

# A Simple, Generalizable Synthesis of PdAu Bimetallic Catalysts with Single Atom Alloy

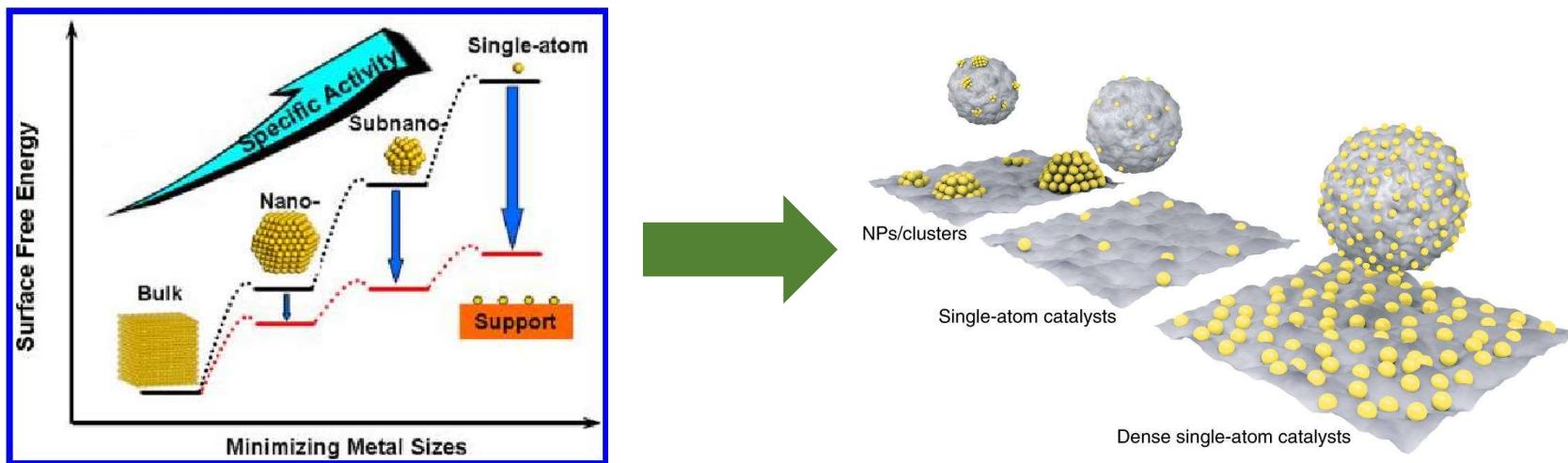
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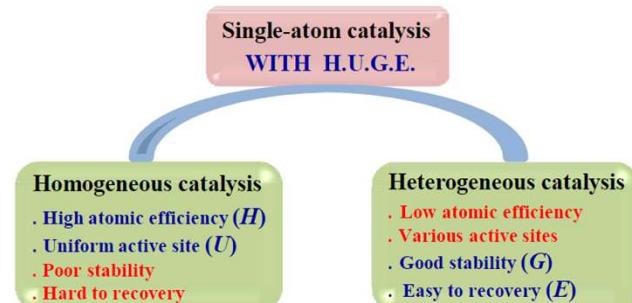
# Overview



- Atomically dispersed noble metal catalysts can increase the efficient resource utilization and cost savings;
- Vacuum physical deposition, galvanic displacement, sequential reduction, coprecipitation, et al.



Acc. Chem. Res. 2018, 51, 1054-1062;  
Fang Chen et al. Chinese Journal of Catalysis 39 (2018) 893–898;  
Nature Catalysis volume 2, pages590–602(2019);  
M. F. Stephanopoulos et al, Annu. Rev. Chem. Biomol. Eng. 2012. 3: 545-74.



# Overview

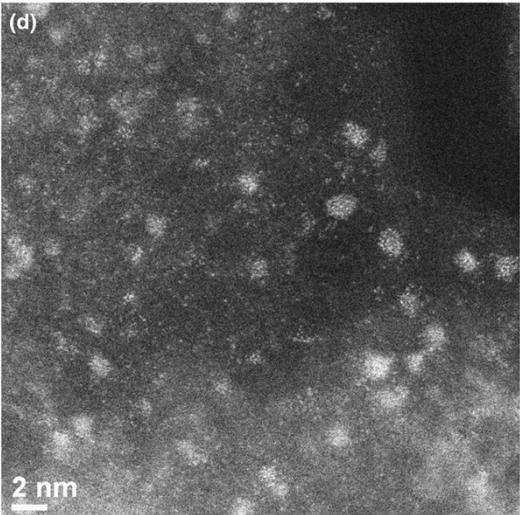


Fig. 2 HRTEM images (d) high magnification image of Au/KBB

## RESEARCH

### CATALYSIS

## Synthesis of ultrasmall, homogeneously alloyed, bimetallic nanoparticles on silica supports

A. Wong,<sup>1</sup> Q. Liu,<sup>1</sup> S. Griffin,<sup>1</sup> A. Nicholls,<sup>2</sup> J. R. Regalbuto<sup>1\*</sup>

Supported nanoparticles containing more than one metal have a variety of applications in sensing, catalysis, and biomedicine. Common synthesis techniques for this type of material often result in large, unalloyed nanoparticles that lack the interactions between the two metals that give the particles their desired characteristics. We demonstrate a relatively simple, effective, generalizable method to produce highly dispersed, well-alloyed bimetallic nanoparticles. Ten permutations of noble and base metals (platinum, palladium, copper, nickel, and cobalt) were synthesized with average particle sizes from 0.9 to 1.4 nanometers, with tight size distributions. High-resolution imaging and x-ray analysis confirmed the homogeneity of alloying in these ultrasmall nanoparticles.

