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Supporting Information

Overcoming Pd/TiO₂ Deactivation during H₂ Production from Photoreforming by Using Cu@Pd Nanoparticles Supported on TiO₂




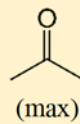

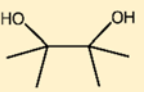

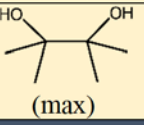





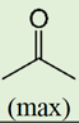
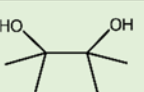
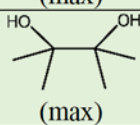




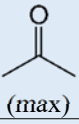
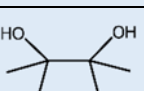
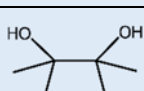
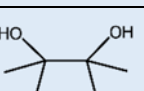
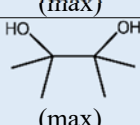
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Table S1. Intermediate evolution in the liquid phase during isopropanol photoreforming reaction (max. indicates the time at which higher signal is observed).

	1 hour	2 hours	3 hours	4 hours	5 hours
Pd _{1.0}				 (max)	
				 (max)	
Cu _{2.0}					 (max)
					 (max)
Pd _{1.0} Cu					 (max)
					 (max)

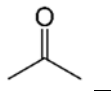
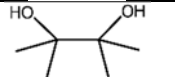
Acetone	
Pinacol: 2,3-dimethyl-2,3-butanediol	

Table S2. Apparent quantum efficiencies (AQE) calculated from reaction rates at 5 and 18 hours for monometallic Cu,Pd and bimetallic Cu@Pd/TiO₂ systems.

Pd (mol%)	AQE after 5 hours		AQE after 18 hours	
	Pd/TiO ₂	Cu@Pd/TiO ₂	Pd/TiO ₂	Cu@Pd/TiO ₂
0	---	4.14	--	2.95
0.03	1.40	4.19	1.35	3.42
0.05	2.59	4.40	2.07	3.88
0.1	5.07	6.05	4.14	4.81
0.2	6.99	7.09	4.14	5.28
0.3	7.76	7.35	4.92	5.69
0.4	8.54	7.50	4.40	5.64
0.5	8.02	10.87	4.50	7.71
1.0	7.87	10.40	4.00	7.35

Table S3. Surface and bulk chemical composition of Cu and Pd doped TiO₂ systems.

Samples	ICP-OES			XPS		
	Cu (at %)	Pd (at %)	Pd/Cu	Cu/Ti	Pd/Ti	Pd/Cu
Pd _{1.0} /TiO ₂	---	1.03	---	---	14·10 ⁻³	---
Cu@Pd _{1.0} /TiO ₂	0.30	1.03	2.32	0.01	18·10 ⁻³	1.79
Cu@Pd _{0.5} /TiO ₂	0.44	0.55	1.96	0.02	13·10 ⁻³	0.72
Cu@Pd _{0.4} /TiO ₂	0.84	0.36	0.42	0.05	10·10 ⁻³	0.21
Cu@Pd _{0.3} /TiO ₂	1.38	0.25	0.18	0.08	9·10 ⁻³	0.09
Cu@Pd _{0.2} /TiO ₂	2.00	0.15	0.07	0.12	8·10 ⁻³	0.07
Cu@Pd _{0.1} /TiO ₂	2.10	0.08	0.02	0.13	2·10 ⁻³	0.02
Cu@Pd _{0.05} /TiO ₂	n.d.	n.d.	n.d.	0.13	1·10 ⁻³	0.01
Cu _{2.0} /TiO ₂	2.13	---	---	0.13	---	---

Table S4. Structural and surface features of Cu and Pd doped TiO₂ systems.

	BET (m ² /g)	Crystallite size* (nm)	Band-gap (eV)
TiO ₂	50	23	3.2
Pd _{1.0} /TiO ₂	51	25	3.2
Cu@Pd _{0.3} /TiO ₂	50	22	3.2
Cu _{2.0} /TiO ₂	51	23	3.2

* Calculated by Rietveld analysis.

Table S5. XPS analysis for Cu and Pd doped TiO₂ systems.

