Supporting Information for:

Revealing the stochastic kinetics evolution of photocatalytic CO_2 reduction

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Supporting information Note

Synthesis of photocatalysts. Al-doped $SrTiO_3$ samples were prepared via a flux method previously reported.[1-3] $SrTiO_3$ (Sinopharm Chemical Reagent Co., Ltd., 99.9%), $SrCl_2$ (Aladdin Co., Inc., 99.5%), and Al_2O_3 (Aladdin Co., Inc., 99.99%, metals basis, 20nm) were mixed uniformly at a molar ratio of 1: 10: 0.02 in a quartz crucible. Then, the mixtures were calcined at 1423 K for 10 h in the air. The Ag-Al/STO photocatalyst was synthesized by a photo-deposition method. Al/STO (50 mg) was added into deionized water (50 mL) in a tubular quartz photoreactor with ultrasonication treatment for 10 min. Then 5 mL of AgNO3 solution (1 g/L) was dropwise added into the Al/STO suspension. The resulting solution was bubbled in dark with high-purity Ar for 1 hour to purge other impurity gases. Afterwards, the mixture was irradiated under a 300 W Xe lamp for 1 hour with stirring. After centrifugation, the precipitation was washed with deionized water 5 times and dried at 80°C for 12 hours to obtain Ag-Al/STO.

Photocatalytic activity evaluation. The photocatalyst (30 mg) was added to 30 mL of deionized water. After ultrasonication treatment for 10 minutes, the reactor was bubbled with high-purity Ar for 1 hour, followed by high-purity CO_2 for 1 hour. A 300 W Xe lamp (PLS-FX300HU, Beijing Perfect Light Technology Co., Ltd.) was used as the light source. Before the activity test, the averaged irradiation intensity was measured by a calibrated fiber optic spectrometer (AvaSpec-ULS2048XL-EVO, Beijing, Avantis Technology Co., Ltd.). The temperature of the system is stabilized by using circulating water first in dark, and then the photocatalytic experiment was carried out for 6 hours. Every combination of reaction conditions is conducted 3 times for reducing experimental errors. A GC9720plus gas chromatography (GC, Zhejiang Fuli Analytical Instrument Co., Ltd China) was used to analyze the gaseous products. Generally, the GC instrument can detect most gas products, including CO, CH_4, C_2H_4, C_2H_2, and H_2. Here the reduction products in the photoactivity testing were CO and H_2.

Photoluminescence spectroscopy measurements. The steady-state PL emission spectra were conducted using the PL spectrometer (FLS 1000, Edinburgh Instruments). The wavelength of excitation was 375 nm. The emission range was collected from 400 nm to 600 nm. The transient PL decay spectra were

collected using a microchannel plate photomultiplier detector with a specified detector response width of ≤ 25 ps at the same PL spectrometer. The PL decay excitation was a 375 nm diode laser of ≤ 90 ps pulse duration (Edinburgh Instruments). The emission decay lifetime was measured at 465 nm. The excitation intensities were adjusted using the built-in attenuation wheel of the PL spectrometer. The temperature of the testing condition was controlled by using the liquid nitrogen low-temperature attachment (OptistatDN-V, range from 77 K to 500 K, Oxford Instruments NanoScience).

Supporting information Figures

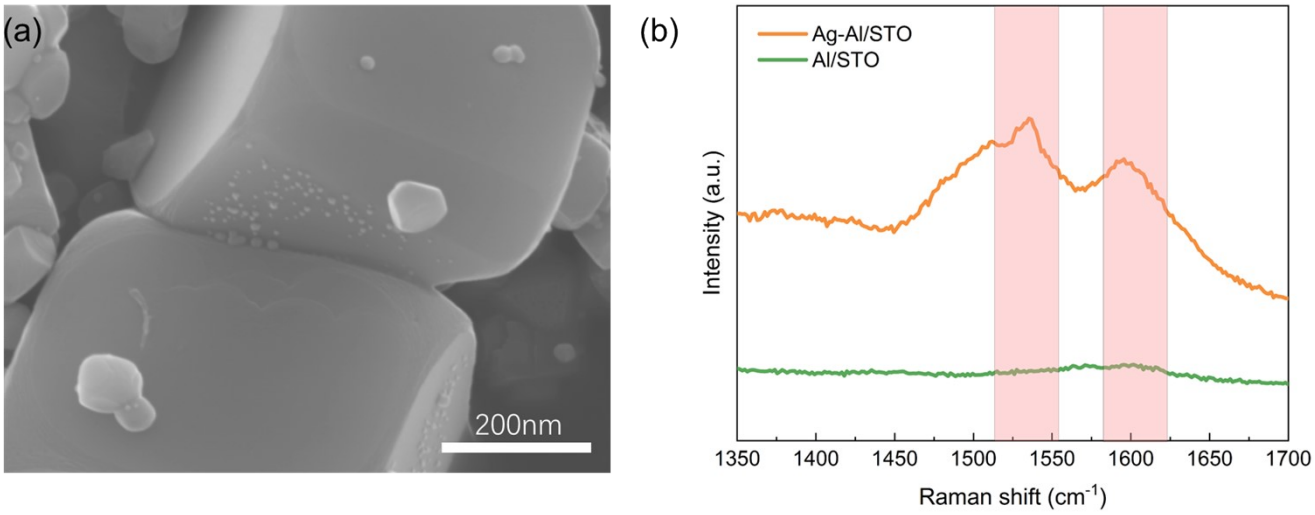

Fig. S1 (a) SEM image and (b) Raman spectra of photocatalysts. The Raman peaks of Ag can be found at about 1525 cm^{-1} and 1600 cm^{-1}.

