Supporting Information

The number of pages: 11

The number of figures: 8

The number of Tables: 0

Light-driven hydrogenation of bicarbonate into formate over nano Pd/TiO_2

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Calculation of the photothermal conversion efficiency

The photothermal conversion efficiency of 5 wt% Pd/TiO_2 NPs was calculated according to previous reports.[1-3] The testing device we conducted is displayed in **Figure S8** and the details of calculation were displayed as follows:

First, all the calculation is based on total energy balance of the irradiation system as follows:

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_{NPs} + Q_s - Q_{loss} \quad \text{...} (1)$$

where m and Cp are the mass (kg) and heat capacity (J/kg/ºC), respectively. The suffix "i" refers to water or catalyst NPs. *T* is the solution temperature. Q_{NPs} is the heat energy generated by 5 wt% Pd/TiO_2 NPs per second:

$$Q_{NPs} = I \times \eta \quad \text{..} (2)$$

where *I* is the energy NPs absorbed and η is the photothermal conversion efficiency of wt% Pd/TiO_2 NPs.

Q_{loss} is thermal energy lost to the surroundings

$$Q_{loss} = hA\Delta T \quad \text{..} (3)$$

Where h is the heat transfer coefficient, A is the surface area of the container, and ΔT is the temperature change, which is referred to $T\text{-}T_{surrounding}$ (T and $T_{surrounding}$ are the solution temperature and ambient temperature of the surrounding, respectively).

Qs is the heat generated by solvent per second. In the case of pure water, the heat input is equal to the heat output at the maximum steady-statue temperature, so the equation (3) can be expressed by equation (4):

$$Q_S = Q_{loss} = \mathrm{h}\mathrm{A}\Delta T_{max,H_2O} \quad \text{..} (4)$$

Where $\Delta T_{max,H2O}$ is the temperature change of water at the maximum steady-state temperature. As it to the experiment of 5 wt% Pd/TiO_2 NPs dispersion, the heat inputs are the heat generated by nanoparticles (Q_{NPs}) and water (Q_s), which is equal to the heat output at the maximum steady-statue temperature, so the equation can be expressed as following:

$$Q_{NPs} + Q_S = Q_{loss} = hA\Delta T_{max,mix} \quad \text{..} (5)$$

Where $\Delta T_{max,mix}$ is the temperature change of the 5 wt% Pd/TiO_2 NPs dispersion at the maximum steady-state temperature. According to the equation (2), (4) and (5), η can be calculated as follows:

$$\eta = \frac{hA(\Delta T_{max,mix} - \Delta T_{max,H_2O})}{I} \quad \text{..} (6)$$

In this equation, only hA is unknown for calculation. To get the hA, we introduce θ here:

$$\theta = \frac{\Delta T}{\Delta T_{max}} \quad \text{(7)}$$

Substituting equation (7) into equation (1):

$$\frac{d\theta}{dt} = \frac{hA}{\sum_i m_i C_{p,i}}\left[\frac{Q_{NPs} + Q_S}{hA\Delta T_{max}} - \theta\right] \quad \text{(8)}$$

When the light source was turned off, the $Q_{NPs} + Q_S = 0$, equation (8) could be expressed as following:

$$dt = -\frac{\sum_i m_i C_{p,i}}{hA}\frac{d\theta}{\theta} \quad \text{(9)}$$

Equation (8) could be expressed as follows after further integration:

$$t = -\frac{\sum_i m_i C_{p,i}}{hA}\ln\theta \quad \text{(10)}$$

Where $\frac{\sum_i m_i C_{p,i}}{hA}$ can be calculated by linear relationship of time versus -lnθ. Considering that the mass of NPs is too little compared with that of solvent and the specific heat of water is much higher than other materials, the m_{NPs} and $C_{p,NPs}$ were neglected. m_{H2O} was 3×10^{-3} Kg and $C_{p,H2O}$ was 4.2×10^{3} J/kg/ºC. So we can get hA equals 0.0233. Subsequently, we substituted every known value into equation (6) to get η. $\Delta T_{max,mix}$ was 51.5 ºC . $\Delta T_{max,H2O}$ is 30.3 ºC . The total energy input of the irradiation was 2.718 W where the irradiation area was 3 cm^2 and the intensity of the light as 906 mW/cm^2. The light intensity decrease to 532 mW/cm^2 after the absorption of solvent, indicating that the energy NPs absorbed (*I*) is 1.596 W. Thus, the photothermal conversion efficiency (η) of 5 wt% Pd/TiO_2 could be 30.9%.

