

Electronic supplementary information

Crystallographic interface control of the plasmonic photocatalyst consisting of gold nanoparticles and titanium(IV) oxide

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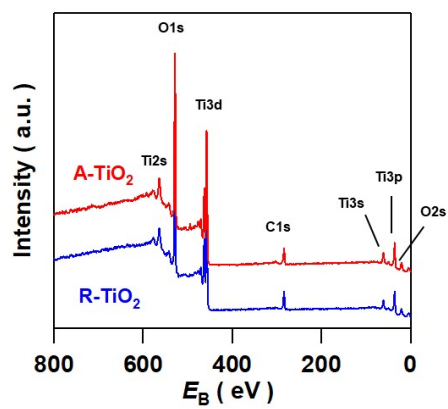


Fig. S1. Wide-scan XPS spectra of anatase TiO_2 (A- TiO_2) and rutile TiO_2 (R- TiO_2).

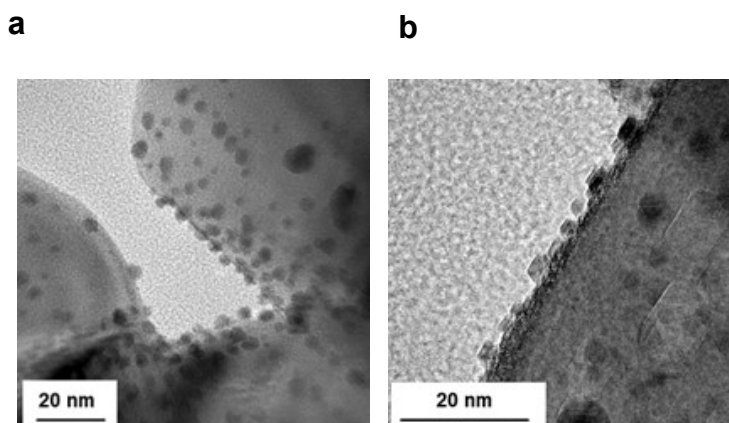


Fig. S2. TEM images of Au/A- TiO_2 (a) and Au/R- TiO_2 (b).

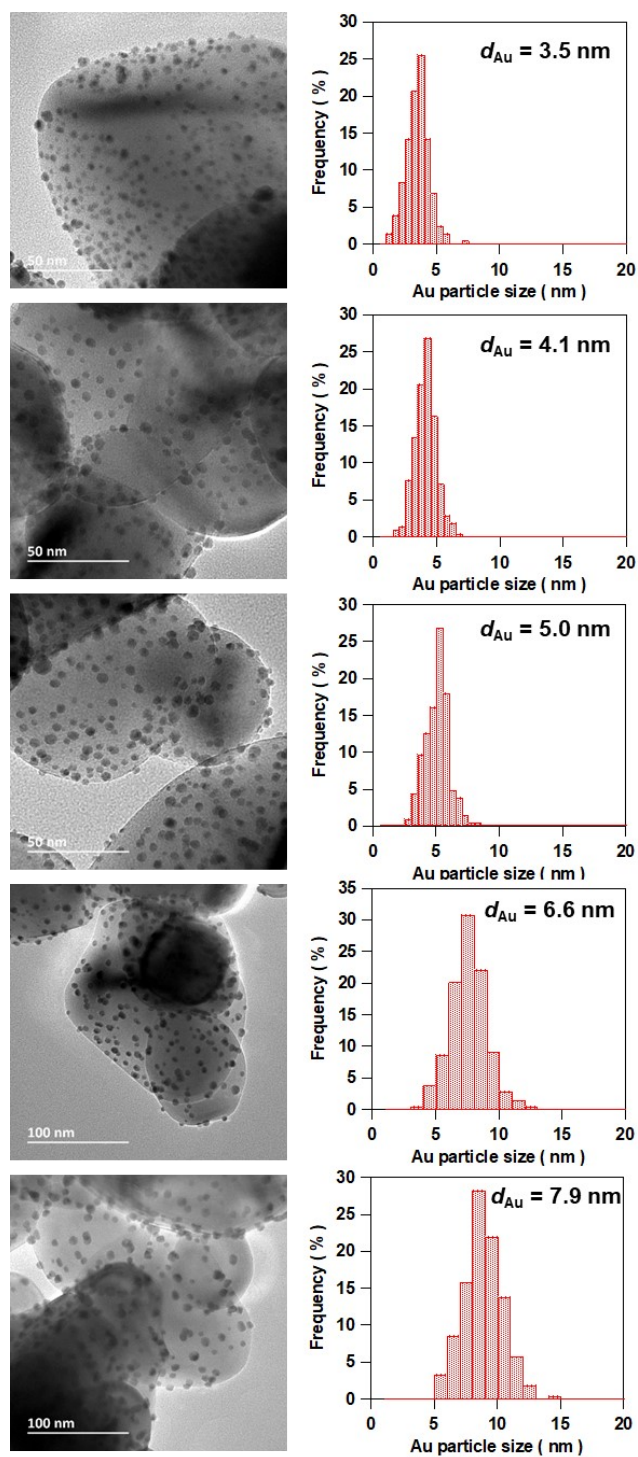


Fig. S3. TEM images and Au size distributions of Au/A-TiO₂ prepared by the deposition precipitation under different conditions.

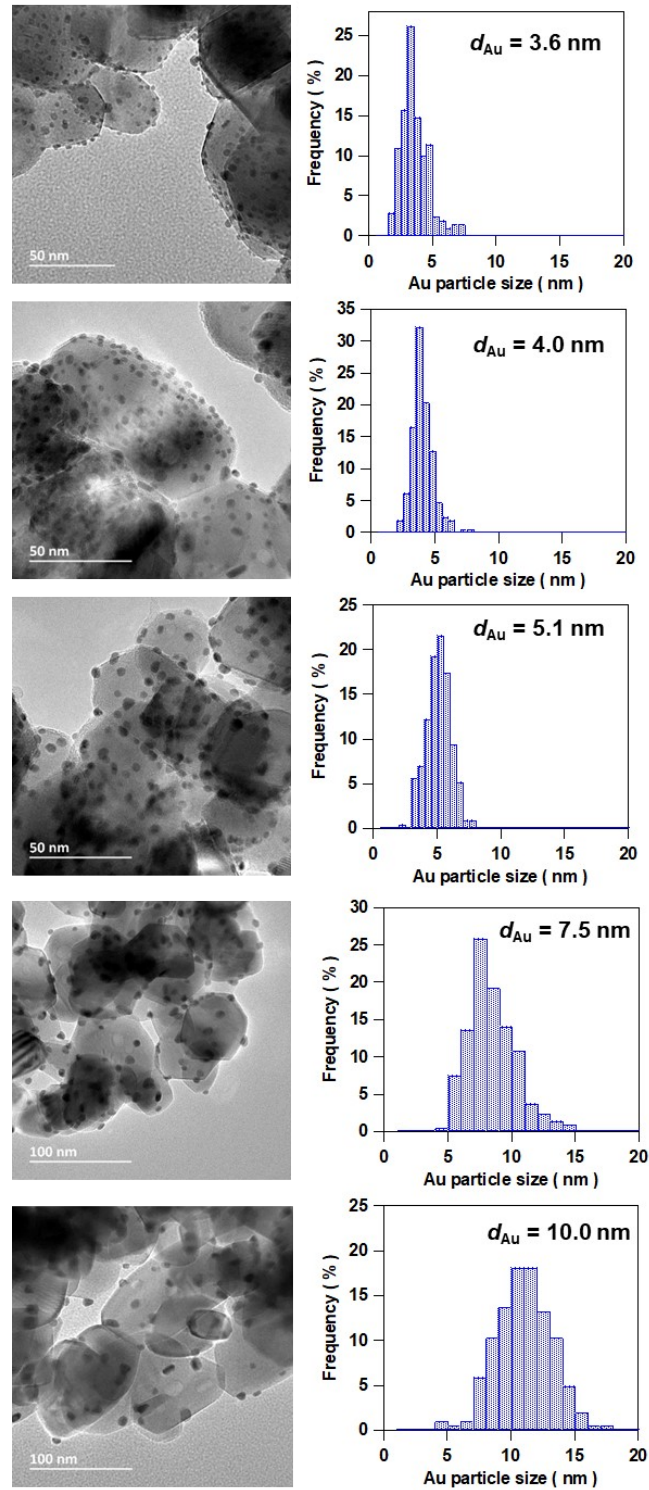


Fig. S4. TEM images and Au size distributions of Au/R-TiO₂ prepared by the deposition precipitation under different conditions.

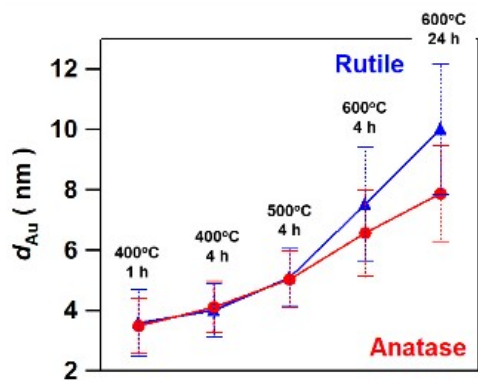


Fig. S5. Au particle size control on anatase and rutile TiO_2 particles. The calcination temperature and time of Au/ TiO_2 are shown above each data point.

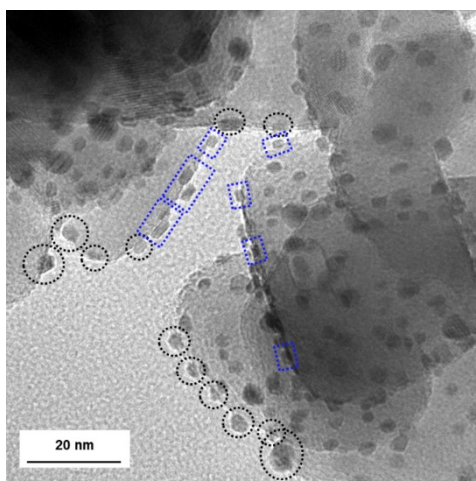


Fig. S6. TEM image of Au/R- TiO_2 prepared at $T_c = 673$ K and $t_c = 1$ h. Faceted and non-faceted Au NPs are shown by dotted blue rectangle and black circle.

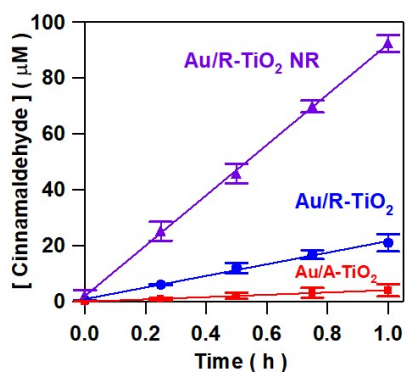
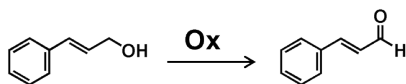


Fig. S7. Time courses for cinnamyl alcohol oxidation under visible-light irradiation ($\lambda_{\text{ex}} > 490$ nm, light intensity integrated from 420 to 485 nm = 3.3 mW cm⁻²) in the presence of Au/A-TiO₂ or Au/R-TiO₂ or Au/R-TiO₂ NR.

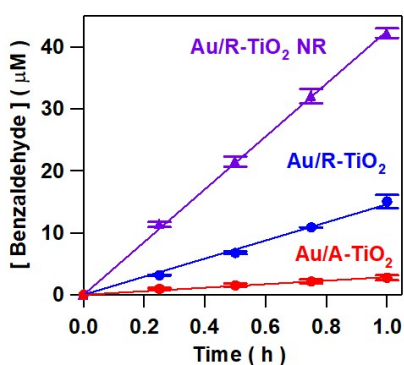
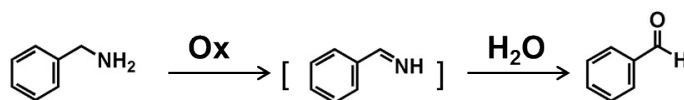


Fig. S8. Time courses for benzylamine oxidation under visible-light irradiation ($\lambda_{\text{ex}} > 430$ nm, light intensity integrated from 420 to 485 nm = 6.0 mW cm⁻²) in the presence of Au/A-TiO₂ or Au/R-TiO₂ or Au/R-TiO₂ NR.