	Cu 2p _{3/2}		Pd 3d _{5/2}	
	BE (eV)	Cu ⁰ /Cu ⁺ *	BE (eV)	Pd ⁰ /(Pd ²⁺ +Pd ⁴⁺) **
Pd _{1.0} /TiO ₂	---	---	334.6	2.8
Cu@Pd _{1.0} /TiO ₂	931.8	---	334.3	3.3
Cu@Pd _{0.5} /TiO ₂	931.5	3.50	334.5	1.9
Cu@Pd _{0.4} /TiO ₂	932.3	0.80	334.5	1.4
Cu@Pd _{0.3} /TiO ₂	932.4	1.55	334.9	1.5
Cu@Pd _{0.2} /TiO ₂	932.4	1.82	335.5	1.4
Cu@Pd _{0.1} /TiO ₂	932.4	1.55	335.5	1.5
Cu@Pd _{0.05} /TiO ₂	932.4	1.20	334.5	n.d.
Cu _{2.0} /TiO ₂	932.4	0.94	1.92	---

* Cu⁰/Cu⁺ ratio calculated from the Cu LMM relative intensities for Cu⁰ and Cu⁺.

** Pd⁰/(Pd²⁺+Pd⁴⁺) ratio calculated from the deconvolution of Pd 3d peak.

Table S6: Computed Bader charges (in electrons) for interface Cu atoms, surface Cu/Pd atoms and reduced Ti atoms in the TiO₂ support. The net charge is the difference between the computed charge and the number of valance electrons. The number of valance electrons is 11 for Cu, 4 for Ti, 16 for Pd and 6 for oxygen.

Structure			
Cu/TiO₂	Cu@Pd₁-TiO₂	Cu-core-Pd-shell-TiO₂	Pd/TiO₂
<i>Interface Cu</i>	<i>Interface Cu</i>	<i>Interface Cu</i>	<i>Interface Pd</i>
10.74 – 10.81	10.73-10.8	10.70-10.79	15.78 – 16.08
<i>Surface Cu</i>	<i>Surface Cu/ Surface Pd</i>	<i>Surface Pd</i>	<i>Surface Pd</i>
10.98 – 11.0	10.85 – 10.90 (Cu)	10.74 – 10.90 (Cu)	16
	16.28 (Pd)	16.05 – 16.1 (Pd)	
<i>Ti in TiO₂</i>	<i>Ti in TiO₂</i>	<i>Ti in TiO₂</i>	<i>Ti in TiO₂</i>
1.66, 1.72, 1.72	1.66, 1.72, 1.72	1.66, 1.72, 1.72	1.39, 1.42

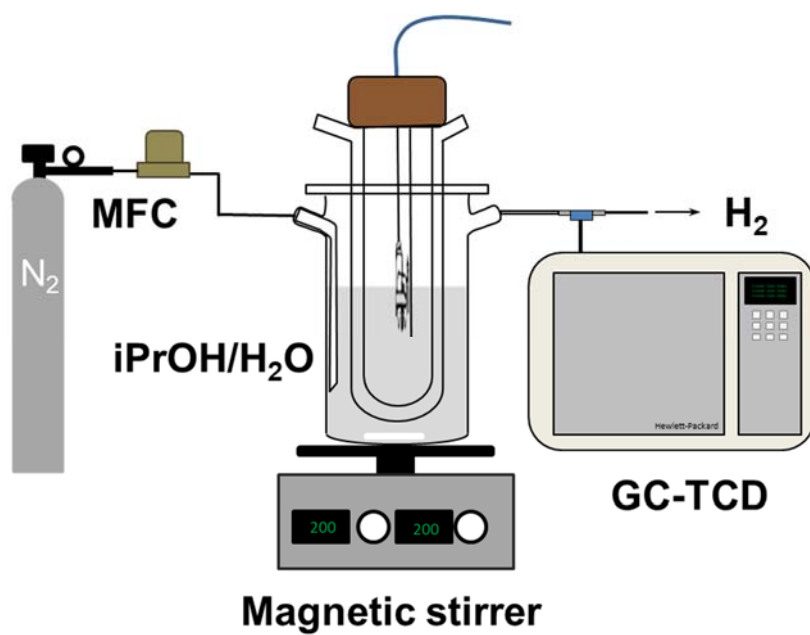


Figure S1. Photocatalytic flow-reactor used for hydrogen production reaction.

