Supporting information

Role of electron Interfacial transfer in Mesoporous Nano-TiO$_2$
Photocatalysis, A Combined Study of In-situ Photoconductivity
and Numerical Kinetic Simulation

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SI1: Physical property characterization

Fig. S1. Surface FE-SEM image of nc-TiO$_2$ coatings (A), cross-sectional FE-SEM image of nc-TiO$_2$ coating (B), XRD pattern of nc-TiO$_2$ coating (C), (D)Pore size distribution of nc-TiO$_2$ coating.
Fig. S2. FT-IR transmittance spectra of pure nc-TiO$_2$ and nc-TiO$_2$ with adding formic acid
SI2: Details of the kinetic model for in-situ photoconductivity (σ) simulation

The experiment results showed that the photocatalysis of formic acid can accord with the quasi-first order reaction.  

\[ r = k_{\text{app}} C(t) \]  

(S1)

where \( C(t) \) is the [HCOOH] at time \( t \). Here, we considered that the photocatalysis takes place by the direct attack of holes, so the Eq. (S1) indicates that the electron injection to the nc-TiO\(_2\) is dependent on \( C(t) \) according to

\[ r_{\text{in}}^e = k_h C(t) \]  

(S2)

where \( k_h \) is the rate constant.

The interfacial transfer (IT) of electrons from CB to to O\(_2\) is considered.

\[ r_{\text{out}}^e = k_{\text{et}} n_c(t) [O_2] \]  

(S3)

By involving Eqn. (S2) and (S3), the Eqn. (6) (main text) can be rewritten as

\[ \int_{0}^{t} r_{\text{in}}^h(x) dx + \int_{0}^{t} r_{\text{out}}^e(x) dx = n(t) \]  

(S4)

where \( n_{c,dark} \), \( C_{O_2}(x) \), and \( t \) are the \( n_c \) in dark, the [O\(_2\)] at time \( x \), and the observation time. The left-hand can be calculated from the dynamic change of [HCOOH] during the photocatalysis.

Since the photocatalysis happens in gaseous condition, the chemically bonding of formic acid on nc-TiO\(_2\) surface is necessary for the hole IT. The IT of holes can take place according to the single-hole mode (Eq. (S5)). The resulted formate radical (●COOH) can inject another electron to TiO\(_2\) by oxidation of another hole (Eqn. (S6)) or the current-doubling effect (Eqn. (S7)).

\[ \text{HCOOH} + h \rightarrow \text{●COOH} \]  

(S5)

\[ \text{●COOH} + h \rightarrow \text{CO}_2 \]  

(S6)

\[ \text{●COOH} \rightarrow \text{CO}_2 + e \]  

(S7)

The reactions (S6) and (S7) have the same effect on the in-situ σ. The Eqn. (S7) is used now that we do not know which one really happens in gaseous condition. The variation of [HCOOH] and the [●COOH] with time are shown in the following equations.

\[ \frac{dC_1(t)}{dt} = -k_{h1}C_1(t) \]  

(S8)

\[ \frac{dC_2(t)}{dt} = k_{h1}C_1(t) - k_{h2}C_2(t) \]  

(S9)
where $C_1(t)$ and $C_2(t)$ are the [HCOOH] and the [$\bullet$COOH] at time $t$. As the $C_1(t)$ can accord with a mono-exponential function ($C_1(t) = Ae^{k_{h1}t} + B$), the $C_2(t)$ is.

$$C_2(t) = \frac{k_{h1}A}{k_{h2} - k_{h1}} e^{-k_{h1}t} + \frac{k_{h1}B}{k_{h2}} - \left(\frac{k_{h1}A}{k_{h2} - k_{h1}} + \frac{k_{h1}B}{k_{h2}}\right)e^{-k_{h2}t}$$

(S10)

the Eqn. (S4) can be written as

$$A - Ae^{-k_{h1}t} + \int_{0}^{t} k_{h2}C_2(x)dx = \int_{0}^{t} k_{et}(n_c(x) - n_{c,dark})C_{O2}(x)dx + n(t)$$

(S11)

The integral of left-hand is the contribution of formate radicals. The “binary search” method was used to search the $n_c(t)$. The integral of the right hand was numerically solved with the Euler method by dividing the integration region as $N$ equal parts.

$$N \int_{0}^{t} k_{et}(n_c(x) - n_{c,dark})C_{O2}(x)dx = \sum_{i=0}^{N} k_{et}[n_c(i \ast \Delta t) - n_{c,dark}]C_{O2}(i \ast \Delta t) \ast \Delta t$$

(S12)

where $\Delta t = t/N$.

In addition, the photocatalysis may also happen via the double-hole mode. In this case, the complete oxidation of one formic acid molecular needs the simultaneous attendance of two holes.

$$HCOOH + 2h\rightarrow CO_2 \ dC_1(t) = -k_{h1}C_1(t)$$

(S13)

This reaction needs that two holes present at the closest sites on nc-TiO$_2$ surface at the same moment, so the probability for the double-hole IT to take place is low. The double-hole IT was also considered to see the difference, and the Eq. (S4) can be transferred to Eqs. (S14)

$$A - Ae^{-k_{h1}t} + \int_{0}^{t} k_{et}(n_c(x) - n_{c,dark})C_{O2}(x)dx + n(t)$$

(S14)

By considering that the $n_{c,dark}$ is not known, the real values of $n_c$ cannot be obtained. Instead, the relative change of $n_c$ was simulated.
SI3: Possible existence of double-hole interfacial transfer.

**Fig. S3** Diagram for the bidentate and monodentate combinations of formic acid on TiO$_2$ surface and single-hole and double-hole transfer from nc-TiO$_2$ to formic acid.

The simulation of the in-situ $\sigma$ indicating the possibility of double-hole IT in the formic acid gaseous photocatalysis. The FT-IR analysis (Fig. S2) and the first-principle calculation$^5$ showed that the formic acid can exist via both bridged bidentate and monodentate combinations on the nc-TiO$_2$ surface, as shown in Fig. S3. The O atom of carbonyl groups of formic acid bonds with the five coordinated Ti (Ti$_{5c}$) in the case of the monodentate combination. The two O atoms of formic acid combine with one pair of adjacent Ti$_{5c}$ atoms for the bidentate combination. Only the single-hole IT can take place for the monodentate combination, which is complicated for the bidentate combination. Generally, two holes cannot locate at the adjacent O sites at the same time, so the photocatalysis is dominated via single-hole IT. When the [HCOOH] is very low, the holes cannot be quickly consumed by formic acid. In this case the hole density becomes high and it is possible for two holes to occupy the adjacent O sites at the same time. This analysis showed that the possibility of double-hole IT is reasonable, although other reasons can also cause the fast decline of in-situ $\sigma$. 
References:


