Electronic Supplementary Information (ESI†)

Quantum Tunneling Injection of Hot Electrons in Au/TiO_2 Plasmonic Photocatalysts

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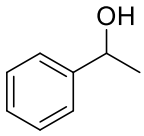
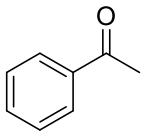
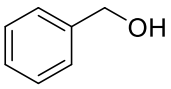
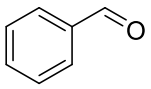
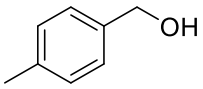
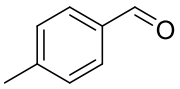
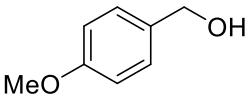
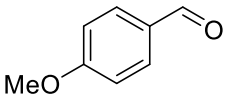
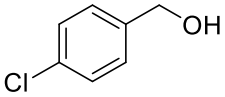
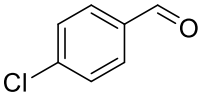
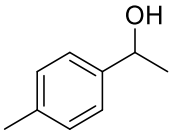
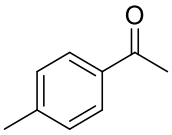
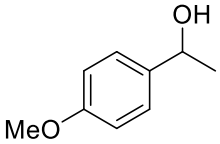
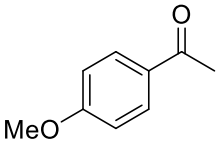
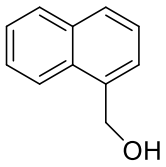
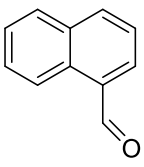
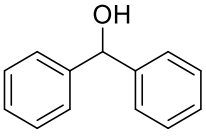
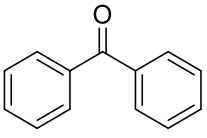
Table S1. Aerobic oxidation of various types of alcohols on Au_2/P25_anatase under visible light irradiation.[a]

run	Substrate	Time / h	Conv. / % [b]	Product	Yield / % [c]
1		8	>99		>99
2		6	>99		95
3		6	>99		99
4		6	>99		92
5		6	98		96
6		12	>99		97
7		12	96		95
8		12	>99		94
9		24	94		91

[a] Reaction conditions: toluene (5 mL), alcohol (5 mM), Au_2/P25_anatase catalyst (20 mg), O_2 (1 atm), Xe lamp (λ >450 nm), light intensity at 450–800 nm (16.8 mW cm^{-2}), temperature (298 ± 0.5 K). [b] = (Alcohol converted) / (initial amount of alcohol) × 100. [c] = (Product formed) / (initial amount of alcohol) × 100.

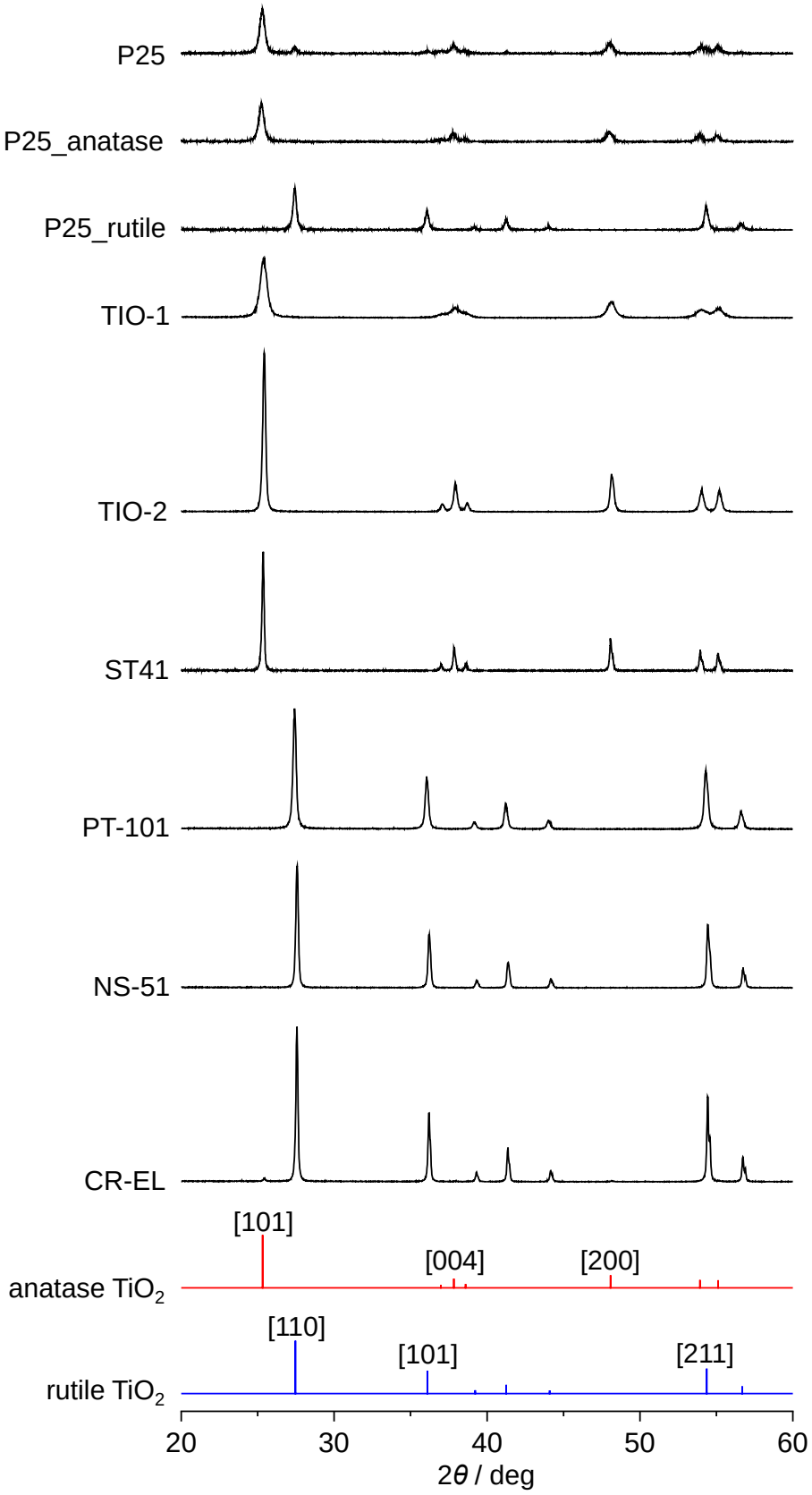


Fig. S1 XRD patterns of TiO_2 supports and standard patterns of anatase (JCPDS 21-1272) and rutile TiO_2 (JCPDS 21-1276).

