Supplementary information

Rational Design of Au@Pd Core–Shell Cocatalysts on Titanium Dioxide Enabling Selective Photocatalytic Formation of Deuterated Alkanes from Lauric Acid and Heavy Water

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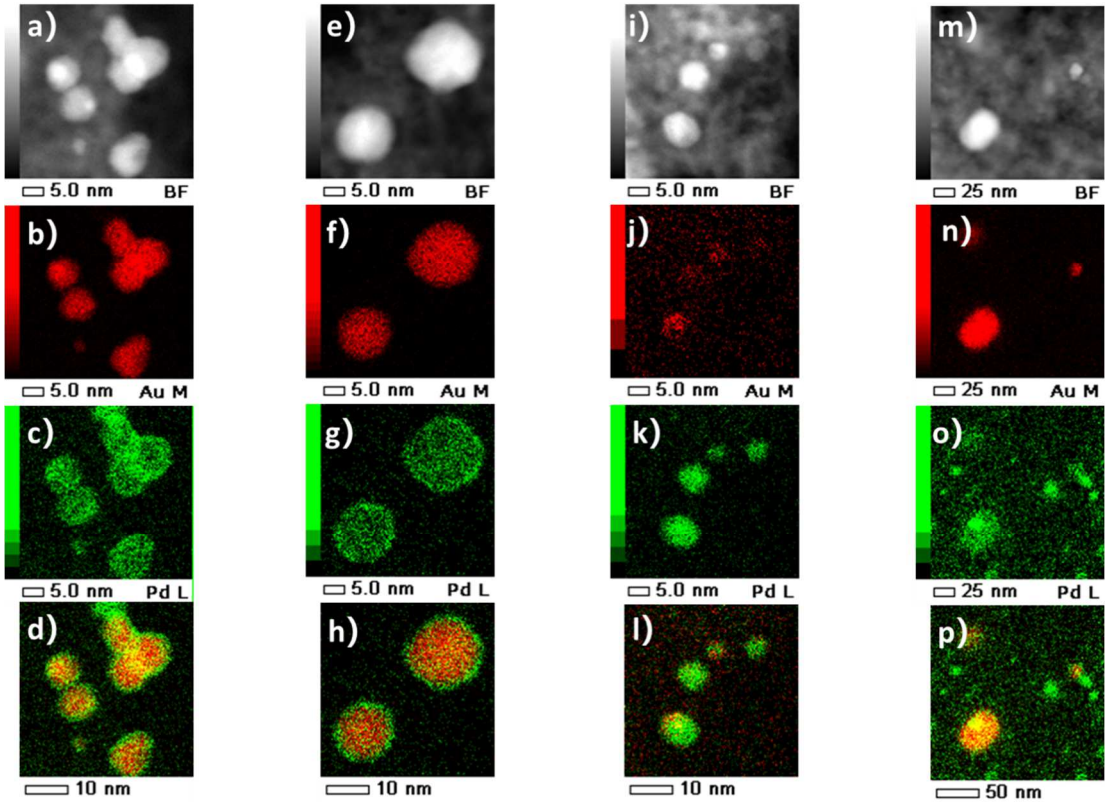

Fig. S1 STEM-EDX elemental mapping of the samples: (a-d) Au1@Pd2/TiO_2, (e–h) Pd2/Au1/TiO_2, (i–l) Au1/Pd2/TiO_2, and (m–p) Pd2(PD)/Au1(CR)/TiO_2. The SPD and PD method was carried out with the light intensity of 76.2 mW cm^{-2} and with methanol as a sacrificial reagent. The images (a-d) are reproduced from reference,[S1] Copyright 2026, Elsevier.

