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## A Dawson-Type Dirhenium(V)-Oxido-Bridged Polyoxotungstate: X-ray Crystal Structure and Hydrogen Evolution from Water Vapor under Visible Light Irradiation

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The synthesis and crystal structure of a Dawson-type dirhenium(V)-oxido-bridged polyoxotungstate are described. The potassium salt  $K_{14}[O{Re^{V}(OH)(\alpha_2 - P_2W_{17}O_{61})}_2] \cdot 21H_2O$  (K-1) was obtained as analytically pure, homogeneous, black-purple crystals by the reaction of a monolacunary Dawson polyoxotungstate with [Re<sup>IV</sup>Cl<sub>6</sub>]<sup>2-</sup> in water, followed by crystallization from an aqueous HCl solution in the dark. Single-crystal X-ray structure analysis revealed that the dimeric dirhenium(V)-oxido-bridged structure has overall  $C_{2h}$  symmetry. Characterization of K-1 was also accomplished by elemental analysis, TG/DTA, and FTIR, UV/Vis absorption, ESR, and solution <sup>31</sup>P NMR spectroscopy. Furthermore, the black-purple compound K-1 was grafted onto a TiO<sub>2</sub> surface by electrostatic binding to give  $TiO_2$  with a cationic quaternary ammonium moiety (1-grafted TiO<sub>2</sub>). Elemental analysis of 1-

### Introduction

The construction of an efficient device for the photosplitting of water to hydrogen is one of the most important subjects from the viewpoint of solar light energy utilization and storage since Honda and Fujishima first demonstrated a photoelectrochemical cell consisting of a TiO<sub>2</sub> photoanode and a Pt cathode to decompose water into hydrogen and oxygen under ultraviolet (UV) irradiation with an external bias.<sup>[1]</sup> The design and preparation of new photocatalysts that are responsive in a similar manner to visible light are a key target for the utilization of solar energy for hydrogen production. To develop efficient photocatalysts that work under visible light irradiation, a number of attempts have been made, e.g., a chemically modified n-type TiO<sub>2</sub> by controlled combustion of Ti metal in a neutral gas flame (this

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grafted TiO<sub>2</sub> indicated that the seven potassium counterions of K-1 were ion-exchanged with seven cationic ammonium moieties to form  ${TiO_2}_{5500}$  = Si(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl]<sub>7</sub> = Si(CH<sub>2</sub>)<sub>3</sub>- $N^{+}(CH_{3})_{3}]_{7}(K_{7}[O{Re(OH)(\alpha_{2}-P_{2}W_{17}O_{61})}_{2}]^{7-})$  and seven molecules of KCl. The diffuse reflectance (DR) UV/Vis spectrum of 1-grafted TiO<sub>2</sub> exhibited two sharp bands at 496 nm and 751 nm due to the  $Re^{V} \rightarrow W^{VI}$  intervalence charge transfer (IVCT) band and the d-d band of the rhenium(V) atom, respectively, in the visible light region, which suggested that polyoxoanion  $\mathbf{1}$  was isolated on the TiO<sub>2</sub> surface. With 1-grafted TiO<sub>2</sub>, hydrogen evolution from water vapor under irradiation with visible light (>400 nm and >420 nm) was achieved.

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material absorbs light at wavelengths below 535 nm).<sup>[2]</sup> visible-light-response TiO<sub>2</sub> thin films prepared by a radio-frequency magnetron sputtering deposition method,<sup>[3]</sup> NiO<sub>x</sub> (partly oxidized nickel) promoted In<sub>0.9</sub>Ni<sub>0.1</sub>TaO<sub>4</sub>,<sup>[4]</sup> (AgIn)<sub>x</sub>- $Zn_{2(1-x)}S_{2}$ ,<sup>[5]</sup> and  $(Ga_{1-x}Zn_{x})(N_{1-x}O_{x})$  with RuO<sub>2</sub>, transition-metal mixed-oxides containing Cr, and noble-metal/ Cr<sub>2</sub>O<sub>3</sub> (core/shell) nanoparticles as co-catalysts.<sup>[6]</sup> These materials are powerful photocatalysts for water splitting under visible light irradiation; however, the search for the use of other materials as visible-light-response photocatalysts is still an interesting objective.

Polyoxometalates (POMs) have attracted considerable attention because of their extreme versatility and unique range of properties, including catalytic and biological activities and/or photochemical, electrochromic, and magnetic properties.<sup>[7]</sup> However, there is no report regarding the use of POMs as photocatalysts for the water splitting reaction under visible light irradiation. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> encapsulated into the titanium-exchanged HY(TiHY) zeolite required both UV and visible light for the water splitting reaction.<sup>[8]</sup> To improve the visible light absorption of POMs, we focused on the synthesis of Dawson-type dirhenium(V)oxido-bridged POM,  $[O{Re^{V}(OH)(\alpha_2 - P_2W_{17}O_{61})}_2]^{14-}$  (1). Then, we prepared a new type of POM-based photocatalyst

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material by the electrostatic grafting of polyoxoanion 1 onto an anatase  $TiO_2$  surface through the cationic ammonium moiety (1-grafted  $TiO_2$ ).

In this paper, we report the full details of the synthesis and characterization of the potassium salt  $K_{14}[O\{Re^{V}-(OH)(\alpha_2-P_2W_{17}O_{61})\}_2]\cdot 21H_2O$  (K-1) and the 1-grafted TiO<sub>2</sub> material. Furthermore, the photocatalytic performance of 1-grafted TiO<sub>2</sub> material in hydrogen formation from water vapor under irradiation with visible light (>400 nm and >420 nm) is investigated.