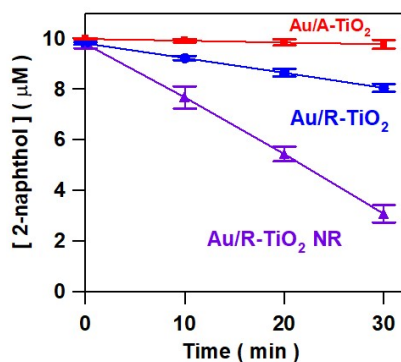
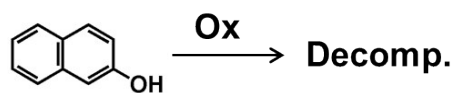


Fig. S9. Time courses for 2-naphthol decomposition under visible-light irradiation ($\lambda_{\text{ex}} > 430$ nm, light intensity integrated from 420 to 485 nm = 6.0 mW cm⁻²) in the presence of Au/A-TiO₂ or Au/R-TiO₂ or Au/R-TiO₂ NR.

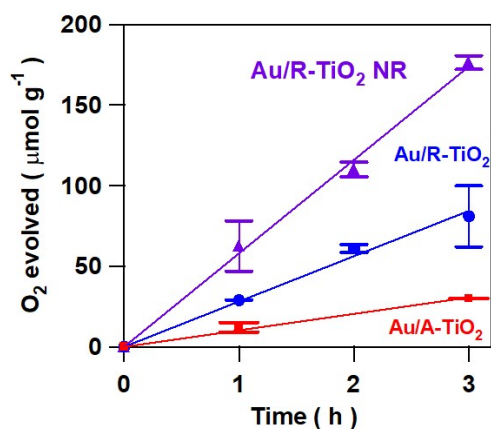
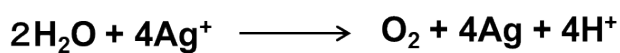


Fig. S10. Time courses for O₂ evolution from 10 mM aqueous solution of AgNO₃ (10 mL) containing La₂O₃ (20 mg) under visible-light irradiation ($\lambda_{\text{ex}} > 470$ nm, light intensity = 30 mW cm⁻²) in the presence of Au/A-TiO₂ or Au/R-TiO₂ or Au/R-TiO₂ NR (10 mg).

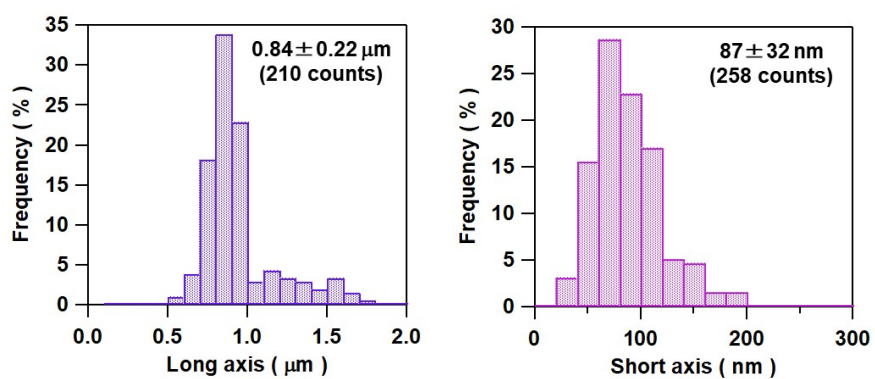
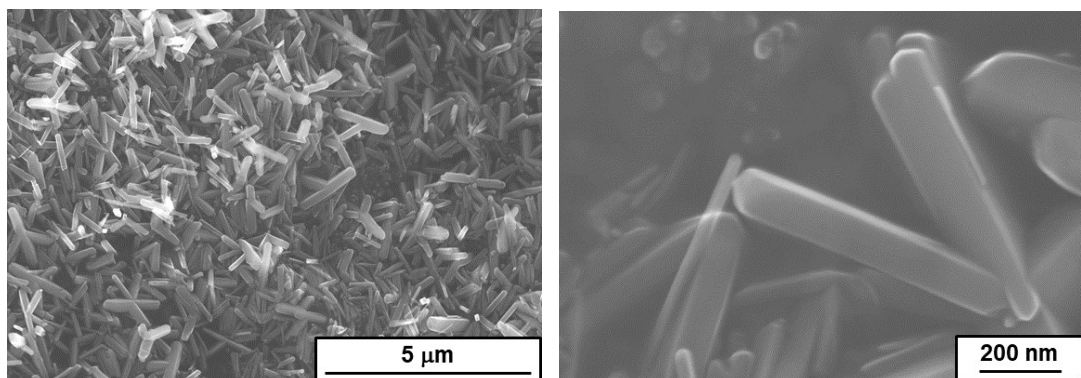


