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Photoredox catalysis for oxygenation/deoxygenation between sulfides and sulfoxides by visible-light-responsive polyoxometalates

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Abstract

In this paper, we report the unique visible-light-responsive photoredox catalysis of a divacant lacunary silicotungstate $\text{TBA}_4\text{H}_4[\gamma\text{-SiW}_{10}\text{O}_{36}]$ (SiW10) for functional group transformations of sulfur-containing compounds; namely, (i) aerobic oxygenation of sulfides to sulfoxides and (ii) deoxygenation of sulfoxides to sulfides. In the presence of suitable additives, such as Ce^{3+} (electron transfer mediator for oxygenation) and an alcohol (electron and proton donor for deoxygenation), SiW10 shows visible-light-induced charge transfers by using the newly formed highest occupied molecular orbitals derived from the coordinating Ce^{3+} or alcohol at the vacant site of SiW10, and consequently oxygenation of sulfides and deoxygenation of sulfoxides can selectively be proceeded by irradiation of visible light ($\lambda > 400$ nm) to afford the corresponding desired products in high yields. The SiW10 photocatalysts can readily be recovered and reused for these transformations. Based on the several experimental evidences, the roles of the additives as well as the reaction mechanisms for these transformations are also discussed.

Introduction

Polyoxometalates (POMs) are a class of anionic molecular metal-oxide clusters with a wide range of structural versatilities.¹ Because their redox properties, photoactivity, and acid/base properties can be controlled by their structures, constituent elements, and additional metal cations, they are emergent and attractive materials in various fields of science, such as catalysis, medicine, and multifunctional materials.^{1,2} In addition, they possess high durability against both oxidation and reduction reactions compared with commonly utilized organic and organometallic catalysts. In particular, by utilizing the photo-induced O-to-W charge transfers of the tungstate-based POM frameworks, they show outstanding photocatalysis for various functional group transformations.³ However, ultra violet light should be required for the O-to-W charge transfers because of their wide energy gaps,³ and therefore, the design of efficient visible-light-responsive POM-based catalysts is an important subject.

We have engaged in design of POM-based molecular catalysts for a long time. Specifically, we focused on the unique properties of lacunary POMs because their vacant sites can be utilized as the inorganic multidentate ligands for construction of not only multimetal clusters but also the coordination sites for substrates and/or oxidants for several functional group transformations.⁴ Moreover, based on the coordination properties at the vacant site of a divacant lacunary silicotungstate $\text{TBA}_4\text{H}_4[\gamma\text{-SiW}_{10}\text{O}_{36}]$ (SiW10, Fig. 1a),^{4h} we have found the unique visible-light-induced charge transfers and the photoredox catalysis, for example, oxidation of amines and one-pot synthesis of *N*-alkylated imines by using the newly formed highest occupied molecular orbitals derived from the coordinating metals or substrates at the vacant site of SiW10.⁵

Oxygenation of sulfur-containing compounds is a noticeable kind of transformations utilized in various fields, such as organic synthesis and pharmaceuticals.⁶⁻⁸ Catalytic oxygenation of sulfides to

sulfoxides has often been performed by using hydrogen peroxide and *tert*-butylhydroperoxide as the oxidants.⁷ Molecular oxygen (O_2) is the most desirable oxidant, and several efficient photocatalytic systems for oxygenation of sulfides using O_2 as the oxidant have recently been reported.⁸ Deoxygenation of sulfoxides to sulfides is also one of the important transformations and applicable to valuable transformations, such as chiral alcohol synthesis and carbon atom homologation.^{9,10} Up to the present, several efficient deoxygenation systems using various reductants have been reported.¹⁰

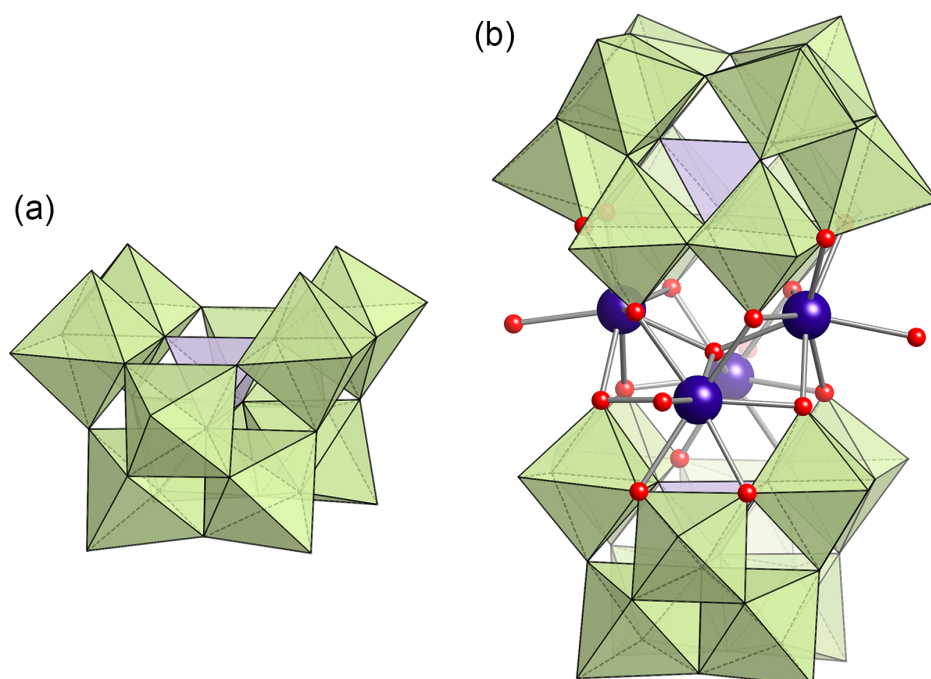
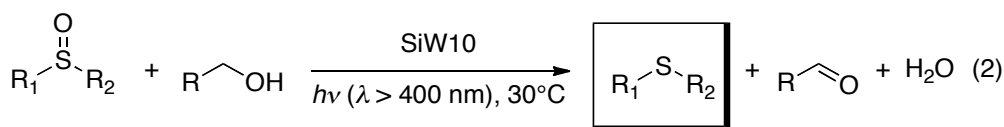
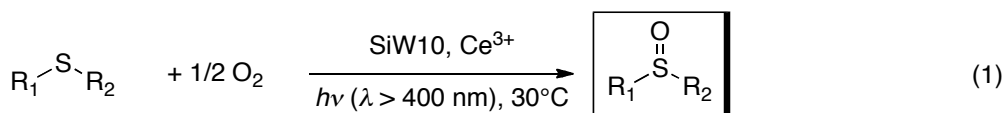


