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COMMUNICATION

A mononuclear cobalt complex with organic ligand acting as precatalyst for efficient visible light-driven water oxidation

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**N, N'-Bis(salicylidene)ethylenediaminecobalt(II) (1) has been investigated as a highly efficient water oxidation precatalyst with TON of 854 at pH=9.0, using $[Ru(bpy)_3](ClO_4)_2$ as a photosensitizer and $Na_2S_2O_8$ as a sacrificial electron acceptor.**

Catalytic water splitting is of fundamental importance to natural and artificial photosynthesis as well as photochemical energy storage and fuel production. Photolysis of water is composed of two half-reactions: the reduction of protons to H_2 and the oxidation of water to O_2 ($H_2O \longrightarrow H_2 + O_2$)[1]. In artificial photosynthesis, the oxidation of water viewed as bottleneck of the overall process, is recognized as the vital step for supplying electron to other half-reaction[2]. Therefore, developing efficient water oxidation catalyst (WOC) is much significant to obtain inexpensive and renewable pollution-free energy sources. In the past few decades, lots of effort has been devoted to develop various metal complexes[3-7] as efficient WOC. Recently, cobalt-based compounds have come to the view of many researchers, in respect that cobalt is much more abundant and cheaper than the noble metal such as ruthenium and iridium. The cobalt complex with organic ligand such as $[Co^{II}(Me_6tren)(OH_2)]^{2+}$(**2**)[8], $[Co^{III}(Cp*)(bpy)(OH_2)]^{2+}$(**3**)[8], $[Co(qpy)(OH_2)_2]^{2+}$(**4**)[9], CoTPPS(**5**)[10] and CoSIp (**6**)[11] and without organic ligand such as $[Co_4(H_2O)_2(\alpha-PW_9O_{34})_2]^{10-}$(**7**)[12], $[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-}$(**8**)[13] have been reported as efficient water oxidation catalysts or precatalyst.

The development of efficient WOCs remains a major scientific challenge despite the above considerable progress, especially for the high TON, TOF and high quantum yield. Herein, we present an efficient photocatalytic water oxidation reaction system using $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) as photosensitizer, $Na_2S_2O_8$ as a sacrificial electron acceptor, borate as buffer reagent in the presence of N,N'-Bis(salicylidene)ethylenediaminecobalt (II) (**1**).

(**1**)
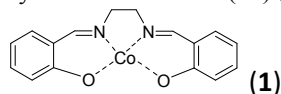
Variables of the photocatalytic reaction including catalyst concentrations, buffer types, pHs, photosensitizers were systemically investigated to obtain the optimal condition (Fig.1, Fig.S8-S10). Oxygen was formed very quickly (Fig.1) and O_2 evolution achieved to a plateau value in 6 min. The sacrificial electron acceptor of $Na_2S_2O_8$ was consumed up, so the amount
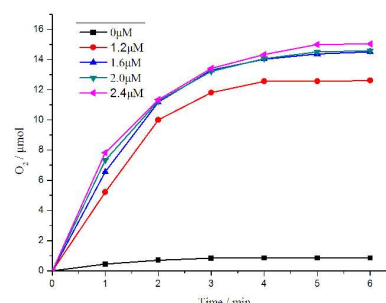

Figure 1. Kinetics of O_2 formation in the photocatalytic system using different concentration of salenCo (0 μM, black; 1.2 μM, red; 1.6 μM, blue; 2.0 μM, green; 2.4 μM, pink).Conditions: LED lamp (≥420 nm), 15.8 mW; 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL and overall volume is ~23 mL; vigorous agitation using a magnetic stirrer.

of formation O_2 is limited to a certain value. A maximum O_2 yield of 54.6% and O_2 evolution amount of 13.7 μmol were achieved when the concentration of **1** was 1.6 μM in 80 mM borate buffer at pH of 9.0. The activity of salen cobalt was compared with other cobalt oxide/hydroxide (Table S6) and Co complexes (Table 1) under the same reaction conditions. The optimum TON of **1** with 854, is among the highest value reported for photocatalytic water oxidation using molecular catalyst so far (Table 1 and Table S1). The initial reaction rate was very fast with an initial rate of O_2 evolution of 6.10 μmol min^{-1} ($TOF_{initial}=TON_{1\ min}/60s = 6.4\ s^{-1}$), which is well comparable to those fastest water systems including thermal and light reactions[14-16]. The quantum yield of Φ_{QY} is ca. 38.6 %, which is the third highest values (Table S1) reported for photocatalytic water oxidation among all the documented compounds containing cobalt so far[17].