#### **Results and Discussion**

### Synthesis, Characterization, and Molecular Structure of a Potassium Salt of the Dawson-Type Dirhenium(V)-Oxido-Bridged POM (K-1)

The potassium salt of compound 1,  $K_{14}[O{Re^{V}(OH)(\alpha_2-P_2W_{17}O_{61})}_2]\cdot21H_2O$  (K-1), was synthesized by a slight modification of the published method for the synthesis of monomeric monorhenium(V)-substituted POM  $K_7[\alpha_2-Re^{V}OP_2W_{17}O_{61}]\cdot2H_2O.^{[9]}$  Compound K-1 was formed by heating at reflux the mixture of  $K_2Re^{IV}Cl_6$  and monolacunary Dawson POM  $[\alpha_2-P_2W_{17}O_{61}]^{10-}$  in an aqueous solution in air followed by reprecipitation from hot water in the dark. The pH of the solution changed from 3.40 to 1.54 during the reaction. The formation of K-1 is given by the ionic balance shown in Equation (1), in which rhenium(IV) is oxidized to rhenium(V).

$$2 \operatorname{Re^{IV}Cl_6^{2-}} + 2 \left[ \alpha_2 \cdot P_2 W_{17} O_{61} \right]^{10-} + 3 \operatorname{H_2O} \rightarrow \\ \left[ O \left\{ \operatorname{Re^V(OH)}(\alpha_2 \cdot P_2 W_{17} O_{61}) \right\}_2 \right]^{14-} + 4 \operatorname{H^+} + 12 \operatorname{Cl^-} (1)$$

The crystallization of K-1 for the single-crystal X-ray analysis was performed by slow evaporation from an aqueous HCl solution (pH = 1.5) in the dark. Good crystals could not be obtained in water. The X-ray crystallographic structural analysis of K-1 exhibits a dimeric dirhenium(V)oxido-bridged structure, as shown in Figure 1. The structure of K-1 is that of a (P<sub>2</sub>W<sub>17</sub>Re)<sub>2</sub>-O dimer with a Re-O-Re linkage, which is similar to the structure of Dawson diruthenium(IV)-oxido-bridged POM  $[O{Ru^{IV}(Cl)}(\alpha_2 - \alpha_2)]$  $P_2W_{17}O_{61}$ }]<sup>16-[10]</sup> Both  $\alpha_2 P_2W_{17}O_{61}^{10-}$  units act as tetradentate chelating and bridging ligands to the Re atoms and possess a center of symmetry for the anion. The two sets of four oxygen atoms attached to the Re atoms in a plane perpendicular to the Re(1)-O(1M)-Re(1A) axis are eclipsed to give a  $C_{2h}$  symmetry. The length of the Re(1)–O(1M) bond coordinated to the four oxygen atoms in the lacunary site is 1.7690(14) Å, which is smaller than that of  $Re^{V}$ –O in O=Re<sup>V</sup>-O-Re<sup>V</sup>=O (ca. 1.9 Å)<sup>[11]</sup> but similar to that in  $[O{Ru^{IV}(Cl)(\alpha_2 - P_2W_{17}O_{61})}_2]^{16-}$  (1.773 Å) (see Table 1).<sup>[10]</sup> The Re-O(1H) bond length [2.369(14) Å; trans to the Re-O-Re in 1] is longer than those of the Re<sup>V</sup>-OH bonds (1.811–1.970 Å) in monomeric complexes of the type  $[\text{Re}^{VO}(\text{OH})L_4]$  (L = pyridine, CN<sup>-</sup>, cyclam, en).<sup>[12]</sup>



Figure 1. Molecular structure of K-1 with 50% probability ellipsoids.

Table 1. Selected bond lengths [Å] and angles [°] for K-1 around the Re–O–Re linkage.

Bond lengths			
Re(1)-O(1M)	1.7690(14)	Re(1)-O(5A)	1.939(17)
Re(1)-O(1H)	2.369(14)	Re(1)-O(9A)	1.917(19)
Re(1)-O(1)	1.942(17)	Re(1)-O(10)	1.951(17)
Bond angles			
O(1M)-Re(1)-O(1H)	178.9(4)	O(9A)-Re(1)-O(1)	90.9(8)
O(1M) - Re(1) - O(1)	90.1(5)	O(1)-Re(1)-O(10)	89.8(7)
O(1M)-Re(1)-O(5A)	90.5(5)	O(9A)-Re(1)-O(5A)	89.1(8)
O(1M)-Re(1)-O(9A)	88.5(5)	O(5A)-Re(1)-O(10)	90.3(7)
O(1M)-Re(1)-O(10)	87.5(5)	O(9A)-Re(1)-O(10)	176.0(7)
O(1)-Re(1)-O(1H)	88.9(6)	W(1)-O(1)-Re(1)	153.6(10)
O(5A)-Re(1)-O(1H)	90.5(6)	W(2)-O(5)-Re(1A)	153.8(10)
O(9A)-Re(1)-O(1H)	92.1(7)	W(6)-O(9)-Re(1A)	167.2(11)
O(10)-Re(1)-O(1H)	91.9(6)	W(7)-O(10)-Re(1)	166.3(10)
O(5A)-Re(1)-O(1)	179.5(8)	Re(1A)-O(1M)-Re(1)	180

The bond valence sum (BVS) value of the Re atom is 5.782; which is in the range 5.556–6.864 that was observed for Re<sup>V</sup>–O–Re<sup>V</sup> complexes,<sup>[11]</sup> above the range of the BVS values observed in Re<sup>III</sup>-O-Re<sup>III</sup> complexes (5.298-5.336),<sup>[13]</sup> but below the range of BVS values observed in Re<sup>VII</sup>–O–Re<sup>VII</sup> complexes (7.557–7.920).<sup>[14]</sup> Therefore, on the basis of Re-oxygen bond lengths, valence sums, bulk diamagnetism, and charge balance from the analytical stoichiometry, we assign the +5 oxidation state to the rhenium atoms. Note also that each Re was clearly 6- and not 7coordinate, as shown in Figure 1. The BVS values of the 17W atoms are in the range 5.912–6.442 (average: 6.229), and those of the two P atoms are in the range 5.002-5.019 (5.011). These values correspond reasonably well to the formal valances W<sup>6+</sup> and P<sup>5+</sup>, respectively (see Tables S1 and S2 in the Supporting Information).