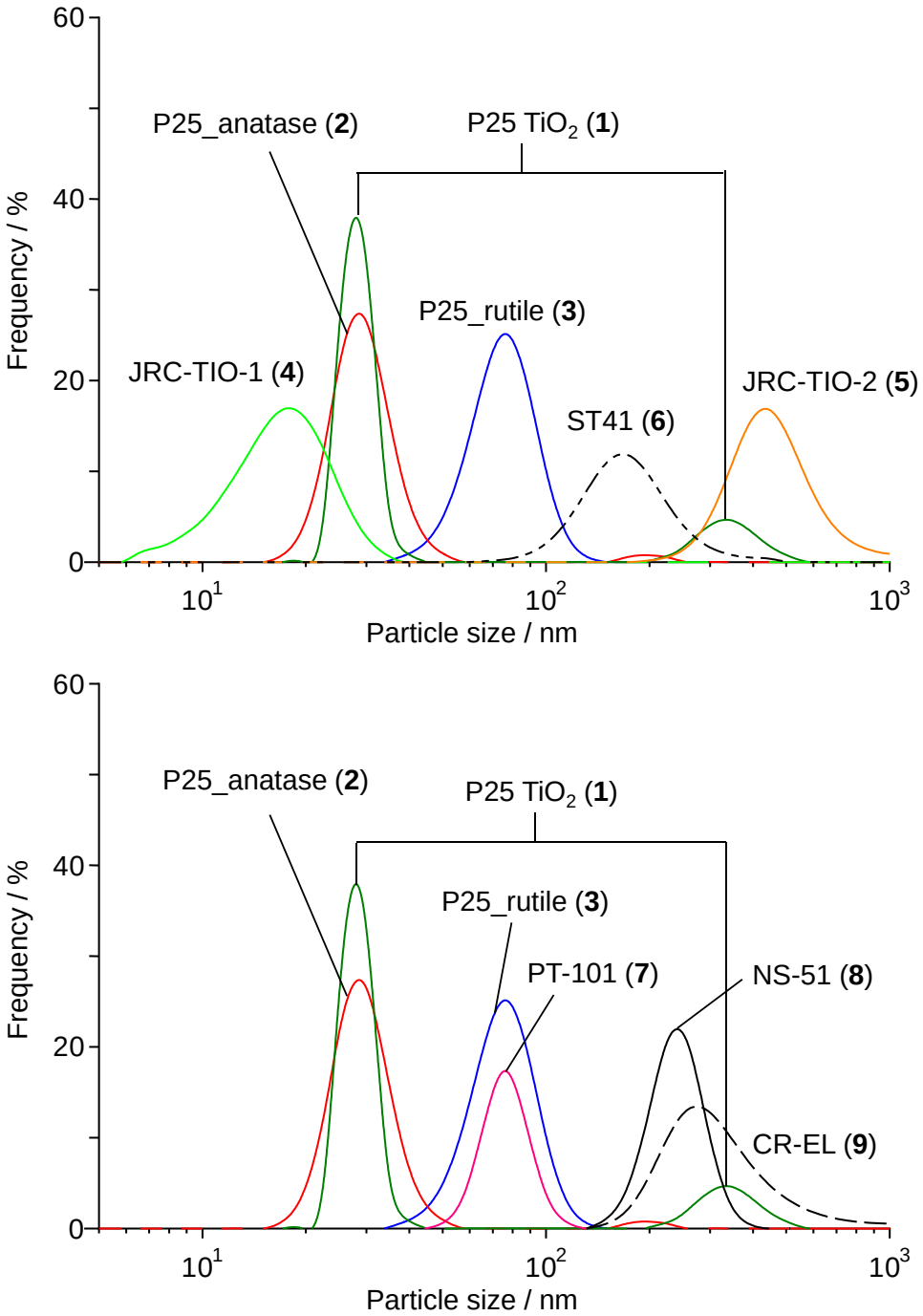
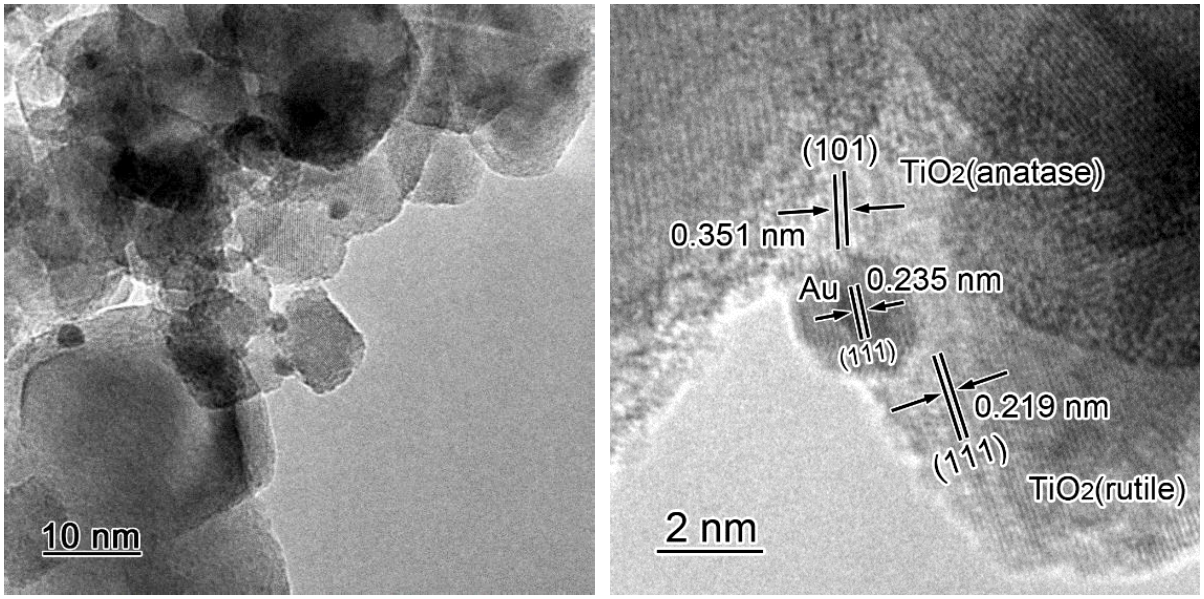


Fig. S2 Size distribution of TiO_2 supports determined by DLS analysis.

Au_2/P25 (1)



Au_2/P25_rutile (3)

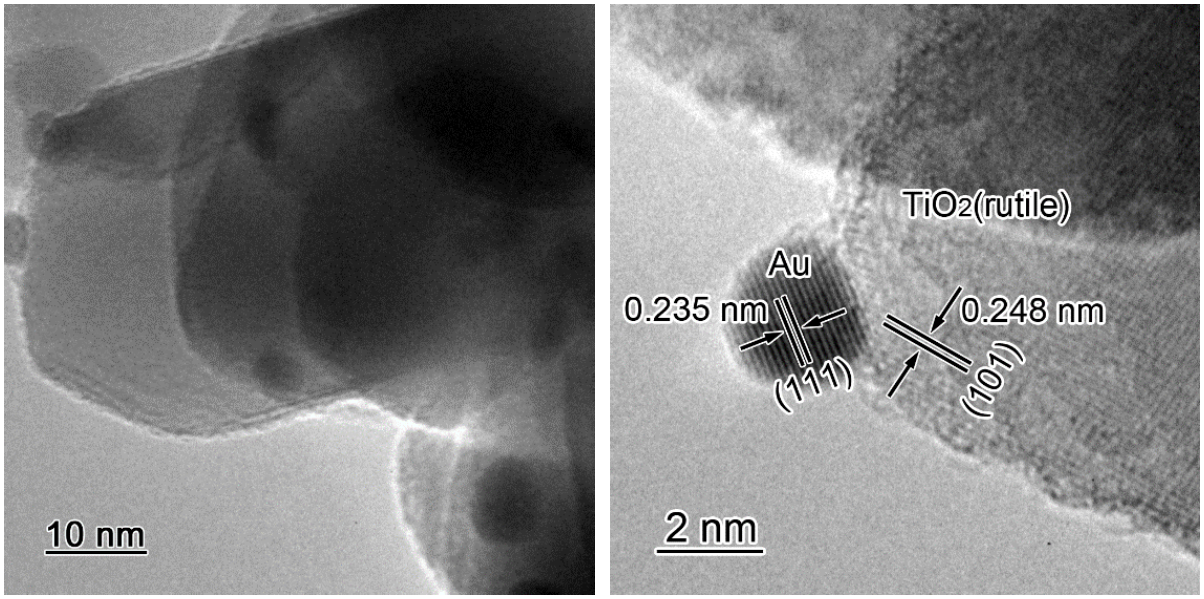
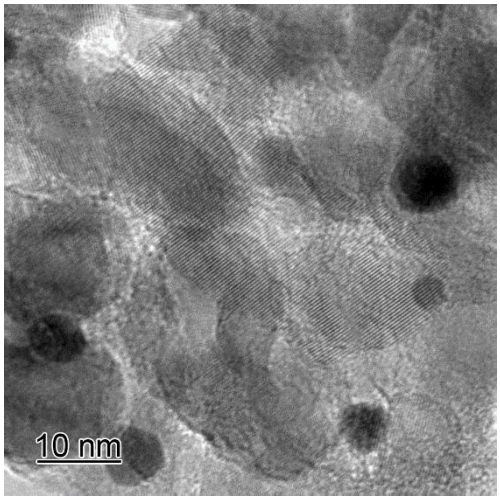
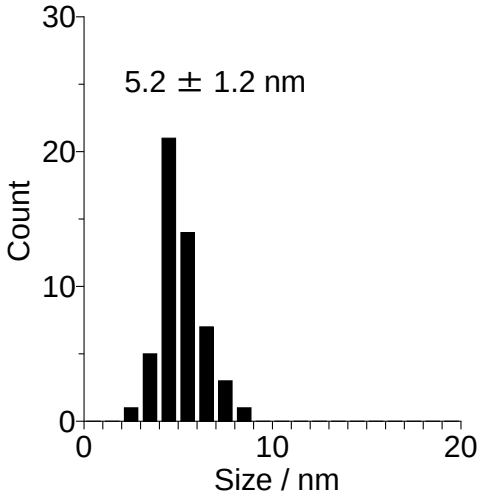