The thermal (dark) water oxidation can also be catalyzed by **1** when using $[Ru(bpy)_3]^{3+}$ as the oxidant. An 83 % oxygen yield, TON of 194 and $TOF_{initial}$ of 2.0 s^{-1} were obtained after 3 minutes reaction, respectively. The O_2 yield and TON are the highest among all dark reactions reported using $[Ru(bpy)_3]^{3+}$ as oxidant so far (Table S2). This result reveals that $[Ru(bpy)_3]^{3+}$ can oxidize **1**. This conclusion was also supported by cyclic voltammetry (CV) measurement of **1** and $[Ru(bpy)_3]^{2+}$. The onset of the catalytic wave due to water oxidation is observed at *ca.* 0. 70 V (Fig. 2), and the redox potential of the $Ru(bpy)_3^{2+/3+}$ in our system is 1.16 V. So, $[Ru(bpy)_3]^{3+}$ thermodynamically capable to promote water oxidation.

Table1. Photocatalytic water oxidation catalyzed by different compounds containing cobalt [a]

Complex	Complex Concentration(μM)	TON [b]	O_2 yield (%) [c]	Ref.
SalenCo(II) (**1**)	1.6	854	54.6	This work
$[Co^{II}(Me_6tren)(OH_2)]^{2+}$ (**2**)	1.6	394	25.2	This work
CoTCPP(**5**)	1.6	191	12.2	This work
CoSIp(**6**)	1.6	17	17.4	This work
$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**7**)	1.6	224	45.0	This work
$[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-}$ (**8**)	1.6	51	30.0	This work
$Co(NO_3)_2$	1.6	762	48.8	This work
SalenCo(II) (**1**)	50.0	35	70.9	This work
$[Co^{III}(Cp^*)(bpy)(OH_2)]^{2+}$ (**3**)	50.0	29	29.0	8

[a] Conditions: LED lamp ($\geq$ 420 nm), 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume 10 ml and overall volume is ~23ml, vigorous agitation using a magnetic stirrer. In calculating these reported values, we subtracted the maximal contribution of O_2 generated from noncatalystic pathways (obtained from the control experiment without catalyst) [b] TON is defined as the total number of moles of O_2 per mole of precatalyst. [c] Yield is difined as twice the number of moles of O_2 per mole of $Na_2S_2O_8$.
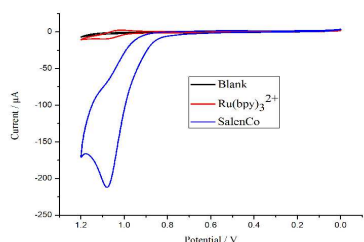

Figure 2. Cycli c voltammogram (CV) of 80 mM sodium borate buffer solution at pH 9.0 with 1mM $[Ru(bpy)_3](ClO_4)_2$ (red line) and 1mM of **1**(blue line). The black line displays the CV of 80 mM sodium borate buffer solution at 1.0M KCl (pH 9.0), Ag/AgCl electrode as reference.

Recently, differentiating homogeneous and heterogeneous water oxidation catalysis has become a very critical issue for researchers using homogeneous WOCs initially. There are three kinds of stability with respect to water oxidation catalyst, i.e. oxidative, hydrolytic and thermal.[18]

Because of experiment carrying out at room temperature, thermal stability is not critical in part for our experiment. In order to know whether it is hydrolytic stable, three experiments were carried out. Firstly, a UV-vis study of **1** shows that the absorbance curve of catalyst **1** in borate buffer (80mM, pH=9.0) almost completely overlap between 0 minute and 60 minute, indicating that the borate buffer does not affect the stability of **1** during the catalytic reaction (Fig. S11). Secondly, kinetics of oxygen formation contrast tests (Fig. S12) was conducted. Complex **1** aged for 1 h gave about 13.6 μmol O_2, which is as same as that of the fresh **1**(13.7 μmol O_2), also suggesting the complex **1** is stable in buffer solution. Thirdly, no nanoparticles were detected after the compound **1** aged for 1 hour in the buffer by dynamic light scattering (DLS) measurements, which meant cobalt hydroxide/oxide nanoparticles did not form during the aging period. These three experiments prove that complex **1** is hydrolytically stable and does not decompose in borate buffer.

