Electronic Supplementary Information (ESI)

Understanding the strain effect of Au@Pd nanocatalysts by in situ surface-enhanced Raman spectroscopy

Jie Wei,[a] Yu-Jin Zhang,[a] Si-Na Qin,[a] Wei-Min Yang,[b] Hua Zhang,*[a] Zhi-Lin Yang,*[b] Zhong-Qun Tian[a] and Jian-Feng Li*[ab]

[a]MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, State Key Laboratory of Physical Chemistry of Solid Surfaces, *i*ChEM, College of Chemistry and Chemical Engineering, College of Materials, Xiamen University, Xiamen 361005, China.

[b]Department of Physics, Xiamen University, Xiamen 361005, China

*Corresponding authors, E-mail: Li@xmu.edu.cn (J. F. Li), zlyang@xmu.edu.cn (Z. L. Yang), zhanghua@xmu.edu.cn (H. Zhang).

Experimental details

Synthesis of Au nanoparticles. The Au nanoparticles were synthesized according to published procedures.[1] Typically, 0.2 g $HAuCl_4 \cdot 3H_2O$ were dissolved in 20 mL oleylamine (OAm). After cooling to 10 ^oC, a mixed solution containing 0.5 mmol of *tert*-butylamine-borane complex (TBAB), tetralin (2 mL), and OAm (2 mL) was injected into the precursor solution. After reaction for 2 h, the mixtures were centrifuged and washed with ethanol for several times. The obtained solid was Au nanocatalysts, which was then dispersed in toluene or hexane for further experiments.

Synthesis of Pd nanoparticles. Pd nanoparticles were synthesized according to published procedures.[2] 150 mg of $Pd(acac)_2$ was mixed with 30 mL OAm in nitrogen atmosphere. The mixed solution was heated to 60°C in 20 min. Then, 600 mg of BTAB in 3 mL OAm was injected into solution. The temperature was raised to 90 °C and kept at this temperature for 60 min. After cooling down to room temperature, the Pd nanoparticles were collected by centrifugation, washed with ethanol, and redispersed in toluene or hexane.

Synthesis of Au@Pd nanoparticles. Typically, 2 mL of the as-prepared Au nanoparticles dispersion was centrifuged and washed with ethanol for several times. Then it was dispersed in 2 mL hexane, followed by the addition of 10 mL of OAm containing 19.6 mg of $Pd(acac)_2$. The solution was then heated to 180 °C at a heating rate of 10 $°C\ min^{-1}$, and kept for 1 h. After cooling down to room temperature, the mixtures were washed with ethanol for several times. The product was dispersed in toluene or hexane for further experiments. The Au@Pd catalysts with different shell thickness were synthesized by the same procedure except that the volumes of Au nanoparticles were changed to 8 mL, 4 mL, 1 mL, and 0.5 mL.

Synthesis of SHINs. SHINs with 55 nm Au cores were synthesized according to our previously reported method.[3, 4]

Au/SiO_2 substrate. A Cr/Au (5/150 nm) film was deposited via electron beam evaporation onto a clean Si. After that, a 2 nm SiO_2 layer was coated on the as-prepared Au film via atomic layer deposition (ALD).

Langmuir–Blodgett (LB) film preparation. Au, Pd, and Au@Pd nanoparticles were dispersed in the mixture of toluene and hexane (volume ratio of 1:1) with a concentration of 5 $mg \cdot mL^{-1}$. The solution was slowly dropped onto water in a LB trough. After evaporation of the toluene and hexane for 30 minutes, the film was compressed until a surface pressure of 20–25 $mN \cdot m^{-1}$ was achieved. The resulting film was aged for 30 minutes and then transferred onto the Au/SiO_2 substrate, forming the nanocatalysts/Au/SiO_2/ substrate.

Fabrication of the SHINERS-gap configuration. 1.5 mL Au SHINs was washed twice with Millio-Q water by centrifugation. Then, the solution was dispersed in 500 μL of a mixture of water and ethanol (volume ratio of 1:2). 5 μL of the solution was dropped on the top of the nanocatalysts/Au/SiO_2/ substrate.

3D-FDTD simulations

In this work, the relevant simulation was based on the finite-difference time-domain (FDTD) methods using Lumerical's 3D-FDTD solutions software. A 2 nm thick SiO_2 was placed on the gold substrate, and then a layer of close-packed nanocatalysts with 4.3 nm Au cores and 1.2 nm Pd shells was placed on it. SHINs with 55 nm Au cores, 2 nm silica shells were placed on the top. The perfectly matched layer (PML) boundary conditions were applied in the all boundaries. Excitation light with a wavelength of 638 nm and a 0.5 nm cell mesh were used.