The crystal structure of K-1 is consistent with the elemental analysis, TG/DTA data, UV/Vis absorption, FTIR, ESR, and solution <sup>31</sup>P NMR spectra. The elemental analysis had to be performed for compound K-1 after drying it at room temperature at  $10^{-3}$ - $10^{-4}$  Torr overnight. The result was consistent with the composition K<sub>14</sub>[O{Re<sup>V</sup>(OH)( $\alpha_2$ -

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 $P_2W_{17}O_{61}$ }<sub>2</sub>]·6H<sub>2</sub>O. The weight loss observed during the course of drying before analysis was 2.8% for K-1; this corresponds to 15–16 weakly solvated or adsorbed water molecules. The TG/DTA measurement performed under ambient conditions showed a weight loss of 3.93% without a clear endothermic point; this value corresponds to 21 water molecules including both the intrinsic water of hydration and the water adsorbed from the atmosphere. Thus, the number of hydrated water molecules in compound K-1 is 21. The elemental analysis of the crystalline sample of K-1 also showed the same composition as the powder sample and the absence of chloride ion after the crystallization from an aqueous HCl solution.

The FTIR spectrum of compound K-1 measured by using a KBr disk is shown in Figure 2. The positions of all the bands (1091, 1018, 954, 907, 787, and 526 cm<sup>-1</sup>) in the polyoxoanion region of this compound are similar to those of  $[\alpha$ -P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> (1091, 1020, 958, 912, 777, and 528 cm<sup>-1</sup>) rather than to those of  $[\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>10-</sup> (1086, 1054, 1016, 940, 885, 811, 741, 601, 527, and 467 cm<sup>-1</sup>), suggesting the coordination of rhenium atoms by the monovacant site of the  $[\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>10-</sup>.



Figure 2. FTIR spectrum, measured by using a KBr disk, in the polyoxoanion region  $(1800-400 \text{ cm}^{-1})$  of K-1.

The <sup>31</sup>P NMR spectrum of K-1 in D<sub>2</sub>O at about 25 °C has a clear two-line spectrum at  $\delta = -12.38$  and -13.39 ppm (referenced to 25%H<sub>3</sub>PO<sub>4</sub>) and  $\delta = -12.06$  and -13.05 ppm (referenced to 85%H<sub>3</sub>PO<sub>4</sub>), showing that K-1 is a diamagnetic compound with an antiferromagnetic interaction between the two Re<sup>V</sup> atoms (see Figure 3). The downfield resonance was assigned to the phosphorus closest to the rhenium sites and the upfield resonance to the phosphorus closer to the W<sub>3</sub> cap. These signals exhibit a shift from those of  $[\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>10-</sup> ( $\delta = -6.96$  and -14.10 ppm; referenced to 25%H<sub>3</sub>PO<sub>4</sub>) and  $[\alpha$ -P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> ( $\delta = -12.75$  ppm;

referenced to 25%H<sub>3</sub>PO<sub>4</sub>), indicating the complete coordination of rhenium atoms by the monovacant site of  $[a_2-P_2W_{17}O_{61}]^{10-}$  and the high purity of K-1. It should be noted that the spectral pattern of K-1 is quite similar to that of the reported monomeric monorhenium(V)-substituted POM K<sub>7</sub>[ $a_2$ -Re<sup>V</sup>OP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]·2H<sub>2</sub>O, but the chemical shift was somewhat different from the values of -11.86 and -12.86 ppm (referenced to 85%H<sub>3</sub>PO<sub>4</sub>) for K<sub>7</sub>[ $a_2$ -Re<sup>V</sup>OP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]·2H<sub>2</sub>O. The <sup>31</sup>P NMR spectrum of the crystalline sample of K-1 crystallized from an aqueous HCl solution also showed the same chemical shifts ( $\delta = -12.46$  and -13.45 ppm; referenced to 25%H<sub>3</sub>PO<sub>4</sub>) as those of the powder sample. No ESR signals of solid K-1 at room temperature were detected over a wide range of magnetic fields, also suggesting that K-1 is diamagnetic compound.



Figure 3. <sup>31</sup>P NMR spectrum of K-1 in D<sub>2</sub>O. The resonance at 0.0 ppm is due to the external reference: 25% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O.



Figure 4. UV/Vis spectrum of K-1 in H<sub>2</sub>O in the range 200–800 nm ( $\times 10^{-6}$  M). Inset: in the range 400–800 nm ( $\times 10^{-4}$  M).

