

## Electronic Supplementary Information

### Understanding water-gas shift reaction mechanisms at palladium-ceria interfaces using in-situ SERS coupled with online mass spectrometry

Di-Ye Wei,<sup>a</sup> Ge Zhang,<sup>a</sup> Hong-Jia Wang,<sup>a</sup> Qing-Na Zheng,<sup>a</sup> Jing-Hua Tian,<sup>b</sup> Hua Zhang\*<sup>a</sup> and Jian-Feng Li\*<sup>a, b, c</sup>

<sup>a</sup>College of Materials, State Key Laboratory of Physical Chemistry of Solid Surfaces, MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, iChEM, Fujian Key Laboratory of Advanced Materials, College of Energy, Xiamen University, Xiamen, 361005, China.

<sup>b</sup>Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM), Xiamen 361102, China.

<sup>c</sup>College of Chemistry, Chemical Engineering and Environment, Minnan Normal University, Zhangzhou 363000, China.

\*Corresponding Authors, E-mail: [Li@xmu.edu.cn](mailto:Li@xmu.edu.cn), [zhanghua@xmu.edu.cn](mailto:zhanghua@xmu.edu.cn)

## Additional Experimental Procedures

The Raman experiments were done on EC-Raman (Xiamen SHINs Technology Co., Ltd.) or a Jobin-Yvon Horiba XplorA confocal Raman system. An excitation laser with a wavelength of 638 nm and a 50× microscope objective with a numerical aperture of 0.55 were used. The laser power was ~0.03 mW, and the spectral resolution was 2 cm<sup>-1</sup>. Approximately 5 μL Au@Pd or Au@CeO<sub>2</sub>-Pd core-shell nanoparticles were concentrated and deposited on a clean silicon surface, dried at room temperature for in-situ experiment. The sample was placed in a home-made Raman cell with atmosphere and temperature controlled to allow the reactant gas flow over the sample surface. Before the Raman measurement, the sample was pre-treated under H<sub>2</sub> at 20 °C for 30 min. The gas coming out of the in-situ Raman cell through a partial split and enters the mass spectrometer for online analysis.

The X-ray photoelectron spectroscopy (XPS) data was collected on Escalab Xi+ from Thermo Fisher. The charging effect was corrected by adjusting the binding energy of C 1s to 284.6 eV. XPS analysis of Pd 3d core-level spectra of Au@Pd and Au@CeO<sub>2</sub>-Pd were conducted. The spin-orbit splitting is fixed at ~5.25 eV, and the peak area ratio of 3d<sub>5/2</sub> and 3d<sub>3/2</sub> is 3:2. The corresponding peak area and positions of Pd 3d are shown in Tables S1-S3. XPS analysis of Ce 3d core-level spectra of Au@CeO<sub>2</sub>-Pd was as followed: The spin-orbit splitting is fixed at ~18.6 eV. The corresponding peak area and positions of Ce<sup>3+</sup> and Ce<sup>4+</sup> are shown in Tables S4-S6. The concentration of Ce<sup>3+</sup> can be calculated by the equation:  $Ce^{3+} = (v_0 + v' + u_0 + u') / (v_0 + v' + u_0 + u' + v'' + v''' + u + u' + u'' + v_0 + v' + u_0 + u')^{1-3}$ .

**Table S1.** Assignment of Pd 3d peaks in XPS over Au@Pd

Assignment		Pd <sup>0</sup>	Pd <sup>2+</sup>
Pd 3d <sub>3/2</sub>	Binding energy/ eV	334.7	336.8
	Area	60360	14490
Pd 3d <sub>5/2</sub>	Binding energy/ eV	339.9	342.0
	Area	40240	9660

**Table S2.** Assignment of Pd 3d peaks in XPS over Au@CeO<sub>2</sub>-Pd

Assignment		Pd <sup>0</sup>	Pd <sup>2+</sup>
Pd 3d <sub>3/2</sub>	Binding energy/ eV	334.7	337.0
	Area	71861	20621
Pd 3d <sub>5/2</sub>	Binding energy/ eV	340.0	342.3
	Area	47907	13747

**Table S3.** Assignment of Pd 3d peaks in XPS over Au@CeO<sub>2</sub>-Pd after WGSR

Assignment		Pd <sup>0</sup>	Pd <sup>2+</sup>
Pd 3d <sub>3/2</sub>	Binding energy/ eV	334.9	338.3
	Area	17003.1	1022.8
Pd 3d <sub>5/2</sub>	Binding energy/ eV	340.2	343.6
	Area	11335.4	681.9

**Table S4.** Assignment of Ce 3d peaks in XPS over Au@CeO<sub>2</sub>

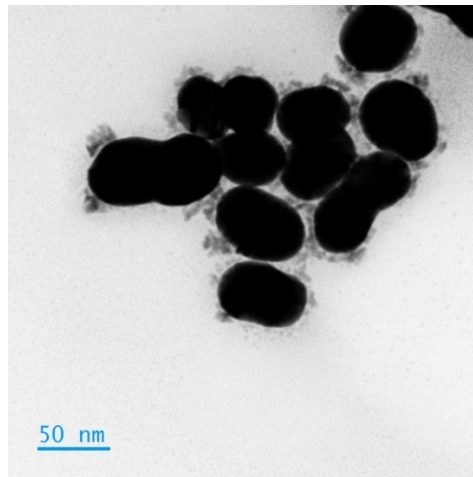
		v <sub>0</sub>	v	v'	v''	v'''
Ce 3d <sub>3/2</sub>	Origin	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>4+</sup>
	Binding energy /eV	881.0	882.9	885.5	888.2	898.8
	Area	449.9	4638.4	2874.1	3563.9	3100.4
		u <sub>0</sub>	u	u'	u''	u'''
Ce 3d <sub>5/2</sub>	Origin	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>4+</sup>
	Binding energy /eV	899.6	901.5	904.1	906.8	917.4
	Area	299.9	3092.3	1916.1	2375.9	2066.9

**Table S5.** Assignment of Ce 3d peaks in XPS over Au@CeO<sub>2</sub>-Pd

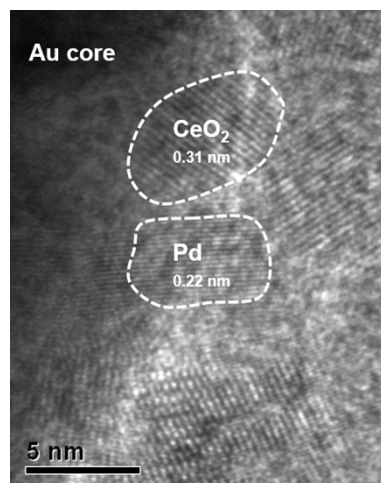
		$v_0$	$v$	$v'$	$v''$	$v'''$
Ce 3d <sub>3/2</sub>	Origin	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>4+</sup>
	Binding energy /eV	880.3	882.1	884.8	887.5	898.2
	Area	4652.5	24078.3	27742.1	20892.4	21173.5
		$u_0$	$u$	$u'$	$u''$	$u'''$
Ce 3d <sub>5/2</sub>	Origin	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>4+</sup>
	Binding energy /eV	898.9	900.7	903.4	906.1	916.8
	Area	3101.7	16052.2	18494.7	13928.3	14115.7