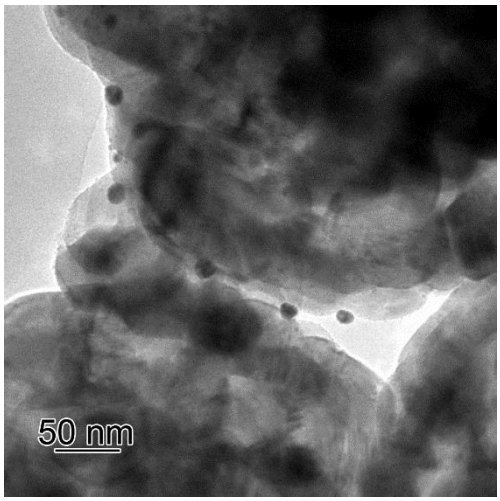
Fig. S3 Typical TEM images of Au_2/P25 and Au_2/P25_rutile catalysts.

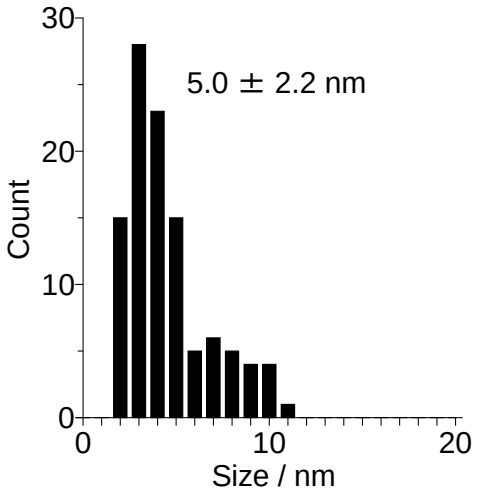
Au_2/TIO-1 (4)



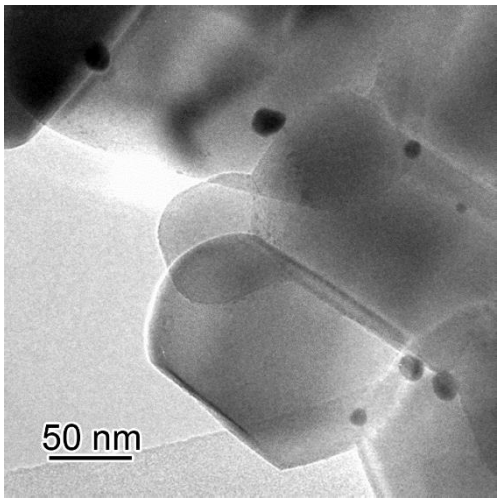


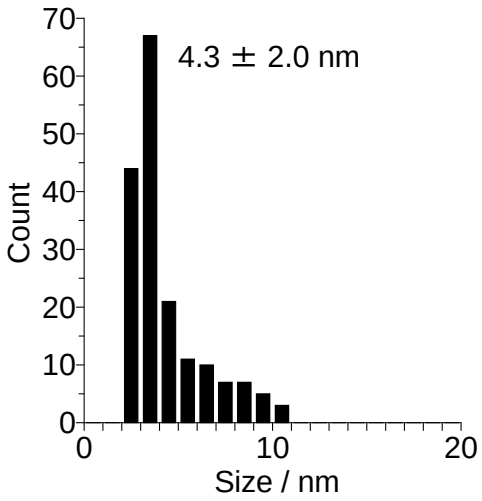
Au_2/TIO-2 (5)



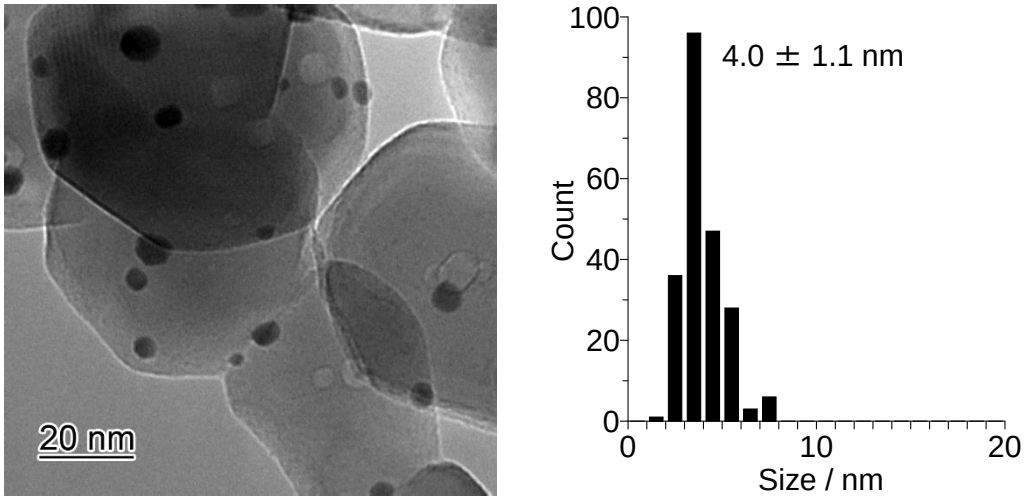


Au_2/ST41 (6)

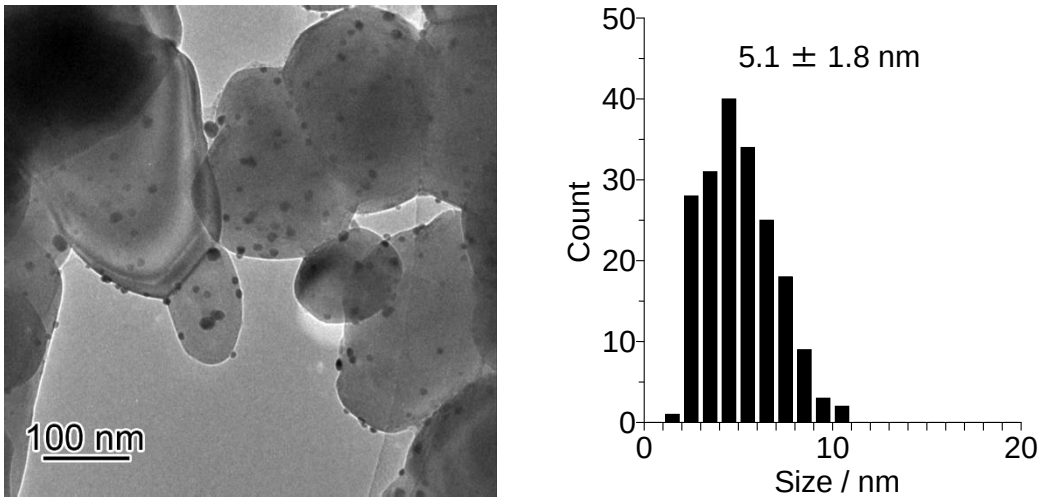




Au_2/PT-101 (7)



Au_2/NS-51 (8)



Au_2/CR-EL (9)