The UV/Vis spectrum of K-1 in water has four absorption bands at 254 nm ( $\varepsilon = 9.39 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ ), 298 nm ( $\varepsilon = 6.28 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ ), 496 nm ( $\varepsilon = 6.61 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$ ), and 737 nm ( $\varepsilon = 4.02 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$ ), as shown in Figure 4. Two large bands at 254 nm and 298 nm were assigned to the charge transfer (CT) bands of W–O, and two small bands at 496 nm and 737 nm were assigned to the Re<sup>V</sup> $\rightarrow$ W<sup>V1</sup> intervalence charge transfer (IVCT) band and d-d band of the rhenium(V) atom, respectively.<sup>[15,16]</sup>

### Preparation, Characterization, and Photocatalytic Performance of Anatase TiO<sub>2</sub> Functionalized by a Cationic Ammonium Moiety by Impregnation with 1

The black-purple compound K-1 that was prepared was grafted onto a TiO<sub>2</sub> surface by electrostatic binding to give TiO<sub>2</sub> functionalized with cationic quaternary ammonium groups according to the published method.<sup>[17]</sup> This material (abbreviated as  $TiO_2-N^+$ ) was obtained by the addition of a 50% methanol solution of N-trimethoxysilylpropyl-N,N,Ntrimethylammonium chloride, (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>-Cl, to a TiO<sub>2</sub> suspension in methanol at 25 °C. In this reaction, the methoxy groups of the silane coupling reagent reacted cleanly with the hydroxy groups of TiO<sub>2</sub> to eliminate methanol and form the isolated surface species  $\equiv$ Si(CH<sub>2</sub>)<sub>3</sub>-N(CH<sub>3</sub>)<sub>3</sub>Cl. Then, polyoxoanion 1 was grafted onto TiO<sub>2</sub>-N<sup>+</sup> by employing the ion-exchange reaction of potassium ion with a cationic ammonium moiety in water at 25 °C. The product obtained is abbreviated as 1-grafted TiO<sub>2</sub>. According to the elemental analysis result, the loading of K-1 was found to be  $2.2 \,\mu mol g^{-1}$  [the amount of the surface cationic quaternary ammonium groups,  $\equiv$ Si(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub>-Cl, was 31.7 µmolg<sup>-1</sup>]. The amount of potassium observed in the elemental analysis of 1-grafted TiO<sub>2</sub> was 0.032%, indicating that the seven potassium counterions of K-1 were ion-exchanged with the seven cationic ammonium moieties to form  ${TiO_2}_{5500} \equiv Si(CH_2)_3N(CH_3)_3Cl]_7 \equiv Si(CH_2)_3N^+$ - $(CH_3)_3]_7(K_7[O{Re(OH)(\alpha_2-P_2W_{17}O_{61})}_2]^{7-})$  and seven molecules of KCl. Thus, 49% of the surface silane coupling reagent of TiO2-N+ was covered by the grafting reaction with K-1. The byproduct KCl can easily be removed by washing with excess water.

The diffuse reflectance (DR) UV/Vis spectrum of 1grafted TiO<sub>2</sub> (2.2 µmol g<sup>-1</sup>) showed two sharp bands at 496 nm and 751 nm in the visible light region (see Figure 5a), suggesting that the surface species 1 is isolated on the TiO<sub>2</sub> surface.<sup>[18]</sup> These bands might be assigned to the Re<sup>V</sup>→W<sup>V1</sup> intervalence charge transfer (IVCT) band and the d–d band of rhenium(V) atom, respectively. The <sup>31</sup>P NMR spectrum of solid 1-grafted TiO<sub>2</sub> was not possible to obtain because of the low loading of 1. The BET surface area was 39.4 m<sup>2</sup>g<sup>-1</sup> after the grafting of 1 onto the TiO<sub>2</sub> surface, which was almost the same as that of the starting TiO<sub>2</sub> material (40.0 m<sup>2</sup>g<sup>-1</sup>).

We initially examined the evolution of  $H_2$  from water vapor under light irradiation greater than 400 nm and 420 nm and catalyzed by 1-grafted TiO<sub>2</sub> at 25 °C without



Figure 5. Diffuse reflectance UV/Vis spectra of (a) as-prepared 1grafted TiO<sub>2</sub>, (b) 1-grafted TiO<sub>2</sub> after H<sub>2</sub> evolution from water vapor (20 Torr) under irradiation with visible light (>400 nm), and (c) 1-grafted TiO<sub>2</sub> after H<sub>2</sub> evolution from water (10 mL) in the liquid-phase reaction containing Na<sub>2</sub>H<sub>2</sub>EDTA·2H<sub>2</sub>O under irradiation with visible light (>400 nm).

any additives in heterogeneous systems, as shown in Table 2. The reaction did not proceed when light irradiation was stopped, even at 60 °C. With regard to the time course of H<sub>2</sub> evolution catalyzed by 1-grafted TiO<sub>2</sub> under light irradiation (>400 nm), a linear increase in H<sub>2</sub> with time was observed, as shown in Figure 6a. After 5 h, the amount of H<sub>2</sub> evolved was 19.8 µmol per g of catalyst [the rate, calculated on the basis of the formula  $(mol g^{-1} \text{ of } H_2)h^{-1}$ , is 3.96  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>]. After 55 h, the amount of H<sub>2</sub> evolved reached 101.6 µmol per g of catalyst [the turnover number (TON), calculated on the basis of the formula (mol of  $H_2$ )/ (mol of 1 per g of catalyst), is 46.2] (Table 2, Entry 1). The catalytic activities were reproducible on five repeated runs. 19.5 µmol water vapor remained in the gas phase after 55 h, and some amounts of water vapor were adsorbed on the TiO<sub>2</sub> surface. O<sub>2</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub> were not detected under the present reaction conditions. The apparent quantum yield (AQY) was quite low, i.e., <0.1% at 405 nm after 25 h; however, there is no report regarding AQY for  $H_2$ 

