

Supporting Information

Kinetics and Mechanism of Photo-Assistant Ag(I)-Catalysed Water Oxidation with $S_2O_8^{2-}$

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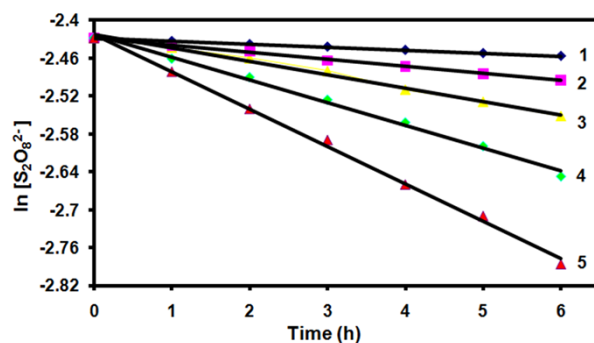


Fig. S1. Plots of $\ln c(\text{S}_2\text{O}_8^{2-})$ vs. time for AgNO_3 - $\text{Na}_2\text{S}_2\text{O}_8$ in 100 ml pure water system without illumination at 24.5 ± 0.5 °C. $\text{Na}_2\text{S}_2\text{O}_8$: 8.82×10^{-2} mol L $^{-1}$. AgNO_3 : (1) 5.88×10^{-4} mol L $^{-1}$; (2) 1.18×10^{-3} mol 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 $^{-1}$.

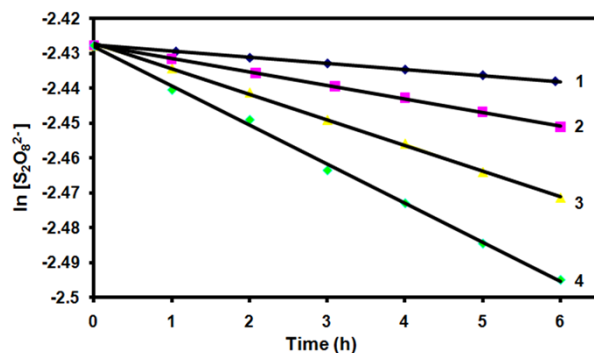


Fig. S2. Plots of $\ln c(\text{S}_2\text{O}_8^{2-})$ vs. time for AgNO_3 - $\text{Na}_2\text{S}_2\text{O}_8$ in 100 ml pure water system at different temperatures without illumination. $\text{Na}_2\text{S}_2\text{O}_8$: 8.82×10^{-2} mol L $^{-1}$. AgNO_3 : 1.18×10^{-3} mol L $^{-1}$. (1) 4.5 ± 0.5 °C; (2) 11.5 ± 0.5 °C; (3) 17.5 ± 0.5 °C; (4) 24.5 ± 0.5 °C.

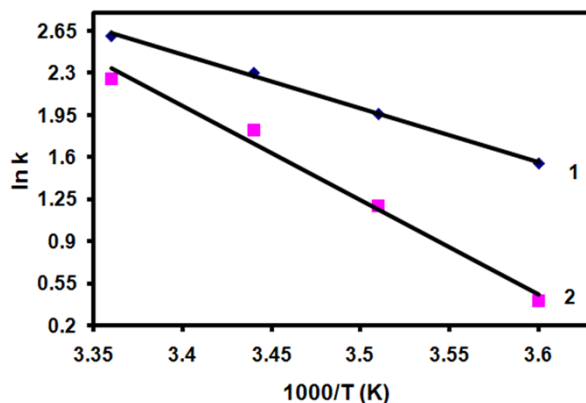


Fig. S3. The activation energy of Ag^+ -catalysed water oxidation of $\text{S}_2\text{O}_8^{2-}$ into O_2 . Plots of $\ln k$ vs. $1000/T(\text{K})$. The k values and the temperatures come from Table 2. 1: under visible light (≥ 400 nm); 2: without illumination.