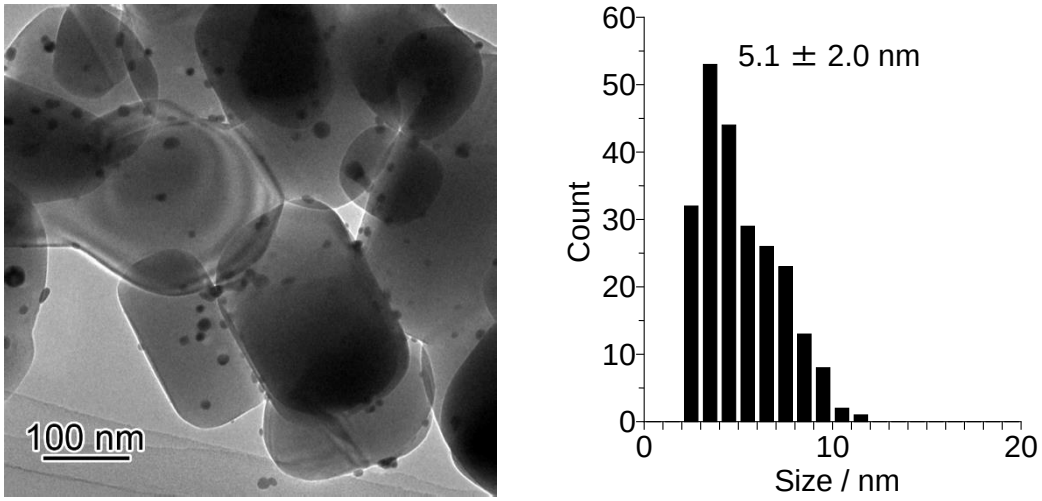


Fig. S4 Typical TEM images and size distributions of Au/TiO_2 catalysts.

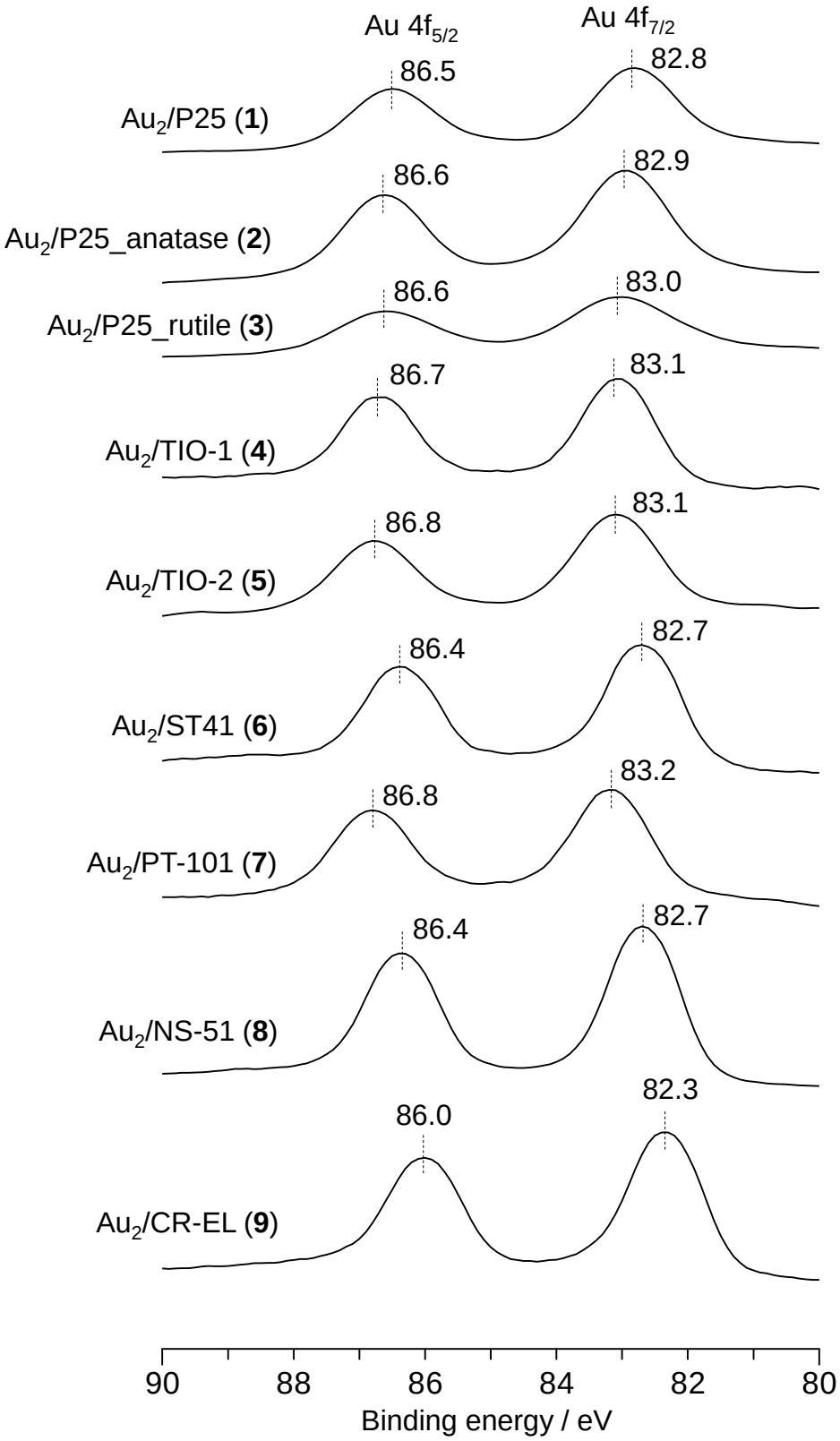


Fig. S5 XPS chart (Au 4f level) of the respective Au_2/TiO_2 catalysts.

The number of surface oxygen vacancies on the respective TiO_2 particles.[a]

sample	TiO_2	Surface oxygen vacancy / μmol g^{-1}
2	P25_anatase	49
3	P25_rutile	40.2
4	TIO-1	1.6
6	ST-41	2.9
7	PT101	81.6
8	NS-51	15.9
9	CR-EL	11.1

[a] The number of surface oxygen vacancies on TiO_2 was determined by DRIFT analysis with nitrobenzene as a probe molecule (Shiraishi, Y.; Hirakawa, H.; Togawa, Y.; Sugano, Y.; Ichikawa, S.; Hirai, T. *ACS Catal.* **2013**, *3*, 2318–2326).

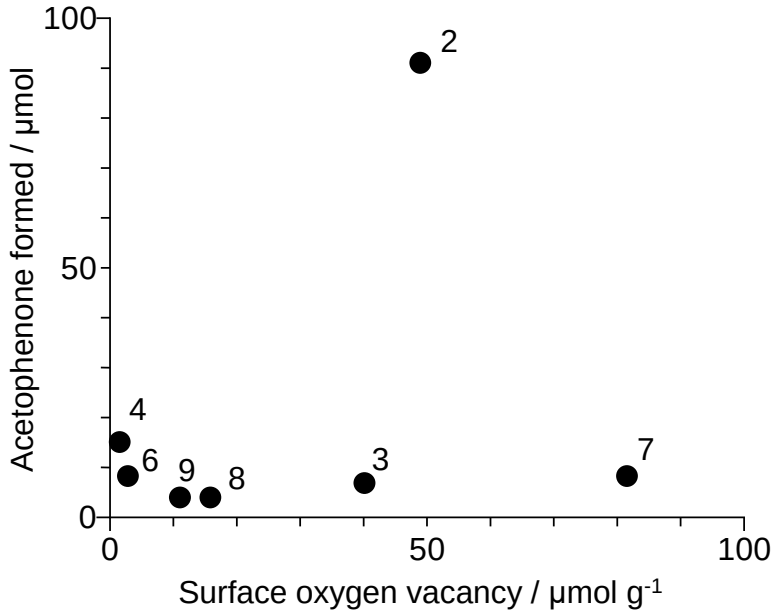
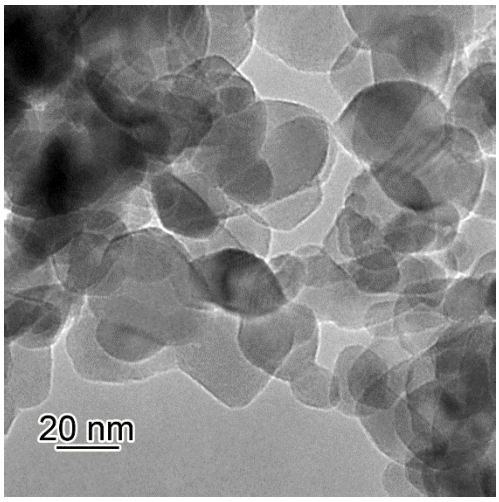
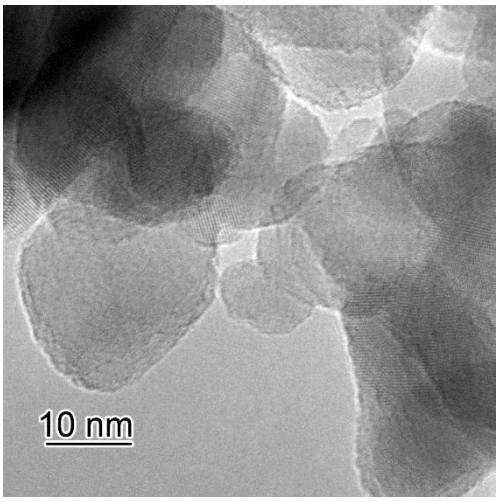