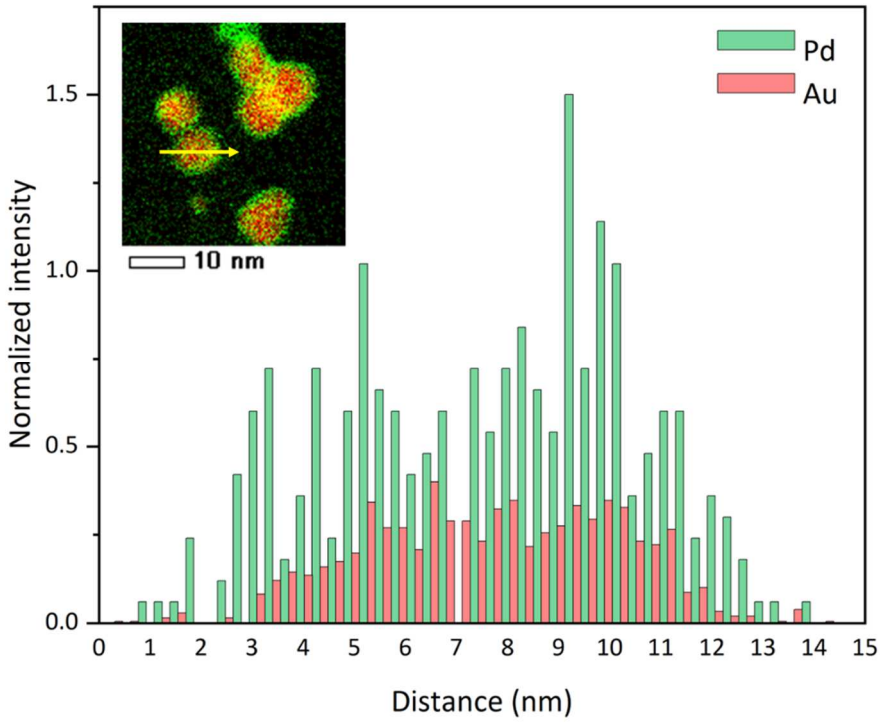

Fig. S2 Line profiles across an Au@Pd particle. The line scan was conducted as indicated by a yellow arow in the inset image. The intensity was normalized with the atomic ratio of Au and Pd.

Table S1 Photocatalytic decarboxylation deuteration of lauric acid with heavy water over various Pd-Au/TiO_2 photocatalyst samples.[a]

Entry	M/TiO_2 sample [b]	Product [c] (μmol)			$Y_{C11\text{-}d}$ (%) [d]	Y_{total} (%) [e]	S_d (%) [f]	R_d (%) [g]
		C_{11}-*d*	C_{11}-*h*	C_{22}				
1	Au1@Pd2	17.2	3.52	0.51	34.4	43.5	79.1	83.0
2	Pd2/Au1	13.5	4.98	0.94	27.1	44.2	66.3	73.1
3	Au1/Pd2	10.0	4.40	0.59	20.1	31.2	64.2	69.5
4	Pd2(PD)/Au1(CR)	7.1	5.51	0.71	14.2	28.0	50.5	56.2

[a] Reaction conditions; catalyst 50 mg, the reaction mixture (5 mL) containing LA 40 mg (50 μmol) in D_2O (3 mL) and CH_3CN (2 mL), reaction time 3 h, light wavelength > 360 nm, irradiated light intensity 41 mW cm^{-2} when measured at 360 ± 20 nm. Pre-heating was conducted before the reaction. [b] Employed TiO_2 was of anatase (ST-01). [c] C_{11}-*d* = *n*-undecane-*d*, $C_{11}H_{23}D$, C_{11}-*h* = *n*-undecane-*h*, $C_{11}H_{24}$, C_{22} = *n*-docosane; [d] Yield of *n*-undecane-*d*, $Y_{C11\text{-}d}$ (%) = 100 × $A_{undecane\text{-}d}$/ $A_{initial\ lauric\ acid}$; [e] Y_{total} (%) = 100 × ($A_{undecane\text{-}d}$+ $A_{undecane\text{-}h}$ + 2×$A_{docosane}$)/$A_{initial\ lauric\ acid}$ [f] Selectivity of $C_{11\text{-}d}$ to the obtained main products (C_{11} and C_{22}) S_d (%)=100 × $A_{undecane\text{-}d}$ /($A_{undecane\text{-}h}$ + $A_{undecane\text{-}d}$ + 2×$A_{docosane}$). [g] Ratio of undecane-*d* to sum of undecane-*d* and undecane-*h*, R_d(%)=100 × $A_{undecane\text{-}d}$/($A_{undecane\text{-}h}$+ $A_{undecane\text{-}d}$).

