

Supporting Information

Size-dependent strong metal-support interaction in Pd/ZnO catalysts for hydrogenation of CO₂ to methanol

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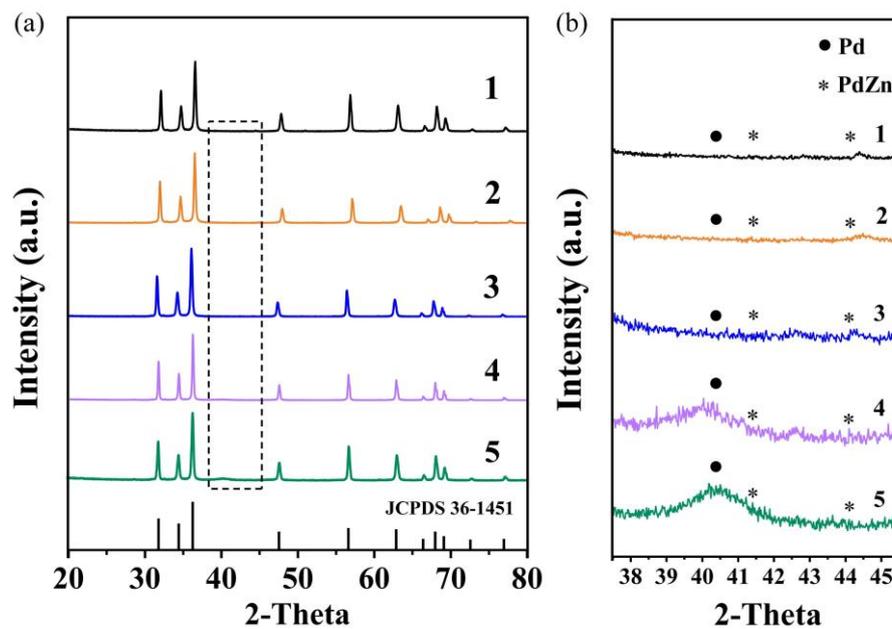


Fig. S1. (a) XRD patterns of the reduced Pd/ZnO catalysts with different size of Pd particles: (1) 1.6 nm, (2) 2.5 nm, (3) 3.3 nm, (4) 5.8 nm, (5) 7.9 nm. (b) Enlarged XRD patterns of the dashed area in (a).