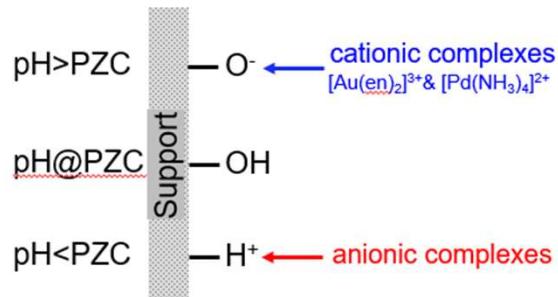
Table 2. Average particle sizes of bimetallic NPs. STEM sizes are number-average diameters; XRD sizes are from the Scherrer equation.

	co-SEA STEM (nm)	IMP XRD (nm)
Pt-Pd	1.0 ± 0.2	9.4
Pt-Cu	1.2 ± 0.3	2.8*
Pt-Ni	1.1 ± 0.3	6.9
Pt-Co	0.94 ± 0.3	4.2
Cu-Co	1.3 ± 0.3	7.3
Cu-Ni	1.1 ± 0.3	14
Ni-Co	1.4 ± 0.3	15.0*
Pd-Ni	1.1 ± 0.2	6.4
Pd-Co	1.0 ± 0.2	7.3
Pd-Cu	1.1 ± 0.2	14.5

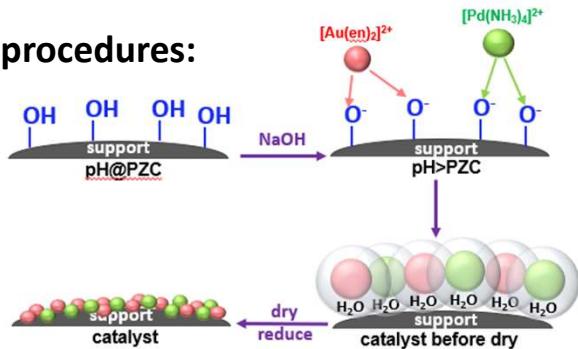
\*2.8 nm is an average of three replicates (3.7, 2.5, and 2.3 nm); 15 is an average of 15.9, 15.2, and 13.9 nm.

# Introduction

SEA mechanism:



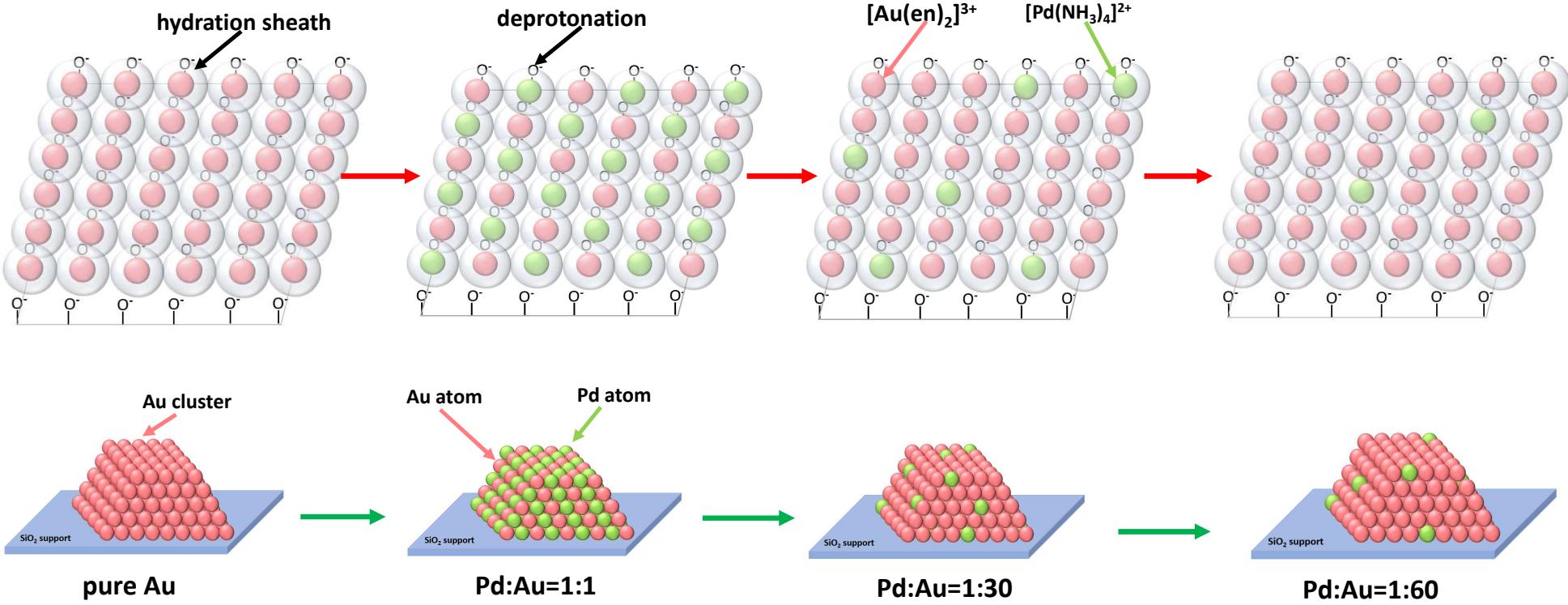
co-SEA procedures:



- ❖ Support surface charged by changing solution pH
- ❖ Adsorb oppositively charged metal precursor(s)
- ❖ Strong metal-support interaction
- ❖ Ultra-small particles

- Homogeneous alloys with high dispersion and ultrasmall nanoparticles can be obtained via co-SEA.

# Part I- Catalysts Synthesis



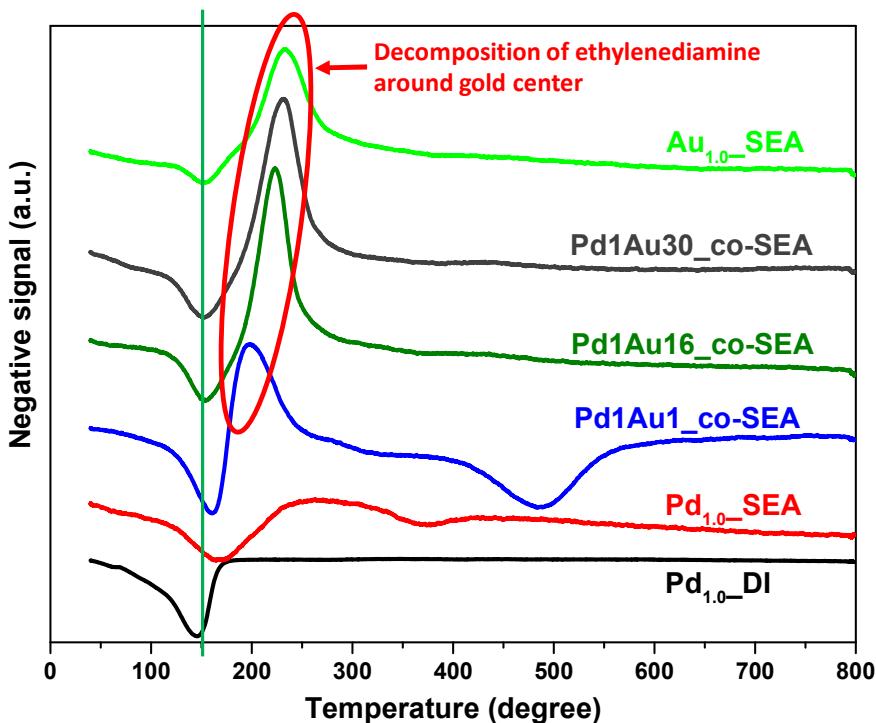
- PdAu catalysts with diluted palladium can be achieved by controlling the concentration of palladium precursor in the co-SEA synthesis process.