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evolution from water vapor without any additives. No H<sub>2</sub> evolution was detected in the absence of water vapor. A mixture of K-1 (5.6  $\mu$ mol) and TiO<sub>2</sub> (1.0 g) in the absence of a silane coupling reagent induced 2.98 µmol g<sup>-1</sup> and  $8.52 \,\mu\text{mol}\,\text{g}^{-1}$  of H<sub>2</sub> evolution after 25 h and 50 h, respectively (rate:  $1.19 \times 10^{-1} \,\mu\text{mol}\,\text{g}^{-1}\,\text{h}^{-1}$  after 25 h; TON: 3.9 after 50 h) (Table 2, Entry 2). In addition, the photodecomposition of D<sub>2</sub>O vapor (20 Torr) was carried out under light irradiation (>400 nm). D<sub>2</sub>, H<sub>2</sub>, and HD were detected after 48 h, which were due to the decomposition of  $D_2O$  vapor, the decomposition of the surface silane coupling reagent, and the H-D exchange reaction of D<sub>2</sub> with H<sub>2</sub>, respectively. These results indicate that H<sub>2</sub> was certainly evolved from water vapor; however, the surface silane coupling reagent of 1-grafted TiO<sub>2</sub> was also decomposed. Under light irradiation at a wavelength greater than 420 nm, a long induction period was observed (see Figure 6b). After 93 h, the amount of  $H_2$  production was  $1.57 \,\mu mol g^{-1}$  of catalyst (rate:  $1.69 \times 10^{-2} \,\mu mol g^{-1} h^{-1}$ ). After 380 h, the amount of  $H_2$  evolved reached 4.35 µmolg<sup>-1</sup> of catalyst (TON: 1.98) (Table 2, Entry 3), which was lower than that under light irradiation at a wavelength greater than 400 nm. The induction period and the low activities under light irradiation (>420 nm) might be due to the light absorption in the range 400–420 nm of 1-grafted TiO<sub>2</sub>, as shown in Figure 5a. In control experiments under irradiation at a wavelength greater than 400 nm, no reactions were observed when K-1, anatase TiO<sub>2</sub>, a mixture of  $H_3PW_{12}O_{40}$  (5.6 µmol) and TiO<sub>2</sub> (1.0 g), tetra-*n*-butylammonium salt of 1 ( $[(n-C_4H_9)_4 N_{14-x}K_{x}[O{Re^{V}(OH)(\alpha_{2}-P_{2}W_{17}O_{61})}_{2}],$  abbreviated as TBA-1), and TiO<sub>2</sub>-N<sup>+</sup> were used as catalysts (Table 2, Entries 4-8). In addition, 1-grafted amorphous SiO<sub>2</sub> (11 µmol 1 per g of sample, 0.055  $\mu$ mol 1 per m<sup>2</sup> of amorphous SiO<sub>2</sub>) prepared by the same method as that of 1-grafted TiO<sub>2</sub>  $(2.2 \,\mu\text{mol 1} \text{ per g of sample}, 0.055 \,\mu\text{mol 1} \text{ per m}^2 \text{ of TiO}_2)$ exhibited no reaction (Table 2, Entry 9). In contrast, H<sub>2</sub> evolution from water vapor under light irradiation (>400 nm) was observed when the  $[\text{Re}^{\text{IV}}\text{Cl}_6]^{2-}$ -grafted TiO<sub>2</sub> (4.4 µmol Re per g of sample) prepared by the same method

as that of 1-grafted TiO<sub>2</sub> (2.2  $\mu$ mol 1 per g of sample, 4.4  $\mu$ mol Re per g of TiO<sub>2</sub>) was used as a catalyst. An induction period was not observed. After 5 h and 72 h, 53.8  $\mu$ molg<sup>-1</sup> and 225  $\mu$ molg<sup>-1</sup> of H<sub>2</sub> were evolved, respectively. These values are higher than those obtained with 1grafted TiO<sub>2</sub> (Table 2, Entry 10). These results suggested that both the rhenium site and TiO<sub>2</sub> support were crucial for hydrogen production from water vapor under the pres-



Figure 6. Time course for  $H_2$  evolution catalyzed by 1-grafted TiO<sub>2</sub> under light irradiation (a) >400 nm and (b) >420 nm. Reaction conditions: see Table 2.

Table 2. Hydrogen evolution from wate	r vapor catalyzed	by 1-grafted TiO <sub>2</sub>	2 under irradiation with	visible light.[a]
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Entry	Catalyst	Light [nm]	Reaction time [h]	$H_2 \left[\mu mol g^{-1}\right]$	Rate $[\mu mol g^{-1} h^{-1}]^{[b]}$
1	1-grafted TiO <sub>2</sub>	>400	5	19.8	3.96
	$(2.2 \mu\text{mol of } 1 \text{ per g of sample})$		55	101.6	
2	A mixture of 1 and $TiO_2$	>400	25	2.98	$1.19 \times 10^{-1}$
	(5.6 µmol of 1 per g of sample)		50	8.52	
3	1-grafted TiO <sub>2</sub>	>420	93	1.57	$1.69 \times 10^{-2}$
	$(2.2 \mu\text{mol of } 1 \text{ per g of sample})$		380	4.35	
4	K-1 <sup>[c]</sup>	>400	30	n.r.	_
5	TiO <sub>2</sub>	>400	30	n.r.	_
6	A mixture of $H_3PW_{12}O_{40}$ and $TiO_2$	>400	30	n.r.	_
	(5.6 $\mu$ mol of H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> per g of sample)				
7	TBA-1 <sup>[d]</sup>	>400	15	n.r.	_
8	TiO <sub>2</sub> –N <sup>+</sup>	>400	15	n.r.	_
9	1-grafted SiO <sub>2</sub>	>400	30	n.r.	_
	(11 µmol of 1 per g of sample)				
10	[Re <sup>IV</sup> Cl <sub>6</sub> ] <sup>2–</sup> -grafted TiO <sub>2</sub>	>400	5	53.8	10.8
	(4.4 µmol of Re per g of sample)		72	225	