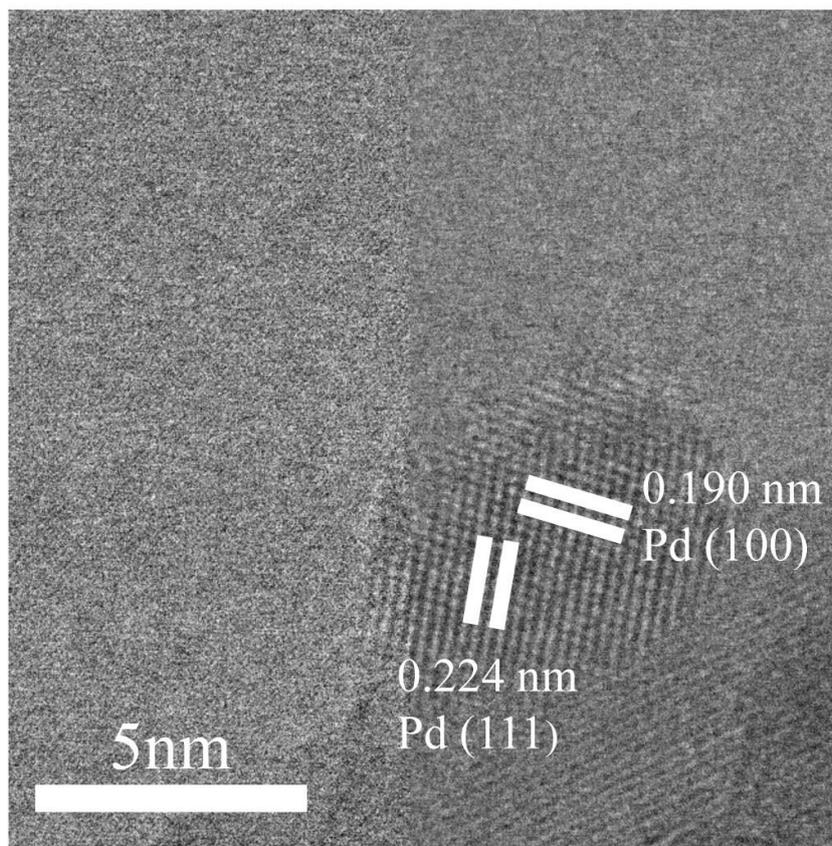


Fig. S2. A representative HRTEM image of the 7.9-nm Pd/ZnO catalyst after reduction in hydrogen at 250 °C.

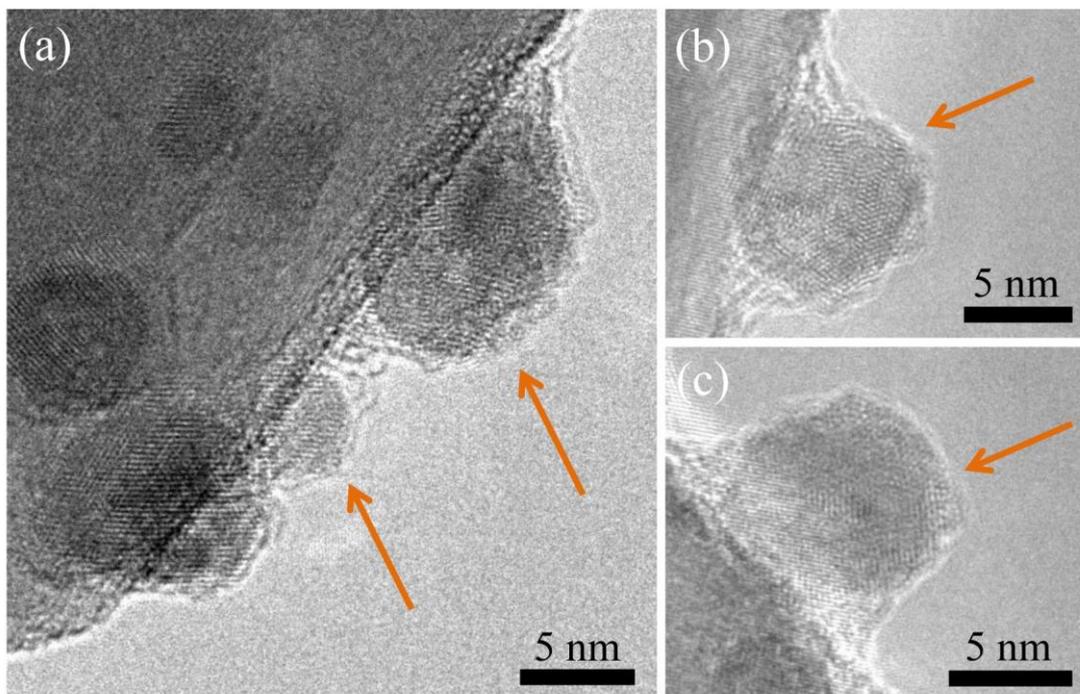


Fig. S3. Representative HRTEM images of the 7.9-nm Pd/ZnO catalyst after reduction in hydrogen at 250 °C at other locations. Arrows in panels indicate the ZnO overlayer via SMSI.