References

(1) Roper, D.K.; Ahn, W.; Hoepfner, M. Microscale heat transfer transduced by surface plasmon resonant gold nanoparticles. *J. Phys. Chem. C* **2007**, *11*, 3636-3641.

(2) Liu, Y.; Ai, K.; Liu, J.; Deng, M.; He, Y.; Lu, L. Dopamine ‐ melanin colloidal nanospheres: an efficient near ‐ infrared photothermal therapeutic agent for in vivo cancer therapy. *Adv. Mater.* **2013**, *25*, 1353-1359.

(3) Zou, Q.; Abbas, M.; Zhao, L.; Li, S.; Shen, G.; Yan, X. Biological photothermal nanodots based on self-assembly of peptide–porphyrin conjugates for antitumor therapy. *J. Am. Chem. Soc.,* **2017**, *139*, 1921-1927.

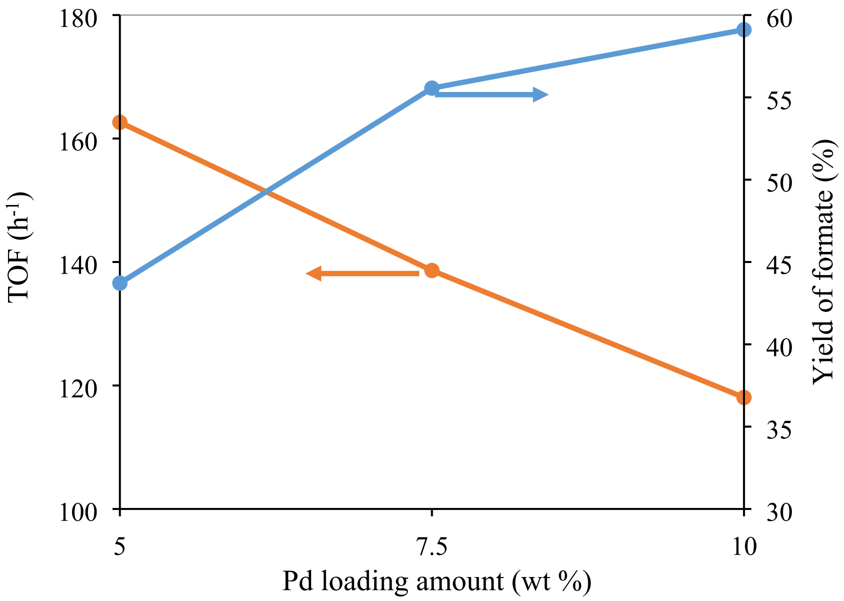

Figure S1. Effect of Pd loading in Pd/TiO_2 on the hydrogenation of $KHCO_3$ under irradiation (reaction conditions: 3 MPa H_2, 5 mL distilled H_2O, 10 mmol $KHCO_3$, 20 mg catalyst, 3 h).

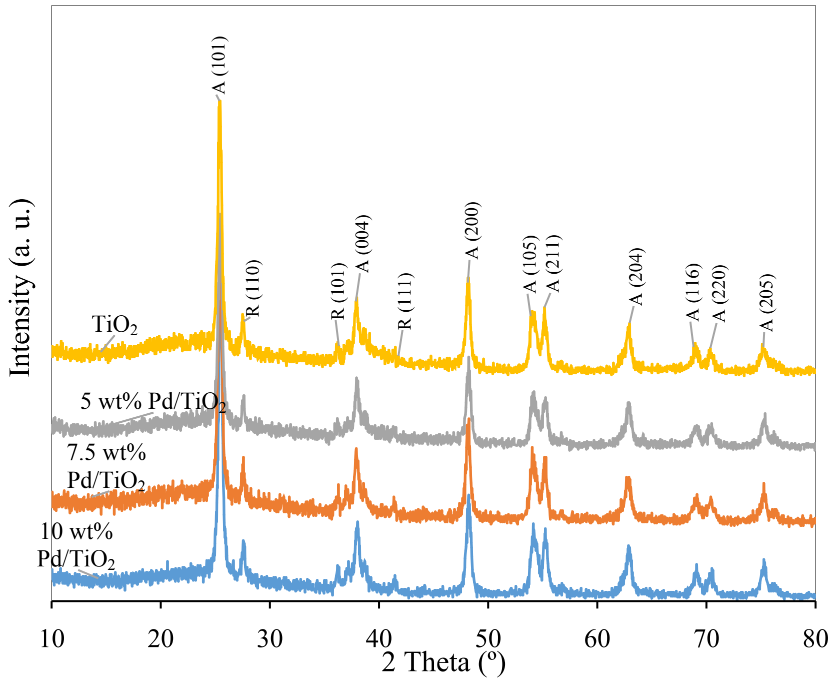

Figure S2. XRD patterns of TiO_2, 5 wt% Pd/TiO_2, 7.5 wt% Pd/TiO_2 and 10 wt% Pd/TiO_2 (A represents anatase, R represents rutile).