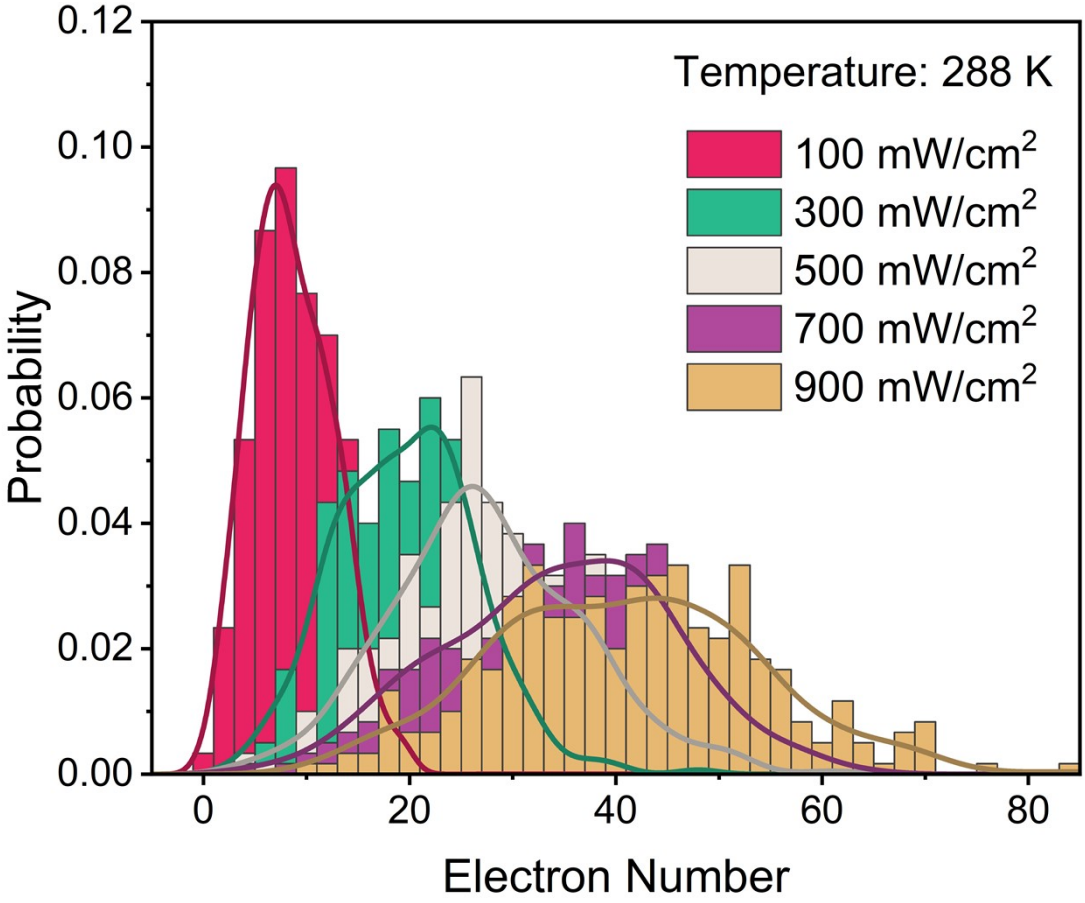

Fig. S2 Probability distributions of surface electron density for various light intensities at a constant temperature of 288 K, the number of surface active sites is 300.