Catalytic performance

4 mL Au@Pd-5ML was purified several times by centrifugation with hexane and ethanol (volume ratio of 1:5) and was dropwise added to a suspension containing 100

mg SiO_2 under vigorously stirring. After stirring for 10 hours, the catalyst was collected by centrifugation and washed with ethanol twice. The catalysts were then dried in an oven allowed to dry before applied to catalytic tests. Other Au@Pd catalysts were prepared with the same number of particles on SiO_2 carrier. Pd catalysts were prepared with the same loading amount as Au@Pd-5ML.

Solvent-free aerobic oxidation of benzyl alcohol using molecular O_2 was carried out in a batch-type reactor under mild conditions. 2.5 mL benzyl alcohol and 10 mg catalysts were added into a 25 mL three-necked glass flask equipped with a reflux condenser. The reactor was heated to 90 ^{o}C and bubbled by O_2 with ultrahigh purity at a flow rate of 10 mL min^{-1}. The reaction mixture was stirred at 1000 rpm and was analyzed by GC.

In situ SERS study

The SHINERS-gap configuration substrate was placed in a Raman cell with reaction temperature and gas flow control (the cell was made in-house).[5] The samples were held at 30 ^{o}C under H_2 for 10 min to remove pre-adsorbed oxygen species and other contaminants. The In situ SERS experiments were carried out using a Jobin-Yvon Horiba Xplora confocal Raman system.

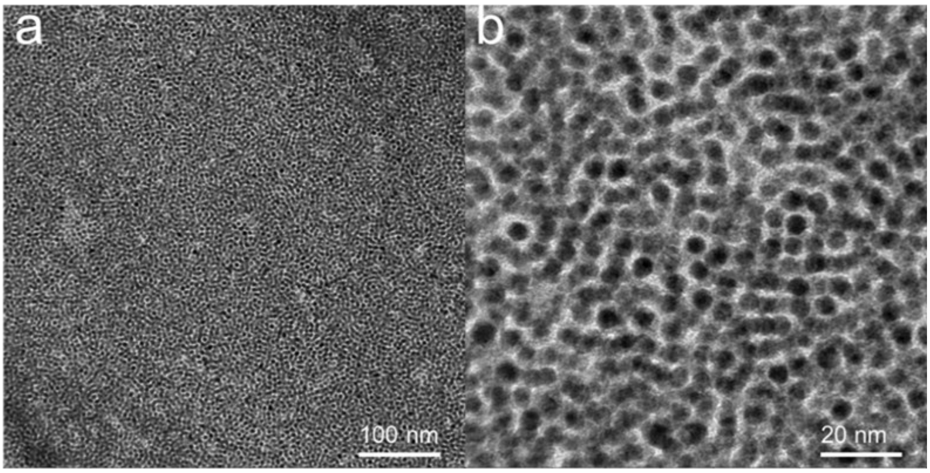

Fig. S1 TEM of a Au@Pd-5ML nanoparticle monolayer prepared by the LB technique.

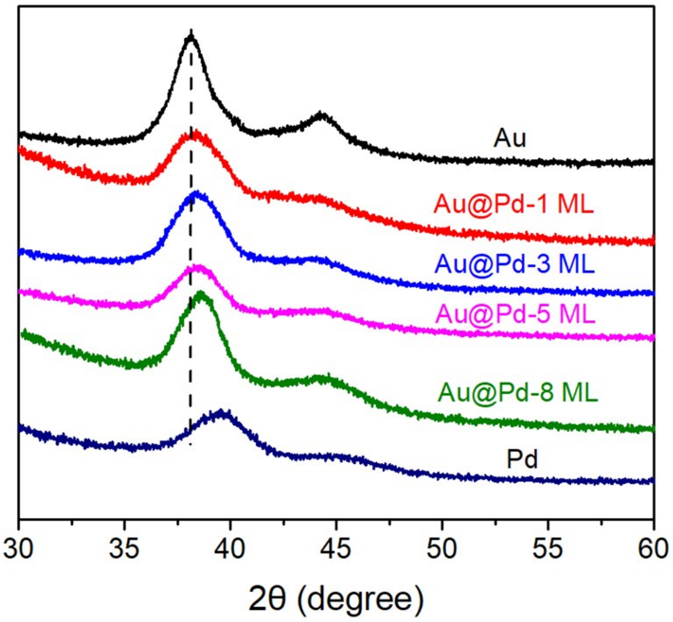

Fig. S2 XRD patterns of Au, Pd and Au@Pd nanocatalysts. The diffraction peaks of Au@Pd-1 ML almost locates at the same position of Au. With increased Pd shell thickness, the diffraction of Au@Pd shifts to higher values and gradually get close to that of Pd, indicating the tensile strain decreases with the increase of the Pd shell thickness.