Table S2 Results of photocatalytic reaction test over several catalyst samples prepared under various light intensity [a].

Entry	Deposition light intensity (mW cm^{-2})	Irradiation time (h)	Product yield (%)			Y_{total}(%)	S_d (%)	R_d (%)
			C_{11}-*d*	C_{11}-*h*	C_{22}			
1	76.2	1	34.44	7.04	2.04	43.53	79.1	83.0
2	38.1	1	31.83	10.38	2.00	44.21	72.0	75.4
3	19.1	1	25.19	10.59	1.60	37.38	67.4	70.4
4	9.5	1	18.00	10.13	2.67	30.79	58.4	64.0
5	9.5	2	26.33	7.88	3.08	37.28	70.6	77.0

[a] Reaction conditions; Au1@Pd2/TiO_2 catalyst 50 mg. For other conditions, see the caption of Table S1.

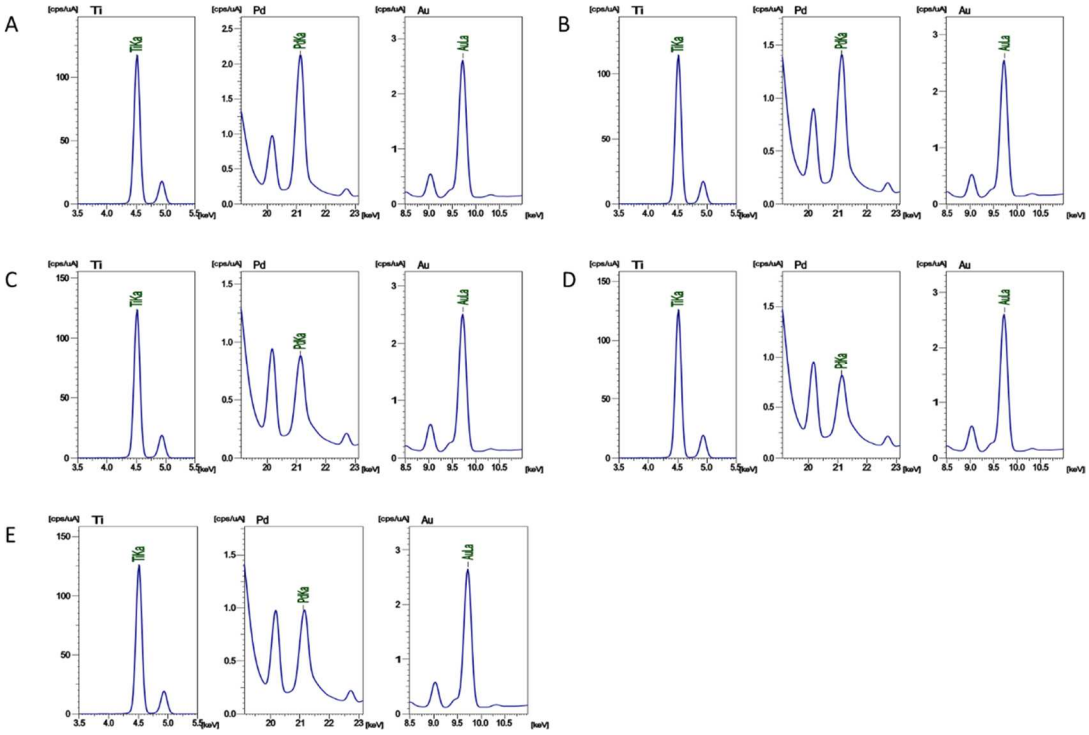

Fig. S3 XRF spectra of each element, Ti, Pd, and Au in the Au1@Pd2/TiO_2 catalysts prepared under different photodeposition light intensities: (A) 76.2, (B) 38.1, (C) 19.1, and (D) 9.5 mW cm^{-2} for 1h, and (E) 9.5 mW cm^{-2} for 2 h. The actual contents of the samples are listed in Table 1.

Fig. S4 Photos of the Au1@Pd2/TiO_2 samples prepared under various SPD light intensity; (left to right) 76.2, 38.1, 19.1, and 9.5 mW cm^{-2}. To enhance the visibility of the sample color, the sample was dispersed in ethanol.