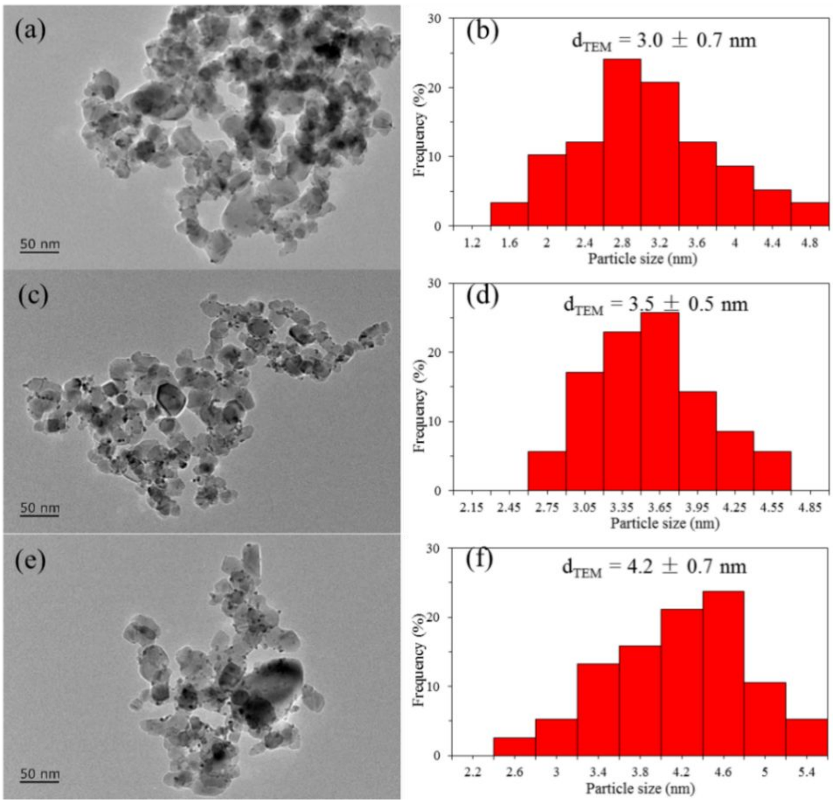

Figure S3. TEM images and Pd NPs size distribution of 5 wt% Pd/TiO_2 (a and b), 7.5 wt% Pd/TiO_2 (c and d), and 10 wt% Pd/TiO_2 (e and f).

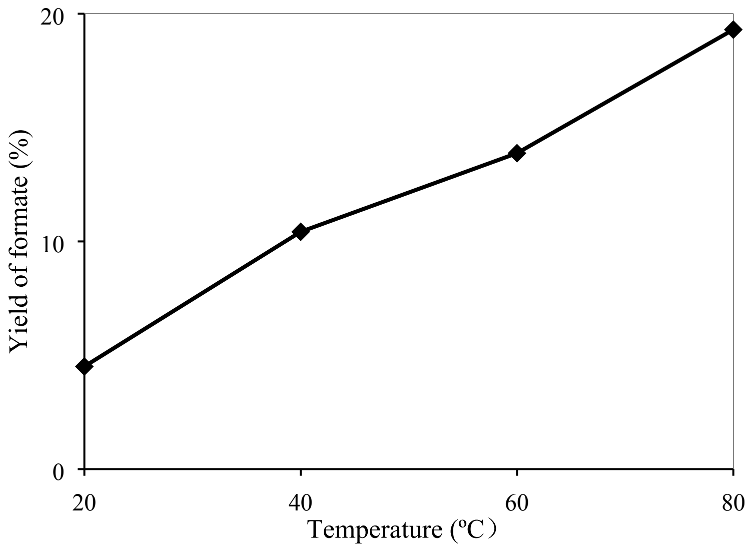

Figure S4. Effect of temperature on the hydrogenation of $KHCO_3$ without irradiation (reaction conditions: 3 MPa H_2, 5 mL distilled H_2O, 10 mmol $KHCO_3$, 20 mg 5 wt% Pd/TiO_2, 3 h).