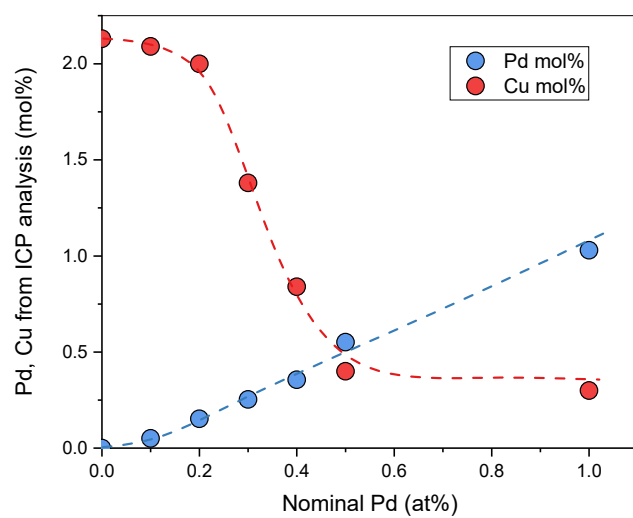


Figure S2. Evolution of Cu and Pd loading measured from ICP analysis with respect to nominal Pd values.

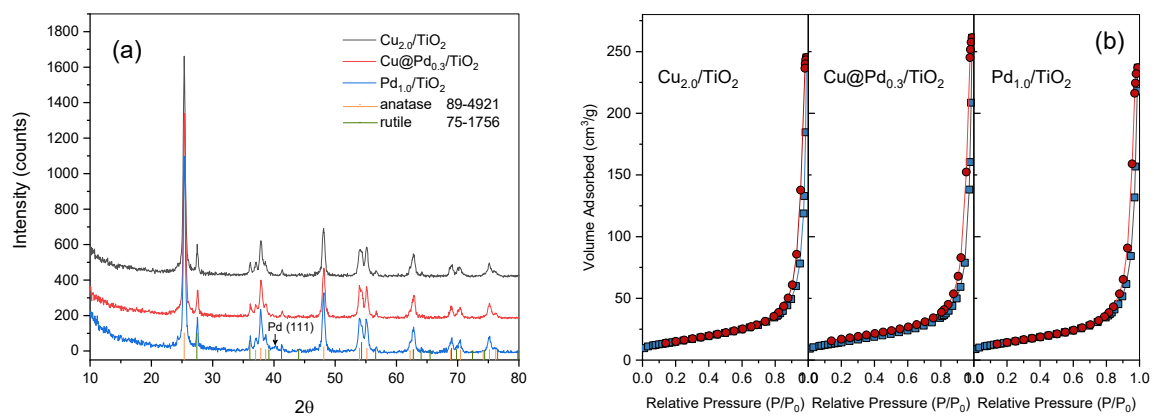


Figure S3. a) XRD pattern and b) N_2 adsorption-desorption isotherms for monometallic Cu/, Pd/ and $\text{Cu}@Pd_{0.3}/\text{TiO}_2$ systems.

