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Kinetics and Mechanism of Photo-Assistant Ag(I)-Catalysed Water Oxidation with S$_2$O$_8^{2-}$

Lihong Yu, Jidan Wang, Dan Guo, Wansheng You,* Meiying Liu, Lancui Zhang, and Can Li*

The kinetics of photo-assistant Ag(I)-catalysed water oxidation into O$_2$ with S$_2$O$_8^{2-}$ has been investigated. It is found that the visible light ($\lambda \geq 400$ nm) can improve the evolution of O$_2$ remarkably. A reasonable mechanism of Ag(I)-catalyzed water oxidation with S$_2$O$_8^{2-}$ has been proposed, in which the reaction (AgO$^+$ + H$_2$O $\rightarrow$ Ag$^+ + $ H$_2$O$_2$) is considered as the rate-determined step. The increase of the O$_2$-evolution rate under visible light illumination results from the absorbance of the AgO$^+$ species at 375 nm, promoting the rate-determined reaction.
Introduction

Efficient water oxidation into O₂ is a bottleneck in the production of H₂ fuel from water splitting and in the reduction of CO₂ by electrolysis, photocatalysis, photodissociation, and other approaches. Therefore, much more attention has been paid to developing viable water oxidation catalysts (WOCs) [1-4]. Since the Meyer and co-workers’ report of the ‘blue dimer’ cis,cis-[bpy]₂(H₂O)RuIIIORuIII(H₂O)(bpy)₂]⁺⁺ [5], a range of homogeneous metal-organic transition WOCs containing the transition metals (Ru, Ir, Co, Mn etc.) have been reported sequentially [6-16]. Much progress has been made in the activity and stability of WOCs, as well as understanding their catalytic mechanisms. Recently, Sun et al. [17] have reported a mononuclear ruthenium complex [Ru(bda)(isooq)] with catalytic activity (TOF > 300 s⁻¹) and chemical stability (TON = 8,360 ± 91) for water oxidation, which is moderately comparable with the reaction rate of the oxygen-evolving complex of photosystem II in vivo. A series of carbon-free polynuclear metallo WOCs, possessing the higher stability towards oxidative degradation, have also been reported [18-32]. In the catalytic process, central metals are oxidized into the high valent species while the aqua ligand is responsible for the proton coupled electron transfer (PCET). The high valent metal ions are responsible for the O₂-forming event, and then O₂ is evolved to bring WOCs into the original state [33,41].

The peroxysulfate ion (S₂O₈²⁻) is not only one of frequently-used sacrificial electron acceptors to evaluate the WOC’s activity and stability, [19,23,25,27,28,30,31,42] but also a general oxidizing agent to oxidize inorganic and organic substances. [31] The oxidation reactions, involving in S₂O₈²⁻, is slow at ordinary temperature in absence of catalysts. The silver ion is the most powerful catalyst for the reactions, including water oxidation into O₂ evolution. In 1980, Kimura et al. [44] have reported the kinetics of the Ag(I)-catalysed water oxidation with S₂O₈²⁻ without illumination, proposed a mechanism for the reaction. They have considered that the rate-determining reaction of the Ag(I)-catalysed water oxidation is the same as that of inorganic and organic substances and thought that the reaction (Ag⁺ + S₂O₈²⁻ → Ag²⁺ + SO₄²⁻ + SO₇⁻) is the rate-determining step. This is obviously different from the modern idea of the catalytic water oxidation based transitional metal complex WOCs of Ru, Ir, Co, Mn etc., in which the rate-determining step is considered as the formation of O-O bonds or the evolution of O₂ [33-41]. Therefore, it is necessary to re-recognize the true essence of the Ag(I)-catalysed water oxidation.

In our research work on the Ag(I)-catalysed water oxidation, it is found that although neither Na₂S₂O₈ nor AgNO₃ absorbs visible light, visible light can accelerate the rate of water oxidation in a solution of Na₂S₂O₈ and AgNO₃. This cannot be explained by the mechanism reported by Kimura et al. It should be an intermediate species which is responsible for the absorption of visible light, and whose reaction may be the rate-determining reaction of the Ag(I)-catalysed water oxidation. In the paper, therefore, the kinetics of photo-assistant Ag(I)-catalysed water oxidation of S₂O₈²⁻ is investigated and a novel mechanism of Ag(I)-catalysed water oxidation into O₂ is proposedrationally.