Fig. S6 Relationship between the number of surface oxygen vacancies on the respective TiO_2 supports and (a) the amount of acetophenone formed on the respective Au/TiO_2 catalysts by aerobic oxidation of 1-phenylethanol under visible light (λ >450 nm, 12 h). The photoreaction conditions are identical to those in Fig. 3 (manuscript).

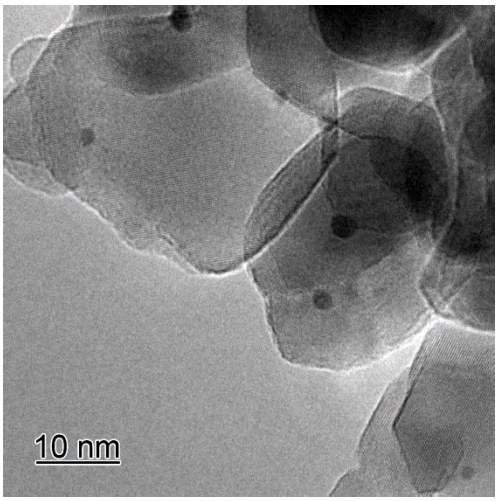
$Au_{0.5}$/P25_anatase

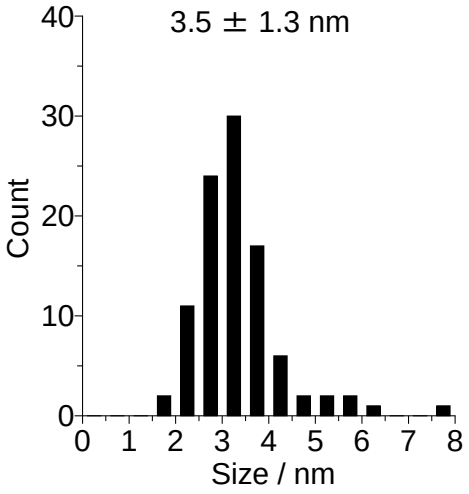


Au_{1}/P25_anatase

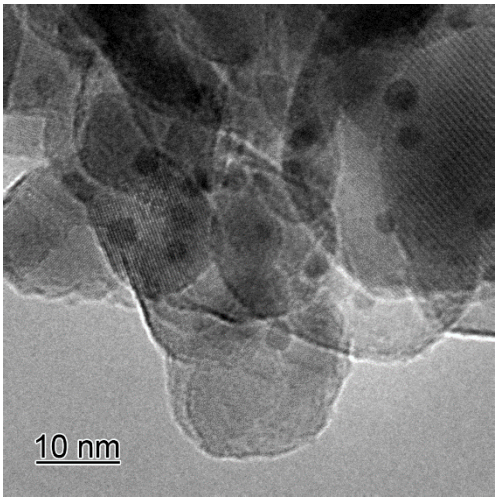


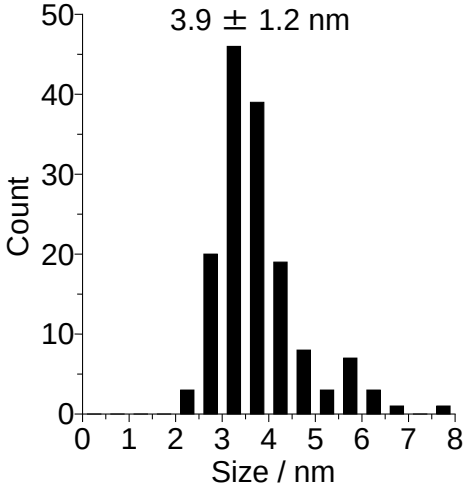
$Au_{1.5}$/P25_anatase



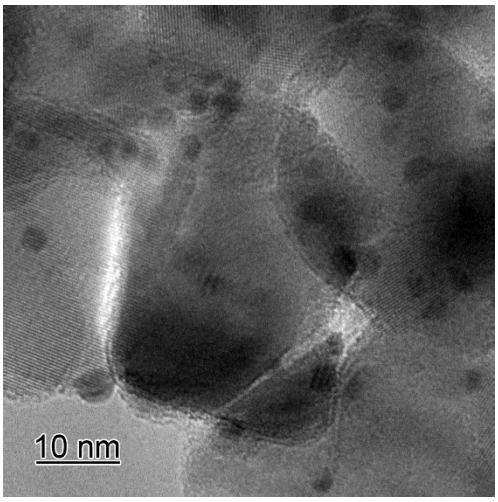


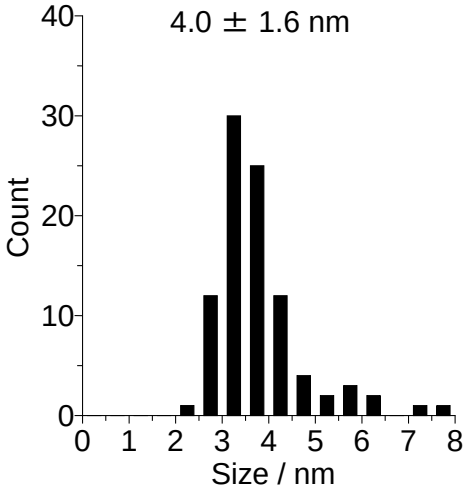
Au_{3}/P25_anatase



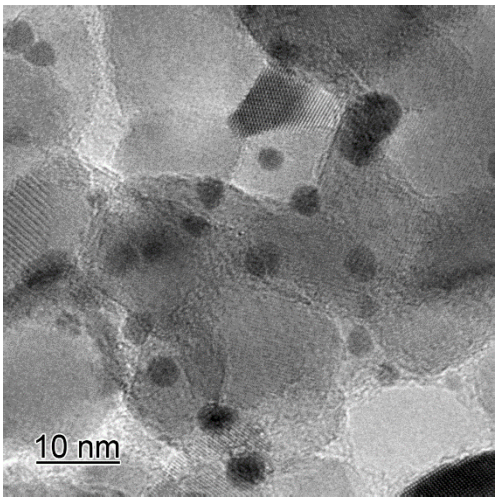