**Table S6.** Assignment of Ce 3d peaks in XPS over Au@CeO<sub>2</sub>-Pd after WGSR.

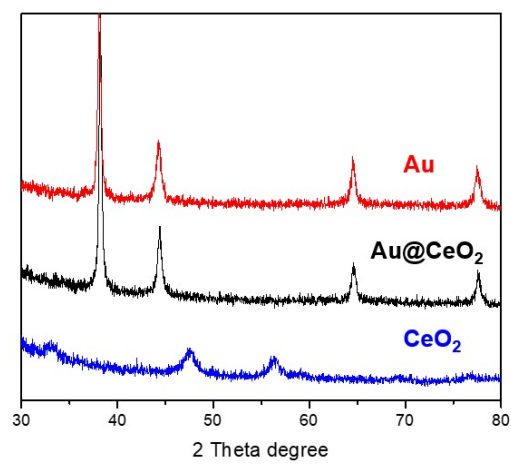
		$v_0$	$v$	$v'$	$v''$	$v'''$
Ce 3d <sub>3/2</sub>	Origin	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>4+</sup>
	Binding energy /eV	881.3	883.0	885.5	888.7	898.6
	Area	8533.8	55542.4	22114.5	53323.1	68444.9
		$u_0$	$u$	$u'$	$u''$	$u'''$
Ce 3d <sub>5/2</sub>	Origin	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>4+</sup>
	Binding energy /eV	899.9	901.6	904.1	907.3	917.2
	Area	5689.2	37028.3	14743.0	35548.7	45629.9



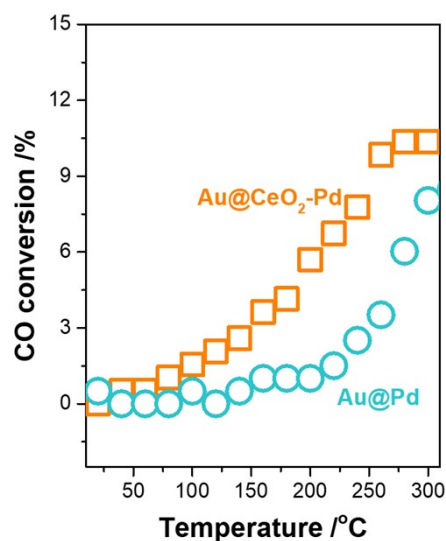
**Figure S1.** TEM image of Au@CeO<sub>2</sub>-Pd NPs.



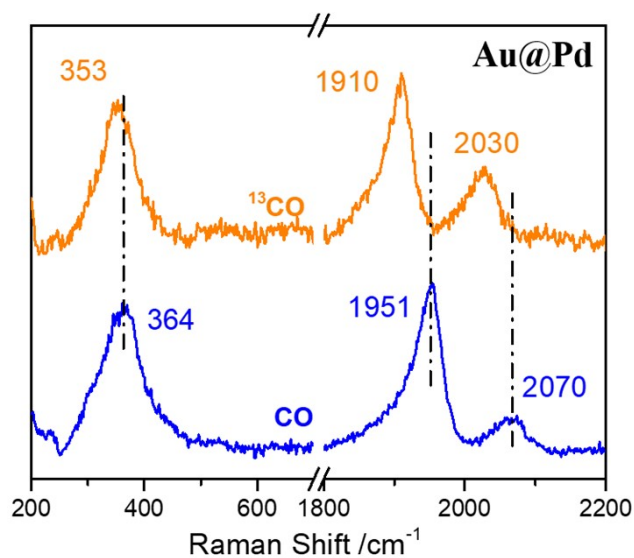
**Figure S2.** HR-TEM image of Au@CeO<sub>2</sub>-Pd.



**Figure S3.** XRD pattern of Au, Au@CeO<sub>2</sub> and CeO<sub>2</sub>.



**Figure S4.** Catalytic performance of Au@CeO<sub>2</sub>-Pd and Au@Pd. Reaction conditions: 1% CO, 2% H<sub>2</sub>O, balance N<sub>2</sub>. The weight hourly space velocity is 20,000 mL·g<sup>-1</sup>·h<sup>-1</sup>.



