

## Supporting Information

### **Direct evidence for long-lived superoxide radical photo-generated on TiO<sub>2</sub> and Other Metal Oxide suspensions**

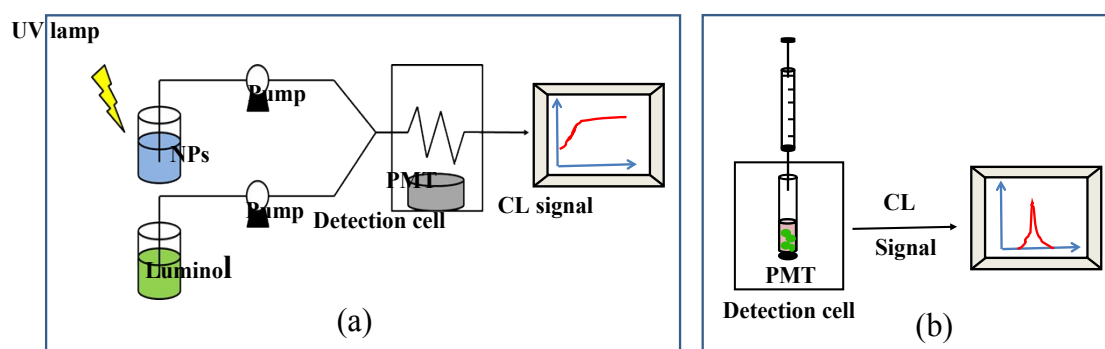
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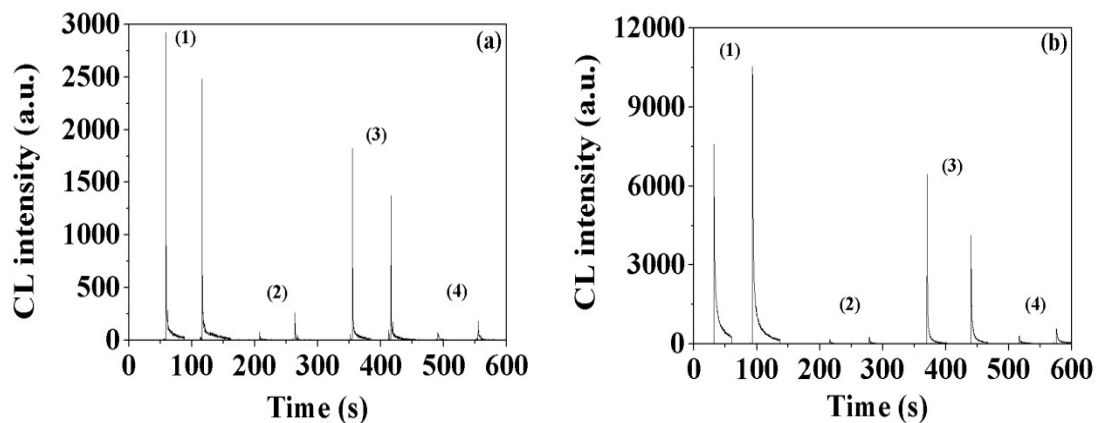
## Supplementary Figures.