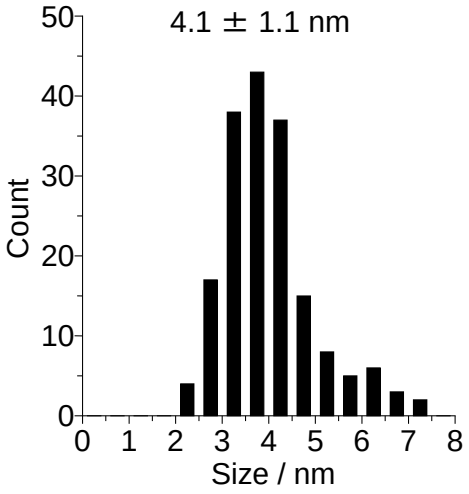
Au_4/P25_anatase



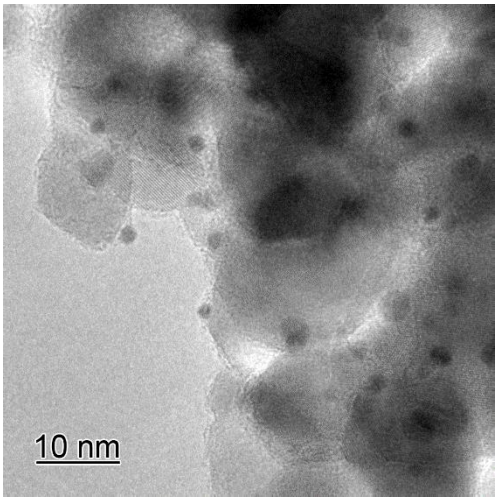


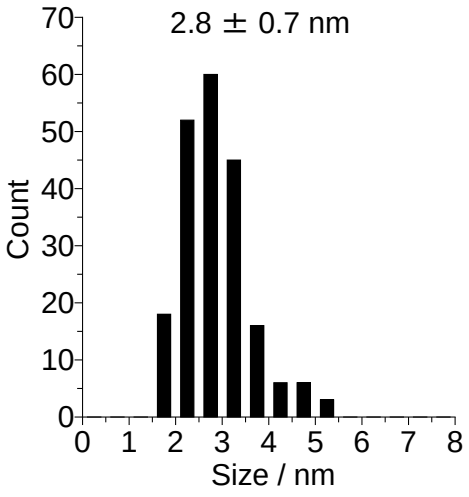
Au_5/P25_anatase



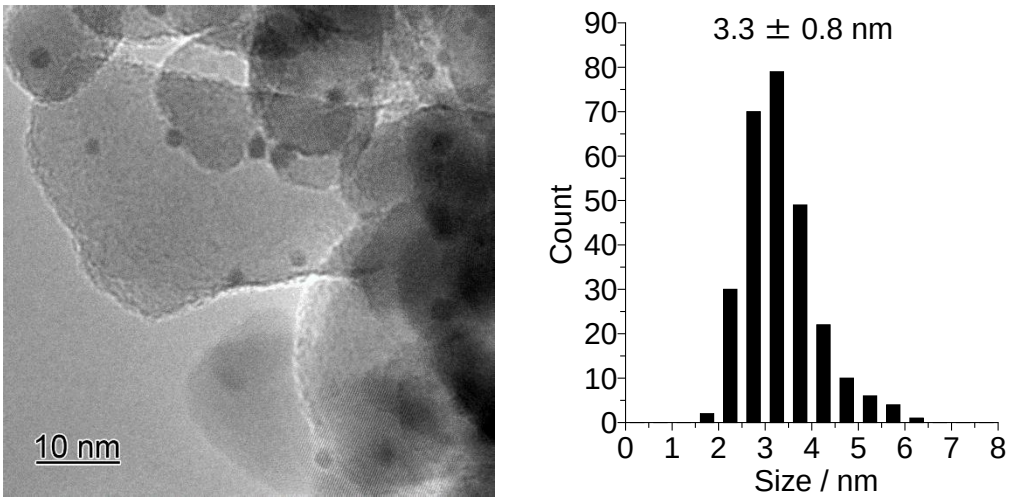


Au_2/P25_anatase prepared by calcination at 473 K

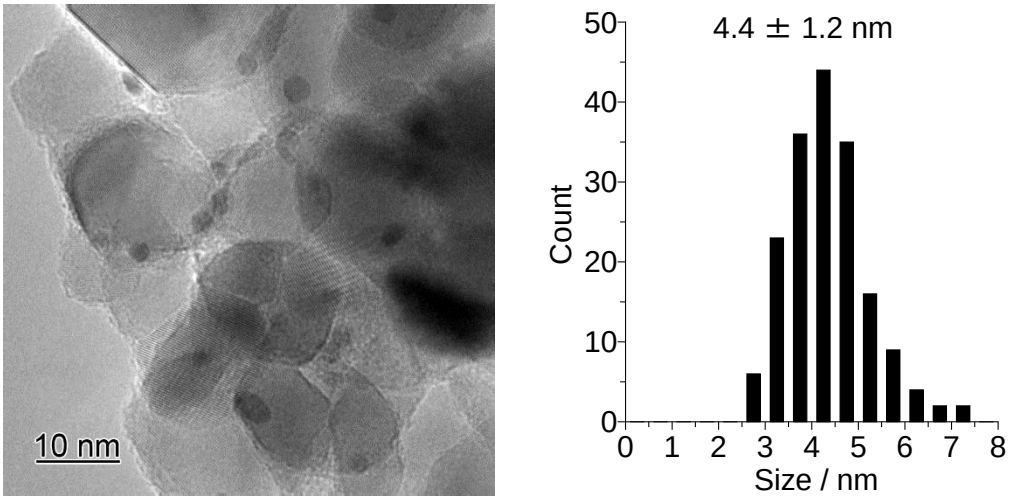




Au_2/P25_anatase prepared by calcination at 573 K



Au_2/P25_anatase prepared by calcination at 723 K



Au_2/P25_anatase prepared by calcination at 773 K

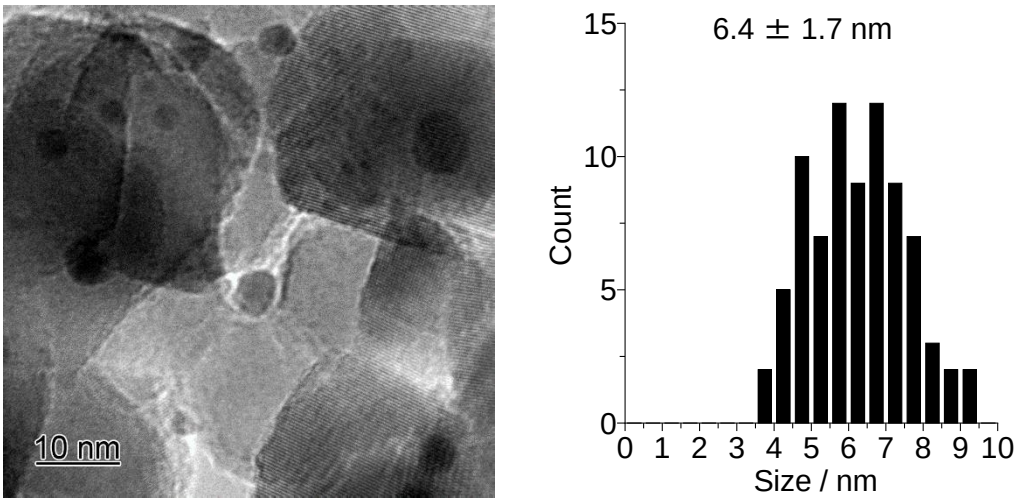
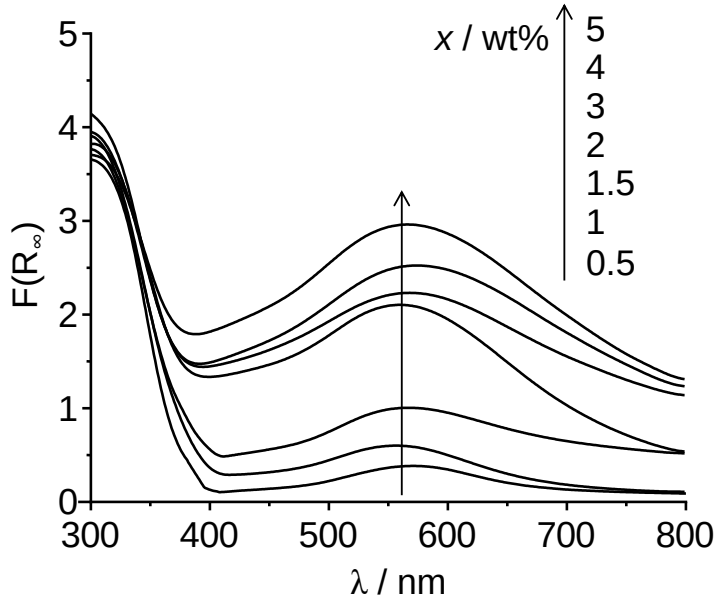


Fig. S7 Typical TEM images and size distributions of the Au_x/P25_anatase and Au_2/P25_anatase catalysts prepared at different calcination temperature.