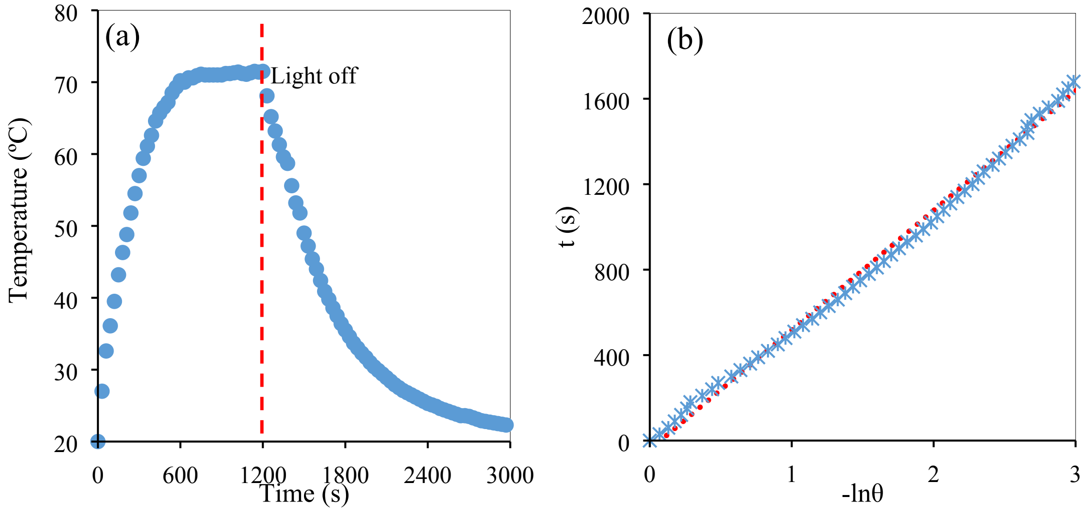

Figure S5. (a) The temperature curve of the 5 wt% Pd/TiO_2 aqueous solution (200 μg/mL) for 1200 s with irradiation and then the light was shut off; (b) Linear time data versus -lnθ obtained from the cooling period of 5 wt% Pd/TiO_2 aqueous solution.

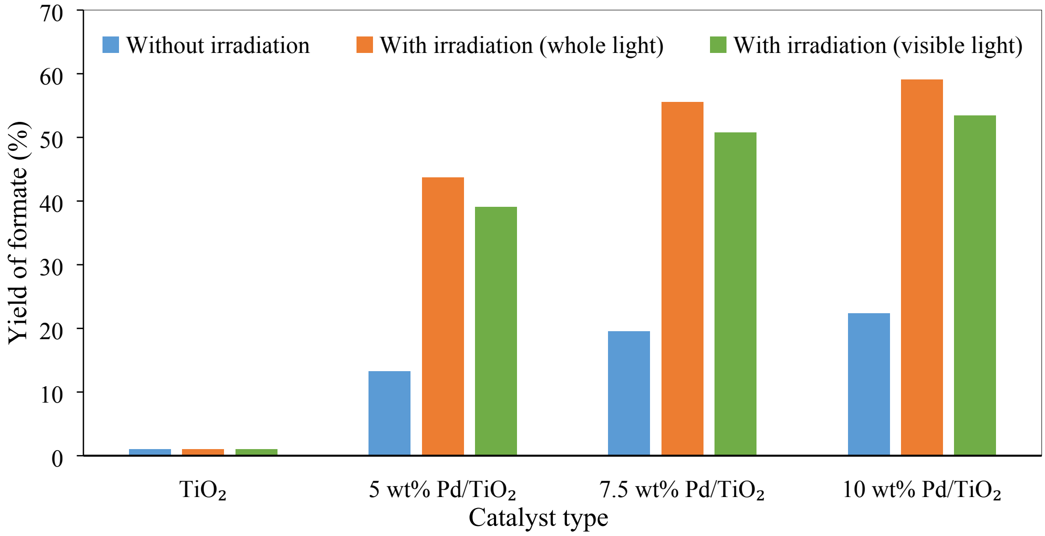

Figure S6. Formate yield obtained over different catalysts (reaction conditions: 3 MPa H_2, 2 mol/L $KHCO_3$, 20 mg catalyst, 3 h)