Fig. S11. SEM images and distribution of long and short axis length of R-TiO₂ NR.

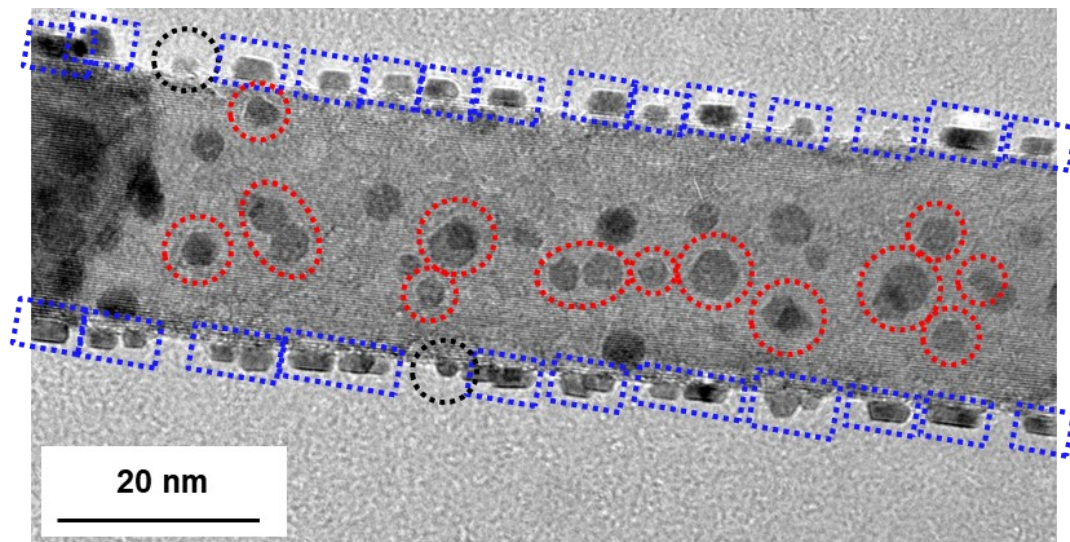


Fig. S12. TEM image of Au/R-TiO₂ NR prepared at $T_c = 673$ K and $t_c = 1$ h. Faceted and non-faceted Au NPs are shown by dotted blue rectangle and black circle.

