

Electronic Supplementary Information for:

Convenient photooxidation of alcohols using dye sensitised metal oxides in combination with silver nitrate and TEMPO – an electron paramagnetic resonance study

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Electronic Supplementary Information

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Table 1 Redox potentials of various components of oxidative cycle.[†]

Compound	E^0 vs. SHE (V)	Reference
E_{cb} (ZnO)	- 0.42	1
TEMPO/TEMPO ⁺	0.64	2
Ag ⁺ /Ag ⁰	0.80	3
AR ⁺ /AR	0.79	4
E_{cb} (TiO ₂)	- 0.50	5
AR [*] /AR ⁺	- 1.57	5

- $E^0_{(AR^*/AR^+)}$ (- 1.57 V vs. SHE) is more negative than $E^0_{(E_{cb} ZnO)}$ (- 0.42 V vs. SHE) and $E^0_{(E_{cb} TiO_2)}$ (- 0.50 V vs. SHE) indicating that the activated state of the dye is capable of injecting electrons into the conduction band of the metal oxide.
- $E^0_{(Ag^+/Ag)}$ (0.79 V vs. SHE) is more positive than $E^0_{(E_{cb} ZnO)}$ (- 0.42 V vs. SHE) and $E^0_{(E_{cb} TiO_2)}$ (- 0.50 V vs. SHE) indicating that the injected electrons can be efficiently trapped by silver (I).
- $E^0_{(AR^+/AR)}$ (0.79 V vs. SHE) is higher than $E^0_{(TEMPO/TEMPO^+)}$ (0.64 V vs. SHE) indicating that the dye radical is able to oxidise the TEMPO radical into the *N*-oxoammonium salt.

[†] AR = Alizarin red

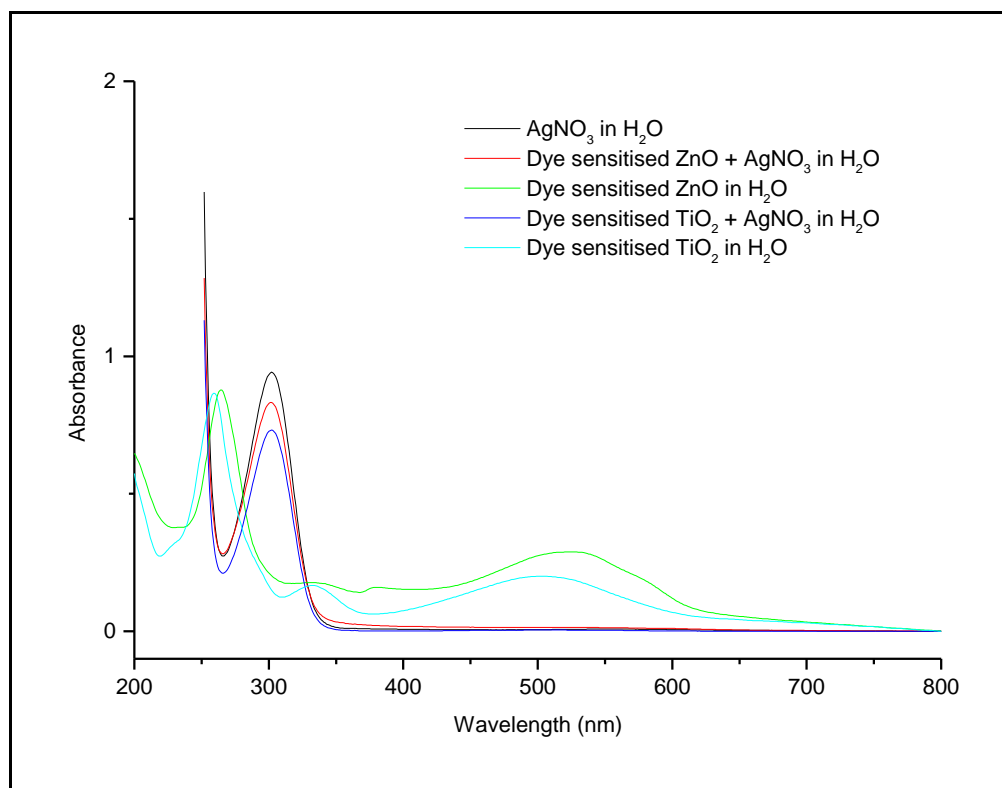


Figure 1

Discussion: Firstly, a concentrated solution of silver nitrate was prepared and a UV/Vis spectrum obtained. Next, the dye sensitised metal oxides were placed in solutions containing pure water and silver nitrate solutions and subjected to analysis by UV/Vis spectroscopy. Both the dye sensitised metal oxides were found to be stable in concentrated silver nitrate solutions with identical spectra to pure silver nitrate solutions obtained. As expected, the dye sensitised metal oxides were found to be unstable in pure water and the dye readily detached from the metal oxide as evidenced by UV/Vis spectra. From these results, it was concluded that both the dye sensitised metal oxides were stable in concentrated silver solutions and unstable in a pure aqueous solution.

General: Chromatograms were obtained using Perkin Elmer Clarus 500 Gas Chromatograph. UV/Vis spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Reactions were irradiated using an OSRAM VIALOX 70 W lamp. EPR measurements were conducted using a Bruker EMX plus, with the following settings: centre field, 3516.87 G; microwave frequency, 9.86 GHz; and power, 2.00 mW. The same quartz tube was used in all experiments to minimise errors.

Procedure for the oxidation of Benzyl alcohol

To a solution of AgNO₃ (306 mg), TEMPO (1.5 mg) and dye sensitised ZnO (20 mg) in H₂O (1.5 ml) was added the appropriate alcohol (0.1 mmol). The mixture was irradiated under visible light (> 450 nm) for 2 hours. The mixture was diluted with ethyl acetate to dissolve any insoluble organic compounds and the resulting mixture was passed through a membrane, with a pore diameter of 2 µm, and analysed by gas chromatography. The structures were confirmed by comparison with authentic samples.

Procedure for the EPR measurements

- A)** EPR study for the dye radical: To a solution of silver nitrate (306 mg) dissolved in distilled water (0.5 ml) was added the dye sensitised semiconductor (10 mg). The mixture was stirred and put into a quartz tube.

- B)** EPR study for the addition of TEMPO: Dye sensitised semiconductor (10 mg), TEMPO (6×10^{-5} M) and benzyl alcohol (0.1 mmol) was added to a solution of silver nitrate (306 mg) in distilled water (0.5 ml). The mixture was stirred and put into a quartz tube.

References:

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