Fig. 1 The structures of the anion parts of (a) SiW10 and (b) CePOM. Green octahedra and light blue tetrahedra represent $\{WO_6\}$ and $\{SiO_4\}$ units, respectively. Blue and red spheres represent cerium and oxygen atoms, respectively.

Toward the development of the selective and efficient photocatalytic systems, molecular design for catalytically active sites, redox potentials, and charge transfer sites should be required. From the above-mentioned desirable properties of the lacunary POMs, we envisioned that efficient photoredox catalysts for oxygenation and deoxygenation of sulfur-containing compounds would be developed. Herein, we report for the first time the photo-induced functional group transformations in

the presence of visible-light-responsive SiW10-based POM catalysts; namely, (i) aerobic oxygenation of sulfides to sulfoxides and (ii) deoxygenation of sulfoxides to sulfides. In the presence of SiW10 together with suitable additives such as Ce^{3+} (electron transfer mediator for oxygenation) and an alcohol (electron and proton donor for deoxygenation), oxygenation of sulfides [eqn (1)] and deoxygenation of sulfoxides [eqn (2)] could selectively be proceeded by irradiation of visible light ($\lambda > 400 \text{ nm}$) to afford the corresponding desired products in high yields. In this paper, the roles of the additives as well as the reaction mechanisms for these transformations are also discussed based on the several experimental evidences.



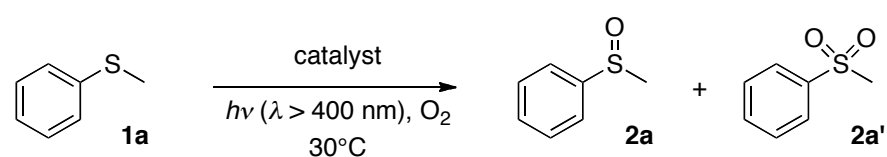
Results and discussion

Photocatalytic aerobic oxygenation of sulfides to sulfoxides

Firstly, the sulfoxidation of thioanisole (**1a**) was investigated in the presence of SiW10 and various metal acetylacetonates ($\text{M}(\text{acac})_n$) as the additives in 1 atm of O_2 with irradiation of visible light ($\lambda > 400 \text{ nm}$). The effect of metal additives is summarized in Table 1. Under the present conditions, SiW10 gave methyl phenyl sulfoxide (**2a**) in only 9% yield (Table 1, entry 14). Notably, $\text{Ce}(\text{acac})_3$ dramatically accelerated the sulfoxidation, and **2a** was obtained in 94% yield (Table 1, entry 1). In contrast, other metal additives, such as $\text{Co}(\text{acac})_2$, $\text{Zn}(\text{acac})_2$, $\text{Mn}(\text{acac})_3$, $\text{Ni}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$, $\text{Cu}(\text{acac})_2$, $\text{Ag}(\text{acac})$, and $\text{Y}(\text{acac})_3$, were much less effective for the sulfoxidation (2–32% yields of **2a**;

Table 1, entries 6–13). The sulfoxidation with $\text{Ce}(\text{acac})_3$ in the absence of SiW10 gave **2a** in only 6% yield (Table 1, entry 15). A mixture of a fully-occupied silicotungstate $\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{Ce}(\text{acac})_3$ was also less effective (28% yield of **2a**; Table 1, entry 16). Thus, both “lacunary” SiW10 and Ce^{3+} are the indispensable components to attain the high yields of **2a**. The sulfoxidation without photo-irradiation or in 1 atm of Ar hardly proceeded (Table 1, entries 17 and 18).

Table 1 Oxygenation of **1a** by irradiation of visible light using various catalysts^a



Entry	Catalyst	Yield (%)	
		2a	2a'
1	SiW10 + $\text{Ce}(\text{acac})_3$	94	6
2 ^b	SiW10 + $\text{Ce}(\text{acac})_3$	94	5
3	SiW10 + $\text{Ce}(\text{OAc})_3$	90	7
4	SiW10 + $\text{Ce}(\text{NO}_3)_3$	16	<1
5	SiW10 + CeCl_3	8	<1
6	SiW10 + $\text{Co}(\text{acac})_2$	3	<1
7	SiW10 + $\text{Zn}(\text{acac})_2$	15	2
8	SiW10 + $\text{Mn}(\text{acac})_3$	4	<1
9	SiW10 + $\text{Ni}(\text{acac})_2$	2	<1
10	SiW10 + $\text{Fe}(\text{acac})_3$	19	2
11	SiW10 + $\text{Cu}(\text{acac})_2$	13	1
12	SiW10 + $\text{Ag}(\text{acac})$	7	<1
13	SiW10 + $\text{Y}(\text{acac})_3$	32	3
14	SiW10	9	1
15	$\text{Ce}(\text{acac})_3$	6	<1
16	$\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}] + \text{Ce}(\text{acac})_3$	<1	<1
17 ^c	SiW10 + $\text{Ce}(\text{acac})_3$	<1	<1
18 ^d	SiW10 + $\text{Ce}(\text{acac})_3$	4	<1
19	CePOM	93	5

^a Reaction conditions: catalyst (SiW10 2 mol%, metal salt 4 mol%, CePOM 1 mol%) **1a** (0.2 mmol), acetonitrile/methanol (1 mL, 2/1 v/v), 30°C , $h\nu$ ($\lambda > 400 \text{ nm}$), O_2 (1 atm), 28 h. Yields were determined by GC using naphthalene as an internal standard. ^b This experiment used retrieved catalyst. ^c Without photo-irradiation. ^d Under Ar (1 atm).