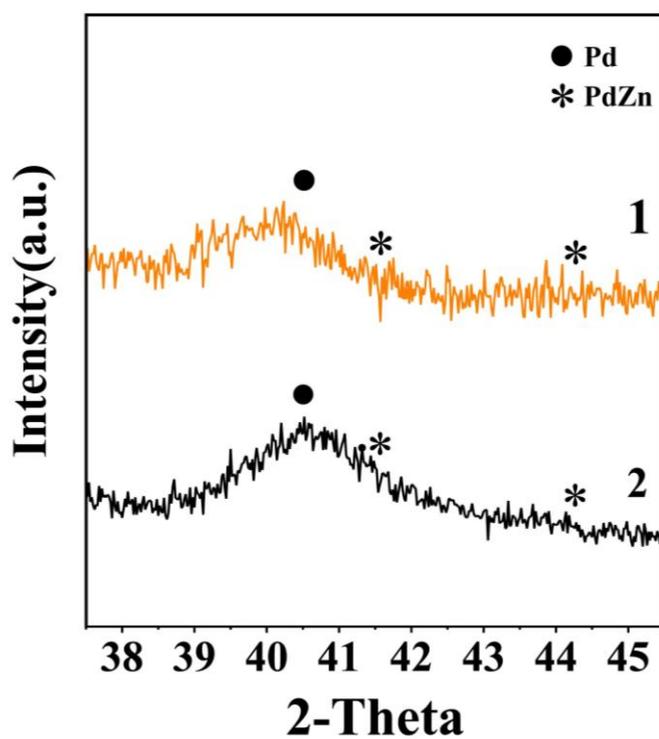


Fig. S4. Magnified XRD spectra of the 5.8-nm Pd/ZnO (1) and the 7.9-nm Pd/ZnO catalyst (2) after subjected to the CO₂ hydrogenation reaction at 250 °C.

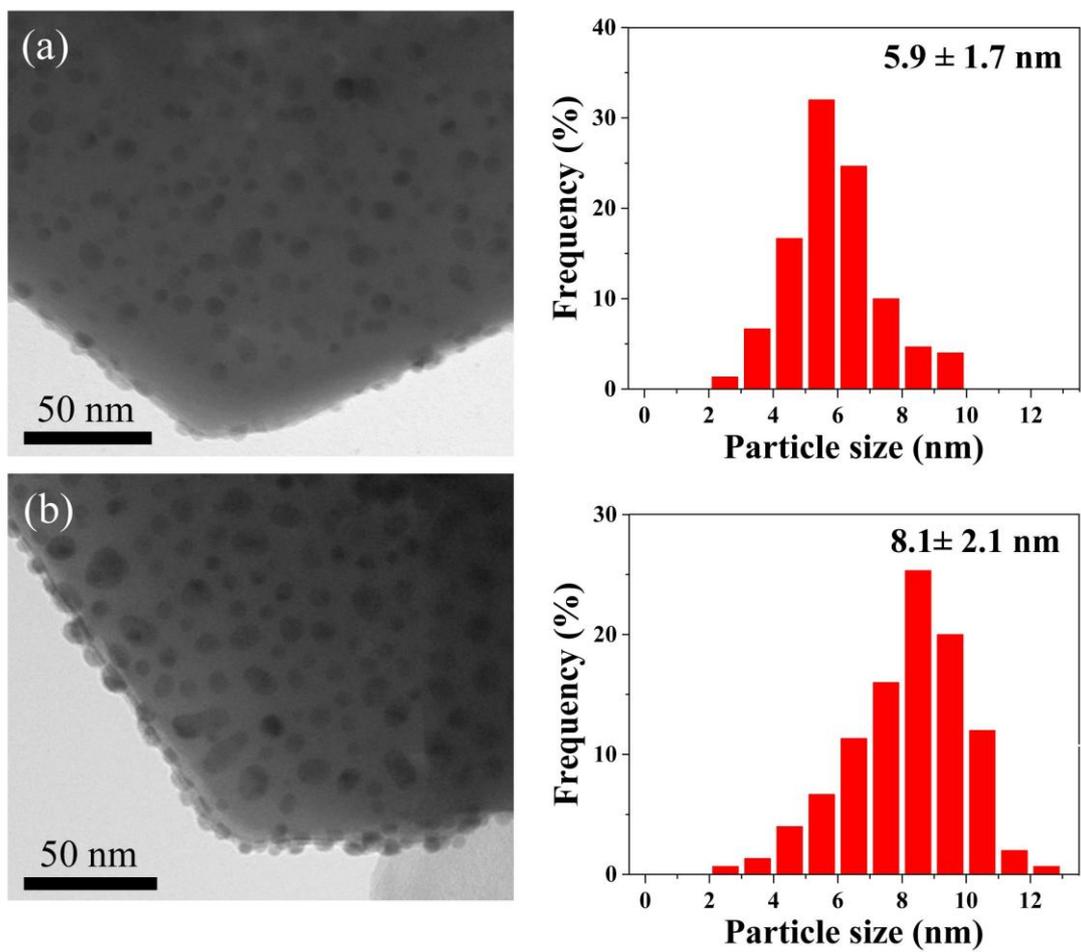


Fig. S5. HRTEM images and the statistical histograms of Pd particle size of (a) 5.8, and (b) 7.9-nm Pd/ZnO catalysts after the CO₂ hydrogenation reaction at 250 °C.