# Part I- Catalysts Synthesis

Catalysts	Mass loading (%)		Actual atomic ratio	Nominal atomic ratio
	Pd	Au	Pd:Au	Pd:Au
Pd <sub>1</sub> Au <sub>0.79</sub> _co-SEA	1.54	2.2	1:0.8	1:1
Pd <sub>1</sub> Au <sub>4.4</sub> _co-SEA	0.28	2.3	1:4.4	1:5
Pd <sub>1</sub> Au <sub>12.4</sub> _co-SEA	0.10	2.3	1:12.4	1:15
Pd <sub>1</sub> Au <sub>28</sub> _co-SEA	0.047	2.4	1:28	1:30
Pd <sub>1</sub> Au <sub>38</sub> _co-SEA	0.031	2.2	1:38	1:45
Pd <sub>1</sub> Au <sub>53</sub> _co-SEA	0.024	2.3	1:53	1:60
Pd <sub>1</sub> Au <sub>81</sub> _co-SEA	0.014	2.2	1:81	1:75
Pd <sub>1</sub> Au <sub>95</sub> _co-SEA	0.013	2.3	1:95	1:120
Au <sub>2.2</sub> _SEA	---	2.2	---	---
Pd <sub>1.0</sub> _SEA	0.97	---	---	---
Pd <sub>0.01</sub> _SEA	0.01	---	---	---
Pd <sub>1.0</sub> _DI	0.97	---	---	---
Pd <sub>1</sub> Au <sub>1</sub> _co-DI	0.88	1.45	---	---
Pd <sub>1</sub> Au <sub>50</sub> _co-DI	0.024	2.32	1:50	1:50

# Part II- Catalysts Characterization

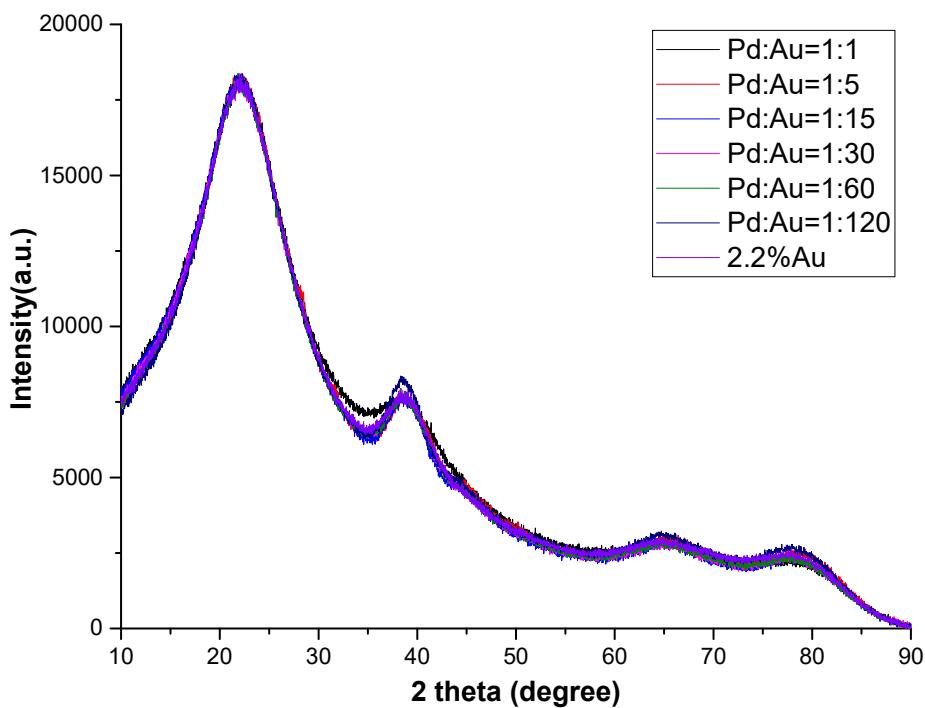
## - Temperature programmed reduction



- Monometallic Pd catalyst by SEA method showed a broader reduction peak at a higher temperature, indicating a stronger metal-support interaction compared with DI sample;
- The reduction temperature for bimetallic catalysts is between monometallic ones;
- Palladium lowers the decomposition temperature of ethylenediamine around gold center.