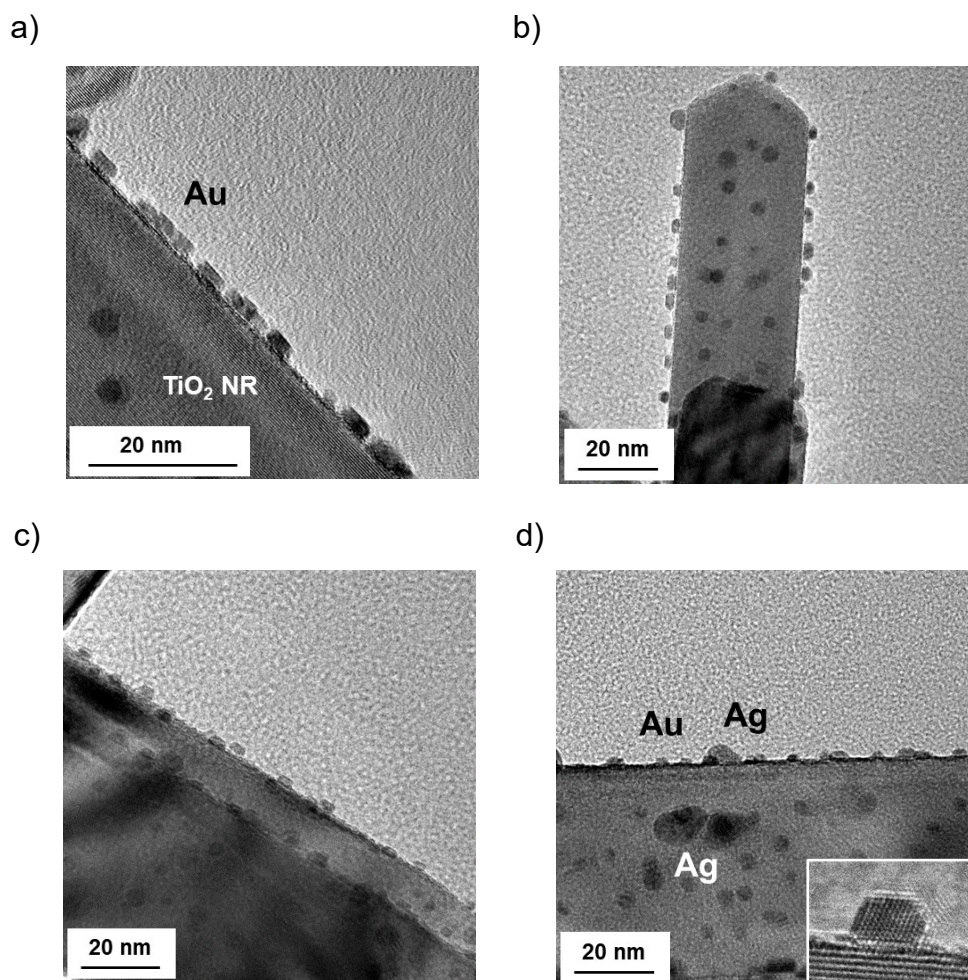


Fig. S13. TEM images of Au/R-TiO₂ NR after reactions: (a) the oxidations of cinnamyl alcohol to cinnamaldehyde, (b) benzylamine to benzaldehyde, (c) the oxidative degradation of 2-naphthol, and (d) O₂ evolution from 10 mM aqueous solution of AgNO₃.