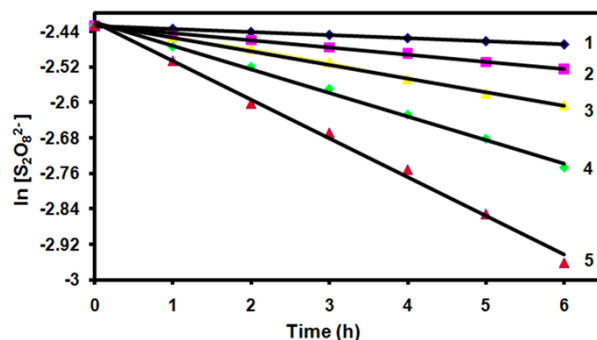


Fig. S4. Plots of $\ln c(\text{S}_2\text{O}_8^{2-})$ vs. time for AgNO_3 - $\text{Na}_2\text{S}_2\text{O}_8$ in 100 ml pure water system under the irradiation of a Xe lamp of 300 W equipped with an ultraviolet cutoff filter to provide visible light ($\lambda \geq 400$ nm) at 24.5 ± 0.5 °C. $\text{Na}_2\text{S}_2\text{O}_8$: 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.

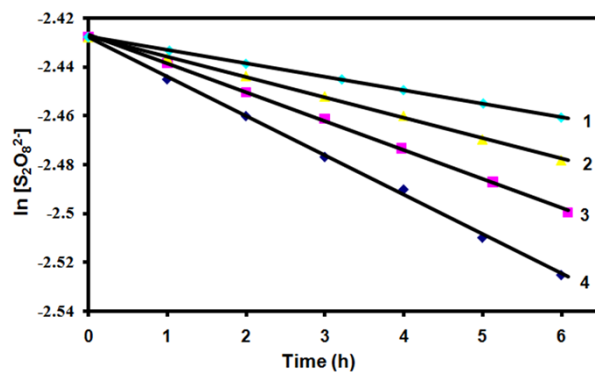


Fig. S5 Plots of $\ln c(\text{S}_2\text{O}_8^{2-})$ vs. time for Ag^+ - $\text{Na}_2\text{S}_2\text{O}_8$ in 100 ml pure water system at different temperatures under the irradiation of a Xe lamp of 300 W equipped with an ultraviolet cutoff filter to provide visible light ($\lambda \geq 400$ nm). $\text{Na}_2\text{S}_2\text{O}_8$: 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.

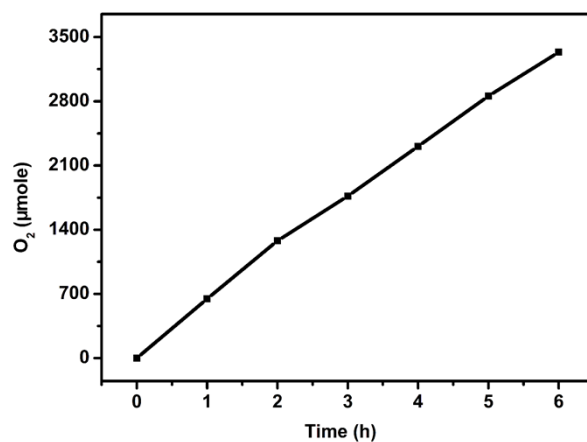


Fig. S6. Time course of O_2 evolution from 100 ml solution of H_2O_2 , AgNO_3 and $\text{Na}_2\text{S}_2\text{O}_8$ without illumination at 24.5 ± 0.5 °C. $\text{Na}_2\text{S}_2\text{O}_8$: 8.82×10^{-2} mol L⁻¹. AgNO_3 : 1.18×10^{-3} mol L⁻¹. 1 ml 30% H_2O_2 .

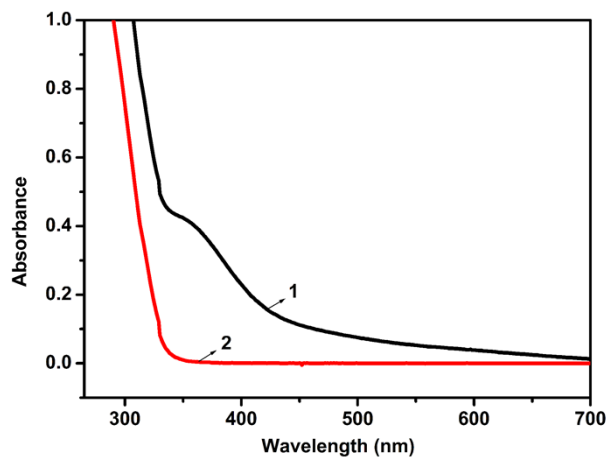


Fig. S7. UV-Visible spectra of the solution of (1) $\text{Na}_2\text{S}_2\text{O}_8$ ($8.82 \times 10^{-2} \text{ mol L}^{-1}$) and AgNO_3 ($7.06 \times 10^{-3} \text{ mol L}^{-1}$); (2) H_2O_2 is added to (1).