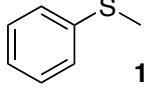
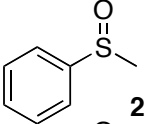
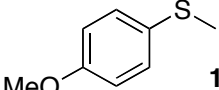
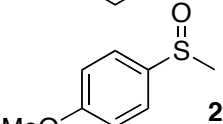
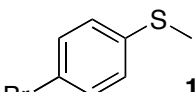
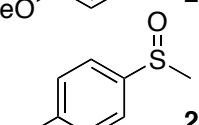
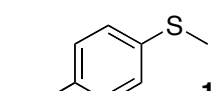
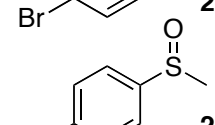
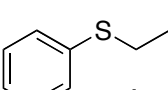
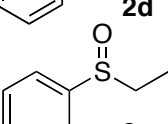
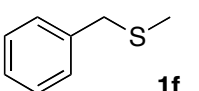
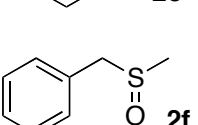
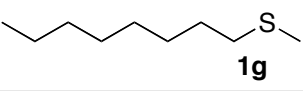
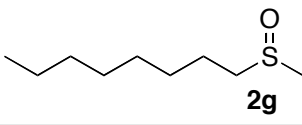
We have recently reported the synthesis and unique visible-light-responsive photoredox property of a tetra-cerium-containing silicotungstate $\text{TBA}_6[\{\text{Ce}(\text{H}_2\text{O})\}_2\{\text{Ce}(\text{CH}_3\text{CN})\}_2(\mu_4\text{-O})(\gamma\text{-SiW}_{10}\text{O}_{36})_2]$ (CePOM, Fig. 1b).^{5a} The DFT calculation showed that the energy gap between the Ce^{3+} -based highest occupied molecular orbital (HOMO) and the $\text{POM}(\text{W}^{6+})$ -based lowest unoccupied molecular orbital (LUMO) was 2.4 eV, and thereby CePOM could possess the visible-light-responsive property (Fig. S1a, ESI†). By irradiation of visible light ($\lambda > 400$ nm), the intramolecular Ce^{3+} -to- $\text{POM}(\text{W}^{6+})$ charge transfer was efficiently induced in CePOM, which could be utilized for the photocatalytic oxidative dehydrogenation of primary and secondary amines and oxidative α -cyanation of tertiary amines.^{5a} The cold-spray ionization (CSI) mass spectrum of a mixture of SiW10 and two equivalents of $\text{Ce}(\text{acac})_3$ in a mixed solvent of acetonitrile and methanol (i.e., the similar solution to that of the photocatalytic sulfoxidation demonstrated in Table 1) showed the signal sets assignable to $[\text{TBA}_8\text{Ce}_4\text{O}(\text{SiW}_{10}\text{O}_{36})_2]^{2+}$ (m/z 3700) and $[\text{TBA}_7\text{Ce}_4\text{O}(\text{SiW}_{10}\text{O}_{36})_2]^+$ (m/z 7158) (Fig. S2a, ESI†), indicating the in-situ formation of CePOM by the reaction of Ce^{3+} and SiW10 under the conditions described in Table 1. Actually, the sulfoxidation of **1a** by CePOM also efficiently proceeded to give **2a** in 93% yield (Table 1, entry 19). The simple mixture of $\text{Ce}(\text{acac})_3$ and SiW10 showed almost the same catalytic performance as that of CePOM and therefore could be utilized as the “in-situ-prepared catalyst” (Table 1, entry 1 vs entry 19). From a practical point of view, the use of such in-situ-prepared catalysts for functional group transformations would be very advantageous because the special synthesis and isolation of the catalysts are not required. For this reason, we have recently developed the several in-situ-prepared metal-containing POM catalysts in organic media for functional group transformations of various kinds of organic substrates.¹¹ In addition, several aqueous in-situ-prepared POM catalysts have been reported to date.¹²

The effect of the counter anions of Ce^{3+} was very significant. $\text{Ce}(\text{OAc})_3$ (OAc = acetate) was equally effective as $\text{Ce}(\text{acac})_3$, and the sulfoxidation of **1a** with $\text{Ce}(\text{OAc})_3$ in the presence of SiW10 also gave **2a** in 90% yield (Table 1, entry 3). The color of the solution containing $\text{Ce}(\text{OAc})_3$ and SiW10 was pale orange and the same as that containing $\text{Ce}(\text{acac})_3$ and SiW10. Thus, the visible-light-responsive CePOM was also possibly formed when using $\text{Ce}(\text{OAc})_3$. In contrast, $\text{Ce}(\text{NO}_3)_3$ and CeCl_3 were much less effective for the sulfoxidation (Table 1, entries 4 and 5). When using $\text{Ce}(\text{NO}_3)_3$ or CeCl_3 , white solid precipitated out from the reaction solutions at the beginning of the sulfoxidation. Recently, we have reported that the transition metal salts of the divacant lacunary silicotungstate can be synthesized by the reaction of SiW10 with various metal nitrates.^{4d} Similarly, the cation exchange of TBA with Ce^{3+} (rather than the formation of CePOM) would take place to form the white Ce^{3+} salt of POM. Most importantly, the simple cations exchange is not effective, and the interaction of Ce^{3+} and SiW10 at the lacunary pocket is indispensable for the present visible-light-responsive catalysis. Therefore, the use of $\text{Ce}(\text{NO}_3)_3$ and CeCl_3 should be avoided in order to generate CePOM in-situ.

