# Supporting Information

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

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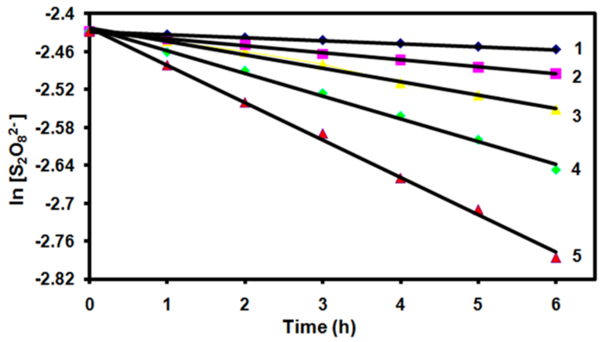


Fig. S1. Plots of ln$c$($S_2O_8^{2-}$) vs. time for $AgNO_3$-$Na_2S_2O_8$ in 100 ml pure water system without illumination at 24.5 ± 0.5 °C. $Na_2S_2O_8$: 8.82×10$^{-2}$ mol L$^{-1}$. $AgNO_3$: (1) 5.88 × 10$^{-4}$ mol L$^{-1}$; (2) 1.18 × 10$^{-3}$ mol L$^{-1}$; (3) 2.35 × 10$^{-3}$ mol L$^{-1}$; (4) 4.71 × 10$^{-3}$ mol L$^{-1}$; (5) 7.06 × 10$^{-3}$ mol L$^{-1}$.

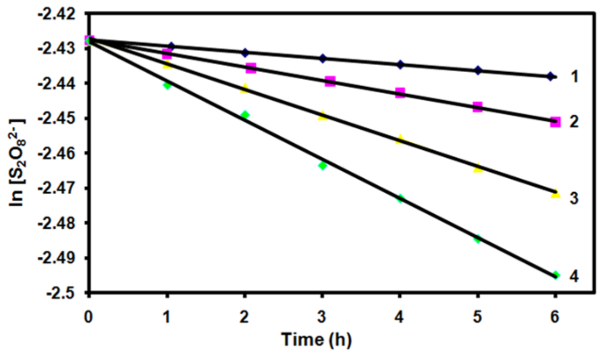


Fig. S2. Plots of ln$c$($S_2O_8^{2-}$) vs. time for $AgNO_3$-$Na_2S_2O_8$ in 100 ml pure water system at different temperatures without illumination. $Na_2S_2O_8$: 8.82 × 10$^{-2}$ mol L$^{-1}$. $AgNO_3$:1.18 × 10$^{-3}$ mol L$^{-1}$. (1) 4.5 ± 0.5 °C; (2) 11.5 ± 0.5 °C; (3) 17.5 ± 0.5 °C; (4) 24.5 ± 0.5 °C.

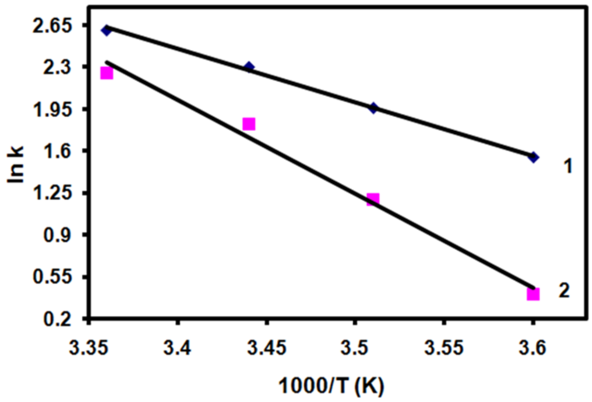


Fig. S3. The activation energy of $Ag^{+}$-catalysed water oxidation of $S_2O_8^{2-}$ into $O_2$. Plots of ln*k* vs. 1000/*T*(K). The *k* values and the temperatures come from Table 2. 1：under visible light (≥ 400 nm); 2: without illumination.

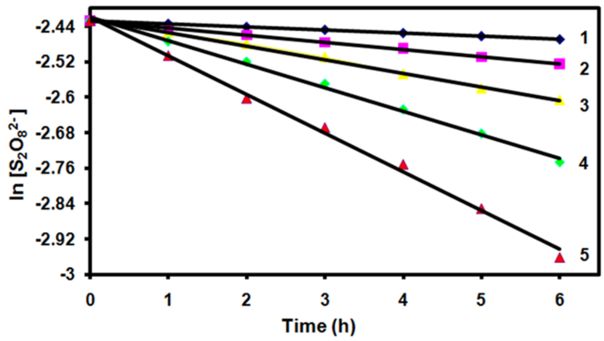


Fig. S4. Plots of ln*c*($S_2O_8^{2-}$) vs. time for $AgNO_3$-$Na_2S_2O_8$ in 100 ml pure water system under the irradiation of a Xe lamp of 300 W equipped with an ultraviolet cutoff filter to provide visible light ($\lambda \geq 400$ nm) at 24.5 ± 0.5 ºC. $Na_2S_2O_8$: 8.82 × $10^{-2}$ mol $L^{-1}$. $AgNO_3$: (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 $L^{-1}$.