[a] Reaction conditions: water (20 Torr; 257.3  $\mu$ mol), catalyst (500 mg), light (>400 nm and >420 nm), 25 °C. [b] The rate was calculated as H<sub>2</sub> (mol g<sup>-1</sup>) per reaction time (h). [c] 1 g K-1 was used. [d] 400 mg TBA-1 was used.

ent conditions, and the formation of  $Re^{IV}$  by the electron transfer reaction of the  $Re^{V}$  site in 1-grafted  $TiO_2$  under light irradiation might accelerate the evolution of hydrogen from water with the decomposition of the surface silane coupling reagent on the  $TiO_2$  support.

When photoreaction of water vapor (20 Torr) was carried out with twice the amount of 1-grafted TiO<sub>2</sub> catalyst under light irradiation at a wavelength greater than 400 nm, the production of hydrogen in the second run decreased to a third of that in the first run; however, the DR UV/Vis spectrum of the 1-grafted TiO<sub>2</sub> after the photoreaction (Figure 5b) showed the same spectral pattern as that of the asprepared 1-grafted TiO<sub>2</sub>. In addition, elemental analysis for the 1-grafted TiO<sub>2</sub> after the photoreaction revealed that the ratio Re/P was about 1:2. These results suggested that 1 was stable under the present photoreaction conditions; however, the change in the surface structure caused by the decomposition of the surface silane species used as an electron donor might influence the catalytic activities.

To prevent the decomposition of the surface silane coupling reagent of 1-grafted TiO<sub>2</sub>, the liquid-phase photoreaction of water (10 mL) in the presence of  $Na_2H_2EDTA \cdot 2H_2O$  (111 mg, 30 mM) as a sacrificial reagent was repeated three times with the same 1-grafted TiO<sub>2</sub> catalyst under light irradiation (>400 nm). For the first run, 5.80  $\mu$ molg<sup>-1</sup> and 19.6  $\mu$ molg<sup>-1</sup> of H<sub>2</sub> were produced after 2 h and 4 h, respectively. In contrast, hydrogen production in the second run was increased to 62.5 µmolg<sup>-1</sup> and 131  $\mu$ molg<sup>-1</sup>, respectively, and the amounts of hydrogen produced were almost the same in the third run  $(60.5 \,\mu\text{molg}^{-1} \text{ and } 111.1 \,\mu\text{molg}^{-1}, \text{ respectively}).$  The DR UV/Vis spectrum of the 1-grafted TiO<sub>2</sub> after the third photoreaction (Figure 5c) also showed the same spectral pattern as that of the as-prepared 1-grafted  $TiO_2$ . These results suggest that neither the surface polyanion 1 nor the surface silane coupling reagent of 1-grafted TiO<sub>2</sub> were decomposed in the presence of a sacrificial reagent. The lower activities in the first run relative to those in the second and third run might be due to the different adsorption state of water molecules on the surface of the catalyst under the present liquid-phase reaction conditions.

With regard to the reaction mechanism, the excitation of  $\text{Re}^{V}$  to  $\text{Re}^{V*}$  by irradiation with visible light and electron transfer from  $\text{Re}^{V*}$  to  $\text{Re}^{IV}$  might occur with the decomposition of the surface silane coupling reagent on  $\text{TiO}_2$  in the absence of a sacrificial reagent.<sup>[19]</sup> In addition, the multielectron collection and transfer for the reduction of H<sup>+</sup> to H<sub>2</sub> were performed by TiO<sub>2</sub>. Further studies regarding the reaction mechanism are in progress.

#### Conclusions

The synthesis and crystal structure of a Dawson-type dirhenium(V)-oxido-bridged polyoxotungstate is presented. We have successfully obtained black-purple single crystals of the water-soluble potassium salt  $K_{14}[O{Re(OH)(\alpha_2-P_2W_{17}O_{61})}_2]\cdot21H_2O$  by treating  $[Re^{IV}Cl_6]^{2-}$  with a monolacunary Dawson polyoxoanion. The characterization of compound K-1 has been accomplished by X-ray structure analysis, elemental analysis, TG/DTA, and UV/Vis absorption, FTIR, ESR, and solution <sup>31</sup>P NMR spectroscopy. The crystal structure of K-1 reveals that the dimeric dirhenium(V)-oxido-bridged structure has overall  $C_{2h}$  symmetry. Polyoxoanion 1 was grafted onto the TiO<sub>2</sub> surface by electrostatic binding to give anatase TiO<sub>2</sub> functionalized by a cationic ammonium moiety. Elemental analysis indicated that the seven potassium counterions of K-1 were ion-exchanged with seven cationic ammonium moieties to form  ${TiO_2}_{5500} \equiv Si(CH_2)_3N(CH_3)_3Cl]_7 \equiv Si(CH_2)_3N^+(CH_3)_3]_7$  $(K_7[O{Re(OH)(\alpha_2 - P_2W_{17}O_{61})}_2]^{7-})$  (1-grafted TiO<sub>2</sub>) and seven molecules of KCl. DR UV/Vis spectrum of 1-grafted TiO<sub>2</sub> exhibited two sharp bands at 496 nm and 751 nm, which suggests that 1-grafted TiO<sub>2</sub> absorbs visible light. With the 1-grafted  $TiO_2$ , the hydrogen evolution from water vapor under visible light irradiation (>400 nm and >420 nm) was achieved. To the best of our knowledge, the Dawson dirhenium(V)-oxido-bridged POM [O{Re<sup>V</sup>(OH)- $(\alpha_2 - P_2 W_{17} O_{61})$   $\}_2$  <sup>14-</sup> is the first example of the use of a POM as a visible-light-response photocatalyst.