In order to make clear the stability of this cobalt complex, DLS measurements were conducted to detect the reaction solution after illumination. It was shown that different sizes of particles were found, ranging from several nm to several thousand nm (Fig. S15). Thus, formation of particles during the reaction was confirmed.

The complete oxidation of ligand of bis(salicylidene)ethylenediamine should produce water, CO_2 and NO_x. Among these products, CO_2 can be detected and quantified by gas chromatography (see Table S7).

To investigate the nature of the catalytic species in photochemical water oxidation by this salen cobalt complex, the following experiments were performed. First, a solution containing 0.2 mM **1**, 2.4 mM of $[Ru(bpy)_3](ClO_4)_2$ and 5.0 mM of $Na_2S_2O_8$ in a borate buffer (80 mM) at pH 9.0 was irradiated under visible light for 6 min at room temperature. Some solid precipitates were obtained after reaction and then were washed completely using CH_2Cl_2. The solution of dichloromethane was then analyzed by electrospray ionization mass spectrometry (ESI/MS). The species observed in the mass spectrum were $[Ru(bpy)_3]^{2+}$ (m/z: 285.2), $[Ru(bpy)_3] (ClO_4)^+$ (m/z: 669.1), $[Ru(bpy)_3](ClO_4)(ClO_2)^+$ (m/z: 737.2) (Fig. S18). No **1**, free salen ligand and other cobalt species (such as simple Co(II) aqua ions) were found at m/z between 50 and 1000. Second, the above precipitates formed after illumination were separated from the reaction solution by centrifugation and washed by pure water repeatedly. The obtained solid then was dried up overnight at 50 ºC. $CDCl_3$ was used to extract the above precipitates and then was analysed by ^1H NMR. No salen ligand and other organic species were observed in the ^1H NMR spectrum except for the solvent signals (Fig. S19). These experimental results revealed that no **1** existed in the precipitates, revealing that **1** was decomposed completely under the photocatalytic reaction condition.

The precipitates derived from **1** using above method were then analyzed by scanning electron microscopy (SEM) and different sizes of particles were observed (Fig. S16). Particles aggregation with the porosity on the surface can be seen clearly. The size of the particles is slightly different accompanied with different degree of aggregation, which form secondary particles of sizes from 100 to 200 nm as shown in SEM.

The X-ray photoelectron spectra (XPS) measurement was carried out for the above particles being washed several times by purified water. Fig. 3 shows the XPS spectrum for Co 2p of the particles, with $2p_{3/2}$ and $2p_{1/2}$ appearing at 781.0 eV and 796.0 eV, respectively. No satellite peaks of Co 2p were observed on the XPS spectrum for the precipitate, indicating no Co(II) species existed on the surface of the precipitate.
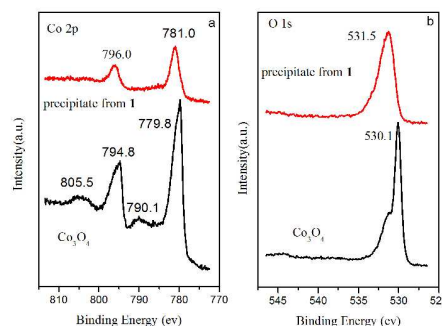

Figure 3. X-Ray photoelectron spectra of Co_3O_4 and precipitates derived from **1** in the energy regions of Co 2p and O 1s. The binding energy of each element was corrected by the C 1s peak (284.8ev)

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Compared to Fukuzumi's XPS binding energy values[8] of particles derived from $[Co^{II}(Me_6tren)(OH_2)]^{2+}$ (**2**), our compounds decomposed from **1** is different to them. Similarly, authentic Co_3O_4 shows two intense peaks at 779.8 eV for Co $2p_{3/2}$ and at 794.8 eV for Co $2p_{1/2}$ with two satellite peaks at 790.1 eV and 805.5 eV, respectively. Contrasted with O1s peak of Co_3O_4(530.1eV), a higher binding energy of 531.5eV for the precipitate appeared, revealing metal hydroxide species existed in the solid.[8] Based on the ESI/MS, ^{1}H NMR and XPS analysis, the precipitates derived from **1** should be Co(III) inorganic species, which would be a mixture of Co(III) containing oxide and/or Co(III) hydroxide.