**Figure S5.** Comparison of the SERS spectra of Au@Pd under <sup>12</sup>CO and <sup>13</sup>CO.

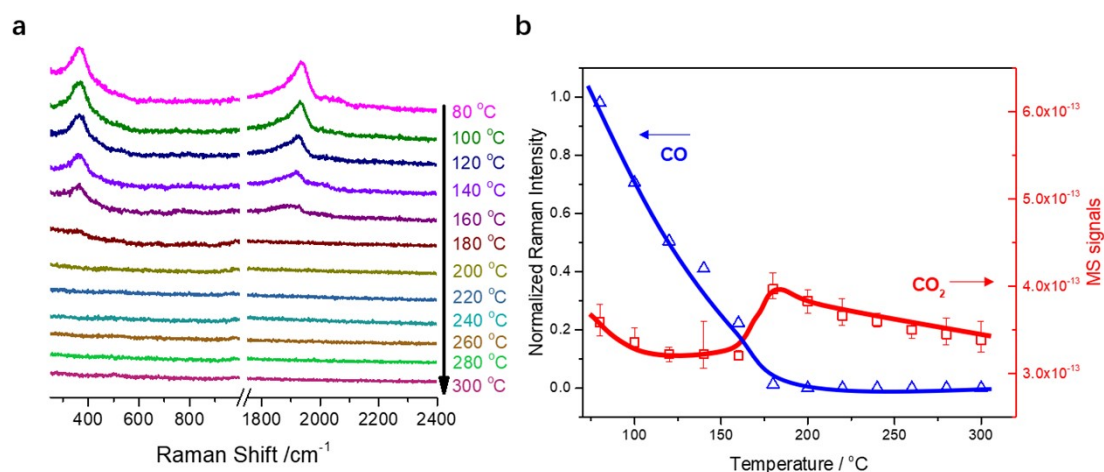
As shown in Figures 2a and S5, the peak at ~364 cm<sup>-1</sup> shifts to ~353 cm<sup>-1</sup> during the <sup>13</sup>CO exchange experiment, leading to a shift ratio of 97.3% (353/364=97.0%). The theoretical shift ratio of the Pd-C stretch mode of CO adsorbed on Pd can be calculated according to the following equation:

$$r = \frac{v(\text{Pd} - {}^{13}\text{C})}{v(\text{Pd} - {}^{12}\text{C})} = \frac{\sqrt{m(\text{Pd}) + m({}^{13}\text{C})}}{\sqrt{m(\text{Pd}) * m({}^{13}\text{C})}} \bigg/ \frac{\sqrt{m(\text{Pd}) + m({}^{12}\text{C})}}{\sqrt{m(\text{Pd}) * m({}^{12}\text{C})}} = \frac{\sqrt{106 + 13}}{\sqrt{106 * 13}} = 96.5\%$$

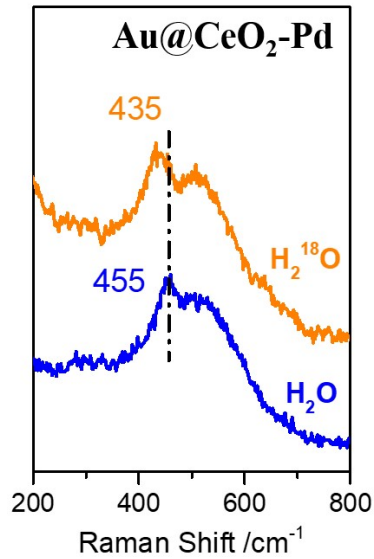
Therefore, it can be confirmed that the band at  $\sim 364 \text{ cm}^{-1}$  is attributed to the Pd-C band.

As shown in Figures 2a and S2, the band at  $\sim 1951 \text{ cm}^{-1}$  redshifts to  $\sim 1910 \text{ cm}^{-1}$  in  ${}^{13}\text{CO}$ , indicating a shift ratio of  $\sim 97.9\%$ . The theoretical shift ratio of the C $\equiv$ O stretch mode according to the following equation is  $\sim 97.8\%$ , which confirms the assignment of this band.

$$r = \frac{v(\text{O} - {}^{13}\text{C})}{v(\text{O} - {}^{12}\text{C})} = \frac{\sqrt{m(\text{O}) + m({}^{13}\text{C})}}{\sqrt{m(\text{O}) * m({}^{13}\text{C})}} \bigg/ \frac{\sqrt{m(\text{O}) + m({}^{12}\text{C})}}{\sqrt{m(\text{O}) * m({}^{12}\text{C})}} = \frac{\sqrt{16 + 13}}{\sqrt{16 * 13}} \bigg/ \frac{\sqrt{16}}{\sqrt{16}}$$