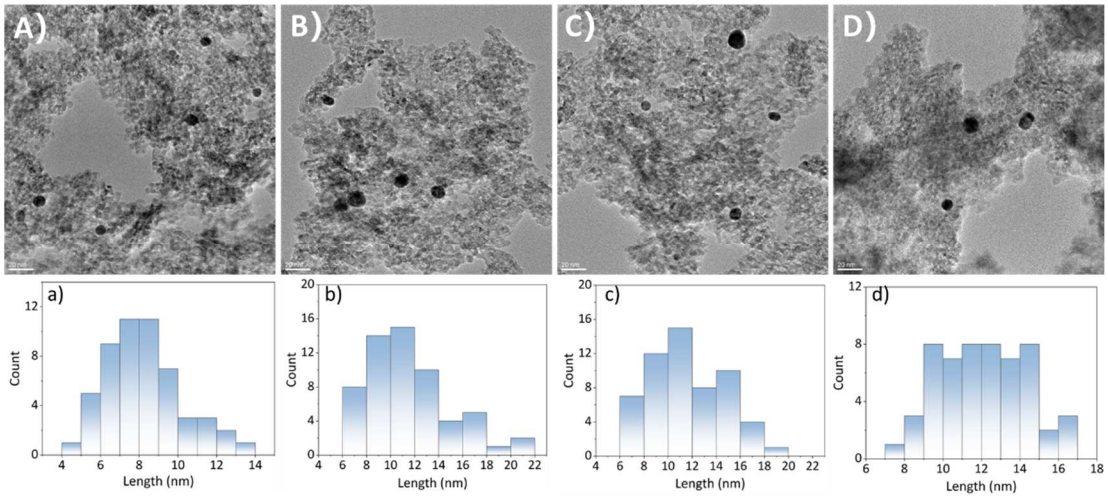

Fig. S5 TEM images of Au1/TiO_2 catalysts prepared under different photodeposition light intensities: (A) 76.2, (B) 38.1, (C) 19.1, and (D) 9.5 mW cm^{-2} and the corresponding particle size distribution (a–d).

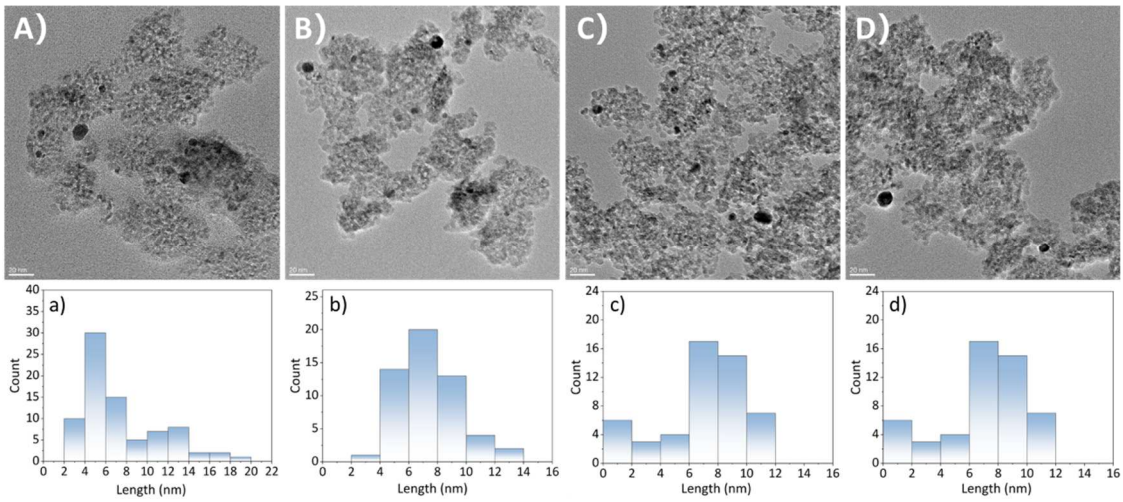

Fig. S6 TEM images of Au1@Pd2/TiO_2 catalysts prepared under different photodeposition light intensities: (A) 76.2, (B) 38.1, (C) 19.1, and (D) 9.5 mW cm^{-2} and the corresponding particle size distribution (a–d).

Table S3 Photocatalytic decarboxylation deuteration of lauric acid over Au1/TiO_2 catalyst samples by different preparation methods [a].