# Part II- Catalysts Characterization

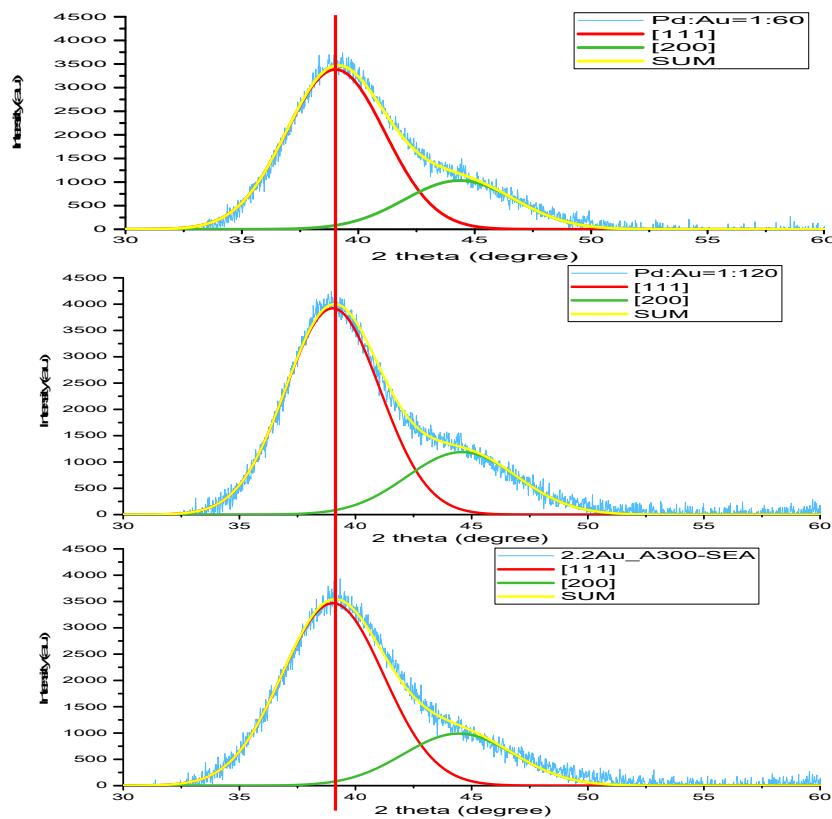
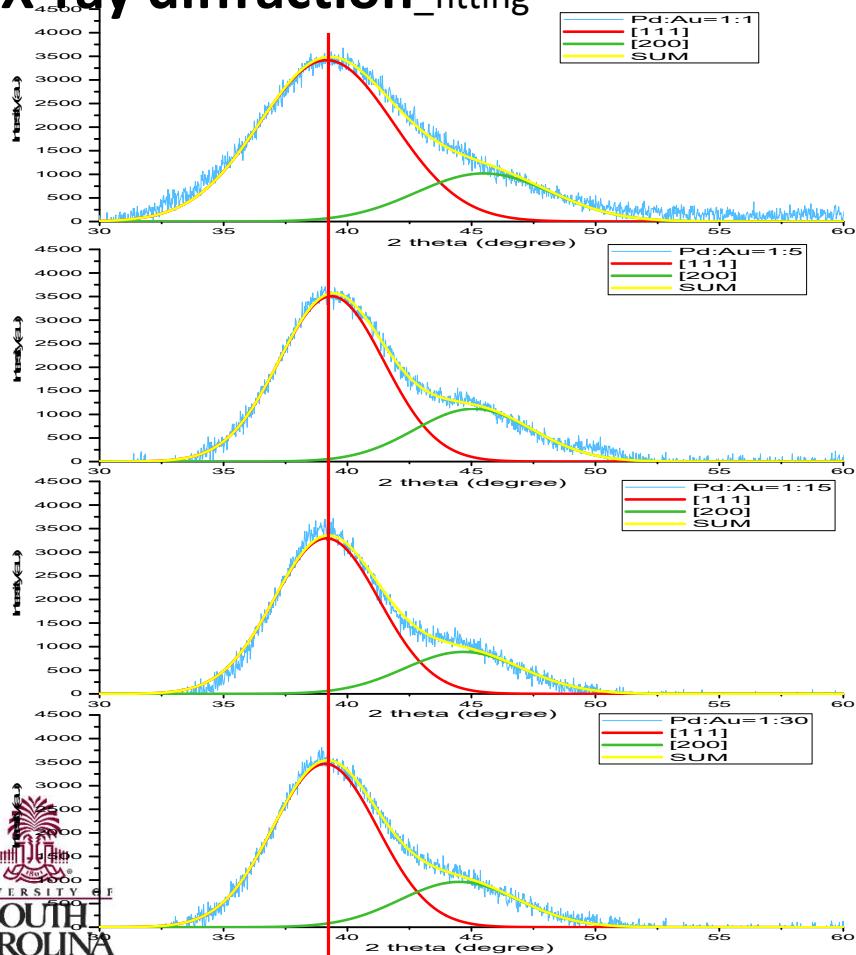
## - X-ray diffraction



- PdAu catalysts by co-SEA method showed broad peaks;
- Pd:Au =1:5 to 1:120 samples showed almost the same peak to the pure gold sample, while Pd:Au=1:1 displayed a much broader peak.