Experimental

Materials and Measurement

All chemicals are of analytical grade and used without further purification. Powder X-ray diffraction measurement is recorded on a D8 Advance instrument in the angular range of 2θ = 10-70° at 293 K with Cu Kα radiation. The ultraviolet-visible spectra are recorded on a Lambda 35 spectrophotometer with the conditions: ...
scan rate, 100 nm min\(^{-1}\); wavelength, 800–200 nm. ESR signals at 77 K and ESR signals of radicals trapped by dimethyl pyridine N-oxide (DMPO) at ambient temperature are recorded on a Brucker ESR A 200 spectrometer. After bubbling O\(_2\) for 10 minutes, the samples are introduced into a homemade quartz cup inside the microwave cavity and illuminated with a 300 W Xe lamp (CERAMAX LX-300). The settings for the ESR spectrometer are as follows: center field, 3350.00 G; sweep width, 200 G; microwave frequency, 9.41 GHz; modulation frequency, 100 kHz; power, 10.00 mW. Magnetic parameters of the radicals are obtained from direct measurements of magnetic field and microwave frequency. The TOF mass spectra were obtained on an Aglient 6224 TOF LC/MS with the negative ESI field and microwave frequency. The TOF mass spectra are as follows: center field, 3350.00 G; sweep rate, 100 nm min\(^{-1}\); fragmentor voltage, 150 V; skimmer voltage, 65 V; OCT RF Vpp, 750 V.

Catalytic water oxidation

The catalytic activity is examined in a self-made closed 500 ml quartz reaction cell containing 100 ml of an aqueous solution of Na\(_2\)S\(_2\)O\(_8\) and AgNO\(_3\). The light source is a 300 W Xe lamp equipped with optical filters (\(\lambda\geq370, 380, 390, 400, 420, 500, 660\) nm). A shutter window and a water filter were placed between the Xe lamp and the reaction cell to filter infrared (IR) light illumination. The reaction is carried out under Ar atmosphere and the temperature of the reaction system is controlled by ice-water bath. The amount of the produced O\(_2\) is analyzed using gas chromatography (with a thermal conductivity detector and an Ar carrier).

Result and Discussion

Kinetics of Ag(I)-catalysed water oxidation into O\(_2\)

The Ag(I)-catalysed water oxidation has been carried out in 100 ml of the aqueous solutions with the initial concentration of 8.82 \times 10^{-2}\ mol\ L^{-1} Na\(_2\)S\(_2\)O\(_8\) and different concentrations of AgNO\(_3\) at 24.5 °C in dark. As shown in Fig. 1, the average rates of O\(_2\) evolution in six hours are 21.0, 47.8, 85.5, 145.0 and 221.6 \mu mol\ h^{-1} for the Ag\(_2\) concentrations of 5.88 \times 10^{-3} to \(7.06 \times 10^{-3}\) mol\ L^{-1} at 24.5 °C. As shown in Fig. 2, the average rates of O\(_2\) evolution in six hours are 7.6, 17.0, 31.4 and 47.8 \mu mol h^{-1} respectively. The rate equation is expressed as

\[
\text{d}c(\text{S}_2\text{O}_8^{2-})/\text{d}t = 2dc(\text{O}_2)/\text{d}t = k_0\ c(\text{S}_2\text{O}_8^{2-})\ c(\text{Ag}^+)\]

where \(k_0\) represents the rate constant. According to the slopes of those lines, the rate constants are obtained (Table 1). The average rate constant at 24.5 ± 0.5 °C is 8.5 ± 1 mol\ L h^{-1}. The result is comparable with that under no illumination reported by Kimura et al.\(^{51}\) However, when the concentration of Ag\(^+\) exceeds 1.14 \times 10^{-2}\ mol\ L^{-1}, it is found that the rate of O\(_2\) does not rise with the concentration of Ag\(^+\) and simultaneously a amount of black precipitate is formed at once.

Kinetic experiments of the Ag(I)-catalysed water oxidation have also been performed with the initial concentrations of 8.82 \times 10^{-2}\ mol\ L^{-1} Na\(_2\)S\(_2\)O\(_8\) and 1.18 \times 10^{-2}\ mol\ L^{-1} AgNO\(_3\) at 4.5, 11.5, 17.5 and 24.5 °C. As shown in Fig. 2, the average rates of O\(_2\) evolution in six hours are 7.6, 17.0, 31.4 and 47.8 \mu mol h^{-1} respectively. The corresponding rate constants (\(k_c\)) (see Fig. S4), are listed in Table 2. According to the Arrhenius equation, \(\ln k_0 = \ln A - E_a/RT\), making the plots of \(\ln k_0\) vs 1/\(T\) (Fig. S3), the activation energy (\(E_a\)) is obtained to be 6.5 \times 10^3 J mol^{-1}.