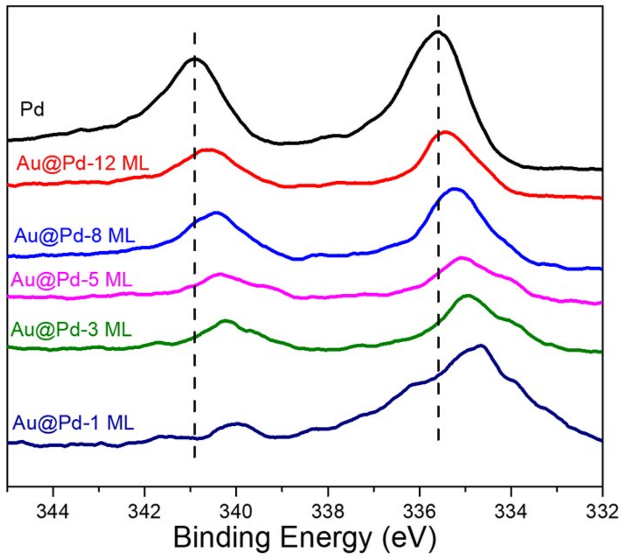

Fig. S3 XPS spectra of Pd $3d_{3/2}$ and Pd $3d_{5/2}$ for Pd and Au@Pd nanocatalysts.

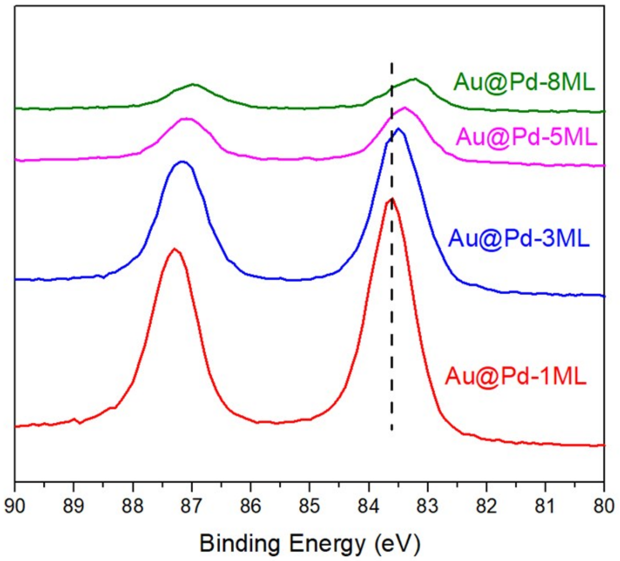

Fig. S4 XPS spectra of Au $4f_{7/2}$ and Au $4f_{5/2}$ of Au@Pd nanocatalysts.

The interactions between core Au and shell Pd were further illustrated by X-ray photoelectron spectroscopy (XPS). As shown in Fig. S3, the peaks at 340.0 and 334.7 eV was corresponded to Pd $3d_{3/2}$ and Pd $3d_{5/2}$ peaks of Pd nanoparticles, respectively. The Pd $3d_{3/2}$ peak of Au@Pd-1ML shift from 340.9 to 340.0 eV referred to Pd nanoparticles. Notably, the binding energies of Pd for Au@Pd-1ML are the lowest among all the catalysts, revealing that the Au core transferred the most d electron to Pd shell. Besides, the binding energies of Pd for Au@Pd approached to that of Pd with increasing Pd shell thickness, indicating that the d electron transfer from Au core to Pd shell was hindered with the increasement of Pd shell thickness. As shown in Fig. S4, the Au $4f_{5/2}$ and $4f_{7/2}$ peaks for the Au@Pd-1ML were 87.3 and 83.6 eV, respectively. The binding energies of Au for Au@Pd shifted to lower energies with increasing Pd shell thickness, indicating that Au core accepted s and p electrons from Pd shell. These results demonstrated that the electronic structure of the Pd atoms in the shell can be modified by Au core. In this case, Pd shell lost s and p electrons but accepted d electrons while Au core accepted s and p electrons but lost d electrons.

