4047. (d) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027–2038.

(26) Contant, R. *Inorg. Synth.* **1990**, *27*, 104–111.

(27) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93–103.

(28) Randall, W. J.; Droege, M. W.; Mizuno, N.; Nomiya, K.; Weakley, T. J. R.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 167–168.

(29) Hervé, G.; Tézé, A. *Inorg. Chem.* **1977**, *16*, 2115–2117.

(30) H<sub>2</sub>PtCl<sub>6</sub> solution (0.038 M) was prepared by dissolving 1.0 g of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in 50.0 mL HCl solution (0.1 M). H<sub>2</sub>PtCl<sub>6</sub> was

reduced to Pt particles in the beginning period (about 45 min for 2, 10 min for 4 and P<sub>2</sub>W<sub>18</sub>) of the photocatalytic reaction.