Entry	Light intensity (mW cm^{-2})	Product yield (%)			Y_{total} (%)	S_d (%)	R_d (%)
		C_{11}-*d*	C_{11}-*h*	C_{22}			
1	76.2	13.96	10.37	3.75	43.53	49.7	57.4
2	38.1	8.37	12.90	2.69	44.21	34.9	39.4
3	19.1	9.01	13.34	2.65	25.00	36.0	40.3
4	9.5	5.86	13.52	1.88	21.25	27.6	30.2

[a] Reaction conditions: Au1/TiO_2 catalyst 50 mg, the reaction mixture (5 mL) containing LA 40 mg (50 μmol), in D_2O (3 mL) and CH_3CN (2 mL), reaction time 3 h, light wavelength > 360 nm, irradiated light intensity 41 mW cm^{-2} when measured at 360 ± 20 nm. Pre-heating was conducted before the reaction. For other conditions, see the caption of Table S1.

Table S4 Photocatalytic decarboxylation deuteration of lauric acid over the Au1@Pd2/TiO_2 catalyst samples by different sacrificial reagents [a].

Entry	Sacrificial reagent	Loading (wt%) [b]		Product yield (%)			Y_{total} (%)	S_d (%)	R_d (%)
		Au	Pd	C_{11}-*d*	C_{11}-*h*	C_{22}			
1	methanol	1.09	2.04	34.4	7.04	2.04	43.5	79.1	83.0
2	ethanol	1.09	1.91	30.6	7.67	1.42	39.7	77.1	79.9
3	2-propanol	1.02	1.98	24.5	9.25	1.64	35.3	69.2	72.6
4	acetic acid	1.03	2.01	19.5	9.36	2.20	31.0	62.7	67.5
5	ethylene glycol	1.17	2.34	21.3	10.6	2.83	34.7	61.4	66.9

[a] Reaction conditions: Au1@Pd2/TiO_2 catalyst 50 mg. For other conditions, see the caption of Table S1.
[b] The intended loading amounts for each sample were 1 and 2 wt% for Au and Pd, respectively. The loading amount is determined by XRF. The XRF spectra are shown in Fig. S5.

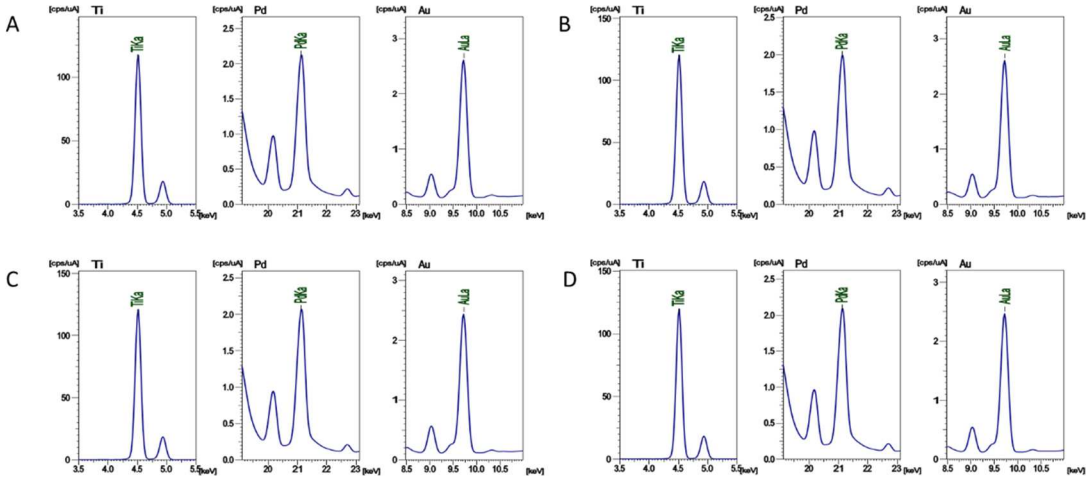

Fig. S7 XRF spectra of each element, Ti, Pd, and Au in the Au1@Pd2/TiO_2 catalysts prepared using various sacrificial reagent: (A) methanol, (B) ethanol, (C) 2-propanol, and (D) acetic acid. The actual contents of the samples are listed in Table 2.