**Table S1.** The BET area, particle size and band gap of metal oxides.

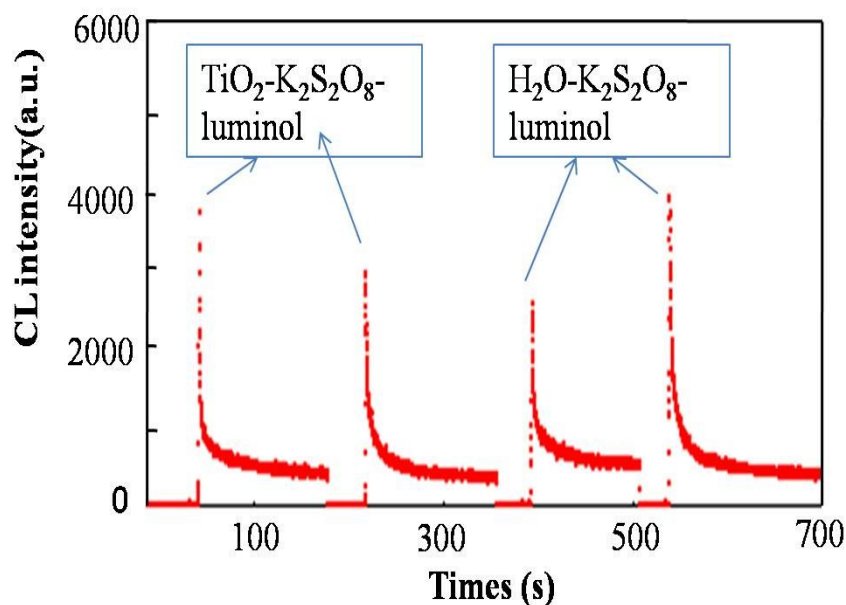
Metal oxide	BET area ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Particles size (nm)	Band gap (eV)
Anatase	82.16	<25	3.2
Rutile	26.18	<100	3.2
P25	48.77	<100	3.2
ZnO	10.8	<50	3.2
SnO <sub>2</sub>	14.2	<50	3.5
CeO <sub>2</sub>	30-50	<25	3.3
Fe <sub>2</sub> O <sub>3</sub>	50-245	<50	2.2



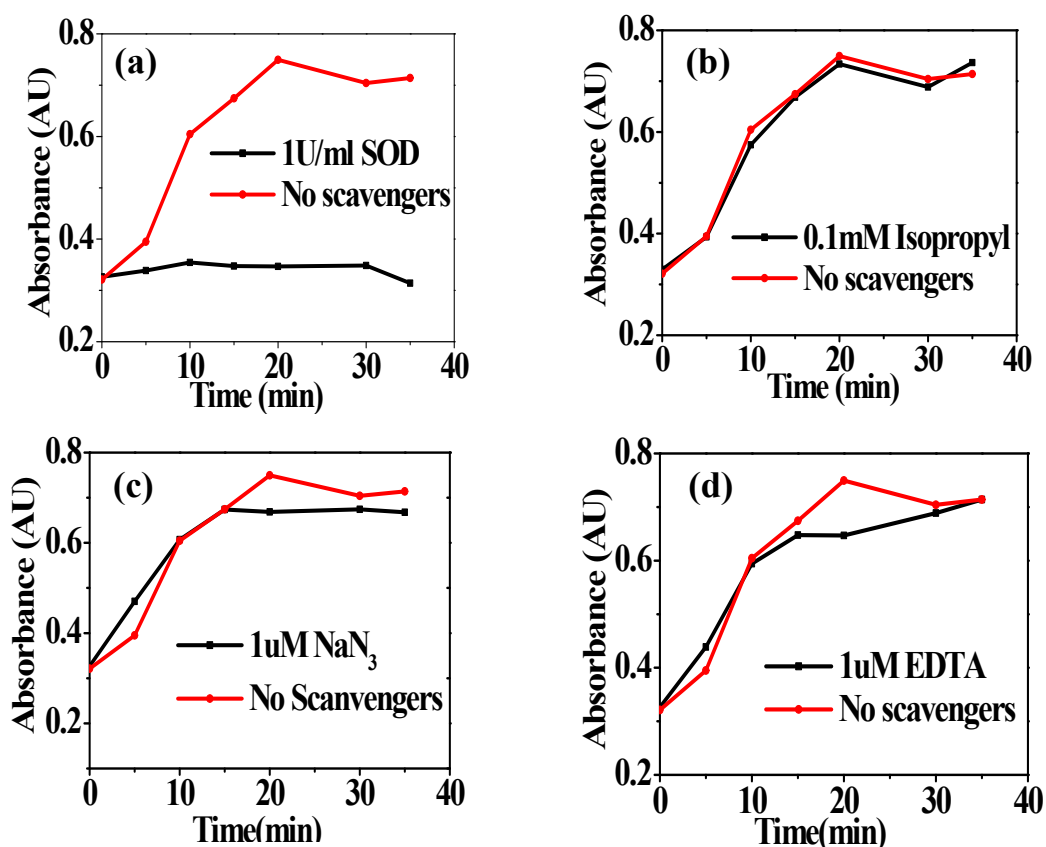
**Figure S1.** CL for the detection of surface-adsorbed  $\text{O}_2^{\cdot-}$ . (a) CFCL apparatus for Online Detection of  $\text{O}_2^{\cdot-}$ . The concentration of luminol and NPs was 50  $\mu\text{M}$  and 0.1  $\text{mg ml}^{-1}$  respectively; The flow rate was 2.2  $\text{mL/min}$ . (b) batch CL for the detection of  $\text{O}_2^{\cdot-}$  on the  $\text{TiO}_2$  nanoparticle and its filtrates. The concentration of luminol was 50  $\mu\text{M}$ .