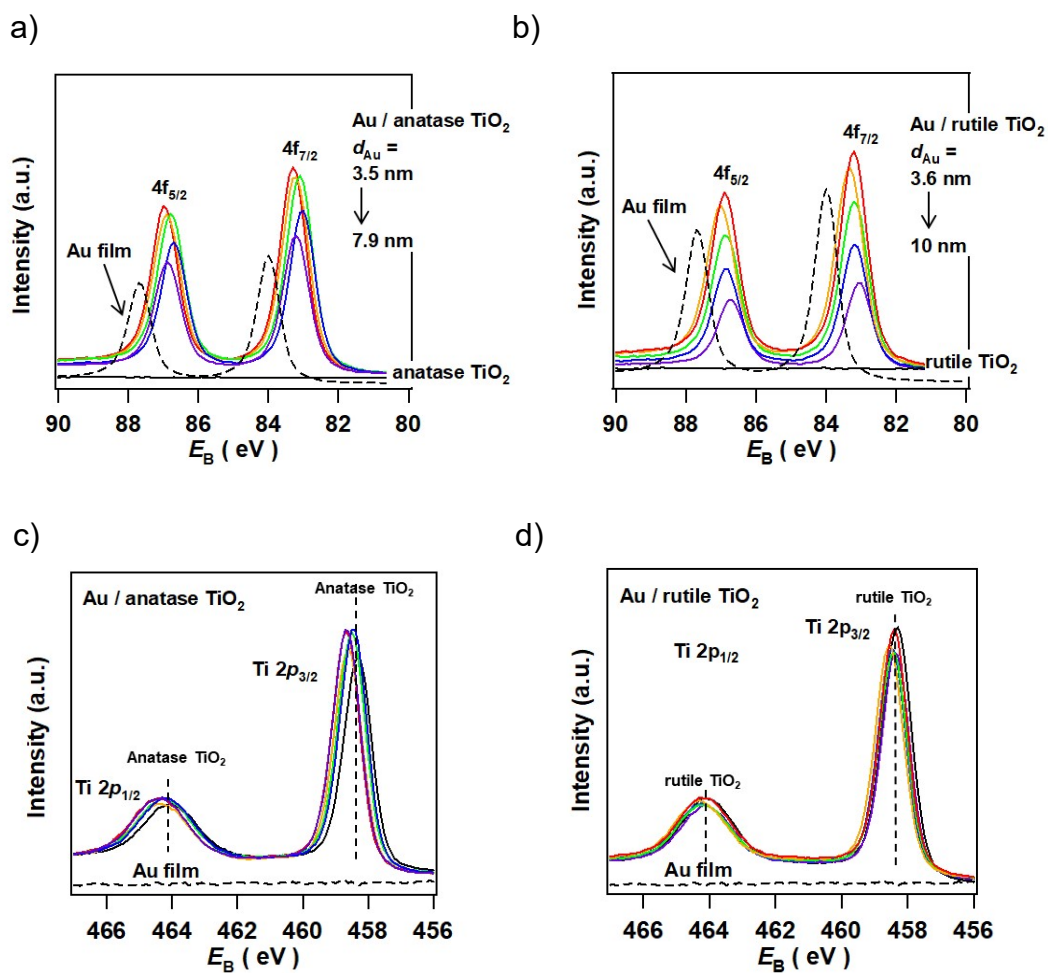


Fig. S14. Au 4f-XPS spectra of Au/A-TiO₂ (a) and Au/R-TiO₂ (b) with varying d_{Au} , and unmodified TiO₂ and Au film-coated glass plate for comparison. Ti 2p-XPS spectra of Au/A-TiO₂ (c) and Au/R-TiO₂ (d) with varying d_{Au} , and unmodified TiO₂ and Au film-coated glass plate for comparison.

Table S1. Crystal-form effect on the plasmonic photocatalytic activity of Au/TiO₂

Reaction	Reaction rate		ratio of R/A	Ref.
	Rutile (R)	Anatase (A)		
2-Propanol oxidation	0.545 $\mu\text{mol h}^{-1}$	0.284 $\mu\text{mol h}^{-1}$	1.96	S1,2
Cinnamyl alcohol oxidation	6.00 $\mu\text{mol h}^{-1}$	1.03 $\mu\text{mol h}^{-1}$	5.81	S3
Benzylamine oxidation	1.82 $\mu\text{mol h}^{-1}$	0.102 $\mu\text{mol h}^{-1}$	17.8	S4
H ₂ evolution	18.5 $\mu\text{mol h}^{-1}$	0 $\mu\text{mol h}^{-1}$	---	S5
Nitrobenzene reduction	7.38 $\mu\text{mol h}^{-1}$	1.04 $\mu\text{mol h}^{-1}$	7.10	S6
Oxygen evolution reaction	10.1 $\mu\text{mol h}^{-1}$	2.24 $\mu\text{mol h}^{-1}$	4.52	S7
Water oxidation	4.46 $\mu\text{A cm}^{-2}$	0.109 $\mu\text{A cm}^{-2}$	40.9	S8
Nonylphenol degradation	2.46 $\mu\text{mol h}^{-1}$	0.321 $\mu\text{mol h}^{-1}$	7.65	S9
2-Naphthol degradation	2.40 $\mu\text{mol h}^{-1}$	0.238 $\mu\text{mol h}^{-1}$	10.1	S10

Reference

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- (S9) S. Naya, T. Nikawa, K. Kimura and H. Tada, Rapid and complete removal of nonylphenol by gold nanoparticle/rutile titanium(IV) oxide plasmon photocatalyst. *ACS Catal.*, 2013, **3**, 903-907.
- (S10) S. Naya and H. Tada, Dependence of the plasmonic activity of Au/TiO₂ for the decomposition of 2-naphthol on the crystal form of TiO₂ and Au particle size. *J. Catal.*, 2018, **364**, 328-333.