# Part II- Catalysts Characterization

## - X-ray diffraction\_fitting



- Support-subtracted patterns could all be fitted with a single set of FCC peaks

# Part II- Catalysts Characterization

## - Particle size from XRD\_particle size

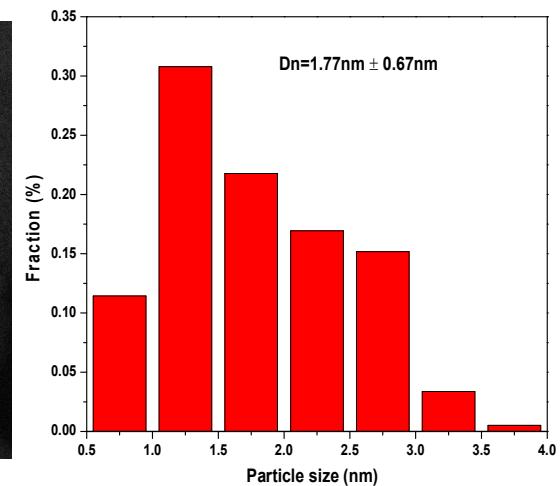
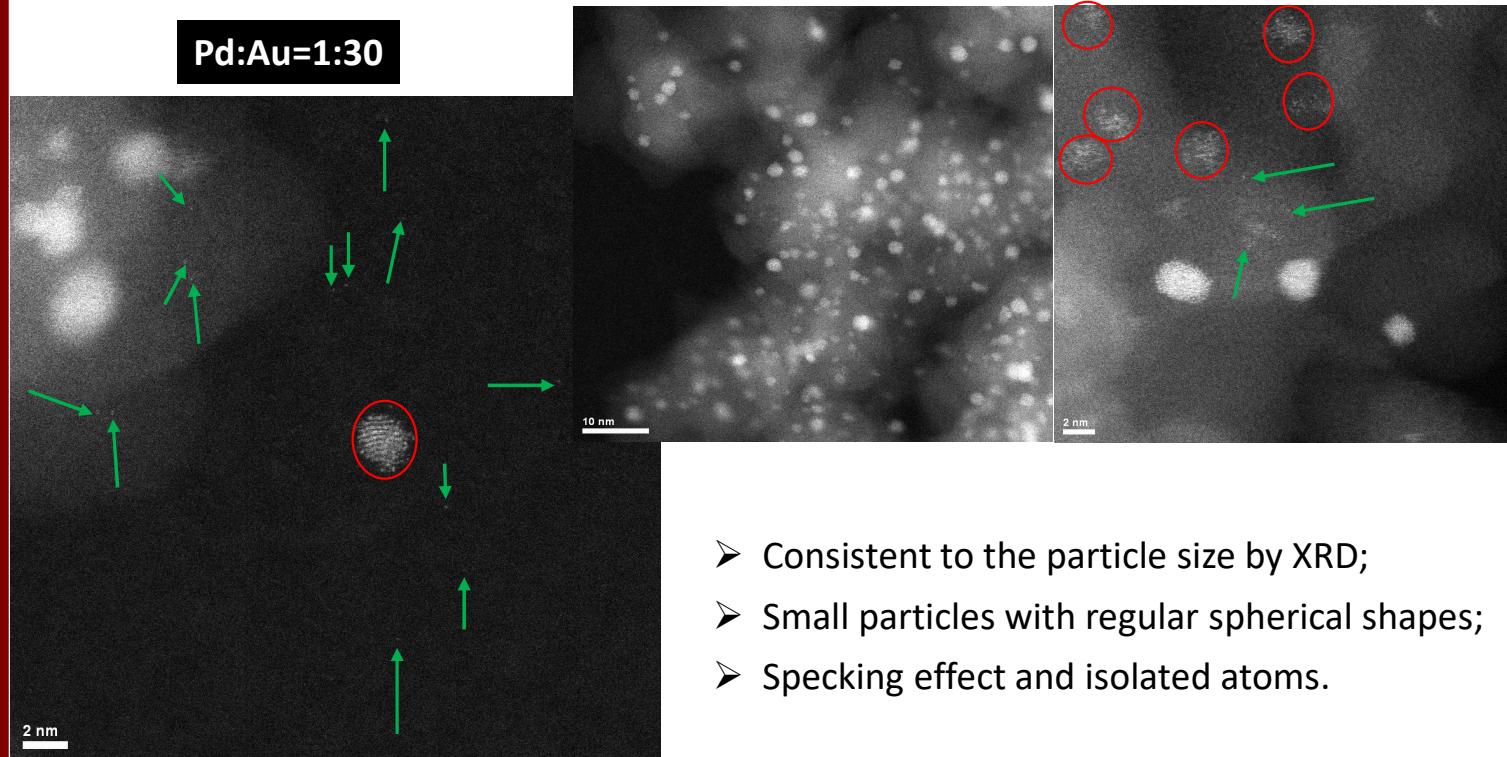
catalysts	peak position		particle size
	[111]	[200]	
Pd:Au=1:1	39.15	45.49	1.4
Pd:Au=1:5	38.52	45.16	1.7
Pd:Au=1:15	38.32	44.74	1.7
Pd:Au=1:30	38.27	44.57	1.7
Pd:Au=1:60	38.19	44.42	1.7
Pd:Au=1:120	38.19	44.65	1.7
2.2%Au/A300_SEA	38.19	44.39	1.7
Au standard	38.19	44.39	
Pd standard	40.12	46.66	

- The peak position obey Vegard's law, indicating homogenous alloy;
- Gold contribute the most the particle size;
- Pd:Au=1:1 sample showed smaller particle size. It may be because the loading of palladium is high enough to break the gold clusters on 1:1 sample.

# Part II- Catalysts Characterization

## - STEM

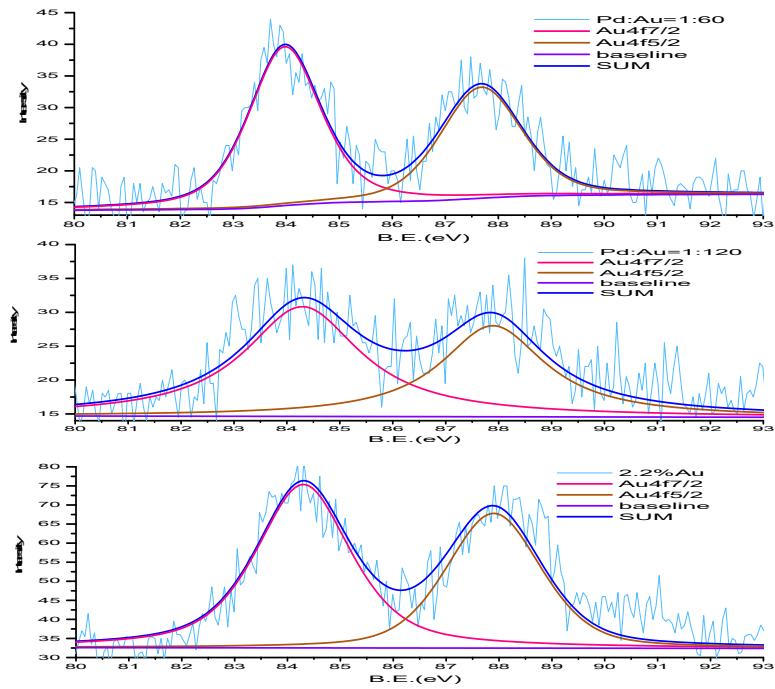
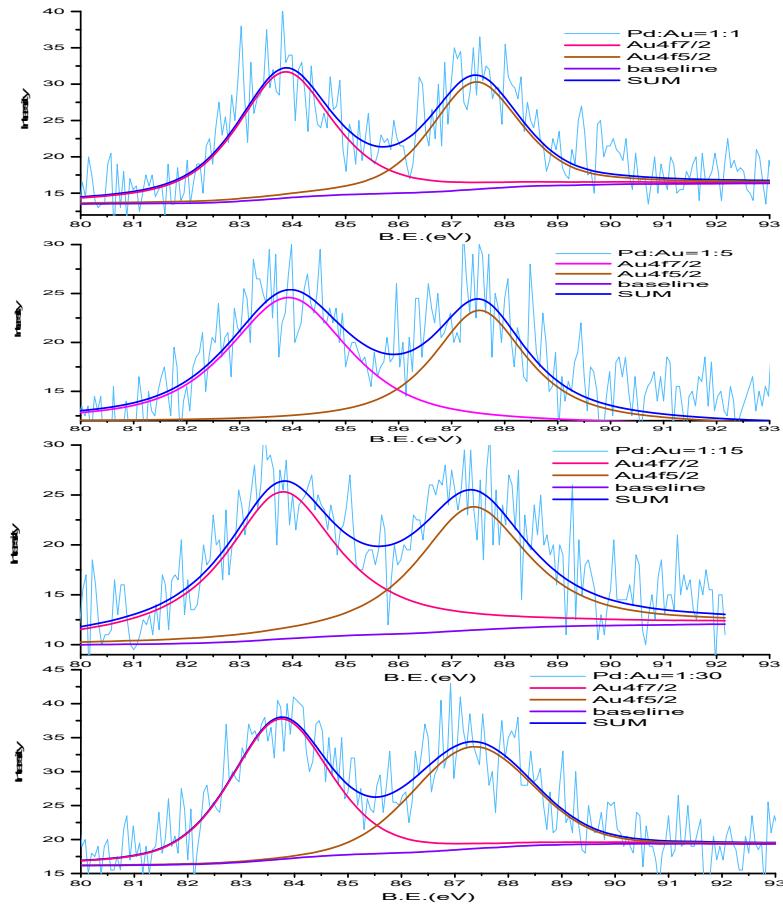
Pd:Au=1:30