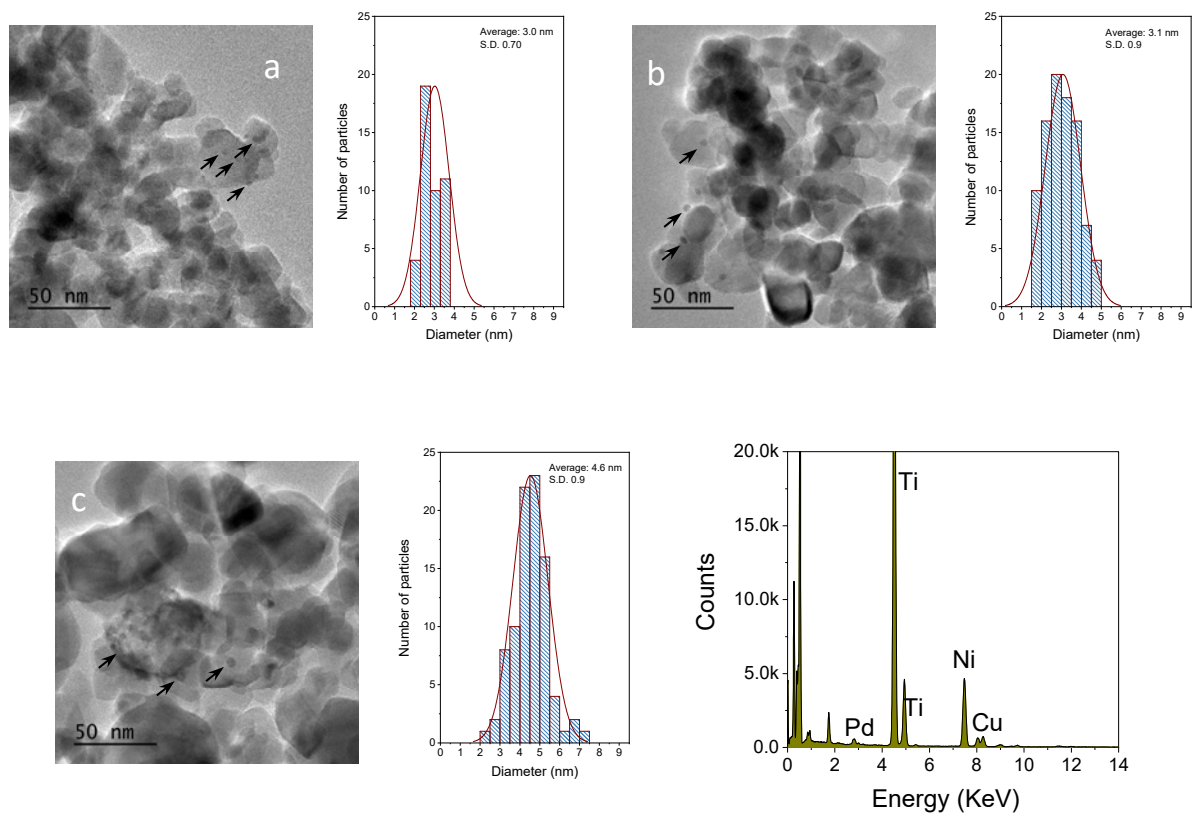


Figure S4. TEM analysis for: a) $\text{Cu@Pd}_{0.1}/\text{TiO}_2$; b) $\text{Cu@Pd}_{0.2}/\text{TiO}_2$; and c) $\text{Cu@Pd}_{0.3}/\text{TiO}_2$ samples.

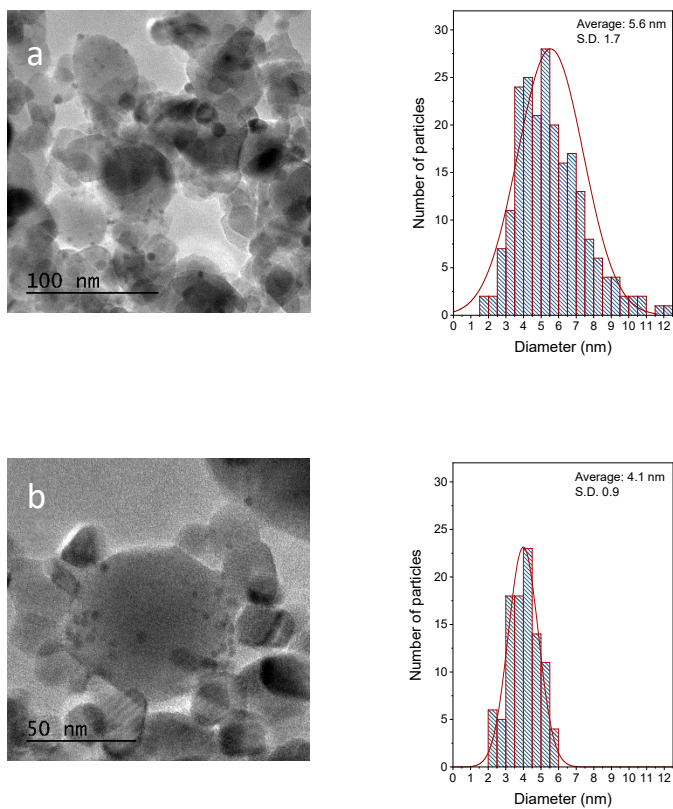


Figure S5. TEM analysis for: a) $\text{Pd}_{1.0}/\text{TiO}_2$; and b) $\text{Cu}@Pd_{1.0}/\text{TiO}_2$ samples after 5 hours of reaction.