![Fig. 1. Time course of O\(_2\) evolution from 100 ml solution of AgNO\(_3\) and Na\(_2\)S\(_2\)O\(_8\) without illumination. Na\(_2\)S\(_2\)O\(_8\): 8.82 \times 10^{-2}\ mol L^{-1}. AgNO\(_3\): (1) 5.88 \times 10^{-3}\ mol L^{-1}; (2) 1.18 \times 10^{-3}\ mol L^{-1}; (3) 2.35 \times 10^{-3}\ mol L^{-1}; (4) 4.71 \times 10^{-3}\ mol L^{-1}; (5) 7.06 \times 10^{-3}\ mol L^{-1}; (6) 9.41 \times 10^{-3}\ mol L^{-1}; (7) 1.18 \times 10^{-2}\ mol L^{-1}; (8) 1.41 \times 10^{-2}\ mol L^{-1}.

![Fig. 2. Time course of O\(_2\) evolution from 100 ml solution of AgNO\(_3\) and Na\(_2\)S\(_2\)O\(_8\) without illumination. Na\(_2\)S\(_2\)O\(_8\): 8.82 \times 10^{-2}\ mol L^{-1}. AgNO\(_3\):1.18 \times 10^{-2}\ mol L^{-1}. (1) 4.5 ± 0.5 °C; (2) 11.5 ± 0.5 °C; (3) 17.5 ± 0.5 °C; (4) 24.5 ± 0.5 °C.

Kinetics of Photo-assistant Ag(I)-catalysed water oxidation into O\(_2\)

Kinetic experiments of the photo-assistant Ag(I)-catalysed water oxidation have been performed with the initial concentration of 8.82 \times 10^{-2}\ mol L^{-1} Na\(_2\)S\(_2\)O\(_8\) and the different concentrations of AgNO\(_3\) (5.88 \times 10^{-2}, 1.18 \times 10^{-2}, 2.35 \times 10^{-2}, 4.71 \times 10^{-2}\) and 7.06 \times 10^{-3}\ mol L^{-1}) at 24.5 °C under visible light illumination (\(I\geq400\) nm). It is found that the evolution rate of O\(_2\) is accelerated under visible light illumination. As shown in Fig. 3, the average rates of O\(_2\) evolution in six hours are 30.2, 68.2, 120.5, 201.3 and 303.8 \mu mol h^{-1} respectively. The corresponding rate constants (\(k_c\)), (see Fig. S4), are listed in Table 1. The average rate constant at 24.5 ± 0.5 °C is 12.4 ± 1 mol L h^{-1}.
4, the average rates of O\textsubscript{2} evolution in six hours are 22.45, 36.22, and 24.5 ± 0.5. The catalytic activity of Ag(I) is 3.7 × 10\textsuperscript{-4} mol L\textsuperscript{-1} J mol\textsuperscript{-1}(see Fig. S6). The rate equation is also expressed as

\[ -dc(S_{2}O_{8}^{2-})/dt = 2dc(O_{2})/dt = k_{c}c(S_{2}O_{8}^{2-})c(Ag^{+}) \]

where \( k_{c} \) represents the rate constant under visible light illumination.

Compared with Ag(I)-catalysed water oxidation without illumination, it is found that visible light can improve the reaction obviously. The differences between \( k_{c} \) and \( k_{o} \) at 4.5, 11.5, 17.5 and 24.5 °C are 3.2, 3.8, 3.8 and 4.1 respectively. Considering the experimental error, they can be regarded as a constant and the average value is 3.8 approximately. This result illustrates that the visible light-increased rates do not vary with the temperature, which is in accord with the law of photochemical reaction.

The mechanism of Ag(I)-catalysed water oxidation into O\textsubscript{2} with \( S_{2}O_{8}^{2-} \)

As known, the Ag\textsuperscript{+} ion is the most powerful catalyst in oxidizing both inorganic and organic substances by \( S_{2}O_{8}^{2-} \). The catalytic universality and high-efficiency of Ag\textsuperscript{+} result from the coexistence of Ag(II) and Ag(III) species as well as radical species generated from Equations 1-5. It is believed that the rate of the oxidation reactions is dependent on the generated rate of the Ag(II)/Ag(III) species or the radical species. In other words, the rate-determined step is Equations 1 and 2.