Au_x/P25_anatase



Au_2/P25_anatase prepared at different calcination temperatures

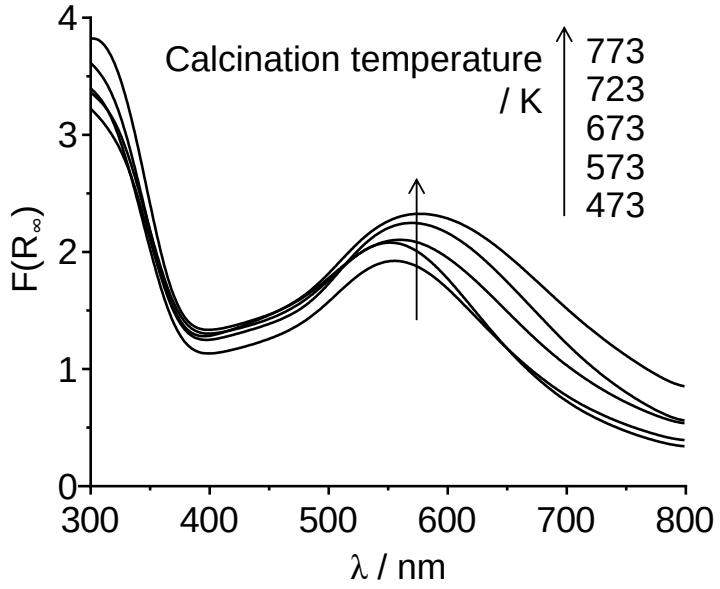


Fig. S8 DR-UV-vis spectra of the catalysts.

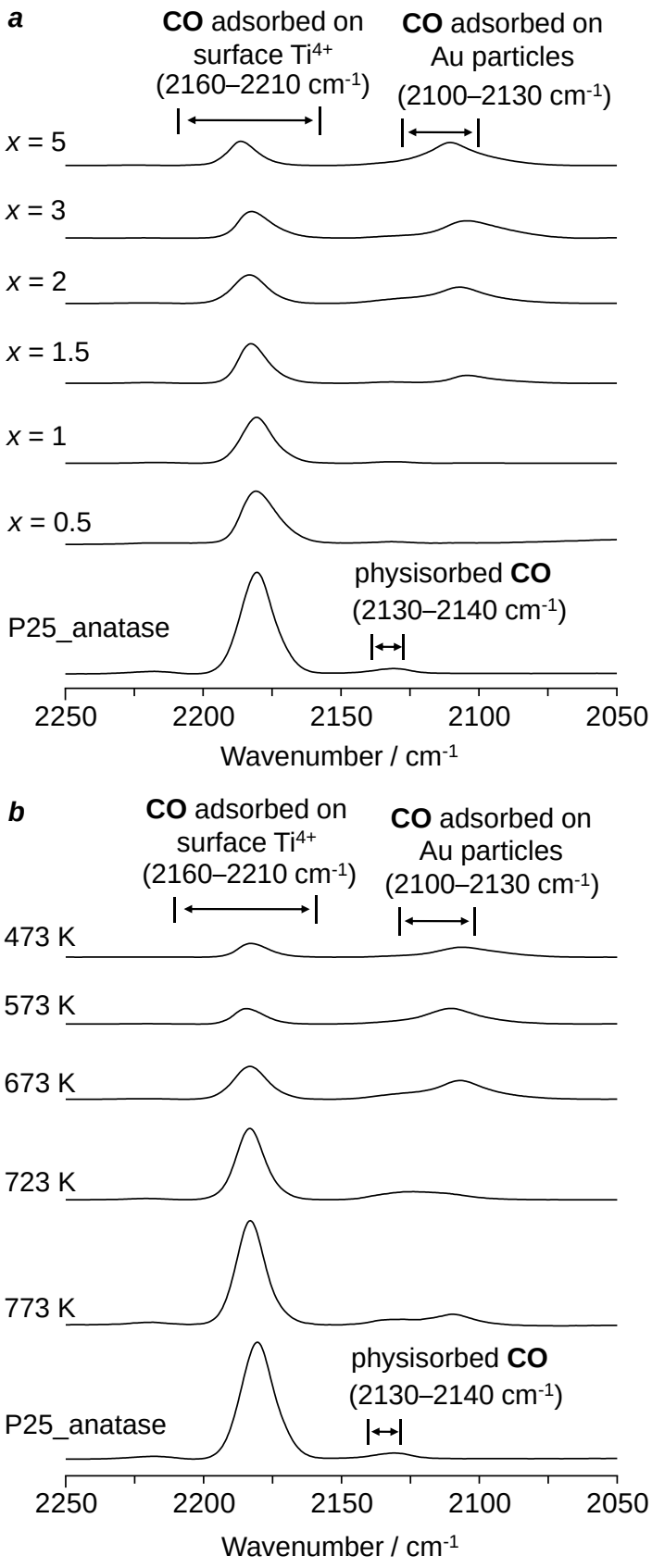


Fig. S9 FTIR spectra of CO adsorbed on (a) Au_x/P25_anatase catalysts and (b) Au_2/P25_anatase catalysts prepared at different calcination temperatures.