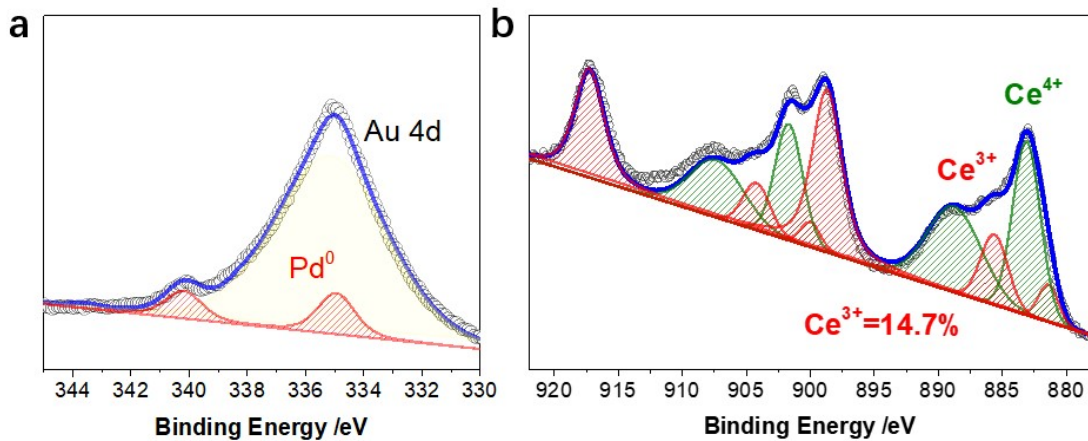
**Figure S6.** (a) In-situ SERS spectra of WGS over Au@Pd switched from CO to H<sub>2</sub>O; (b) The corresponding Raman intensities and MS signals of CO<sub>2</sub> as function of temperature during the in-situ SERS-MS study. The blue line shows the normalized CO Raman intensity, and the red line is the MS signal of CO<sub>2</sub>.



**Figure S7.** Comparison of the SERS spectra of Au@Pd-CeO<sub>2</sub> under H<sub>2</sub><sup>18</sup>O and H<sub>2</sub>O.

As shown in Figure S7, the peak at ~455 cm<sup>-1</sup> shifts to ~435 cm<sup>-1</sup> during the H<sub>2</sub><sup>18</sup>O exchange experiment, leading to a shift ratio of 97.3% (435/455=95.6%). The theoretical shift ratio of the Ce-O stretch mode can be calculated according to the following equation. Therefore, it can be confirmed that this band is attributed to the Ce-O band.

$$r = \frac{v(\text{Ce} - ^{18}\text{O})}{v(\text{Ce} - ^{16}\text{O})} = \frac{\sqrt{m(\text{Ce}) + m(^{18}\text{O})}}{\sqrt{m(\text{Ce}) * m(^{18}\text{O})}} \bigg/ \frac{\sqrt{m(\text{Ce}) + m(^{16}\text{O})}}{\sqrt{m(\text{Ce}) * m(^{16}\text{O})}} = \frac{\sqrt{140 + 18}}{\sqrt{140 * 18}} = 94.9\%$$



**Figure S8.** XPS spectra of (a) Pd 3d and (b) Ce 3d in Au@Pd-CeO<sub>2</sub> after WGSR.



## References

1. L. Artiglia, F. Orlando, K. Roy, R. Kopelent, O. Safonova, M. Nachtegaal, T. Huthwelker and J. A. van Bokhoven, *J. Phys. Chem. Lett.*, **2017**, *8*, 102-108.
2. X. Ye, H. Wang, Y. Lin, X. Liu, L. Cao, J. Gu and J. Lu, *Nano Res.*, **2019**, *12*, 1401-1409.
3. F. Zhang, P. Wang, J. Koberstein, S. Khalid and S.-W. Chan, *Surf. Surf. Sci.*, **2004**, *563*, 74-82.