- Consistent to the particle size by XRD;
- Small particles with regular spherical shapes;
- Specking effect and isolated atoms.

# Part II- Catalysts Characterization

## - *In-situ* XPS \_Au4f



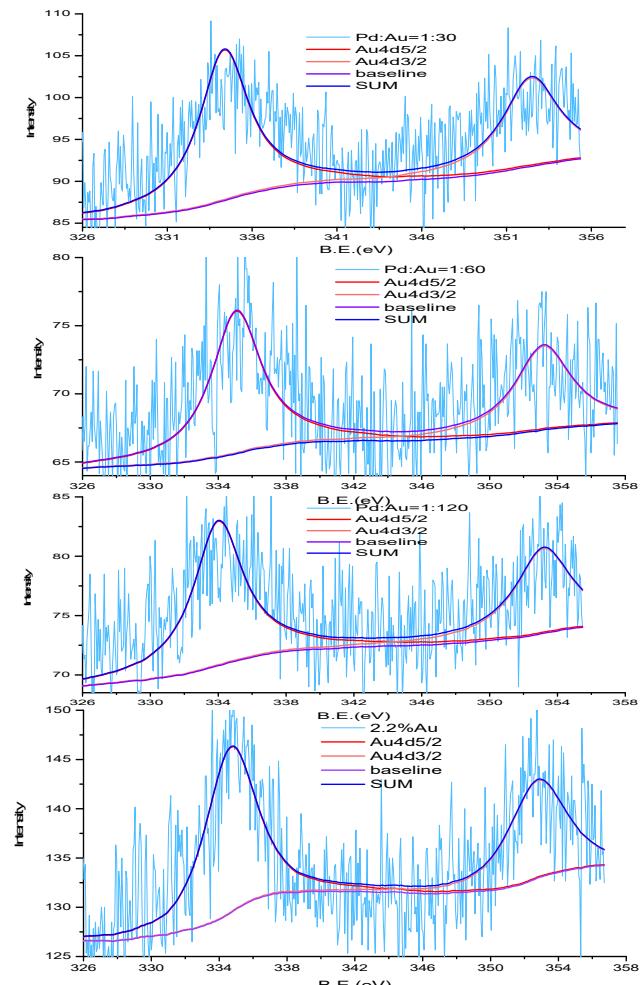
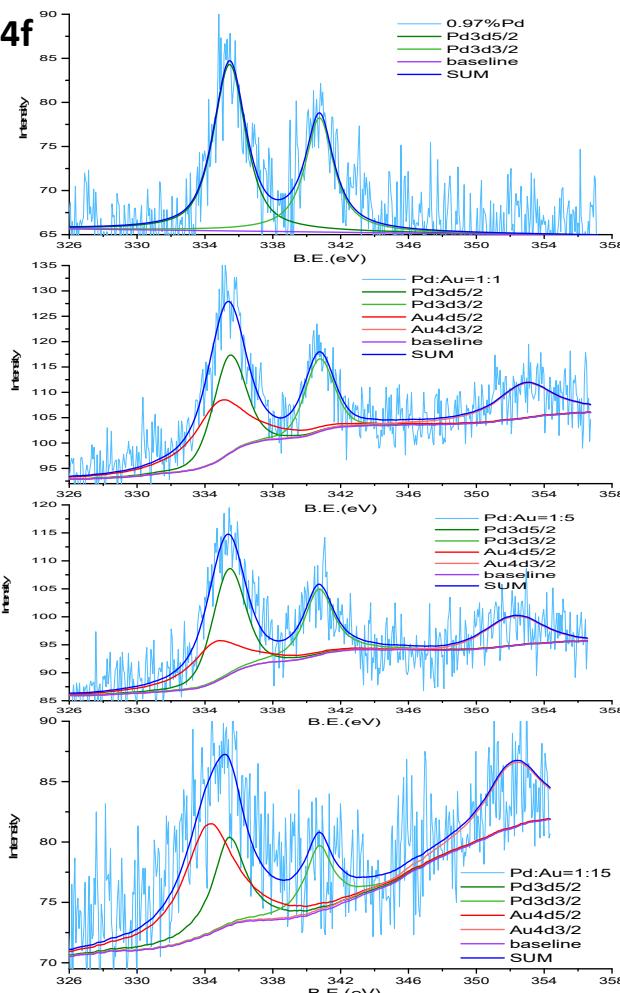
# Part II- Catalysts Characterization