### **Experimental Section**

**Materials:**  $K_{10}[\alpha_2-P_2W_{17}O_{61}]$ ·19H<sub>2</sub>O was prepared as described in the literature.<sup>[20]</sup> The number of solvated water molecules was determined by TG/DTA analysis. All the reagents and solvents were obtained and used as received from commercial sources.

Instrumentation/Analytical Procedures: Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature at  $10^{-3}$ -10<sup>-4</sup> Torr overnight before analysis. The microanalysis of Re an K elements was specially ordered for the 1-grafted TiO<sub>2</sub> sample. Infrared spectra were recorded with a Jasco 4100 FTIR spectrometer by using KBr disks at room temperature. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) data were performed with a Rigaku Thermo Plus 2 series TG/DTA TG 8120 instrument. TG/DTA measurements were performed in air with a temperature ramp of 4 °C per min between 20 and 500 °C. The <sup>31</sup>P{<sup>1</sup>H} NMR (161.70 MHz) spectra in solution were recorded in 5-mm-outer-diameter tubes with a JEOL JNM-EX 400 (Kanagawa University) and a JEOL ECA-600 (Shizuoka University) NMR spectrometer. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to an external standard of 25% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O or 85% H<sub>3</sub>PO<sub>4</sub> in a sealed capillary. Chemical shifts were reported as negative on the  $\delta$  scale with resonances upfield of  $H_3PO_4$  ( $\delta = 0$  ppm). Solution UV/Vis spectra and diffuse reflectance (DR) UV/Vis spectra were recorded with a Jasco V-570 spectrophotometer. For the DR UV/Vis measurement, a Jasco diffuse reflectance attachment was used. Specific surface areas were measured by the BET method by using an ASAP 2010 (Shimadzu) instrument. X-band EPR spectra were recorded with a JEOL JES-RE Series EPR spectrometer at room temperature.

Synthesis and Characterization of K-1: A mixture of  $K_2ReCl_6$ (0.701 g, 1.47 mmol) and  $K_{10}[\alpha_2-P_2W_{17}O_61]$ ·17H<sub>2</sub>O (7.14 g, 1.47 mmol) in water (80 mL) was heated at reflux for 30 min in air. During the refluxing, the color of the solution became a dark purple-black. The solvent was removed by rotary evaporation at 50 °C. The sample obtained was dissolved in hot water (ca. 9 mL) at 80 °C

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and placed in a refrigerator to yield a purple-black precipitate, which was collected on a membrane filter (JG, 0.2 µm), and washed with ethanol  $(3 \times 20 \text{ mL})$  and ether  $(3 \times 20 \text{ mL})$ . Yield: 6.38 g (89.7%). For  $K_{14}[O{Re^{V}(OH)(\alpha_2 - P_2W_{17}O_{61})}_2] \cdot 6H_2O, H_{14}K_{14}O_{131}$ P<sub>4</sub>Re<sub>2</sub>W<sub>34</sub> (9404.277): calcd. H 0.15, Cl 0, K 5.82, P 1.32, Re 3.96; found H 0.13, Cl<0.1, K 5.91, P 1.24, Re 3.93. A weight loss of 2.8% (from K-1) was observed during the course of drying at room temperature at 10<sup>-3</sup>-10<sup>-4</sup> Torr overnight before analysis, suggesting the presence of 15-16 weakly solvated or adsorbed water molecules. TG/DTA data: a weight loss of 3.93% was observed below 500 °C; calcd. 3.91% for x = 21 in  $K_{14}[O{Re^{V}(OH)(\alpha_2 - P_2W_{17}O_{61})}_2] \cdot xH_2O$ . IR (KBr):  $\tilde{v} = 1091$ , 1018, 954, 907, 787, 527 cm<sup>-1</sup>. <sup>31</sup>P NMR (in D<sub>2</sub>O, at 25 °C, referenced to 25 % H<sub>3</sub>PO<sub>4</sub>):  $\delta = -12.38, -13.39$  ppm. <sup>31</sup>P NMR (in D<sub>2</sub>O, at 25 °C, referenced to 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta = -12.06$ , -13.05 ppm. UV/Vis (water):  $\lambda$  ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>) = 254 (9.39 × 10<sup>4</sup>), 298  $(6.28 \times 10^4)$ , 496  $(6.61 \times 10^3)$ , 737  $(4.02 \times 10^3)$  nm. ESR (20 °C): silent.

**Crystallization of K-1:** The sample (1.0 g) was dissolved in aqueous HCl solution (pH = 1.5; 3 mL) at >90 °C, and the purple-black crystals were obtained by slow evaporation at 25 °C in the dark for 6 d. <sup>31</sup>P NMR (D<sub>2</sub>O, 25 °C):  $\delta$  = -12.46, -13.45 ppm. For K<sub>14</sub>[O{Re<sup>V</sup>(OH)(\alpha\_2-P\_2W\_{17}O\_{61})}\_2]·6H\_2O, H\_{14}K\_{14}O\_{131}P\_4Re\_2W\_{34} (9404.277): calcd. H 0.15, Cl 0, K 5.82, P 1.32, Re 3.96; found H 0.17, Cl < 0.1, K 6.19, P 1.28, Re 4.00.