The scope of the present Ce^{3+} -SiW10-catalyzed photocatalytic sulfoxidation system was next investigated (Table 2). Thioanisole (**1a**) and its derivatives with electron-withdrawing as well as electron-donating substituents on the phenyl rings (**1b–1d**) could efficiently be converted into the corresponding sulfoxides (**2a–2d**) in high yields (Table 2, entries 1–4). Notably, the sulfoxidation of nitro-substituted thioanisole (**1d**) efficiently proceeded to afford the corresponding sulfoxide (**2d**) in 86% yield although some of the reported photocatalysts showed low catalytic activities for the sulfoxidation of **1d**.⁸ Ethyl phenyl sulfide (**1e**) was also converted into ethyl phenyl sulfoxide (**2e**) in 91% yield (Table 2, entry 5). It should be noted that not only aryl sulfides but also less reactive alkyl ones (**1f** and **1g**) could efficiently be oxygenated (Table 2, entries 6 and 7).

By addition of an excess amount of diethyl ether (ca. 20 mL) to the reaction solution, the catalyst (originally $\text{Ce}(\text{acac})_3 + \text{SiW}_{10}$) spontaneously precipitated out and could easily be retrieved by simple filtration ($\geq 95\%$ recovery based on CePOM). The IR spectrum of the retrieved catalyst indicated that the $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ framework was preserved after the photocatalytic sulfoxidation (Fig. S3, ESI \dagger). The CSI-mass spectrum of the retrieved catalyst in acetonitrile showed the signal sets assignable to $[\text{TBA}_8\text{Ce}_4\text{O}(\text{SiW}_{10}\text{O}_{36})_2]^{2+}$ (m/z 3700) and $[\text{TBA}_7\text{Ce}_4\text{O}(\text{SiW}_{10}\text{O}_{36})_2]^+$ (m/z 7158), indicating that a part of Ce^{3+} was introduced to the vacant site of SiW₁₀ to form CePOM (Fig. S2b, ESI \dagger). Moreover, the retrieved catalyst could be reused for the sulfoxidation of **1a** without an appreciable loss of its high catalytic performance (Table 1, entry 2).

Table 2 Scope of the Ce³⁺-SiW10-catalyzed oxygenation of sulfides by irradiation of visible light^a

Entry	Substrate	Time (h)	Product	Yield (%)	
				2	2'
1		28		94	6
2		24		92	8
3		24		92	7
4		24		86	12
5		24		91	8
6		28		93	7
7		32		90	9

^a Reaction conditions: **1** (0.2 mmol), SiW10 (2 mol%), Ce(acac)₃ (4 mol%), acetonitrile/methanol (1 mL, 2/1 v/v), 30°C, $h\nu$ ($\lambda > 400$ nm), O₂ (1 atm). Yields were determined by GC using naphthalene as an internal standard. Under the conditions, sulfides (**1**) were quantitatively converted into the corresponding oxygenated products (**2** and **2'**).

A possible reaction mechanism for the present photocatalytic oxygenation of sulfides by Ce³⁺-SiW10 (equally CePOM) is shown in Fig. 2. As above-mentioned, we have reported that CePOM shows the intramolecular Ce³⁺-to-POM(W⁶⁺) charge transfer in response to visible light.^{5a} By irradiation of visible light to CePOM, the intramolecular Ce³⁺-to-POM(W⁶⁺) charge transfer efficiently occurs, followed by one electron transfer from a sulfide to the resulting Ce⁴⁺ to afford a

sulfide cation radical species. Then, the reduced POM(W^{5+}) is reoxidized to POM(W^{6+}) by O_2 , and a superoxide anion radical species is likely formed.^{5a} By the reaction of the sulfide cation radical and the superoxide anion radical species, the corresponding sulfoxides are successively obtained as the final products.¹³

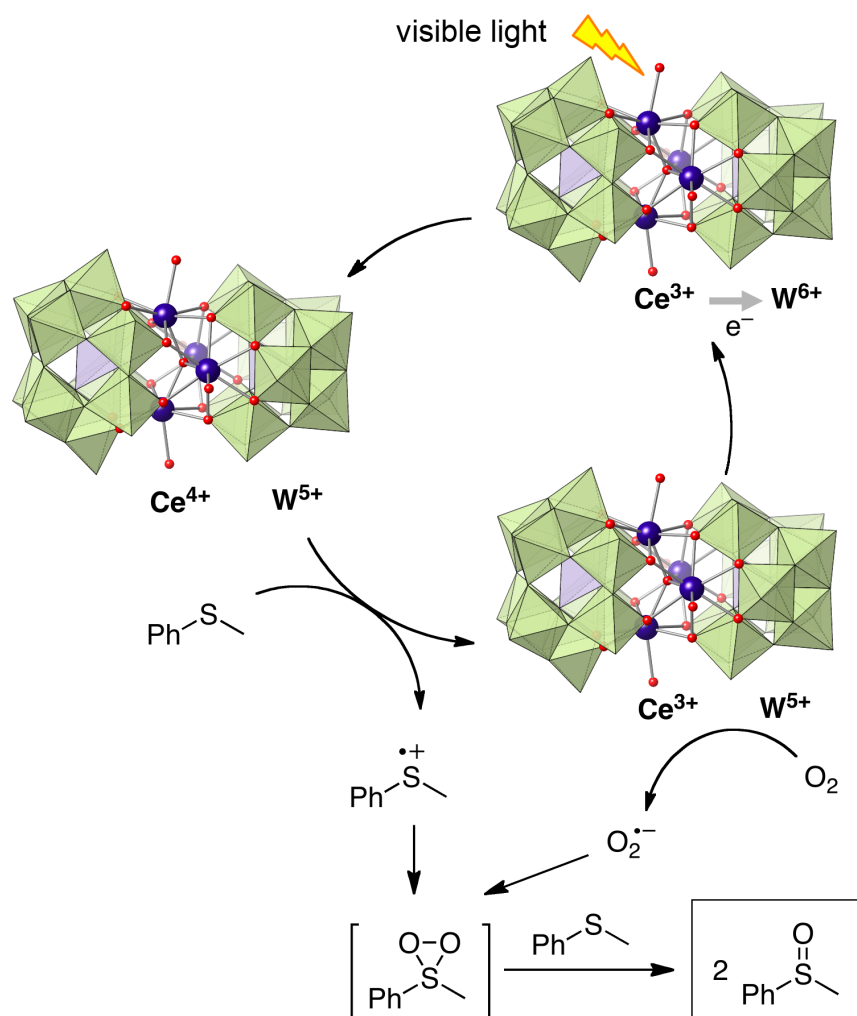


Fig. 2 Visible-light-responsive photocatalytic oxygenation of sulfides by CePOM.