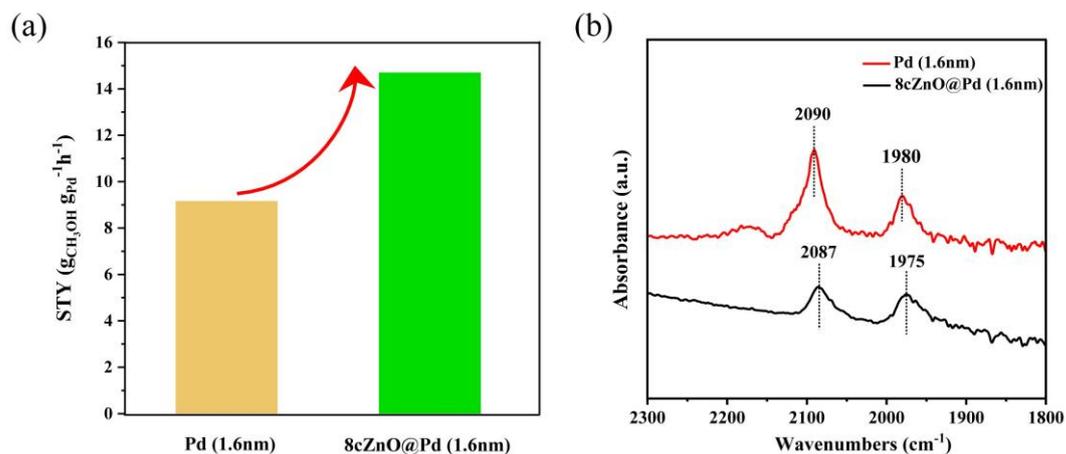


Fig. S6. (a) STY of methanol on 1.6-nm Pd/ZnO and 1.6-nm Pd/ZnO@8cZnO. (b) DRIFTS of CO chemisorption on 1.6-nm Pd/ZnO and 1.6-nm Pd/ZnO@8cZnO after reduction in hydrogen at 250 °C at the saturation coverage.