X-ray Crystallography: Crystals of compound K-1 were surrounded by liquid paraffin to prevent their degradation. The crystal size was  $0.13 \times 0.06 \times 0.01$  mm. Data collection was carried out with a Bruker SMART APEX CCD diffractometer at 90 K. The intensity data were automatically corrected for the Lorentz and polarization effects during integration. The structure was determined by direct methods (SHELXS-97),<sup>[21]</sup> followed by the subsequent difference Fourier calculation, and refined by the full-matrix least-squares procedure (SHELXL-97).[22] Absorption correction was performed with SADABS (empirical absorption correction).<sup>[23]</sup> For complex 1, 34 tungsten atoms, two rhenium atoms, and four phosphorus atoms were clearly identified. Thus, the main feature of the molecular structure of the polyoxometalate was clarified. However, the resolution obtained for the structure of the salt was limited by the poor quality of the available crystals and by the considerable disorder of the countercations and the solvent of crystallization. These features are common in polyoxometalate crystallography.<sup>[24]</sup>

**Crystal Data for K-1:** Triclinic space group  $P\bar{1}$ , purple-black granular crystals, a = 12.663(5) Å, b = 12.824(5) Å, c = 25.348(9) Å,  $a = 92.348(7)^\circ$ ,  $\beta = 103.666(7)^\circ$ ,  $\gamma = 114.919(6)^\circ$ , and Z = 1. The data were collected with a Bruker SMART APEX CCD sealed-tube diffractometer with Mo- $K_a$  (0.71073 Å) radiation [temperature = 90(2) K] in the range  $0.84 < \theta < 28.41^\circ$ . The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (all W, Re, P, K atoms), and isotropic thermal parameters (all O atoms) converged at  $R_1 = 7.23\%$  and  $wR_2 = 15.87\%$  ( $F_o > 2\sigma F_o$ ). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [Fax: +49-7247-808-666], email: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-416410 for K-1.

**1-Grafted TiO<sub>2</sub>:** TiO<sub>2</sub> (anatase,  $40 \text{ m}^2 \text{g}^{-1}$ ) was pretreated by being dried in the oven (at 50 °C) overnight. The dried TiO<sub>2</sub> support (2.0 g) was dispersed in methanol (160 mL) at 25 °C. A 50% methanol solution of (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl (556 µL; 1.0 mmol) was added to this. This mixture was heated at reflux for 6 h at 85 °C. The obtained white powder was collected on a membrane filter (JG, 0.2 µm), washed with methanol (25 mL × 3), and then

dried in the oven (at 50 °C) overnight (TiO<sub>2</sub>–N<sup>+</sup> was obtained). TiO<sub>2</sub>–N<sup>+</sup> [1.5 g, 31.7 µmol of  $\equiv$ Si(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl groups per g] was suspended in water (45 mL) for 10 min at 25 °C. Solid K-1 (1.0 g, 0.10 mmol) was added to this suspension. The resulting mixture was stirred at 25 °C overnight. The solid product was collected on a membrane filter (JG, 0.2 µm), washed with water (25 mL × 3), and then dried in the oven (at 50 °C) overnight. [Note: if the 1-grafted TiO<sub>2</sub> sample was contaminated by K-1 after the washing with water, the catalytic activity decreased.] Yield: 1.38 g. For [(TiO<sub>2</sub>)<sub>5500</sub>][Si(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>Cl]<sub>7</sub>[Si(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>7</sub>(K<sub>7</sub>[O{Re<sup>V</sup>-(OH)( $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)}<sub>2</sub>])·(H<sub>2</sub>O)<sub>200</sub> (2.2 µmol of 1 per g): calcd. C 0.22, H 0.14, K 0.06, Re 0.08, Si 0.09, Ti 58.00, found C 0.41, H 0.20, K 0.032, Re 0.025, Si 0.16, Ti 58.2. DR UV/Vis spectrum in the visible region: 496, 751 nm. BET surface area: 39.4 m<sup>2</sup>g<sup>-1</sup>.

Catalytic Reaction Experiments: H<sub>2</sub> evolution from water vapor was carried out at 25 °C. A catalyst (500 mg) was placed into a glass reaction vessel, which was connected to a conventional Pyrex closed gas circulation system (238.8 cm<sup>3</sup>). Water vapor (20 Torr; 257.3 µmol) was introduced after evacuation at 25 °C, followed by irradiation with a 500-W Xe lamp equipped with a cut-off filter  $(\lambda > 400 \text{ nm and } \lambda > 420 \text{ nm})$ . H<sub>2</sub>, O<sub>2</sub>, CO, and CH<sub>4</sub> were analyzed by GC (TCD, Molecular Sieve 5A stainless steel columns), and water and CO2 were analyzed by GC (TCD, Porapak Q stainless steel columns), and assignments were made after comparing these with the authentic samples analyzed under the same conditions. D<sub>2</sub>, H<sub>2</sub>, and HD were detected with a quadruple mass spectrometer (Pheiffer Vacuum Prisma QME200). The AQY, defined by the following equation, was measured by using combined band-pass and cut-off (Kenko) filters and a photodiode (PM3; COHERENT). AQY = (number of reacted electrons)/(number of incident photons)  $\times$  100 = (number of evolved H<sub>2</sub> molecules  $\times$  2)/(number of incident photons)  $\times$  100.<sup>[25]</sup>

**Supporting Information** (see also the footnote on the first page of this article): bond lengths, bond angles, and bond valence sums for compound K-1 (Tables S1 and S2).

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