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

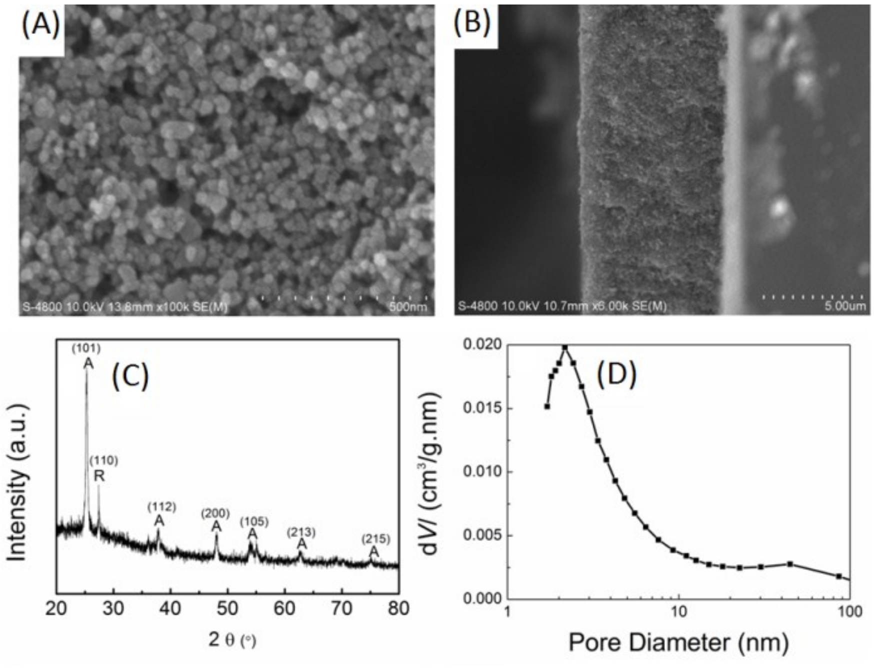

Fig. S1. Surface FE-SEM image of nc-TiO_2 coatings (A), cross-sectional FE-SEM image of nc-TiO_2 coating (B), XRD pattern of nc-TiO_2 coating (C), (D)Pore size distribution of nc-TiO_2 coating.

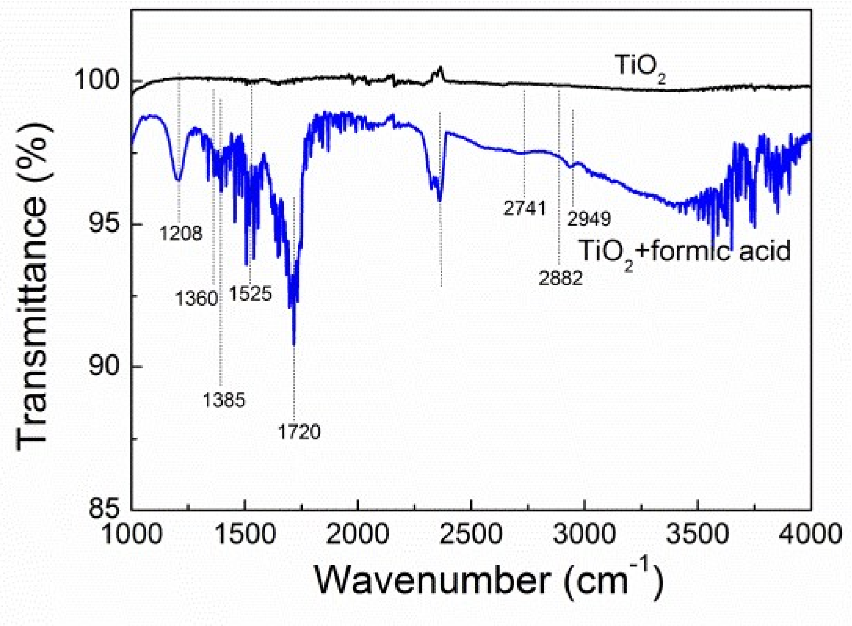

Fig. S2. FT-IR transmittance spectra of pure nc-TiO_2 and nc-TiO_2 with adding formic acid

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. [11]

$$r = k_{app}C(t) \tag{S1}$$

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

$$r_e^{in} = k_h C(t) \tag{S2}$$

where k_{ht} is the rate constant.