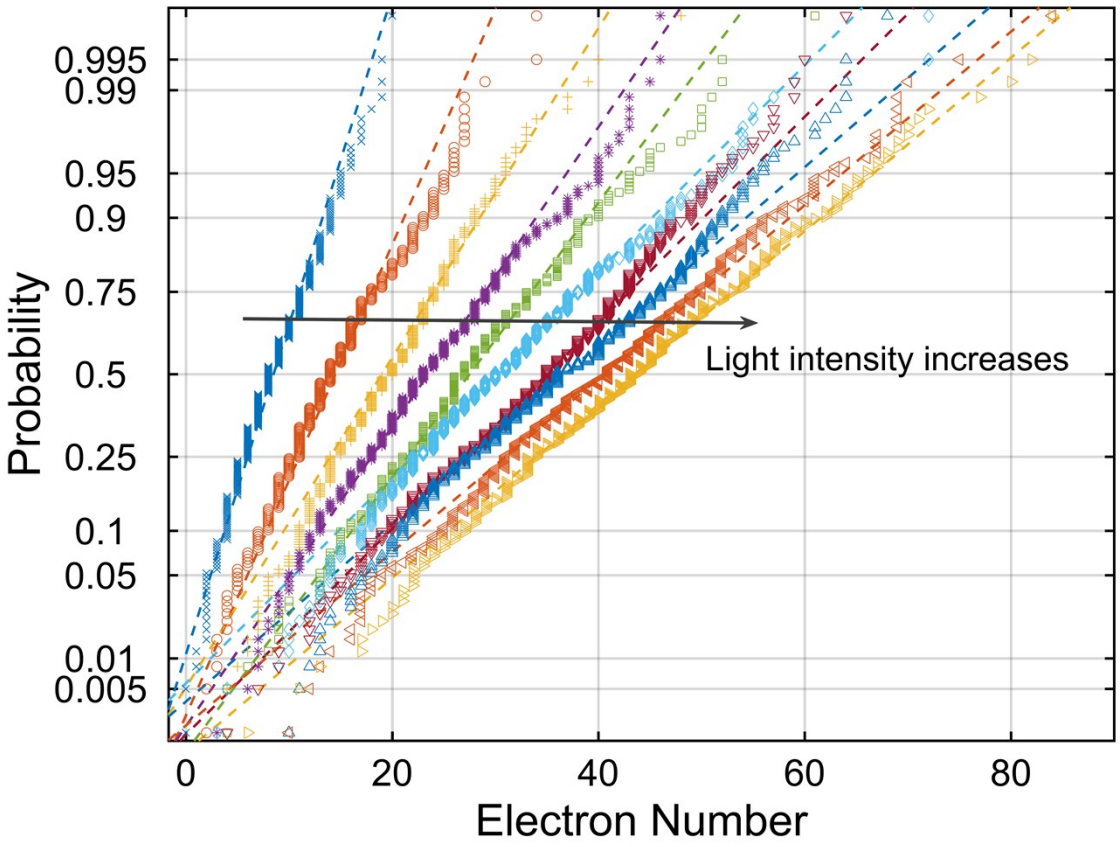

Fig. S3 Probability plot of surface electron density for various light intensities at a constant temperature of 288 K.

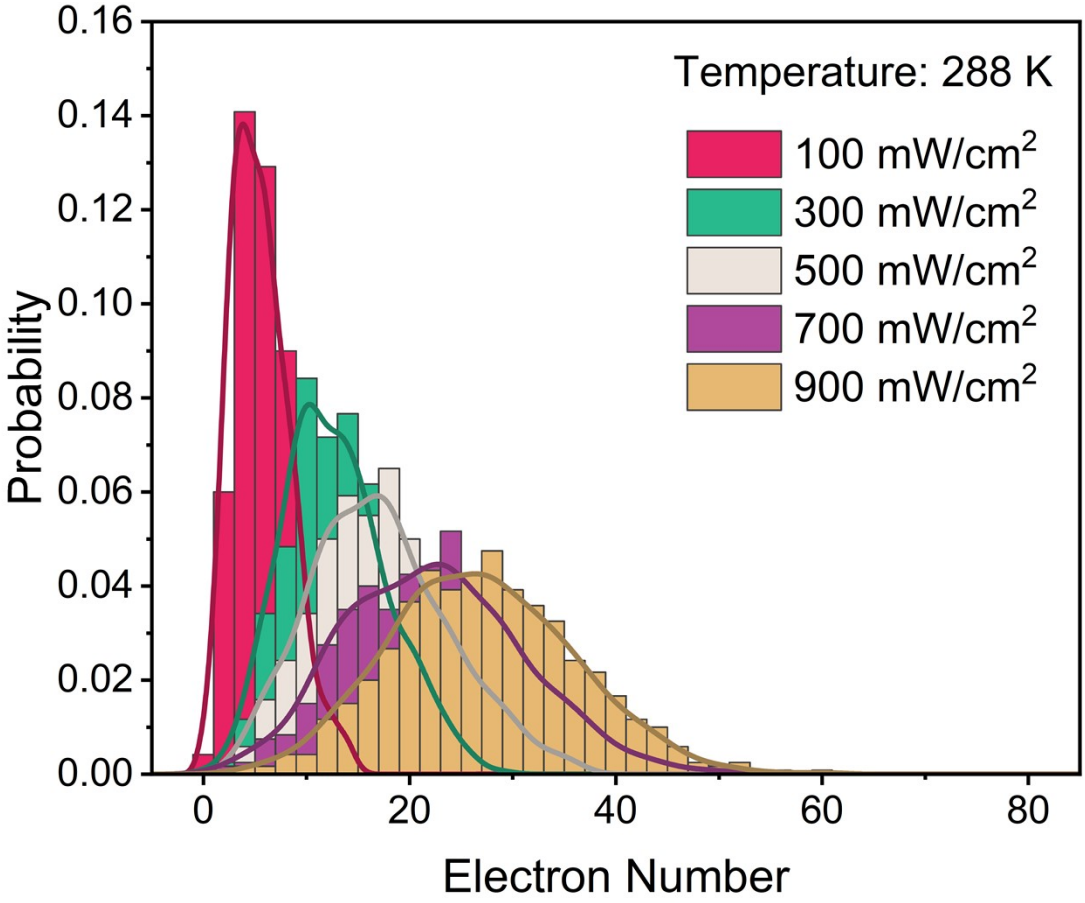

Fig. S4 Probability distributions of surface electron density for various light intensities at a constant temperature of 288 K, the number of surface active sites is 600.