For Ag(I)-catalysed water oxidation, however, some experimental phenomena cannot be explained by the mechanism reported by Kimura et al.\textsuperscript{12} Therefore, we have employed modern techniques to characterize the intermediates and analyzed scientifically the experimental phenomena in Ag(I)-catalysed water oxidation. Based on those, a new mechanism of Ag(I)-catalysed water oxidation is proposed in the paper.

The time of flight mass spectrum of a solution of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} and AgNO\textsubscript{3} is investigated. As shown in Fig. 5, A peak set of five mass-to-charge rations at 298.8090, 299.8093, 300.8086, 301.8701 and 302.8061 is observed, which agrees well with the
Fig. 3. Time course of O$_2$ evolution from 100 ml solution of AgNO$_3$ and Na$_2$S$_2$O$_8$ under the irradiation of a 300 W Xe lamp equipped with an ultraviolet cutoff filter (λ ≥ 400 nm) at 24.5 ± 0.5 °C. Na$_2$S$_2$O$_8$: 8.82×10$^{-2}$ mol L$^{-1}$, AgNO$_3$: (1) 5.88 × 10$^{-4}$ mol L$^{-1}$; (2) 1.18 × 10$^{-3}$ mol L$^{-1}$; (3) 2.35 × 10$^{-3}$ mol L$^{-1}$; (4) 4.71 × 10$^{-3}$ mol L$^{-1}$; (5) 7.06 × 10$^{-3}$ mol L$^{-1}$.

Fig. 4. Time course of O$_2$ evolution from 100 ml solution of AgNO$_3$ and Na$_2$S$_2$O$_8$ under the irradiation of a 300 W Xe lamp equipped with an ultraviolet cutoff filter (λ ≥ 400 nm). Na$_2$S$_2$O$_8$: 8.82×10$^{-2}$ mol L$^{-1}$, AgNO$_3$: 1.18 × 10$^{-3}$ mol L$^{-1}$ (1) 4.5 ± 0.5 °C; (2) 11.5 ± 0.5 °C; (3) 17.5 ± 0.5 °C; (4) 24.5 ± 0.5 °C.

Fig. 5. Time of flight mass spectrogram for the mixed solution of 0.01 mol L$^{-1}$ AgNO$_3$ and 0.01 mol L$^{-1}$ Na$_2$S$_2$O$_8$. Insert: fitting figure of [S$_2$O$_8^{2-}$ + Ag$^+$].

Fig. 6. ESR spectrum of a solution of Na$_2$S$_2$O$_8$ (8.82 × 10$^{-2}$ mol L$^{-1}$) and AgNO$_3$ (1.18 × 10$^{-3}$ mol L$^{-1}$) at 100 K.

This shows that a {AgS$_2$O$_8^-$} complex be formed in the process of Ag(I)-catalysed water oxidation. Employing DMPO as an ESR spin trap, consecutive ESR spectra of the solution Na$_2$S$_2$O$_8$ and AgNO$_3$ is obtained. As shown in Fig. 6, ESR signals are centered at $g = 2.0065$. The typical quartets with intensity of 1: 2: 1 and hyperfine coupling constants of $\alpha_N = 14.9$ G and $\alpha_H = 14.9$ G for DMPO-OH adducts appear, indicating that OH· radicals are formed via Equation 3 in the process of Ag$^+$-catalysed water oxidation.