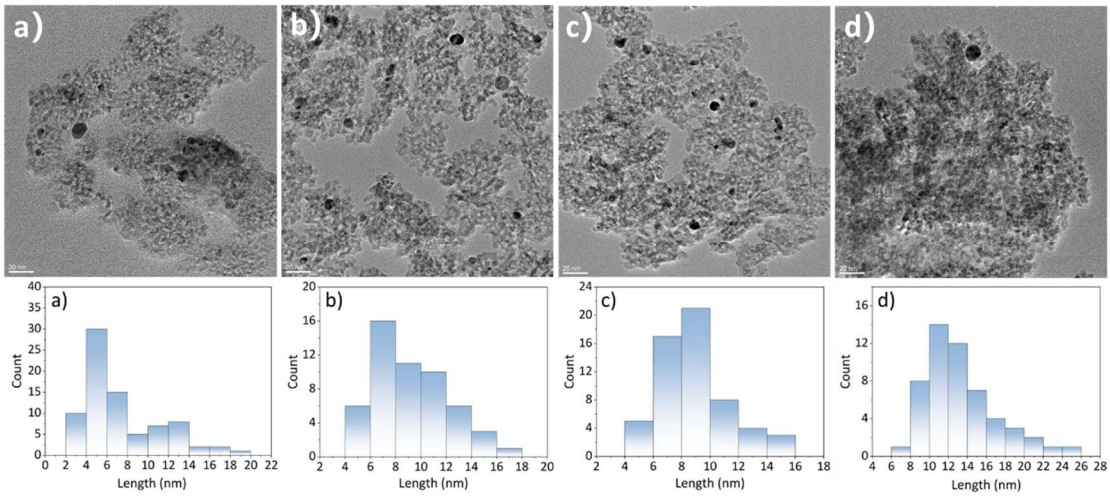

Fig. S8 TEM images of Au1@Pd2/TiO_2 catalysts prepared using various sacrificial reagent: (A) methanol, (B) ethanol, (C) 2-propanol, and (D) acetic acid and the corresponding particle size distribution (a–d).

Table S5 Photocatalytic decarboxylation deuteration of lauric acid over the Au1@Pd2/Pt*x*/TiO_2 catalyst samples by different preparation methods [a].

Entry	Au1@Pd2/Pt*x*/TiO_2 samples	Product yield (%)			Y_{total} (%)	S_d (%)	R_d (%)
		C_{11}-*d*	C_{11}-*h*	C_{22}			
1	0.01	26.82	6.00	1.72	34.54	77.7	81.7
2	0.1	24.89	7.41	1.32	33.62	74.0	77.1
3	0.5	23.32	7.58	2.03	32.93	70.8	75.5
4	1.0	11.24	8.60	0.21	20.06	56.0	56.6

[a] Reaction conditions: catalyst 50 mg, the reaction mixture (5 mL) containing LA 40 mg (50 μmol), in D_2O (3 mL) and CH_3CN (2 mL), reaction time 3 h, light wavelength > 360 nm, irradiated light intensity 41 mW cm^{-2} when measured at 360 ± 20 nm. Pre-heating was conducted before the reaction. See the caption of Table S1 for other conditions.

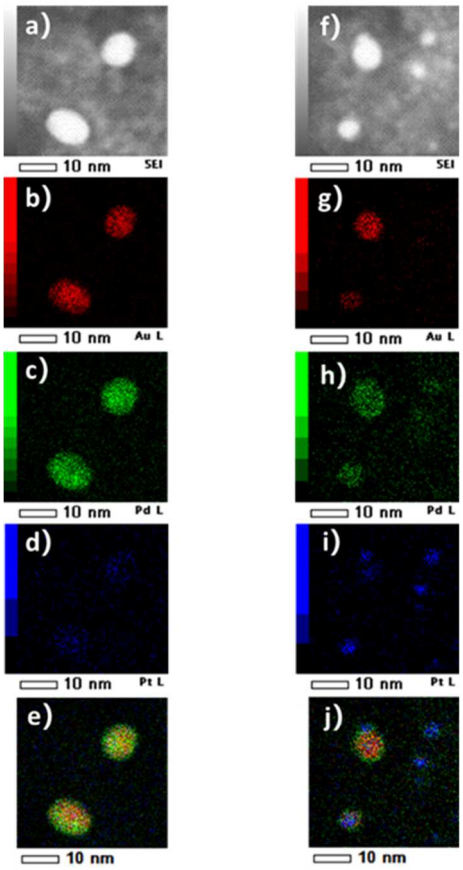

Fig. S9 STEM-EDX elemental mapping of the: (a–e) Au1@Pd2/Pt0.01/TiO_2 and (f–j) Au1@Pd2/Pt1.0/TiO_2catalysts.