## - *In-situ* XPS \_ Pd3d & Au4f

Standard binding energy

Pd	B.E.(ev)
Pd3d5/2	335.2
Pd3d3/2	340.5

Au	B.E.(ev)
Au4d5/2	335.1
Au4d3/2	353.2



# Part II- Catalysts Characterization

## - *In-situ* XPS \_peak parameter and qualification analysis

Sample	Binding energy of core electrons (eV)			Atomic ratio by XPS	
	Au4f7/2	Pd3d5/2	Au4d5/2	Pd:Au (increased)	Si/Au(nominal)
0.97%Pd	---	335.45	---	No Au detected	---
Pd:Au=1:1	83.76	335.44	334.82	1:0.67	164(143)
Pd:Au=1:5	83.78	335.41	334.57	1:0.87	146(138)
Pd:Au=1:15	83.80	335.43	334.22	1: 1.4	172(139)
Pd:Au=1:30	83.81	ND	334.34		170(133)
Pd:Au=1:60	84.02	ND	335.25		211(139)
Pd:Au=1:120	84.26	ND	334.41		193(139)
2.2%Au	84.30	ND	334.68		226(146)

\*ND: no detected or overlapped with Au4d peak and hardly distinguish

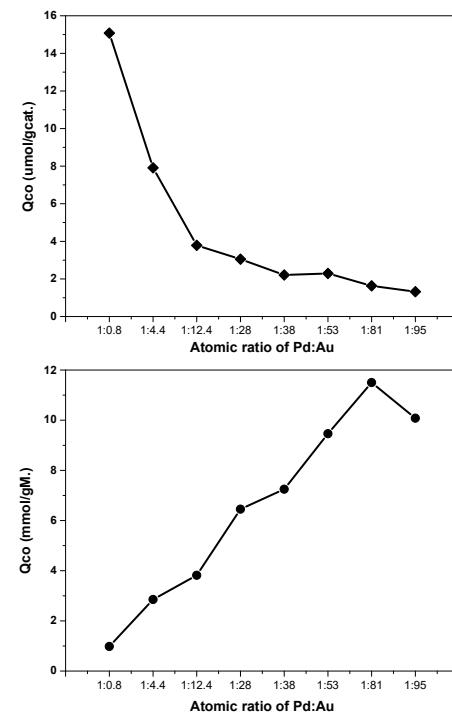
- One Pd specie suggests homogenous alloy of PdAu;
- Au4f peak of PdAu DLA catalysts shifts to lower binding energy, demonstrating electron transfer occurred on Au;
- XPS derived a higher ratios of Pd/Au. The lower Pd added, the greater the deviation, which seems the microstructure of PdAu alloy can be tuned by the Pd/Au ratio.
- It is reported that with more Au, PdAu catalyst is prone to form Au-rich surface clusters\*. Fixed Au loading, as palladium is diluted, relatively more palladium is on the surface.

\*X. Yan et al./Journal of Catalysis 291 (2012)36-43.

# Part II- Catalysts Characterization

## - CO chemisorption

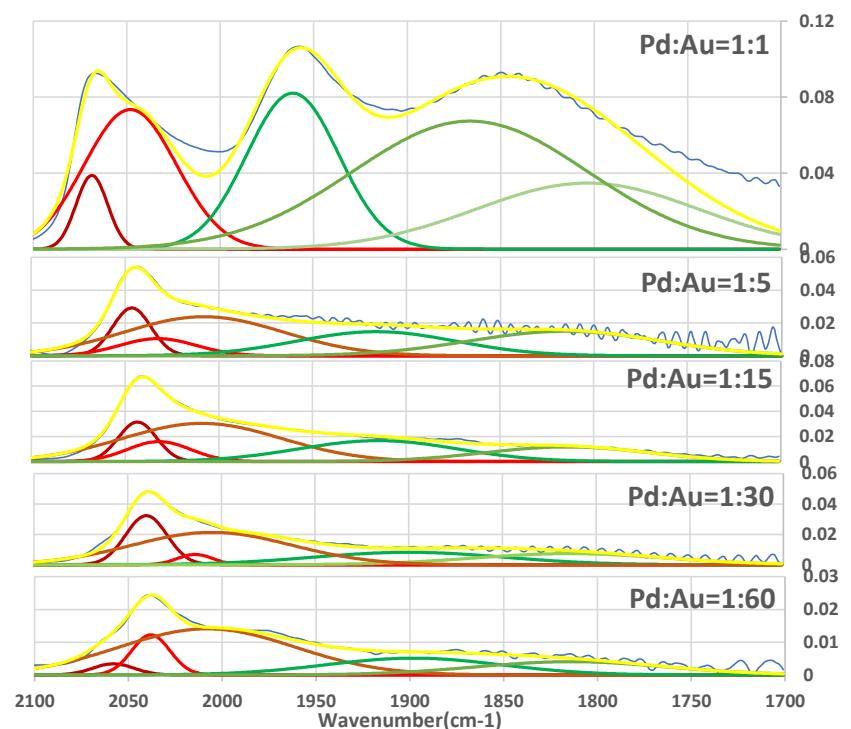
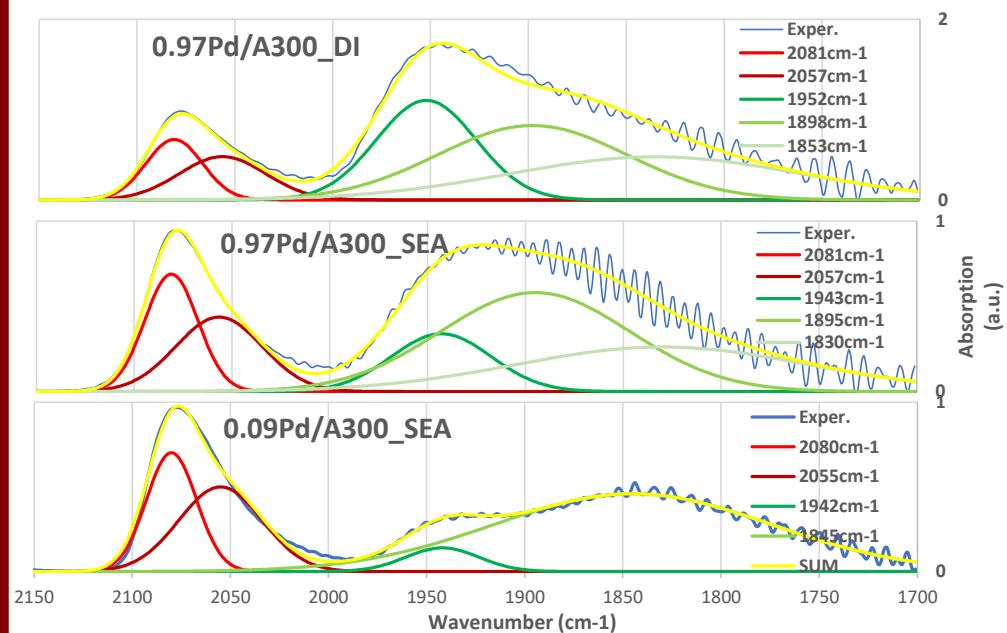
Sample (weight percent of Pd )	CO (umol/g <sub>cat.</sub> )	CO (mmol/g <sub>M</sub> )	SA (m <sup>2</sup> /g <sub>M</sub> )
Pd-Au=1:1 (1.54%)	15.08	0.98	46.5
Pd-Au=1:5 (0.28%)	7.91	2.85	83.7
Pd-Au=1:15 (0.10%)	3.79	3.82	180.9
Pd-Au=1:30 (0.05%)	3.05	6.45	305.8
Pd-Au=1:45 (0.03%)	2.21	7.25	343.6
Pd-Au=1:60 (0.02%)	2.29	9.46	448.4
Pd-Au=1:75 (0.014%)	1.63	11.50	545.0
Pd-Au=1:120 (0.013%)	1.32	10.08	477.8