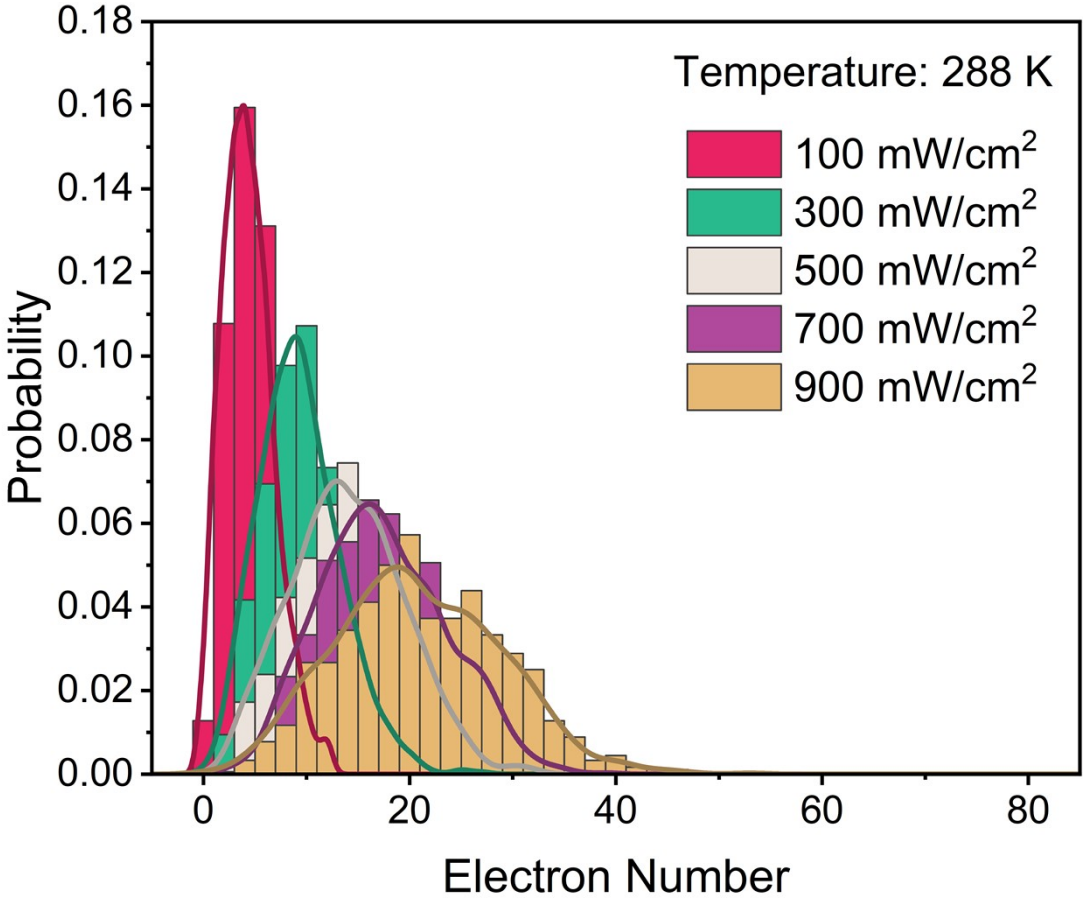

Fig. S5 Probability distributions of surface electron density for various light intensities at a constant temperature of 288 K, the number of surface active sites is 900.

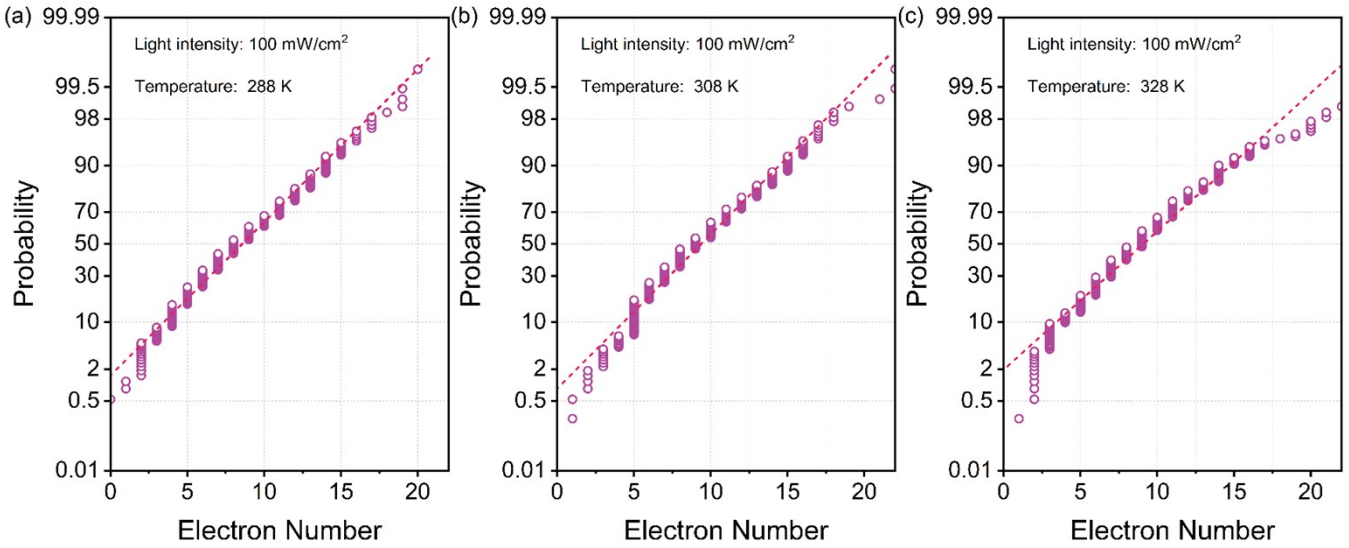

Fig. S6 Probability plot of surface electron density at different temperatures (a) 288 K, (b) 308 K, and (c) 328K.