Photocatalytic deoxygenation of sulfoxides to sulfides

Besides the sulfoxidation, we found that deoxygenation of sulfoxides to sulfides, that is, an inverse reaction to sulfoxidation, efficiently proceeded with SiW10 in 1 atm of Ar using a suitable electron and proton donor (reductant), 4-methoxybenzyl alcohol (**3**). Unlike the above-mentioned sulfoxidation,

the SiW10-catalyzed deoxygenation did not require any metal additives; the deoxygenation of **2a** with SiW10 gave **1a** in 99% yield, while the yield of **2a** was 38% when using SiW10 and Ce(acac)₃ (Table 3, entry 1 vs entry 4).

Table 3 Scope of the SiW10-catalyzed deoxygenation of sulfoxides by irradiation of visible light^a

Entry	Substrate	Time (h)	Product	Yield (%)
1		8		99
2 ^b		8		95
3 ^b		8		99
4 ^c		8		38
5 ^d		8		<1
6 ^e		8		<1
7 ^f		8		<1
8 ^g		8		2
9		8		99
10		8		99
11		3		98
12		6		98
13		10		94

^a Reaction conditions: SiW10 (1 mol%), **2** (0.2 mmol), acetonitrile/toluene (2 mL, 1/9 v/v), 4-methoxybenzyl alcohol (**3**, 1 mmol), 30 °C, $h\nu$ ($\lambda > 400$ nm), Ar (1 atm).

^b These experiments used retrieved SiW10; the first reuse (entry 2), the second reuse (entry 3). ^c Without SiW10 (1 mol%) and Ce(acac)₃ (2 mol%). ^d Without SiW10. ^e Without **3**. ^f Without photo-irradiation. ^g With TBA₄H₄[SiW₁₂O₄₀].

The cyclic voltammogram showed that the reduction current of **2a** was observed below -1.8 V vs NHE in acetonitrile (light blue line in Fig. 3). Thus, the reduction of **2a** is essentially difficult due to its high reduction potential.¹⁴ Upon addition of SiW10 (1 mol% with respect to **2a**) to the acetonitrile solution of **2a**, the reduction current due to **2a** was significantly shifted to the more positive potential at ca. -1.5 V (red line in Fig. 3), indicating that **2a** was efficiently reduced by the presence of SiW10. Indeed, upon addition of **2a** (100 equivalents with respect to SiW10) to an acetonitrile solution of the electrochemically two-electron-reduced SiW10, the dark blue solution (due to the reduced SiW10) changed to colorless within 10 min, indicating the electron transfer from the reduced SiW10 to **2a** possibly took place to form **1a**. In contrast, even by addition of **2a** to the two-electron reduced “fully occupied” $\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]$ in acetonitrile (100 equivalents of **2a** with respect to $\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]$), the dark blue color of the solution did not change (even after 4 h), and the formation of **1a** was hardly observed. Needless to say, the deoxygenation of **2a** hardly proceeded with $\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]$ under the conditions described in Table 3. The CSI-mass spectrum of the mixture of SiW10 and **2a** in acetonitrile showed the signal sets at m/z 1932, 2003, 2072, 3763, and 3903 assignable to $[\text{TBA}_6(\text{SiW}_{10}\text{O}_{34})]^{2+}$, $[\text{TBA}_6(\text{SiW}_{10}\text{O}_{34})(\mathbf{2a})]^{2+}$, $[\text{TBA}_6(\text{SiW}_{10}\text{O}_{34})(\mathbf{2a})_2]^{2+}$, $[\text{TBA}_5(\text{SiW}_{10}\text{O}_{34})(\mathbf{2a})]^+$, and $[\text{TBA}_5(\text{SiW}_{10}\text{O}_{34})(\mathbf{2a})_2]^+$, respectively (Fig. 4a). In contrast, the CSI-mass spectrum of the mixture of $\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]$ and **2a** showed only the signal sets assignable to $[\text{TBA}_6(\text{SiW}_{12}\text{O}_{40})]^{2+}$ (m/z 2165) and $[\text{TBA}_5(\text{SiW}_{12}\text{O}_{40})]^+$ (m/z 4086) (Fig. 4b). These results indicate that the vacant site of SiW10 can act as the coordination site for **2a**, which is likely responsible for the efficient reduction of **2a** by the electron transfer from the reduced SiW10.

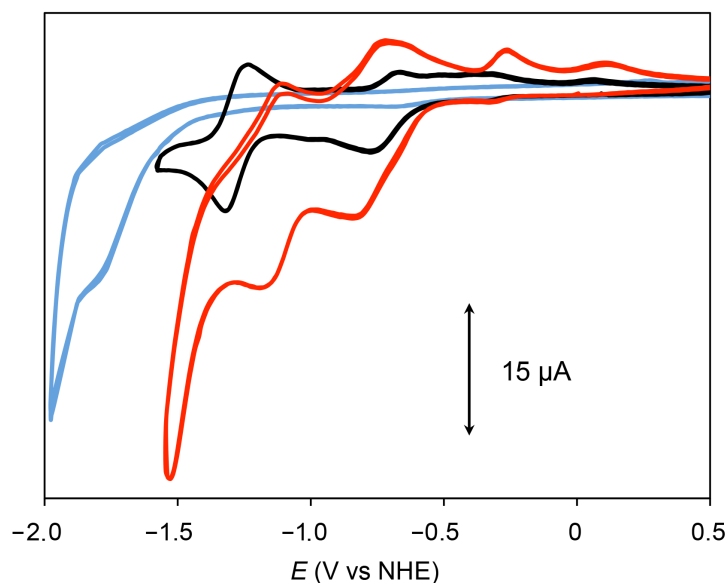


Fig. 3 Cyclic voltammogram of **2a** (light blue line), SiW10 (black line), and the mixture of **2a** and SiW10 (red line) in acetonitrile (SiW10 1 mM, **2a** 100 mM, TBAClO₄ 100 mM).