Table S2. Characterization results of the Au/A-TiO₂ and Au/R-TiO₂ plasmonic photocatalysts.

Catalysts	$d_{\text{Au}} / \text{nm}$ (counts)	$x_{\text{Au}} / \text{mass}\%$	Faceting probability / % (counts)	T_c / K	t_c / h
Au/A-TiO ₂	3.5 ± 0.9 (203)	4.25	negligible (1032)	673	1
Au/A-TiO ₂	4.1 ± 0.8 (208)	4.20	negligible (1045)	673	4
Au/A-TiO ₂	5.0 ± 0.9 (205)	4.21	negligible (1021)	773	4
Au/A-TiO ₂	6.6 ± 1.4 (208)	4.24	0.1 (1032)	873	4
Au/A-TiO ₂	7.9 ± 1.6 (209)	4.21	0.2 (1037)	873	24
Au/R-TiO ₂	3.6 ± 1.1 (210)	4.22	14.1 (1017)	673	1
Au/R-TiO ₂	4.0 ± 0.9 (211)	4.16	3.6 (1013)	673	4
Au/R-TiO ₂	5.1 ± 1.0 (213)	4.21	1.8 (1009)	773	4
Au/R-TiO ₂	7.5 ± 1.9 (213)	4.31	0.9 (1037)	873	4
Au/R-TiO ₂	10.0 ± 2.2 (204)	4.19	0.8 (1019)	873	24
Au/R-TiO ₂ NR	3.5 ± 0.7 (223)	4.20	94.2 (1029)	673	1
Au/R-TiO ₂ NR	6.3 ± 1.1 (205)	4.18	88.7 (1034)	873	24

Table S3. Au 4f and Ti 2p-XP binding energies

Samples	$d_{\text{Au}} / \text{nm}$	Au		Ti	
		4f _{7/2} / eV	4f _{5/2} / eV	2p _{3/2} / eV	2p _{1/2} / eV
A-TiO ₂	---	---	---	458.3	464.0
Au/A-TiO ₂	3.5 ± 0.9	83.3	87.0	458.7	464.4
Au/A-TiO ₂	4.1 ± 0.8	83.2	86.9	458.6	464.3
Au/A-TiO ₂	5.0 ± 0.9	83.1	86.8	458.5	464.3
Au/A-TiO ₂	6.6 ± 1.4	83.0	86.7	458.5	464.3
Au/A-TiO ₂	7.9 ± 1.6	83.2	86.9	458.7	464.3
R-TiO ₂	---	---	---	458.3	464.2
Au/R-TiO ₂	3.6 ± 1.1	83.2	86.9	458.4	464.3
Au/R-TiO ₂	4.0 ± 0.9	83.3	87.0	458.6	464.3
Au/R-TiO ₂	5.1 ± 1.0	83.2	86.9	458.4	464.3
Au/R-TiO ₂	7.5 ± 1.9	83.2	86.9	458.5	464.2
Au/R-TiO ₂	10.0 ± 2.2	83.1	86.7	458.4	464.2

Table S4. Comparison of the local electric field between HS Au/A-TiO₂ and t-Oh Au/R-TiO₂ systems calculated by the 3D-FDTD method

Model	$d_{\text{Au}} / \text{nm}$	λ / nm	Monitor plane	Maximum E / E_0	Maximum $ E ^2 / E_0 ^2$
HS Au/A-TiO ₂	3.5	702	xz	49.6	2.5E+03
			xy	59.9	3.6E+03
t-Oh Au/R-TiO ₂	3.6	675	xz	138	1.9E+04
			xy	382	1.5E+05
			xz	272	7.4E+04
		704	xy	453	2.1E+05
			xz	448	2.0E+05
			xy	448	2.0E+05