**Figure S2.** (a) CL intensity of  $\text{TiO}_2$  particles and filtrate from the  $\text{TiO}_2$  aqueous suspension at pH=7 pre- and post- UV irradiation: (1)  $\text{TiO}_2$  particles post-irradiation, (2) filtrate post-irradiation, (3)  $\text{TiO}_2$  particles pre-irradiation, (4) filtrate pre-irradiation; (b) CL intensity of  $\text{TiO}_2$  particles and filtrate from the  $\text{TiO}_2$  aqueous suspension at pH=11 pre- and post- UV irradiation: (1)  $\text{TiO}_2$  particles post-irradiation, (2) filtrate post-irradiation, (3)  $\text{TiO}_2$  particles pre-irradiation, (4) filtrate pre-irradiation.



**Figure S3.** CL intensity of  $K_2S_2O_4$ -luminol- $TiO_2$  and  $K_2S_2O_4$ -luminol- $H_2O$  system, in which 50 $\mu$ M luminol, 60 mM  $K_2S_2O_8$ , 0.1g/L  $TiO_2$

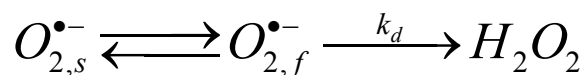


**Figure S4.** (a) Change of Formazan absorption spectra obtained from NBT chemical transformation induced by  $O_2^{\cdot-}$  before and after the addition of the  $O_2^{\cdot-}$  scavengers, SOD (a),  $\cdot OH$  scavengers, isopropanol (b),  $^1O_2$  scavengers,  $NaN_3$  (c) and Hole scavengers, EDTA (d) in the photocatalytic  $TiO_2$  (0.1 mg/ml) suspensions.

## Supplementary Discussion.

### Decay Model of $O_{2,s}^{\bullet-}$ in $TiO_2$ suspensions in darkness after UV irradiation.

Though the self-disproportionation of  $O_2^{\bullet-}$  is a second order reaction, the decay process of  $O_2^{\bullet-}$  in darkness was yet supposed to obey to the pseudo first order decay kinetics when its concentration in solution was low because almost all the  $O_2^{\bullet-}$  were adsorbed on  $TiO_2$  surface [1]. Given that the  $O_2^{\bullet-}$  in solution is desorbed from the  $TiO_2$  surface, so the overall decay process of  $O_2^{\bullet-}$  in darkness after the UV irradiation is shown as follows:



Where  $O_{2,s}^{\bullet-}$  denotes the  $O_2^{\bullet-}$  adsorbed on  $TiO_2$  surface,  $O_{2,f}^{\bullet-}$  is the  $O_2^{\bullet-}$  in solution desorbed from  $TiO_2$  surface,  $H_2O_2$  is originated from the disproportionation of  $O_2^{\bullet-}$  in solution,  $k_d$  is the decay rate constant of  $O_2^{\bullet-}$  in darkness after the irradiation.