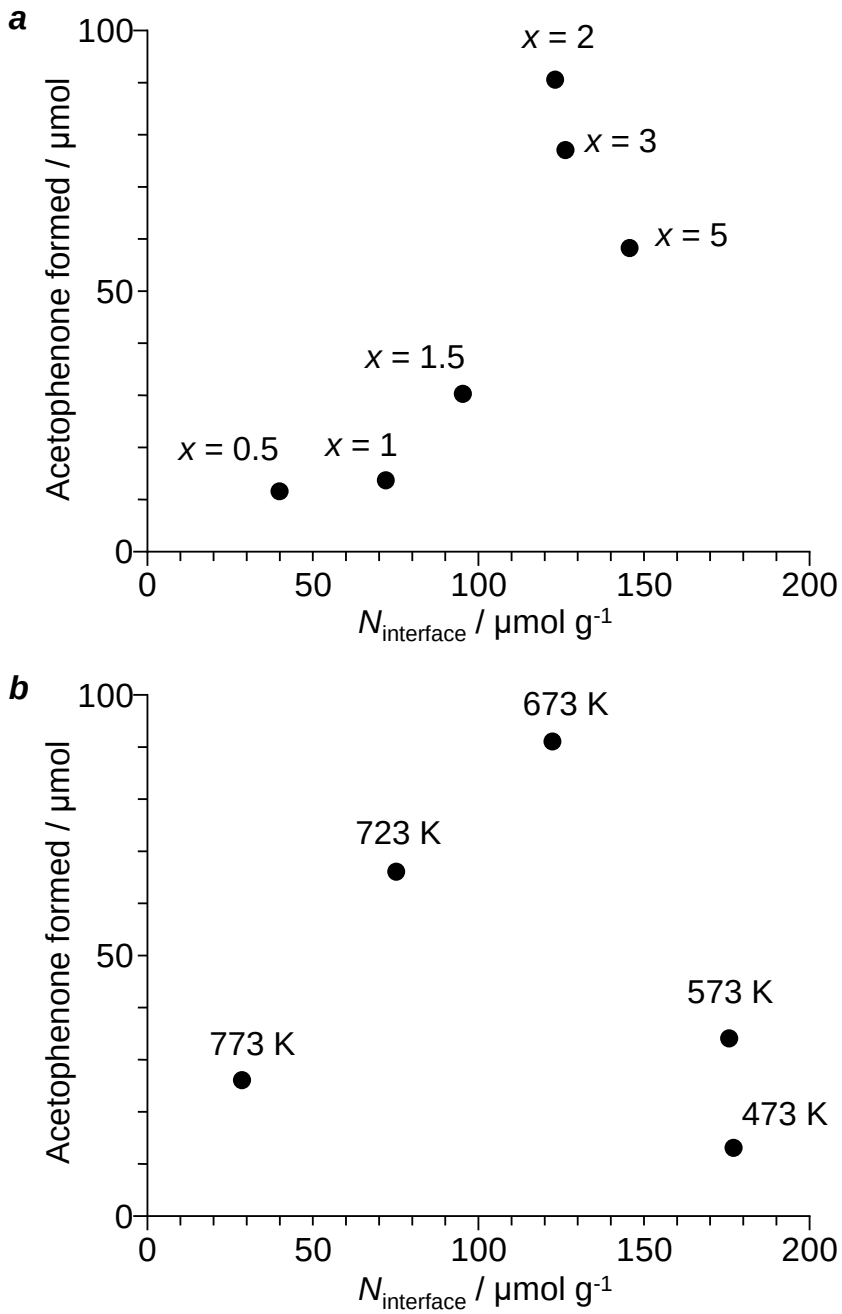


Fig. S10 Relationship between $N_{interface}$ and the amount of acetophenone formed by aerobic oxidation of 1-phenylethanol (12 h) performed under visible light irradiation, with (a) Au_x/P25_anatase catalysts and (b) Au_2/P25_anatase catalysts prepared at different calcination temperature. Reaction conditions are identical to those in Fig. 3 (manuscript).

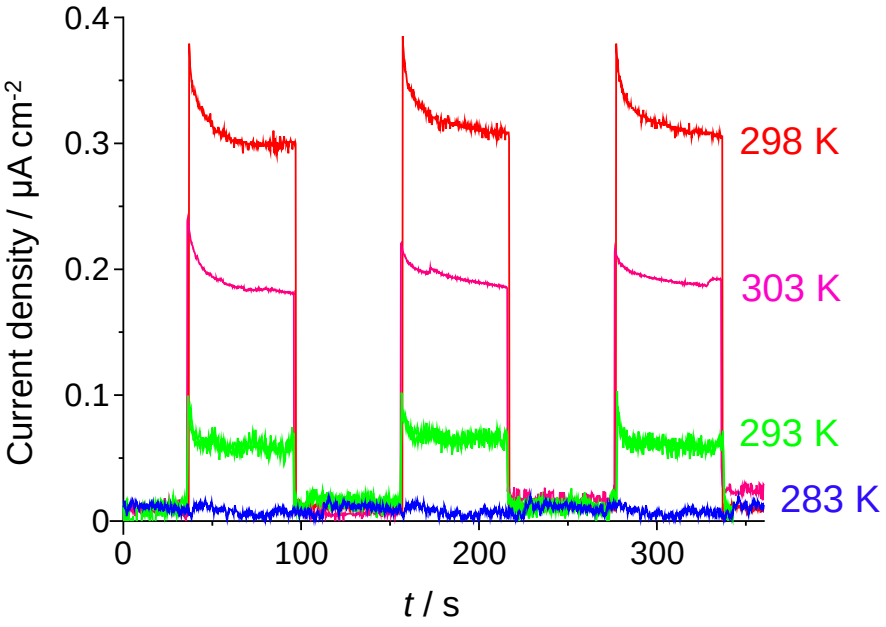


Fig. S11 Photocurrent response of Au_2/P25_anatase measured on a FTO glass electrode at different temperatures. The measurements were carried out in 0.5 M Na_2SO_4 under visible light (λ >450 nm) at a bias of 0.1 V.

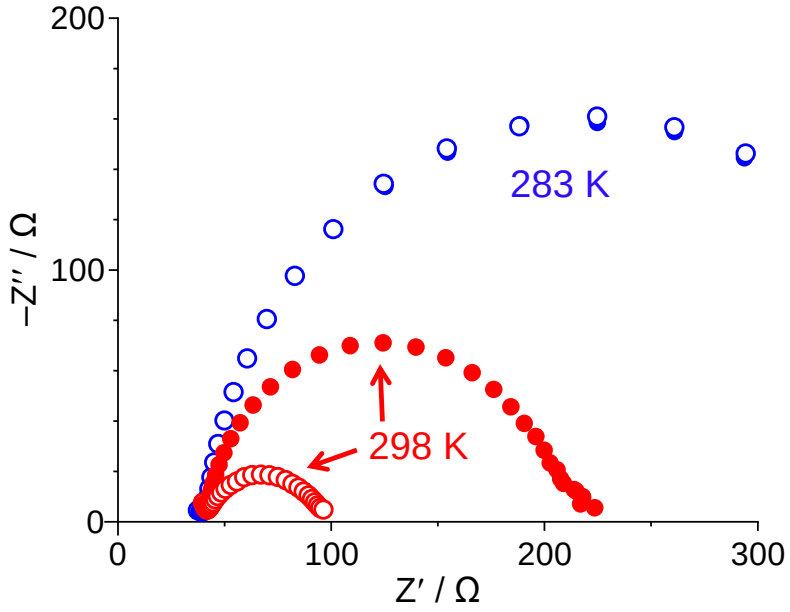


Fig. S12 EIS Nyquist plots of Au_2/P25_anatase in 0.5 M Na_2SO_4 solution at a bias of 2 V (vs open circuit) in the frequency range of 10 mHz to 100 kHz, measured (closed symbols) in the dark or (open symbols under visible light irradiation at different temperatures.

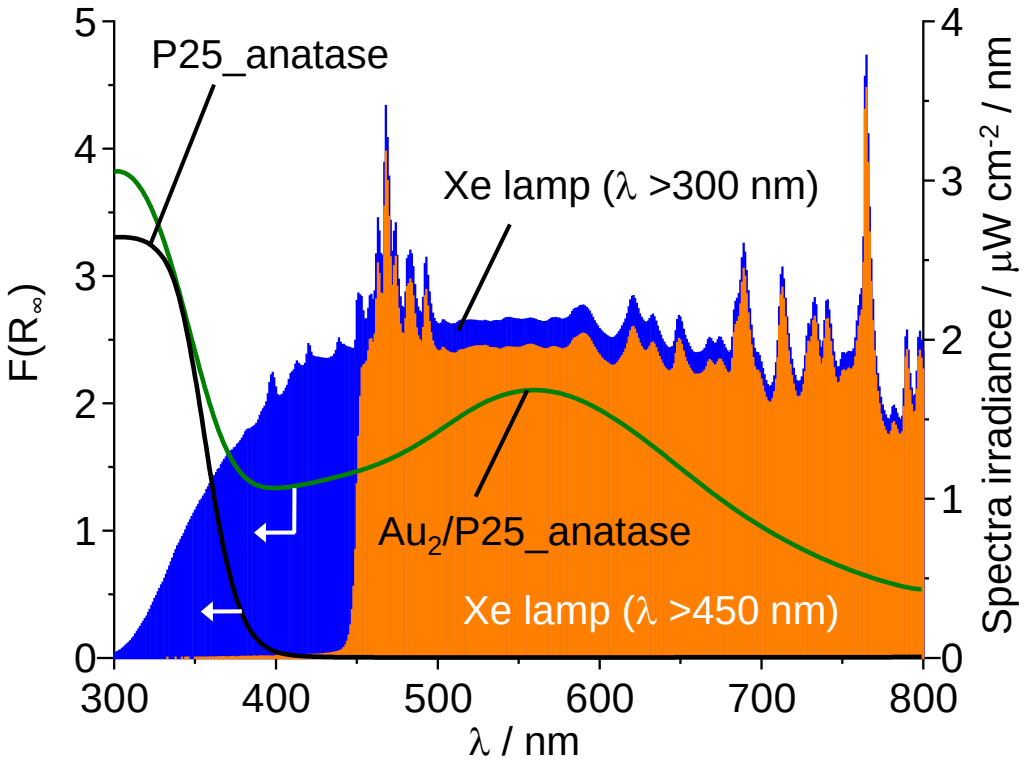


Fig. S13 Light emission spectra of Xe lamp (blue) without filter, (orange) with λ >450 nm filter. DR UV-vis spectra of (green) Au_2/P25_anatase and (black line) P25_anatase are also shown here.