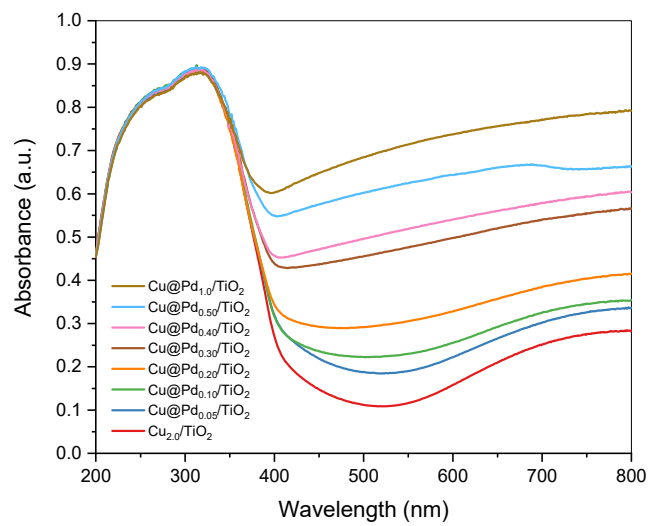


Figure S6. Diffuse reflectance UV-vis spectra for Cu@Pd/TiO₂ systems.

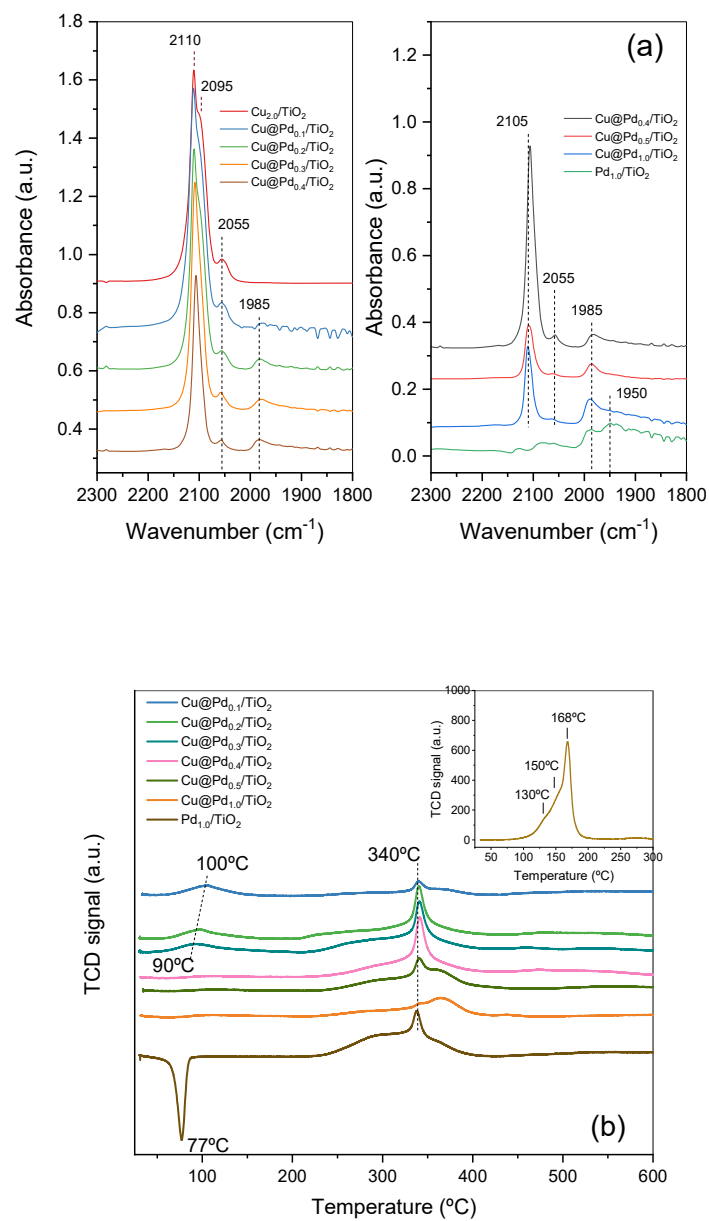


Figure S7. a) FTIR spectra of CO irreversibly adsorbed; b) H₂-TPR curves for different Cu@Pd doped TiO₂ systems. Inset: H₂-TPR for Cu_{2.0}/TiO₂.