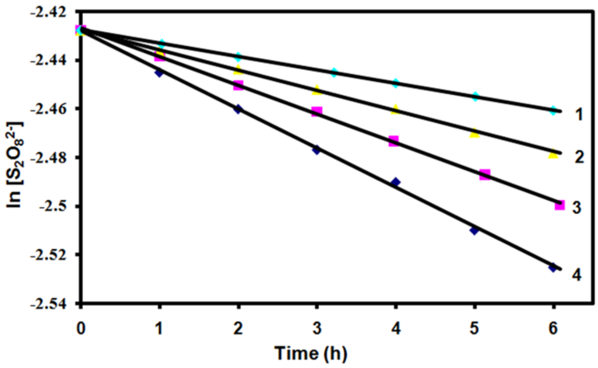


Fig. S5 Plots of ln$c(S_2O_8^{2-})$ vs. time for $Ag^+$-$Na_2S_2O_8$ in 100 ml pure water system at different temperatures under the irradiation of a Xe lamp of 300 W equipped with an ultraviolet cutoff filter to provide visible light ($\lambda \geq 400$ nm). $Na_2S_2O_8$: 8.82 × $10^{-2}$ mol $L^{-1}$. $AgNO_3$: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.

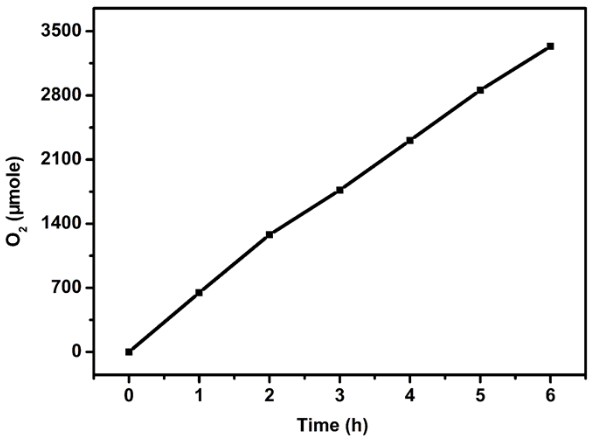


Fig. S6. Time course of $O_2$ evolution from 100 ml solution of $H_2O_2$, $AgNO_3$ and $Na_2S_2O_8$ without illumination at 24.5 ± 0.5 °C. $Na_2S_2O_8$: 8.82 × $10^{-2}$ mol $L^{-1}$. $AgNO_3$:1.18 × $10^{-3}$ mol $L^{-1}$. 1 ml 30% $H_2O_2$.

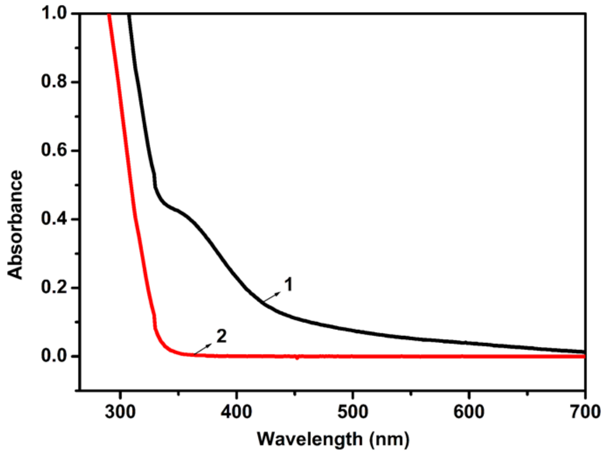


Fig. S7. UV-Visible spectra of the solution of (1) $Na_2S_2O_8$ (8.82 × $10^{-2}$ mol $L^{-1}$) and $AgNO_3$ (7.06 × $10^{-3}$ mol $L^{-1}$); (2) $H_2O_2$ is added to (1).

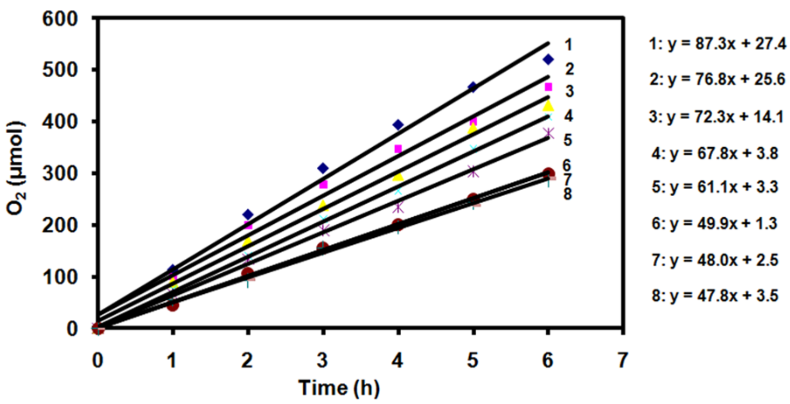


Fig. S8. Plots of $O_2$ vs. time for 100 ml solution of $AgNO_3$ (1.18 × $10^{-3}$ mol $L^{-1}$) and $Na_2S_2O_8$ (8.82 × $10^{-2}$ mol $L^{-1}$) at 24.5 ± 0.5 °C under the irradiation of a 300 W Xe lamp equipped with cutoff filters of (1) $\lambda \geq 370$ nm, (2) $\lambda \geq 380$ nm, (3) $\lambda \geq 390$ nm, (4) $\lambda \geq 400$ nm, (5) $\lambda \geq 420$ nm, (6) $\lambda \geq 500$ nm and (7) $\lambda \geq 660$ nm and (8) without illumination.

## Steady State Analysis of the Proposed Mechanism

Several differential equations can be set up from this mechanism

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

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

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

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

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

Thus, from (S2) and (S4)

$K_8\,c(AgO^+) = k_4\,c(Ag^{2+})\,c(OH^{\cdot})$ S5

from (S3) and (S4)

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

Substitution of (S6) in (S5) gives

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

Substitution of (S7) in (S1) gives

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

which is simplified into

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