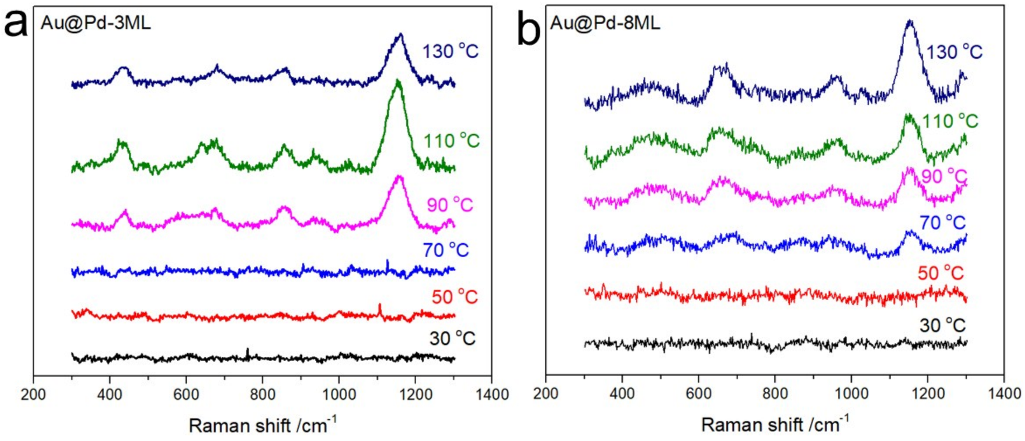

Fig. S5 In-situ SERS spectra of (a) Au@Pd-3ML and (b) Au@Pd-8ML nanocatalysts with different temperature in the oxygen using the SHINERS-gap configuration.

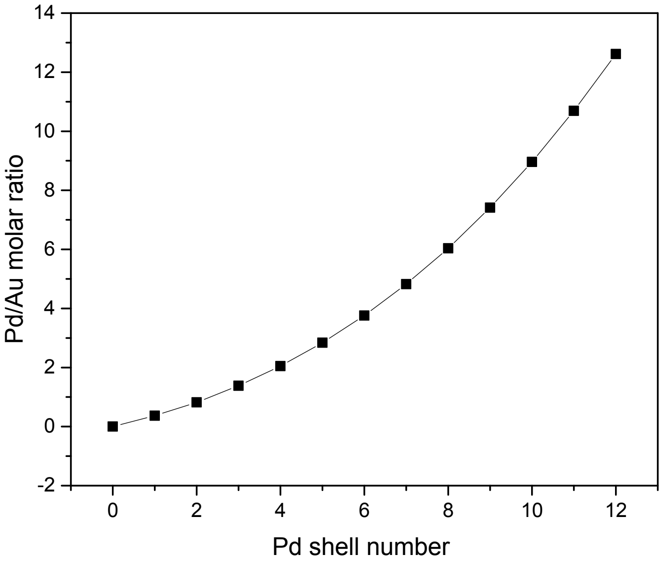

Fig. S6 Pd/Au molar ratio as a function of the amount of Pd shell number according to the ‘‘magic clusters model’’ based on a 4.3 nm Au core.

Table S1 Chemical composition of the catalysts according to the ‘‘magic clusters model’’ based on a 4.3 nm Au core, which contains 1980 Au atoms.[6]

Pd shell number (n)	Number of Pd atoms in shell (n_{atom})[a]	Total number of Pd atoms in shell (n_{atom})	Pd/Au mol ratio
1	724.5	724.5	0.366
2	904.5	1629	0.823
3	1104.5	2733.5	1.381
4	1324.5	4058	2.049
5	1564.5	5622.5	2.839
6	1824.5	7447	3.761
7	2104.5	9551.5	4.824
8	2404.5	11956	6.038
9	2724.5	14680.5	7.414
10	3064.5	17745	8.962
11	3424.5	21169.5	10.692
12	3804.5	24974	12.613

[a] $n_{atom} = 10 * (n + 7.5)^2 + 2$

Table S2 Pd shell number of Au@Pd nanoparticles calculated based on ICP-AES according to the ‘‘magic clusters model’’.

Catalyst	Au (wt%)	Pd (wt%)	Pd/Au molar ratio	Size calculated according to ICP-AES results	Size distribution according to TEM results
Au@Pd-1ML/SiO_2	1.6	0.5	0.58	5.0	4.8
Au@Pd-3ML/SiO_2	1.6	1.0	1.16	5.5	5.6
Au@Pd-5ML/SiO_2	1.7	2.0	2.18	6.2	6.6
Au@Pd-8ML/SiO_2	1.5	3.9	4.81	7.5	8.0
Au@Pd-12ML/SiO_2	1.5	7.6	9.38	8.9	9.7

Table S3 Catalytic results of the selective oxidation of benzyl alcohol on Au, Pd and Au@Pd nancatalysts.

Samples	Time (h)	Conversion (%)	Selectivity (%)			
			Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate
Pd	1	1.0	4.6	95.4	0.00	0.00
	8	8.2	4.7	93.0	2.3	0.1
Au@Pd-1ML	1	1.2	0.9	88.5	6.7	3.9
	8	6.9	3.2	86.8	5.3	4.7
Au@Pd-3ML	1	3.3	0.9	97.7	0.5	1.0
	8	15	2.5	94.4	1.4	1.8
Au@Pd-5ML	1	9.5	2.0	93.0	2.6	2.3
	8	63.8	1.1	88.1	2.6	8.2
Au@Pd-8ML	1	4.3	0.6	94.4	0.8	4.2
	8	33.2	1.9	89.6	5.4	3.1
Au@Pd-12ML	1	2.5	0.7	94.6	0.8	3.9
	8	19.7	2.4	86.5	4.4	6.7

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