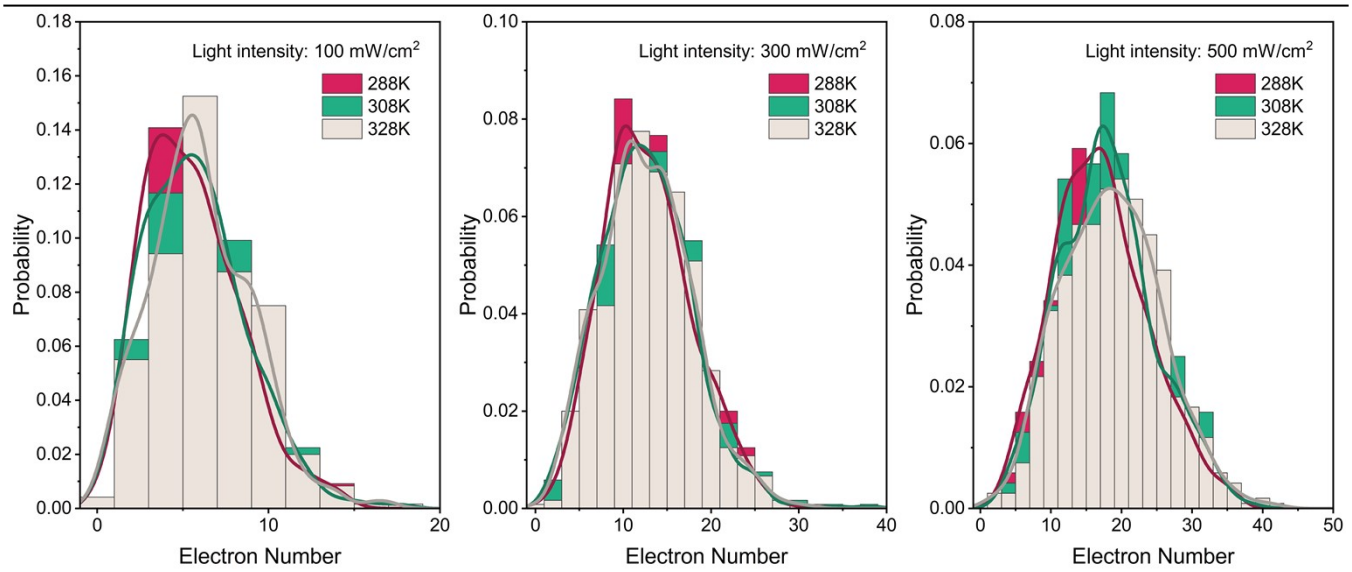

Fig. S7 Probability distributions of surface electron density for various temperatures at three light intensities (a) 100, (b) 300, and (c) 500 mW/cm^2, and the number of active sites is set as 600.

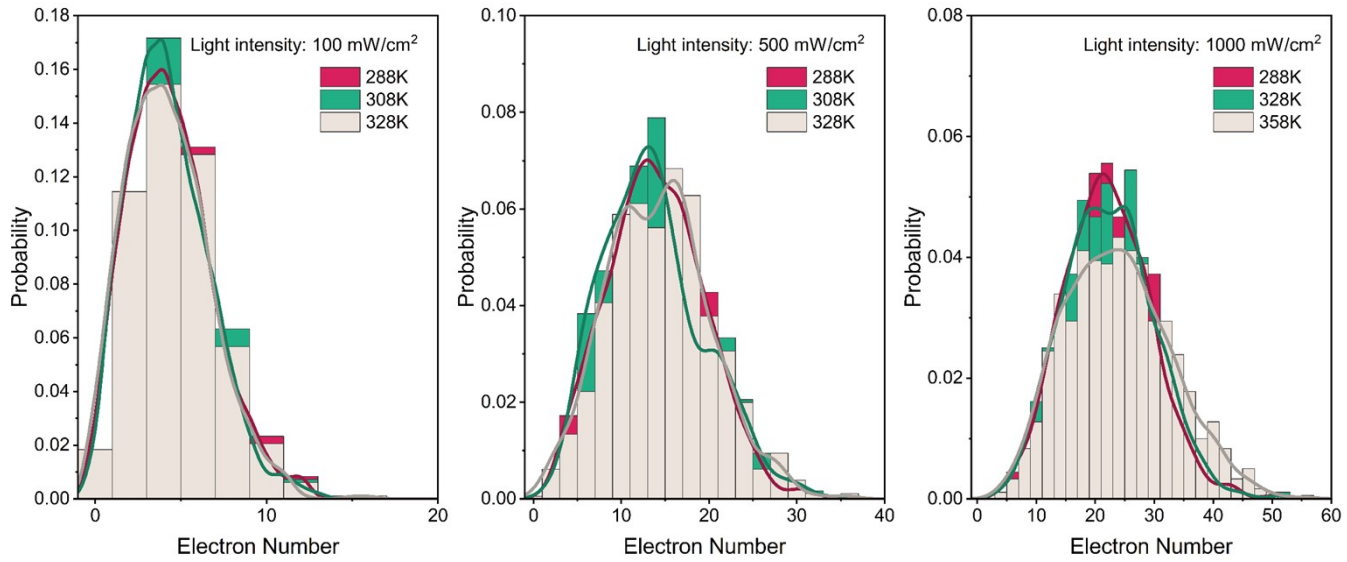

Fig. S8 Probability distributions of surface electron density for various temperatures at three light intensities (a) 100, (b) 300, and (c) 500 mW/cm^2, and the number of active sites is set as 900.