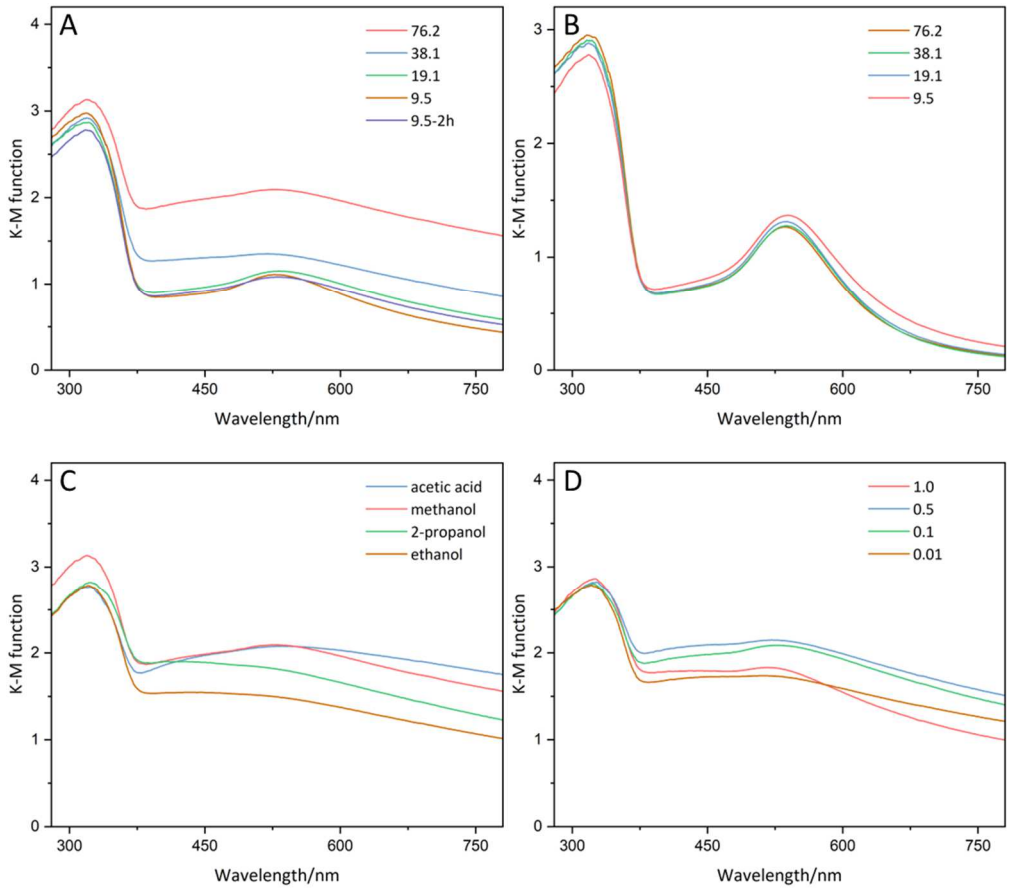

Fig. S10 DR UV-vis spectra of various samples, (A) Au1@Pd2/TiO_2 prepared under series PD light intensity, (B) Au1/TiO_2 prepared under series PD light intensity, (C) Au1@Pd2/TiO_2 prepared using various PD sacrificial reagent, and (D) Au1@Pd2/Pt*x*/TiO_2, *x*=1.0, 0.5, 0.1, and 0.01 wt%.

References

S1 H. Huang, A. Yamamoto, R. Sugiyama, A. Tanaka, H. Kominami and H. Yoshida, *Catal Today*, 2026, **461**, 115520.