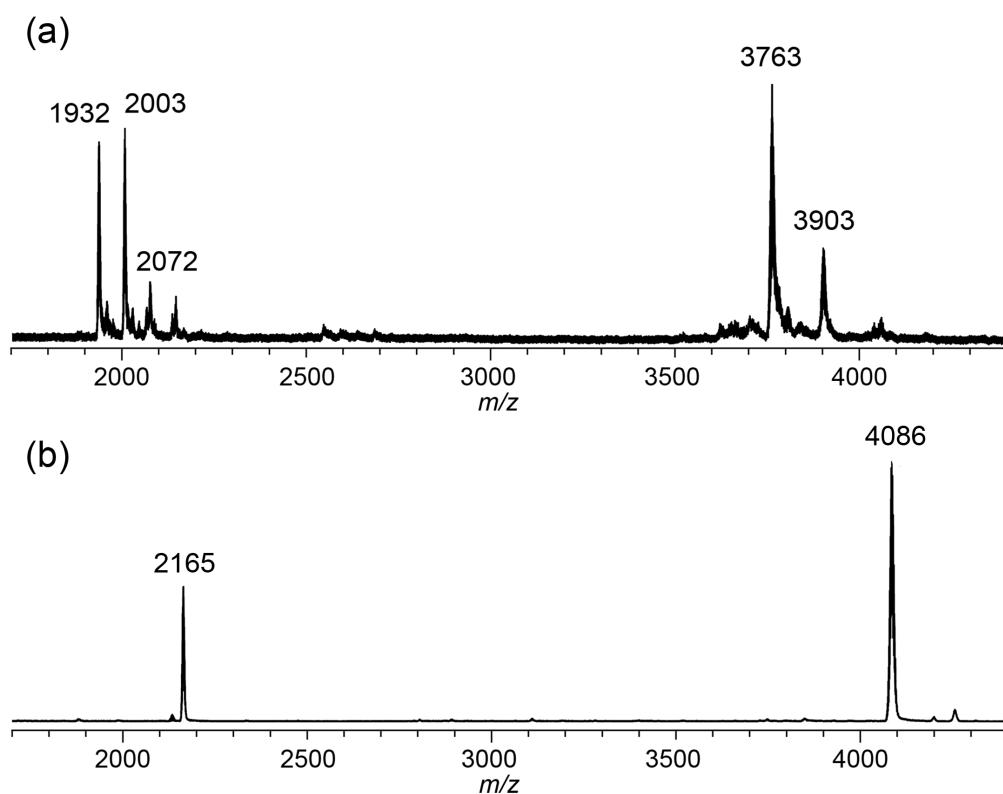


Fig. 4 CSI-mass spectra of (a) the mixture of SiW10 and **2a** in acetonitrile (100 equivalents with respect to SiW10) and (b) the mixture of TBA₄[SiW₁₂O₄₀] and **2a** in acetonitrile (100 equivalents with respect to TBA₄[SiW₁₂O₄₀]). The signal sets at m/z 1932, 2003, 2072, 3763, 3903, 2165, and 4086 were assignable to [TBA₆(SiW₁₀O₃₄)]²⁺, [TBA₆(SiW₁₀O₃₄)(**2a**)]²⁺, [TBA₆(SiW₁₀O₃₄)(**2a**)₂]²⁺, [TBA₅(SiW₁₀O₃₄)(**2a**)]⁺, [TBA₅(SiW₁₀O₃₄)(**2a**)₂]⁺, [TBA₆(SiW₁₂O₄₀)]²⁺, and [TBA₅(SiW₁₂O₄₀)]⁺, respectively.

We have recently reported the visible-light-responsive multielectron redox catalysis of SiW10 by the in-situ coordination of **3** to the vacant site of SiW10.^{5b} By the coordination of **3** to the vacant site, the new HOMO was generated as the electron donor level due to the molecular orbital of **3**, and the energy gap between the newly generated HOMO and the POM(W⁶⁺)-based LUMO became much narrower (2.82 eV) than that between the POM(O²⁻)-based HOMO and the POM(W⁶⁺)-based LUMO in SiW10 (4.58 eV) (Fig. S1b, ESI†). This would enable the visible-light-responsive charge transfer from **3** to SiW10. As the result, up to two electrons and two protons could efficiently be transferred from **3** and stored in SiW10 by irradiation of visible light. Therefore, the vacant site of SiW10 could play a dual role on the present deoxygenation, that is, not only the electron transfer site from **3** to SiW10 but also the electron transfer site from the reduced SiW10 to **2a**. Based on these results, we envisioned that the present visible-light-responsive photoredox system with SiW10 is desirable for photocatalytic deoxygenation of various kinds of sulfoxides, and we next investigated the photocatalytic deoxygenation of sulfoxides by SiW10 in 1 atm of Ar in more detail.