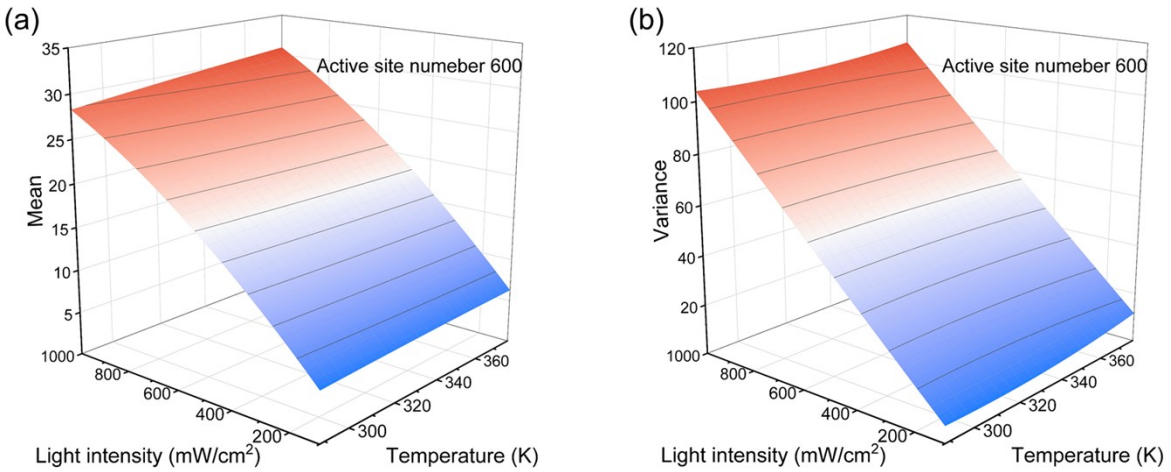

Fig. S9 RSM plots depicting effects of interaction between light intensity and temperature on (a) mean and (b) variance of electron distribution, and the number of active sites is set as 600.

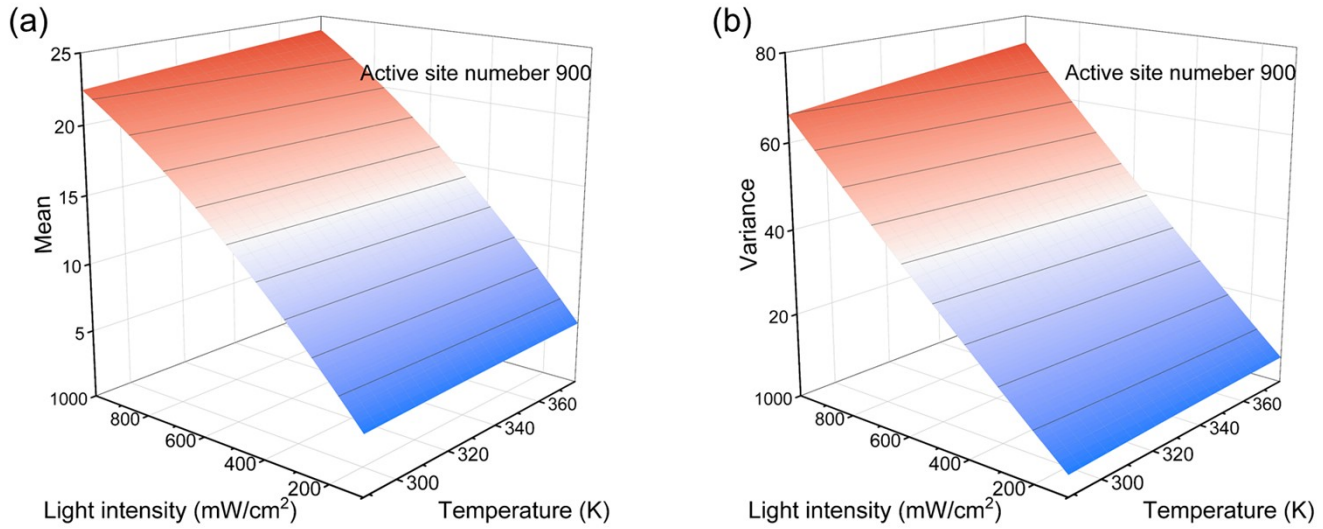

Fig. S10 RSM plots depicting effects of interaction between light intensity and temperature on (a) mean and (b) variance of electron distribution, and the number of active sites is set as 900.