For the aqueous solution of 8.8×10$^{-2}$ mol L$^{-1}$ S$_2$O$_8^{2-}$, when the concentration of adding Ag$^+$ is more than 1.41 × 10$^{-2}$ mol L$^{-1}$, an important phenomenon is observed that the evolution rate of O$_2$...
does not rise with the concentration of adding Ag⁺ (Fig. 1), and simultaneously a black precipitate is formed as soon as the amount of Ag⁺ is added. After the precipitate is washed several times with distilled water, XRD analysis indicated the presence of a single compound, which was identified as silver (III) oxide \( \text{Ag}_2\text{O}_3 \) (Fig.8). As early as 1926, Yost \(^31\) have employed the accurate chemical analysis to determine the precipitate to be a Ag(III) oxide, formulated as \( \text{Ag}_2\text{O}_3 \). The \( \text{Ag}_2\text{O}_3 \) precipitate should be formed via a soluble Ag(III) species in the solution, recognized as \( \text{AgO}^+ \) \(^43,44,52\). As shown in Fig. 9, no absorption (> 350 nm) is observed for the individual solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) or \( \text{AgNO}_3 \). For the mixed solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) and \( \text{AgNO}_3 \), however, an obvious absorption band is observed with the maximum peak at 375 nm, which is attributed to a \( \text{AgO}^+ \) species. \(^33,54\) In addition, the band intensity is dependent on the concentrations of \( \text{Ag}^+ \). This confirms the existence of Ag(III) in the process of \( \text{Ag}^+ \)-catalysed water oxidation. Because the \( \text{OH}^- \) radicals has a strong oxidizing ability, it is deduced reasonably that the \( \text{AgO}^+ \) species should be generated through oxidizing \( \text{Ag}^+ \) ions with the \( \text{OH}^- \) radicals. (Equation 4). Theoretically, there are two pathways to produce the \( \text{AgO}^+ \) species: (1) oxidation of \( \text{Ag(II)} \) ions with the radicals (equation 4); (2) disproportionation of \( \text{Ag(II)} \) ions (equation 6). It has been recognized generally that Equations 3, 4, 5 and 6 are fast reactions. A process of \( \text{Ag}^+ \rightarrow \text{Ag}_2\text{O}_3 \) can be imaged reasonably below. Firstly, \( \text{Ag}^+ \) ions are oxidized into the \( \text{AgO}^+ \) species through Equations 1-6, then the \( \text{Ag}_2\text{O}_3 \) precipitate is produced after the \( \text{AgO}^+ \) species reaches supersaturation. In this case, the evolution rate of \( \text{O}_2 \) does not increase with the concentration of adding \( \text{Ag}^+ \). For the saturated solution of \( \text{AgO}^+ \), its concentration should be fixed so that the evolution rate of \( \text{O}_2 \) is not changed. The experimental evidence shows that the evolution rate of \( \text{O}_2 \) is dependent on the concentration of \( \text{AgO}^+ \). The above experimental phenomena cannot be explained by the mechanism proposed by Kimura et al.

\[ \text{Ag}^+ + \text{OH}^- \rightarrow \text{AgO}^+ + \text{H}^+ \]

**Fig. 7.** In situ ESR spectra of DMPOX generated in the solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) and \( \text{AgNO}_3 \) without illumination. The signal is denoted as ‘1.4 min’ when the reaction is conducted for 1.4 minutes, as ‘14 min’ for 14 minutes and as ‘28 min’ for 28 minutes.

**Fig. 9.** UV-Visible spectra of (1) \( \text{AgNO}_3 \) (7.06 \( \times \) \( 10^{-3} \) mol L\(^{-1} \)); (2) \( \text{Na}_2\text{S}_2\text{O}_8 \) (8.82 \( \times \) \( 10^{-2} \) mol L\(^{-1} \)); (3) the solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) (8.82 \( \times \) \( 10^{-2} \) mol L\(^{-1} \)) and \( \text{AgNO}_3 \) (1.18 \( \times \) \( 10^{-3} \) mol L\(^{-1} \)); (4) the solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) (8.82 \( \times \) \( 10^{-2} \) mol L\(^{-1} \)) and \( \text{AgNO}_3 \) (2.35 \( \times \) \( 10^{-3} \) mol L\(^{-1} \)); (5) the solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) (8.82 \( \times \) \( 10^{-2} \) mol L\(^{-1} \)) and \( \text{AgNO}_3 \) (4.71 \( \times \) \( 10^{-3} \) mol L\(^{-1} \)); (6) the solution of \( \text{Na}_2\text{S}_2\text{O}_8 \) (8.82 \( \times \) \( 10^{-2} \) mol L\(^{-1} \)) and \( \text{AgNO}_3 \) (7.06 \( \times \) \( 10^{-3} \) mol L\(^{-1} \)); (7) the filtrate of mixing \( \text{Na}_2\text{S}_2\text{O}_8 \) (0.1 mol L\(^{-1} \)) and \( \text{AgNO}_3 \) (0.1 mol L\(^{-1} \)).