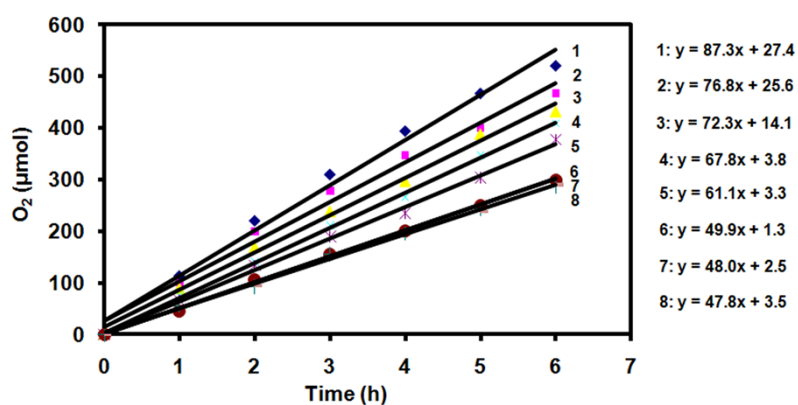


Fig. S8. Plots of O_2 vs. time for 100 ml solution of AgNO_3 ($1.18 \times 10^{-3} \text{ mol L}^{-1}$) and $\text{Na}_2\text{S}_2\text{O}_8$ ($8.82 \times 10^{-2} \text{ mol L}^{-1}$) at $24.5 \pm 0.5 \text{ }^\circ\text{C}$ under the irradiation of a 300 W Xe lamp equipped with cutoff filters of (1) $\lambda \geq 370 \text{ nm}$, (2) $\lambda \geq 380 \text{ nm}$, (3) $\lambda \geq 390 \text{ nm}$, (4) $\lambda \geq 400 \text{ nm}$, (5) $\lambda \geq 420 \text{ nm}$, (6) $\lambda \geq 500 \text{ nm}$ and (7) $\lambda \geq 660 \text{ nm}$ and (8) without illumination.

Steady State Analysis of the Proposed Mechanism

Several differential equations can be set up from this mechanism

$$dc(O_2)/dt = -dc(AgO^+)/dt = k_7 c(AgO^+) \quad S1$$

$$dc(AgO^+)/dt = k_4 c(Ag^{2+}) c(OH^-) - k_8 c(AgO^+) \quad S2$$

$$dc(Ag^{2+})/dt = k_1 c(Ag^+) c(S_2O_8^{2-}) - k_4 c(Ag^{2+}) c(OH^-) \quad S3$$

By the steady state hypothesis, $c(AgO^+)$ and $c(Ag^{2+})$ are constant, therefore

$$dc(AgO^+)/dt = dc(Ag^{2+})/dt = 0 \quad S4$$

Thus, from (S2) and (S4)

$$k_8 c(AgO^+) = k_4 c(Ag^{2+}) c(OH^-) \quad S5$$

from (S3) and (S4)

$$k_4 c(Ag^{2+}) c(OH^-) = k_1 c(Ag^+) c(S_2O_8^{2-}) \quad S6$$

Substitution of (S6) in (S5) gives

$$c(AgO^+) = k_1 k_8^{-1} c(Ag^+) c(S_2O_8^{2-}) \quad S7$$

Substitution of (S7) in (S1) gives

$$dc(O_2)/dt = k_7 k_1 k_8^{-1} c(Ag^+) c(S_2O_8^{2-}) \quad S8$$

which is simplified into

$$dc(O_2)/dt = k c(Ag^+) c(S_2O_8^{2-}) \quad S9$$