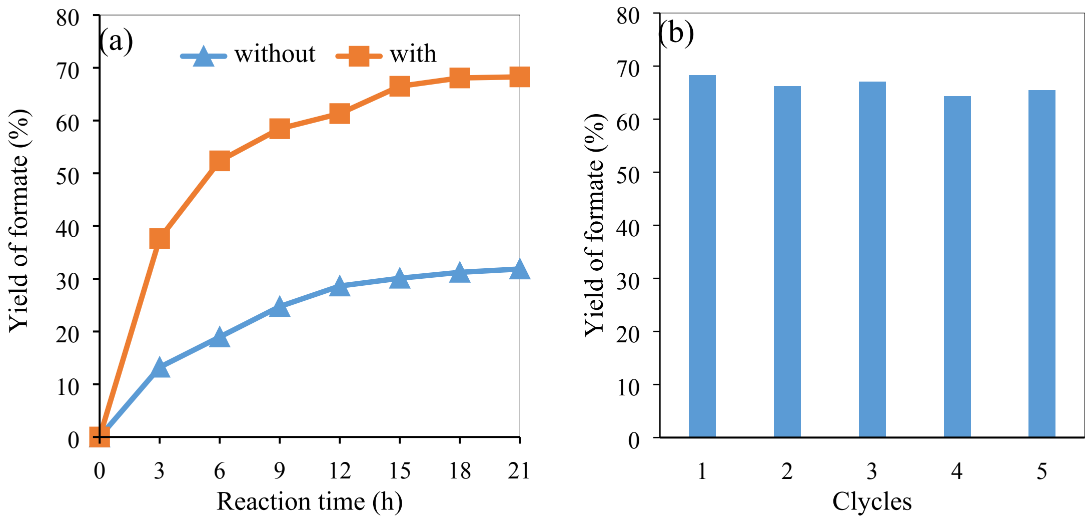

Figure S7. (a) Effect of reaction time on the hydrogenation of $KHCO_3$ with/without irradiation (reaction conditions: 3 MPa H_2, 5 mL distilled H_2O, 10 mmol $KHCO_3$, 20 mg 5 wt% Pd/TiO_2 catalyst). (b) Catalyst recycle in hydrogenation of $KHCO_3$ (reaction conditions: 3 MPa H_2, 5 mL distilled H_2O, 10 mmol $KHCO_3$, 20 mg 5 wt% Pd/TiO_2 catalyst, 21 h).

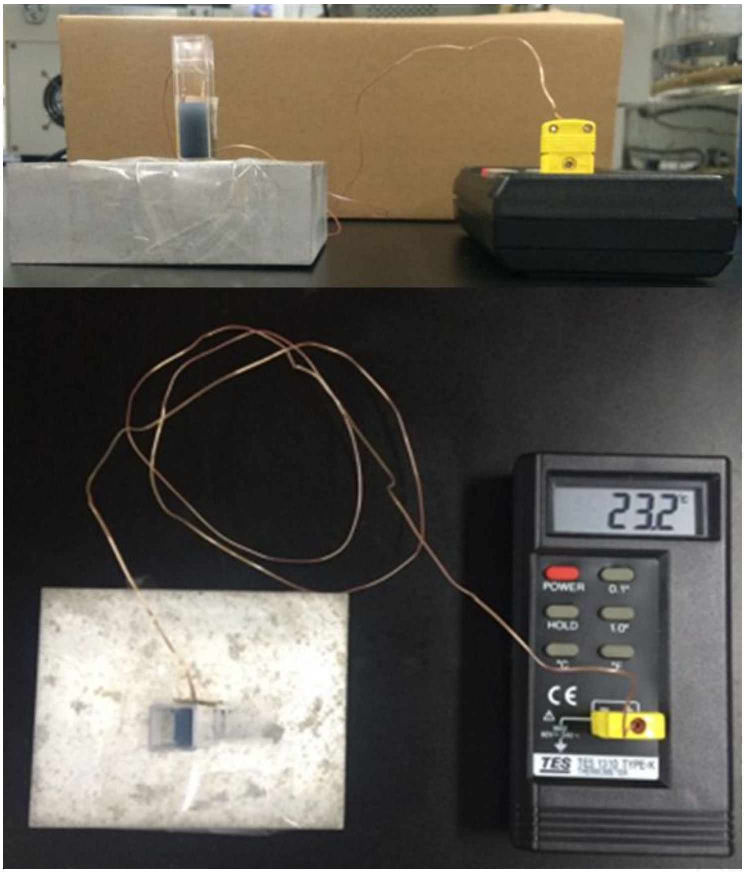

Figure S8. Camera photo of the testing device for photothermal conversion efficiency calculation