H\(_2\text{O}_2 \) is analogous to \( \text{H}_2\text{O} \) in composition, but the oxidation rate of H\(_2\text{O}_2 \) is more than one hundred times faster than that of \( \text{H}_2\text{O} \) (Fig. S6). The former differs from the later in structure that it consists of O-O bonds. If the rate-determined steps of oxidation of \( \text{H}_2\text{O} \) is the same as that of \( \text{H}_2\text{O}_2 \), their rates of \( \text{O}_2 \) evolution should be comparable or water oxidation should be faster because water is of high concentration. The difference of the rate in their oxidation reactions may reflect from the different reaction pathways. In addition, when H\(_2\text{O}_2 \) is added to the solution of \( \text{Ag}^+ \) and \( \text{S}_2\text{O}_8^{2-} \), the band at 375 nm disappears immediately (Fig. S7), indicating that oxidation of \( \text{H}_2\text{O}_2 \) by \( \text{AgO}^+ \) is very fast. Therefore, this shows that the mechanism of oxidation of \( \text{H}_2\text{O}_2 \) must be different from that of \( \text{H}_2\text{O} \). It is not entirely true that mechanism
of oxidation of water into $\text{O}_2$ has been considered as general oxidation of inorganic and organic substances.

In 1968, Po et al. proposed a concept that AgO$^+$ oxidizes water into $\text{H}_2\text{O}_2$ while they investigated the mechanism of water oxidation by Ag(II). If the concept is introduced in the mechanism of Ag(I)-catalysed water oxidation into $\text{O}_2$ with $\text{S}_2\text{O}_8^{2-}$ (equation 7), a new mechanism, involving the formation of O-O bonds, is proposed, in which equation 7 is considered as a rate-determined step. Afterwards, $\text{H}_2\text{O}_2$ is oxidized very fast into $\text{O}_2$ by Ag(II), AgO$^+$ or radicals. It is not surprised that no $\text{H}_2\text{O}_2$ is detected in the system because the oxidation of $\text{H}_2\text{O}_2$ is very fast (Fig. S6).

$$\text{Ag}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \{\text{AgS}_2\text{O}_6\}^+ \quad 1$$

$$\{\text{AgS}_2\text{O}_6\}^- \rightarrow \text{Ag}^{2+} + \text{SO}_4^{2-} + \text{SO}_2^{2-} \quad 2$$

$$\text{H}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{OH}^- + \text{H}^+ + \text{SO}_4^{2-} \quad 3$$

$$\text{Ag}^{2+} + \text{OH}^- = \text{AgO}^+ + \text{H}^+ \quad 4$$

$$\text{Ag}^+ + \text{OH}^- = \text{Ag}^{2+} + \text{OH}^- \quad 5$$

$$2\text{Ag}^{2+} + \text{H}_2\text{O} = \text{Ag}^{+} + \text{AgO}^+ + 2\text{H}^+ \quad 6$$

$$\text{AgO}^+ + \text{H}_2\text{O} \rightarrow \text{Ag}^+ + \text{H}_2\text{O}_2 \quad 7$$

$$2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{Ag}^+ + \text{O}_2 + \text{H}_2\text{O} \quad 8$$

$$2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{Ag}^+ + \text{O}_2 + 2\text{H}^+ \quad 9$$

The overall reaction:

$$2\text{H}_2\text{O} + 2\text{S}_2\text{O}_8^{2-} \rightarrow 4\text{SO}_4^{2-} + \text{O}_2 + 4\text{H}^+ \quad 10$$

For the mechanism, if Equation 7 is considered as a slow reaction or a rate-determined step, the experimental phenomena can be explained very well. Firstly, the Ag$_2$O$_3$ precipitate can be generated when the high concentration of Ag$^+$ is employed. Secondly, the AgO$^+$ species can be detected obviously in the reaction system, and Ag$_2$O$_3$ precipitate can be formed when the concentration of Ag$^+$ is more than 1.41 $\times$ 10^{-2} mol L$^{-1}$. Thirdly, the rate of Ag(I)-catalysed oxidation of water is much slower than that of H$_2$O$_2$.