As we expected, the SiW10-catalyzed deoxygenation of **2a** quantitatively proceeded to afford **1a** by irradiation of visible light ($\lambda > 400$ nm) in the presence of **3** as the electron and proton donor (Table 3, entry 1). By irradiation of visible light, the color of the reaction solution promptly changed from pale yellow to dark blue, indicating the efficient electron transfer from **3** to SiW10 to form the photo-reduced SiW10. 4-Methoxybenzaldehyde (0.2 mmol, an equimolar amount with respect to **1a** produced) was also produced as the two-electron oxidation product of **3**, and no hydrogen (H₂) was detected in the gas-phase confirmed by the GC-TCD (thermal conductivity detector) analysis. These results support that the electrons stored in SiW10 can mostly be used for the deoxygenation of **2a**. In contrast, the reactions did not proceed without SiW10 (Table 3, entry 5), **3** (Table 3, entry 6), or photo-

irradiation (Table 3, entry 7). As above-mentioned, when a fully-occupied TBA₄[SiW₁₂O₄₀] was used, the color of the reaction solution did not change, and the reaction hardly proceeded (Table 3, entry 8).

Based on the above-mentioned experimental evidences, a possible reaction mechanism for the present SiW10-catalyzed photocatalytic deoxygenation of sulfoxides to sulfides is proposed (Fig. 5). By irradiation of visible light, the efficient electron transfer from the coordinated alcohol (**3**) at the vacant site to SiW10 occurs, and up to two electrons and two protons are stored on SiW10. Then, the sulfoxide coordinated at the vacant site is possibly deoxygenated to the corresponding sulfide by using the electrons and protons.

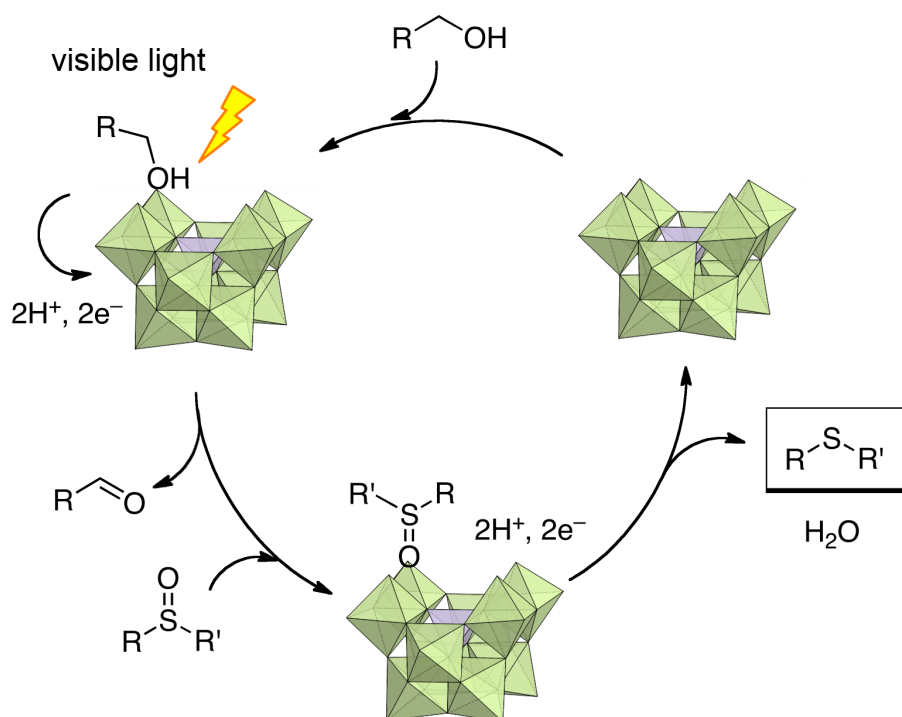


Fig. 5 Visible-light-responsive photocatalytic deoxygenation of sulfoxides by SiW10.

Finally, we turned our attention to the examination of the scope of the present SiW10-catalyzed deoxygenation system. Various kinds of aryl sulfoxides (**2h–2k**) could quantitatively be converted into the corresponding sulfides (Table 3, entries 9–12). Notably, this catalytic system was

applicable to sulfoxides with other reducible substituents, such as C=C double bond (**2i**) and Cl (**2j**), and the deoxygenation of sulfoxides selectively proceeded to give the corresponding sulfides (**1i** and **1j**) without reduction of the C=C and Cl moieties (Table 3, entries 10 and 11). Alkyl sulfoxide (**2l**) was also converted into the corresponding sulfide (**1l**) though a longer reaction time was required (Table 3, entry 13).¹⁵ After the reaction, the catalyst could easily be retrieved as precipitates by addition of an excess amount of diethyl ether (ca. 15 mL) to the reaction solution (>95% recovery based on SiW10). The CSI-mass and IR spectra showed that the structure of the retrieved catalyst was preserved (Figs. S4 and S5, ESI†). In addition, the retrieved catalyst could be reused at least twice without an appreciable loss of its high catalytic performance (Table 3, entries 2 and 3).

Conclusions

We have successfully developed for the first time the visible-light-responsive photoredox catalysis of the lacunary polyoxometalate (TBA₄H₄[γ -SiW₁₀O₃₆]) for oxygenation/deoxygenation reactions between sulfides and sulfoxides. In the presence of the simple mixture of TBA₄H₄[γ -SiW₁₀O₃₆] and Ce³⁺ (in-situ-prepared catalyst) or the cerium-containing polyoxometalate (TBA₆[{Ce(H₂O)}₂{Ce(CH₃CN)}₂(μ_4 -O)(γ -SiW₁₀O₃₆)₂]), selective aerobic oxygenation of various kinds of structurally diverse sulfides to the corresponding sulfoxides efficiently proceeded by irradiation of visible light. The visible-light-induced Ce³⁺-to-W⁶⁺ charge transfer was the key for the oxygenation. In the presence of the suitable electron and proton donor, the photoredox system of TBA₄H₄[γ -SiW₁₀O₃₆] could be further utilized for deoxygenation of sulfoxides, giving the corresponding sulfides with high efficiencies and selectivity even in the presence of other reducible substituents. In the deoxygenation, the vacant site of TBA₄H₄[γ -SiW₁₀O₃₆] acted as not only for the

electron transfer site form an alcohol to $\text{TBA}_4\text{H}_4[\gamma\text{-SiW}_{10}\text{O}_{36}]$ but also the electron transfer site from the reduced $\text{TBA}_4\text{H}_4[\gamma\text{-SiW}_{10}\text{O}_{36}]$ to a sulfoxides.