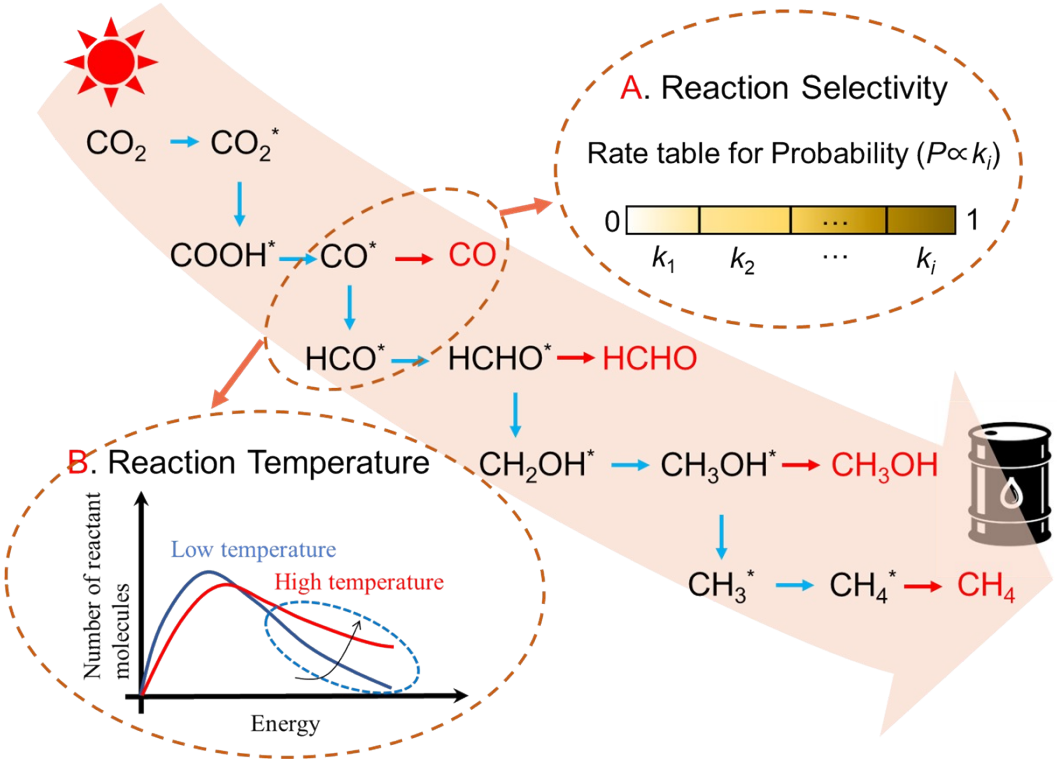

Fig. S11 the possible reaction pathways of photocatalytic CO_2 reduction.[4]

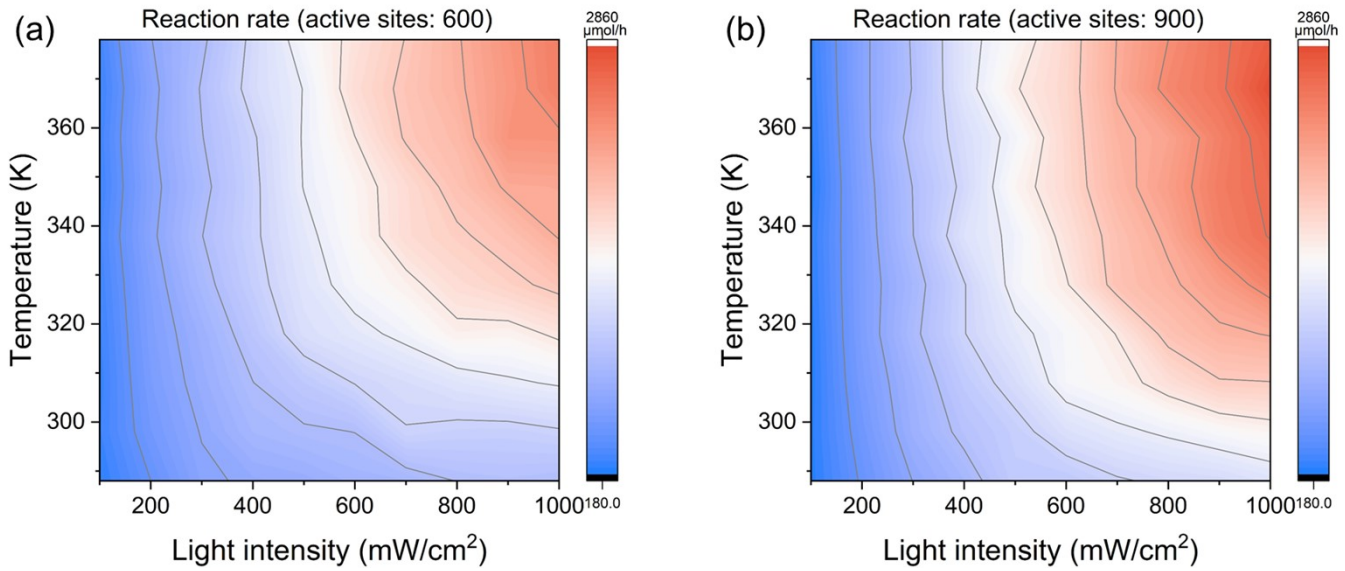

Fig. S12 Contour plots displaying the relationship between two operating variables and reaction rates, and the number of active sites is set as (a) 600 and (b) 900, respectively.

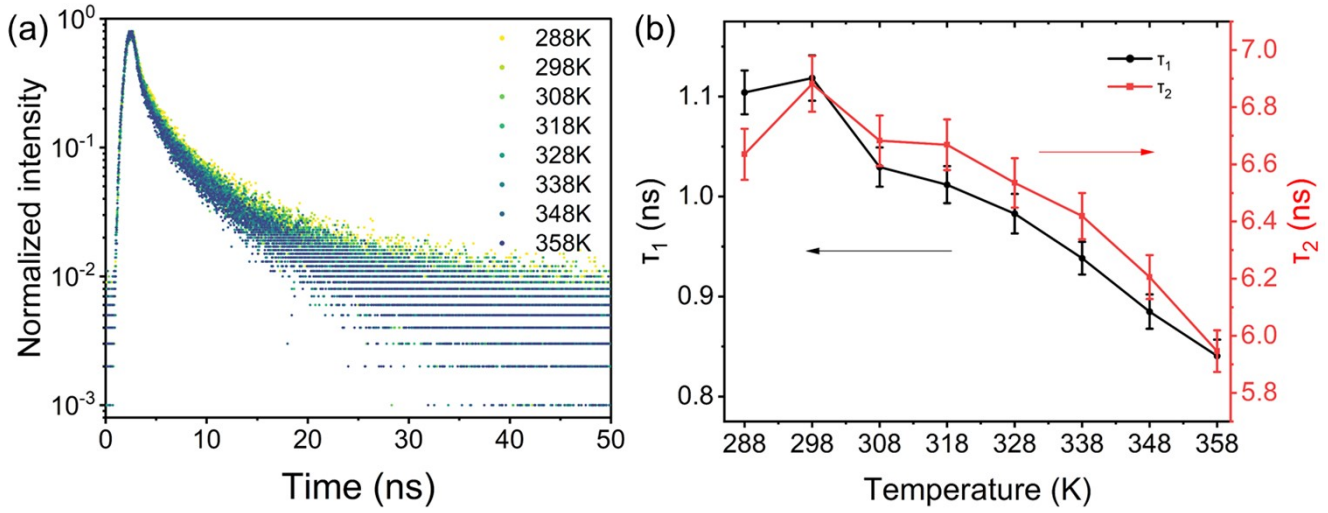

Fig. S13 (a) The plot of transient PL decay dynamics and (b) comparison of the fitting lifetime under different temperature conditions.