As mentioned above, the  $O_{2,s}^{\bullet-}$  remained long-lived in darkness after UV irradiation, while the  $O_{2,f}^{\bullet-}$  from the desorption of  $O_{2,s}^{\bullet-}$  occurred the rapid disproportionation reaction. Therefore, the decay process of  $O_{2,s}^{\bullet-}$  in darkness was actually attributed to the self-disproportionation of  $O_{2,f}^{\bullet-}$  in solution as shown in equation (S1).

$$\frac{-d[O_{2,s}^{\bullet-}]}{dt} = \frac{-d[O_{2,f}^{\bullet-}]}{dt} = k_d [O_{2,f}^{\bullet-}] \quad (S1)$$

Where  $[O_{2,s}^{\bullet-}]$  is the concentration of  $O_{2,s}^{\bullet-}$ ,  $[O_{2,f}^{\bullet-}]$  is the concentration of  $O_{2,f}^{\bullet-}$ . Because there is adsorption/desorption equilibrium between  $O_{2,s}^{\bullet-}$  and  $O_{2,f}^{\bullet-}$  as shown in equation (3), the dissociation equilibrium constant ( $K_d$ ) of  $O_{2,s}^{\bullet-}$  could be expressed as follows.

$$K_d = \frac{[TiOH][O_{2,f}^{\bullet-}]}{[O_{2,s}^{\bullet-}][OH^-]} \quad (S2)$$

$[TiOH]$  is the concentration of adsorption sites for  $O_2^{\bullet-}$ , and  $[OH^-]$  is the concentration of  $OH^-$ . In the certain  $TiO_2$  suspensions, the solution pH and number of the surface  $-Ti^{4+}-OH$  during the decay process of  $O_2^{\bullet-}$  are almost unchanged, thus the

[OH<sup>-</sup>] and [TiOH] are viewed as the constants. Based on this, equation (S2) could be transformed as follows.

$$K'_d = \frac{[O_{2,f}^{\bullet-}]}{[O_{2,s}^{\bullet-}]} = \frac{K_d [OH^-]}{[TiOH]} \quad (S3)$$

Where  $K'_d$  is presumed as the apparent dissociation equilibrium constant, it denotes the ratios of  $O_{2,f}^{\bullet-}$  to  $O_{2,s}^{\bullet-}$ , then  $K'_d$  is determined by the  $K_d$ , [TiOH] and [OH<sup>-</sup>]. By substituting equation (S3) into the right side term of equation (S1), we can obtain the equation (S4) as follows

$$\frac{-d[O_{2,s}^{\bullet-}]}{dt} = k_d K'_d [O_{2,s}^{\bullet-}] \quad (S4)$$

In equation (S4), there is only one variable,  $[O_{2,s}^{\bullet-}]$ , in certain suspension. Therefore, after assuming that  $[O_{2,s}^{\bullet-}] = mCL + n$ , which is a linear relationship between the  $O_{2,s}^{\bullet-}$  concentration and CL intensity, the equation (S4) is converted to equation (S5).

$$\frac{-d[mCL + n]}{dt} = k_d K'_d [mCL + n] \quad (S5)$$

If the equation (S5) is integrated from  $t_0$  to  $t$ ,  $t_0$  is the time when irradiation is stopped, equation (S6) with respect to time as independent variable and CL intensity as dependent variable respectively is obtained as follows.

$$CL = \frac{mCL_0 + n}{m} e^{-k_d K'_d (t-t_0)} - \frac{n}{m} \quad (S6)$$

## Reference

- (1) A. L. Rose, J. W. Moffett, T. D. Waite, *Anal. Chem.* **2008**, 80, 1215-1227.