Experimental section

Materials

Substrates and solvents were obtained from Aldrich, TCI, Kanto Chemical, and Wako Pure Chemical Industries, and purified prior to use (if necessary).¹⁶ $\text{Ce}(\text{acac})_3$ (Aldrich), $\text{Co}(\text{acac})_2$ (Kanto Chemical), $\text{Zn}(\text{acac})_2$ (Kanto Chemical), $\text{Mn}(\text{acac})_3$ (Aldrich), $\text{Ni}(\text{acac})_2$ (Kanto Chemical), $\text{Fe}(\text{acac})_3$ (Aldrich), $\text{Cu}(\text{acac})_2$ (Aldrich), $\text{Ag}(\text{acac})$ (Aldrich) and $\text{Y}(\text{acac})_3$ (Aldrich) were used as received. POMs SiW_{10} ,^{4h} CePOM ,^{5a} and $\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]$ ¹⁷ were synthesized according to the reported procedures.

Instruments

IR spectra were measured on a Jasco FT/IR-4100 spectrometer using KBr disks. Cold-spray ionization (CSI) mass spectra were recorded on JEOL JMS-T100CS. ICP-AES analyses were performed on a Shimadzu ICPS-8100. Elemental analysis for C, H, and N were performed on a Yanaco MT-6 at the Elemental Analysis Center of the School of Science, the University of Tokyo. GC analyses were performed on a Shimadzu GC-2014 instrument with a flame ionization detector (FID) equipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a TC-1 capillary column (internal diameter = 0.32 mm, length = 30 m). GC analyses for H_2 were performed on a Shimadzu GC-8A with a thermal conductivity detector (TCD) with a 5 Å molecular sieve column (internal diameter = 3.2 mm, length = 3.0 m). GC mass spectra were measured on a Shimadzu GCMS-QP2010 at an ionization voltage 70 eV.

Electrochemistry

Cyclic voltammetric measurements were carried out with a Solartron SI 1287 Electrochemical Interface. A standard three-electrode arrangement was employed with a BAS glassy carbon disk electrode as the working electrode, a platinum wire as the counter electrode, and a silver wire electrode as the pseudoreference electrode. The voltage scan rate was set at 100 mV s^{-1} , and TBAClO₄ was used as an electrolyte. The potentials were measured using Ag/AgNO₃ reference electrode (10 mM AgNO₃, 100 mM TBAClO₄ in acetonitrile, 0.55 V vs NHE) and were converted to NHE. Electrochemical reduction of TBA₄[SiW₁₂O₄₀] (20 μmol) was carried out in acetonitrile (40 mL, 50 mM TBAClO₄) at -1.05 V vs NHE with an Electrochemical Analyzer ALS 600A using a BAS glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and a silver wire electrode as the pseudoreference electrode.

Oxygenation of sulfides

A typical procedure for oxygenation of sulfides is as follows: Into a Schlenk flask (volume: ca. 20 mL) were successively placed SiW10 (4 μmol , 2 mol% with respect to **1a**), Ce(acac)₃ (8 μmol , 4 mol% with respect to **1a**), **1a** (0.2 mmol), acetonitrile/methanol (1 mL, 2/1 v/v), and a Teflon-coated magnetic stir bar under O₂ (1 atm). The reaction was initiated by irradiation of visible light ($\lambda > 400 \text{ nm}$) with a Xe-lamp equipped with a 400 nm cut off filter at 30°C. The detailed reaction conditions are shown in the footnotes of Tables 1 and 2. The products were confirmed by comparison of their GC retention times and GC-MS spectra with those of authentic data. The yields of products were periodically determined by GC analysis using an internal standard technique. The reactions were also carried out by using CePOM (2 μmol , 1 mol% with respect to **1a**) instead of the mixture of SiW10 and Ce(acac)₃. After the reaction, the catalyst was retrieved as precipitate by addition of diethyl ether (ca.

20 mL) to the solution (>95% recovery based on CePOM). The retrieved catalyst was washed with diethyl ether, and then dried prior to being used for the reuse experiment.

Deoxygenation of sulfoxides

A typical procedure for deoxygenation of sulfoxides is as follows: Into a Schlenk flask (volume: ca. 20 mL) were successively placed SiW10 (2 μmol , 1 mol% with respect to **2a**), **2a** (0.2 mmol), **3** (1 mmol), acetonitrile/toluene (2 mL, 1/9 v/v), and a Teflon-coated magnetic stir bar under Ar (1 atm). The reaction was initiated by irradiation of visible light ($\lambda > 400$ nm) with a Xe-lamp equipped with a 400 nm cut off filter at 30°C. The products were confirmed by comparison of their GC retention times and GC-MS spectra with those of authentic data. The yields of products were periodically determined by GC analysis using an internal standard technique. After the reaction, the catalyst was retrieved as precipitate by addition of diethyl ether (ca. 15 mL) to the solution (>95% recovery based on SiW10). The retrieved catalyst was washed with diethyl ether, and then dried prior to being used for the reuse experiment.

Quantum chemical calculations

The DFT calculations were performed with Gaussian 09 software.¹⁸ For the calculation of CePOM, the anionic part of CePOM was optimized at the B3LYP level theory¹⁹ with 6-31+G* (for H, O) and 6-31G* (for Si), LanL2DZ (for W),²⁰ and Stuttgart RSC 1997 ECP basis set (SDD, for Ce)²¹ by using the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)²² with the universal force field (UFF) radii for acetonitrile. For the calculation of SiW10 and the complex of SiW10 and **3**, anionic parts were optimized at the B3LYP level theory with 6-31++G* (for C, H, and O), 6-31G* (for Si), and LanL2DZ (for W) by using conductor-like polarizable continuum model (CPCM)²³ with the parameters of the United Atom Topological Model (UAHF) for acetonitrile.

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