The interfacial transfer (IT) of electrons from CB to to O_2 is considered. [43,44]

$$r_e^{out} = k_{et} n_c(t)[O_2] \tag{S3}$$

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

$$\int_0^t k_h C(x)dx = \int_0^t k_{et}(n_c(x) - n_{c,dark}) C_{O2}(x)dx + n(t) \tag{S4}$$

where $n_{c,dark}$, $C_{O2}(x)$, 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)).27

$$HCOOH + h \rightarrow \bullet COOH \tag{S5}$$

$$\bullet COOH + h \rightarrow CO_2 \tag{S6}$$

$$\bullet COOH \rightarrow CO_2 + e \tag{S7}$$

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.

$$dC_1(t)/dt = - k_{h1}C_1(t) \tag{S8}$$

$$dC_2(t)/dt = k_{h1}C_1(t) - k_{h2}C_2(t) \tag{S9}$$

where *C₁(t)* and *C₂(t)* are the [HCOOH] and the[•COOH] at time *t*. As the *C₁(t)* can accord with a mono-exponential function ($C_1(t) = Ae^{-k_{h1}t} + B$), the *C₂(t)* is.

$$C_2(t) = \frac{k_{h1}A}{k_{h2} - k_{h1}}e^{-k_{h1}t} + \frac{k_{h1}B}{k_{h2}} - \left(\frac{k_{h1}A}{k_{h2} - k_{h1}} + \frac{k_{h1}B}{k_{h2}}\right)e^{-k_{h2}t} \tag{S10}$$

the Eqn. (S4) can be written as

$$A - Ae^{-k_{h1}t} + \int_0^t k_{h2}C_2(x)dx = \int_0^t k_{et}\left(n_c(x) - n_{c,dark}\right)C_{O2}(x)dx + n(t) \tag{S11}$$

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.

$$\int_0^t k_{et}\left(n_c(x) - n_{c,dark}\right)C_{O2}(x)dx = \sum_{i=0}^{N} k_{et}\left[n_c(i * \Delta t) - n_{c,dark}\right]C_{O2}(i * \Delta t) * \Delta t \tag{S12}$$

where Δt=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.

$$HCOOH + 2h \rightarrow CO_2 \quad dC_1(t) =- k_{h1}C_1(t) \tag{S13}$$

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 Eq. (S14)

$$A - Ae^{-k_{h1}t} = \int_0^t k_{et}\left(n_c(x) - n_{c,dark}\right)C_{O2}(x)dx + n(t) \tag{S14}$$

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.

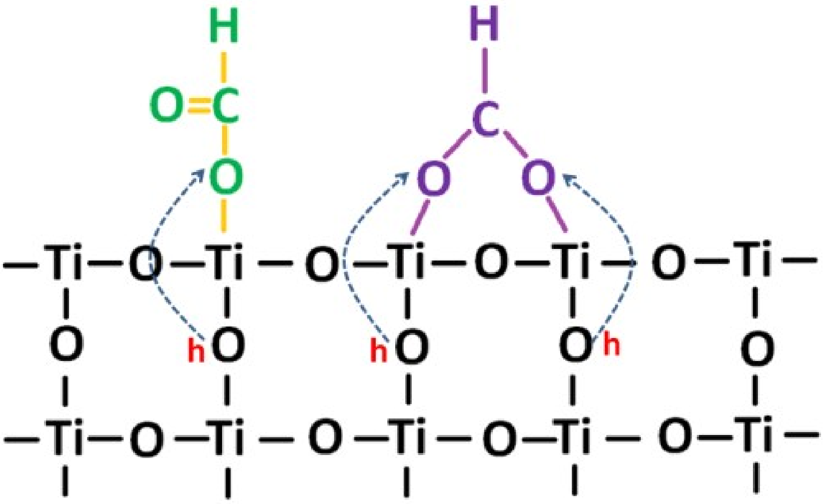

Fig. S3 Diagram for the bidentate and monodentate combinations of formic acid on TiO_2 surface and single-hole and double-hole transfer from nc-TiO_2 to formic acid.

The simulation of the in-situ σ 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 σ.

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