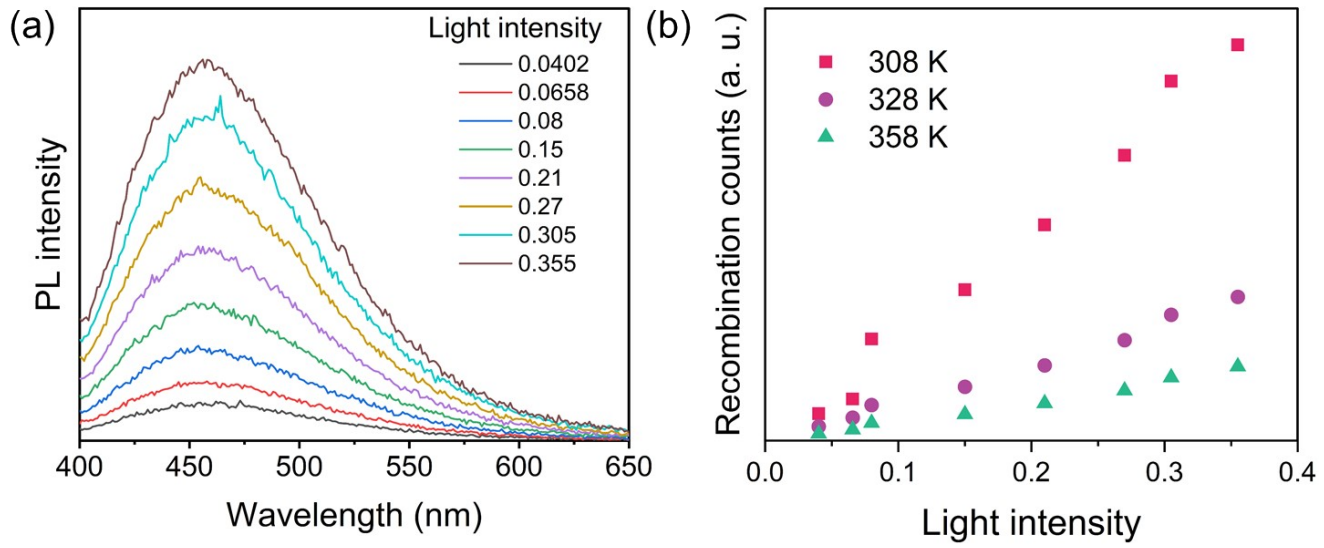

Fig. S14 (a) Excitation-dependent steady-state PL spectra at 288 K, and (b) integrated PL intensities under various temperature conditions from 288 K to 358 K. The unit of light intensity is mW/cm^2.

Supporting information Table

I \ *T*	288	298	308	318	328	338	348	358	368
100	0.015	0.058	0.046	0.042	0.010	0.024	0.017	0.023	0.145
200	0.033	0.028	0.007	0.027	0.037	0.043	0.058	0.038	0.011
300	0.010	0.021	0.024	0.054	0.038	0.013	0.007	0.046	0.015
400	0.002	0.011	0.048	0.044	0.051	0.013	0.068	0.026	0.007
500	0.026	0.038	0.014	0.028	0.026	0.025	0.015	0.012	0.009
600	0.009	0.077	0.000	0.012	0.026	0.034	0.017	0.009	0.041
700	0.011	0.034	0.007	0.042	0.022	0.013	0.001	0.027	0.011
800	0.007	0.006	0.031	0.028	0.005	0.005	0.038	0.021	0.002
900	0.009	0.002	0.029	0.008	0.011	0.035	0.016	0.023	0.030
1000	0.032	0.005	0.003	0.009	0.024	0.036	0.042	0.003	0.004

Table S1 The relative error of surface reaction rates. *I* and *T* represent the light intensity (mW/cm^2) and temperature (K), respectively.

The relative error is calculated by

$$\varepsilon_{\mathrm{r}} = \frac{\frac{1}{n}\sum_{s=1}^{n}\left|x_{\mathrm{s}} - x_{\mathrm{k}}\right|}{x_{\mathrm{k}}} \times 100\%$$

where ε_{r}, x_{s}, and x_{k} are the relative error, the statistical result, and the results of reaction rate equation, respectively.

Supplementary References

1. T. H. Chiang, H. Lyu, T. Hisatomi, Y. Goto, T. Takata, M. Katayama, T. Minegishi and K. Domen, *ACS Catal.*, 2018, **8**, 2782-2788.
2. S. Zong, L. Tian, X. Guan, C. Cheng, J. Shi and L. Guo, *J. Colloid Interface Sci.*, 2022, **606**, 491-499.
3. H. Lyu, T. Hisatomi, Y. Goto, M. Yoshida, T. Higashi, M. Katayama, T. Takata, T. Minegishi, H. Nishiyama, T. Yamada, Y. Sakata, K. Asakura and K. Domen, *Chem. Sci.*, 2019, **10**, 3196-3201.
4. J. Fu, K. Jiang, X. Qiu, J. Yu and M. Liu, *Mater. Today*, 2020, **32**, 222-243.