Wavelength dependence of the photo-assistant Ag(I)-catalysed water oxidation have been performed in the solution of 8.82 $\times$ 10^{-2} mol L$^{-1}$ Na$_2$S$_2$O$_3$ and 1.18 $\times$ 10^{-3} mol L$^{-1}$ AgNO$_3$ at 24.5 $\pm$ 0.5 °C under the irradiation of a 300 W Xe lamp equipped with the cutoff filters of (1) $\lambda$ ≥ 370 nm, (2) $\lambda$ ≥ 380 nm, (3) $\lambda$ ≥ 390 nm, (4) $\lambda$ ≥ 400 nm, (5) $\lambda$ ≥ 420 nm, (6) $\lambda$ ≥ 500 nm and (7) $\lambda$ ≥ 660 nm and (8) without illumination. As shown in Fig. 10 and Fig. S8, the average rates of O$_2$ evolution in six hours are 87.3, 76.8, 72.3, 67.8, 61.1, 49.9, 48.0 and 47.8 $\mu$mol h$^{-1}$ respectively. It is found that the photo-reaction system with the cutoff filter of $\lambda$ ≥ 370 nm shows the highest rate obviously, and the rates are decreased gradually as the ranges of the radiation wavelength are deduced, or far away from 370 nm. When the radiation light wavelength is more than 500 nm, the rates are almost the same as that without illumination. This illustrates that the photo-assistant catalytic water oxidation results from the AgO$^+$ species. Because the absorption of the AgO$^+$ species at 350 - 450 nm accelerates equation 7, so that the evolution rate of O$_2$ is increased by visible light illumination.

Application of the steady state hypothesis to equations 1-7 in the mechanism (see supporting information) leads to the rate law

$$\frac{dc(\text{O}_2)}{dt} = k \left(\text{S}_2\text{O}_8^{2-}\right) c(\text{Ag}^+)$$

which is consistent with the experimental rate law (the concentrations of Ag$^+$ are less than 1.41 $\times$ 10^{-2} mol L$^{-1}$). Therefore, not only that, but the experimental phenomena can be explained very well. This shows that the mechanism is more reasonable. It is significant for understanding of water oxidation into O$_2$ and to develop high-efficiency WOCs based on silver complexes.

![Fig. 10. Time course of O$_2$ evolution from 100 ml solution of AgNO$_3$ (1.18 $\times$ 10^{-3} mol L$^{-1}$) and Na$_2$S$_2$O$_3$ (8.82$\times$10^{-2} mol L$^{-1}$) at 24.5 $\pm$ 0.5 °C. under the irradiation of a 300 W Xe lamp equipped with the cutoff filters of (1) $\lambda$ ≥ 370 nm, (2) $\lambda$ ≥ 380 nm, (3) $\lambda$ ≥ 390 nm, (4) $\lambda$ ≥ 400 nm, (5) $\lambda$ ≥ 420 nm, (6) $\lambda$ ≥ 500 nm and (7) $\lambda$ ≥ 660 nm and (8) without illumination.](image)

**Summary**

1. Visible light ($\lambda$ ≥ 400 nm) can increase the rate of Ag(I)-catalysed water oxidation with S$_2$O$_8^{2-}$ into O$_2$ further. The rate equation is $-\frac{dc(\text{S}_2\text{O}_8^{2-})}{dt} = 2dc(\text{O}_2)/dt = k_c(\text{S}_2\text{O}_8^{2-})c(\text{Ag}^+)$, where $k_c$ is 8.5 ± 1 at 24.5 °C and the activation energy is ca. 3.7 $\times$ 10^{3} J mol$^{-1}$.

2. Based on the intermediate species of {Ag$^+$···S$_2$O$_8^{2-}$}, Ag$^{2+}$, OH$^-$, Ag$_2$O$_3$, AgO$^+$ detected in Ag(I)-catalysed water oxidation with S$_2$O$_8^{2-}$, the mechanism of has been developed, where the reaction (AgO$^+$ + H$_2$O → Ag$^+$ + H$_2$O$_2$) is the rate-determined step. The increase of oxidation rate under visible light illumination results from the absorption of the AgO$^+$ species at 375 nm, promoting the reaction (AgO$^+$ + H$_2$O → Ag$^+$ + H$_2$O$_2$).

3. The above results show that the high valent silver ion possesses not only the applicable potential for water oxidation, but also the ability of the formation of O–O bonds. Some silver complexes would become high-efficient WOCs.

**Acknowledgment**
This work is financially supported by the National Science Foundation of China (No. 20773057) and the State Key Laboratory of Fine Chemicals of China (KF 1204) and Key Laboratory of Polyoxometalates Science of Ministry of Education of China for support of this research.

Notes and references