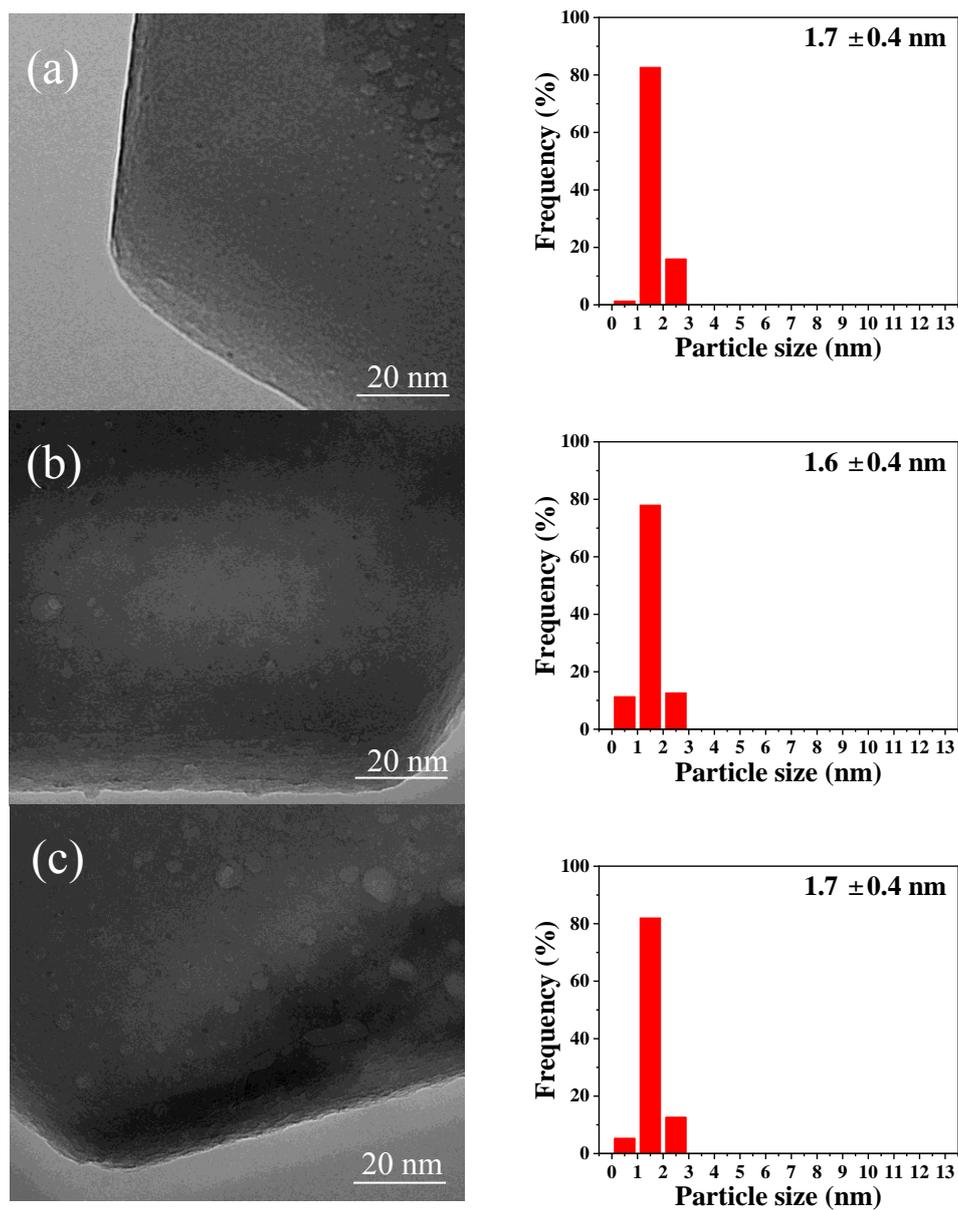


Fig. S7. HRTEM images and the statistical histograms of Pd particle size of the (a) 1.6-nm Pd/ZnO catalyst after the CO₂ hydrogenation reaction at 250 °C, (b) 1.6-nm Pd/ZnO@8cZnO catalyst after reduction in hydrogen at 250 °C, and (c) 1.6-nm Pd/ZnO@8cZnO catalyst after the CO₂ hydrogenation reaction at 250 °C.

Table S1. Pd content and dispersion over Pd-ZnO catalysts.

Catalyst	Cycles of Pd ALD	Pd particle size (nm) ^a	Pd particle size (nm) ^b	Pd content (wt%) ^c	Dispersion (%) ^d	
					150 °C	250 °C
Pd/ZnO	1	1.6	1.6	0.27	65.93	53.44
	3	2.5	2.4	0.41	44.00	19.14
	4	3.3	3.1	0.76	34.38	15.65
	10	5.8	6.7	2.48	15.65	7.14
	15	7.9	12.6	5.21	8.38	2.67

^a Determined by TEM measurements.

^b Calculated based on the Pd dispersion.

^c Determined by ICP results.

^d Pd dispersion determined by CO pulse chemisorption.

Table S2. Catalytic performance of the 1.6-nm Pd/ZnO and 1.6-nm Pd/ZnO@8cZnO catalysts in the reaction of CO₂ hydrogenation^a.

Catalyst	Pd content (wt%) ^b	CO ₂ conversion (%)	CH ₃ OH selectivity (%)
1.6-nm Pd/ZnO	0.27	1.38	35
1.6-nm Pd/ZnO@8cZnO	0.26	1.71	44

^a Reaction Conditions: catalyst, 60 mg; 1CO₂: 3H₂ mixture, 15 mL/min; 250 °C, 4.5 MPa. All catalysts were pre-treated in situ at 250 °C with H₂ flow for 30 min.

^b Determined by ICP results.