The recycle of the true catalytic active species was evaluated (Table S8). The catalytic activity (40.9 % O_2 yield) of the isolated precipitate derived from salen Co towards visible-light-driven water oxidation was found to be considerably lower than that of fresh salen Co (54.6 % O_2 yield). The sizes of most particles in situ formed during the photocatalytic process (Fig. S15) are less than 100nm. However, the sizes of isolated precipitates derived from salen Co (Fig. S16) are from 100 to 200 nm. The number of active cobalt oxo sites on the surface of the active intermediate available for O_2 formation is expected to be more for these small particles in situ formed. So, the catalytic activity of fresh catalyst of salen Co was better than the recovered one.

A proposed mechanism was shown in scheme 1. The reaction is started upon the absorption of two photons by two $[Ru^{II}(bpy)_3]^{2+}$ under the illumination. Then the products, two excited $[Ru^{II*}(bpy)_3]^{2+}$ were quenched by two $S_2O_8^{2-}$ through visible-light-accessible metal-to-ligand charge-transfer, resulting in the generation of two $[Ru^{III}(bpy)_3]^{3+}$ complexes, two SO_4^{2-} and two SO_4^{-} radical anions. The latter which is also a strong oxidant, oxidizes two another $[Ru^{II}(bpy)_3]^{2+}$ to give two more $[Ru^{III}(bpy)_3]^{3+}$ with itself into SO_4^{2-}. The light induced products of $[Ru(bpy)_3]^{3+}$ ($Ru(bpy)_3^{2+/3+}$ in our system is 1.16 V) and $SO_4^{\bullet-}$ $[E°(SO_4^{-}/SO_4^{2-}) \approx 2.4$ V][18] are both strong oxidants, and the organic ligand of complex **1** is subjected to be oxidized deeply. Some active intermediates generated from the decomposition of salen Co(II) in situ should be the true catalytic active species, which are answered for the fast oxygen evolution. Further research is underway in order to make clear what species and the quantity content are.
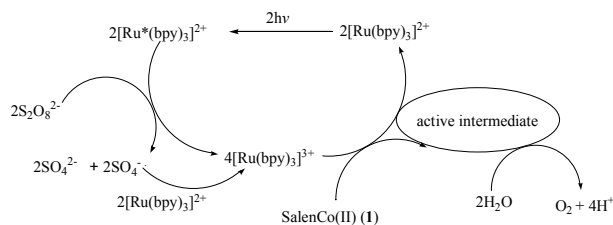
Scheme 1

In conclusion, an efficient water oxidation system was developed using a precatalyst of N, N'-Bis(salicylidene)ethylenediaminecobalt(II). A TON of 854 and TOF of 6.4 s^{-1} were achieved, which are among the highest values reported for photocatalytic water oxidation using molecular catalyst so far.

Notes and references

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Graphic abstract
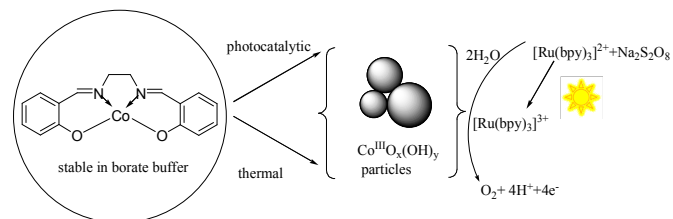
A precatalyst of N, N'-Bis(salicylidene)ethylenediaminecobalt (Ⅱ) showed a TON of 854 and TOF$_{initial}$ of 6.4 s^{-1} for efficient visible light-driven water oxidation.