- More CO per gram palladium was obtained on lower ratio of Pd/Au, meaning a higher surface palladium concentration. The declined CO amount on Pd/Au=1:120 is due to the extremely low palladium on the surface;
- Increased metallic palladium surface area signified a larger number of palladium atoms have access to reactants;

# Part II- Catalysts Characterization

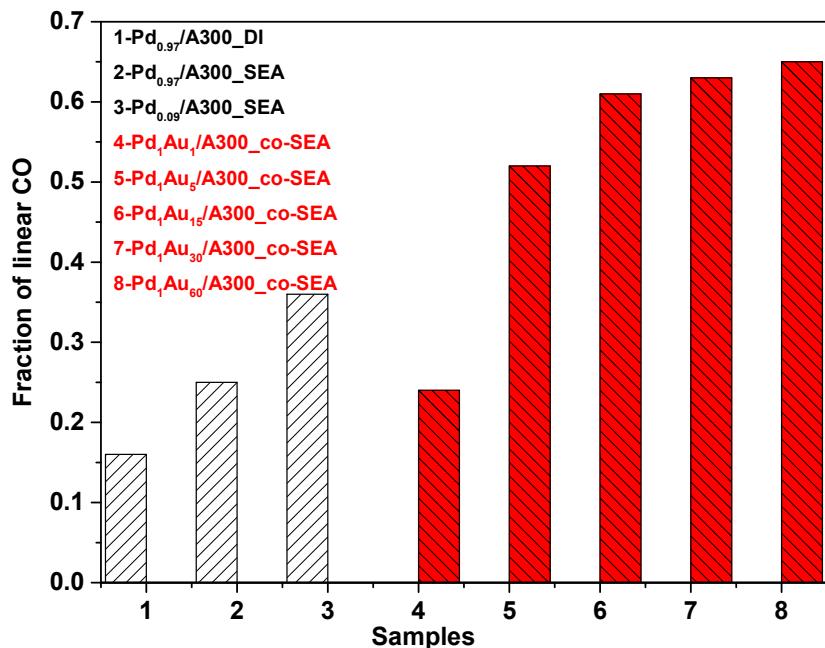
## --CO adsorbed FTIR patterns



- 2080, 2056cm<sup>-1</sup>-linear CO on low coordinated Pd (corners, edges, steps or kinks);
- 1950cm<sup>-1</sup>-bridging CO with twofold on Pd[110], Pd[100];
- 1895, 1845cm<sup>-1</sup>-bridging CO with threefold on Pd[111].

# Part II- Catalysts Characterization

## --Fraction of linearly/bridging adsorbed CO



- Compared with DI sample, SEA showed higher ratio of linearly adsorbed CO;
- Lower loading of Pd sample also showed higher fraction of bridging adsorbed CO;
- In case of bimetallic NPs with constant content of gold, diluting the loading of Pd, the ratio of linearly adsorbed CO increased significantly, suggesting isolated palladium atoms can be obtained by co-SEA.

# Part II- Catalysts Characterization

## - *Evaluation* Partial oxidation of 1-phenylethanol to acetophenone

50ml pure phenylethanol, 50 psig of O<sub>2</sub>, T=160 °C, stirring rate=400 rpm

Catalyst	Pd (10 <sup>-3</sup> mol/L)	Au (10 <sup>-3</sup> mol/L)	TOF <sub>total-metal</sub> (h <sup>-1</sup> )	TOF <sub>Pd</sub> (h <sup>-1</sup> )
Pd	19.4	0	0.5	0.5
Au	0	24.75	0.4	0.4 <sup>o</sup>
1:5 Pd:Au	3.2	20.4	5.2	31
1:14 Pd:Au	1.8	25.8	4.4	68
1:28 Pd:Au	1	25.8	31	833
1:53 Pd:Au	0.4	24.75	74	4654

- Little activity was observed on monometallic Pd or Au catalysts;
- As Pd is diluted into the Au cluster on SiO<sub>2</sub> support, the turnover frequency per total moles of metals or per moles of Pd increased by two to four orders of magnitude;
- This correlate with the increase of linearly adsorbed Pd in IR analysis.

# Part III- Conclusion and Future Work

## Conclusion:

- Ultrasmall nanoparticles with single atoms can be achieved by co-SEA method;
- Over PdAu catalysts with dilute palladium, there is electron transfer between Au and Pd;
- With diluting the loading of palladium, the fraction of single atoms increased.

## Future work

- Finish CO-FTIR on PdAu catalysts with even lower loading of palladium;
- Evaluate PdAu catalysts with more diluted Pd for the partial oxidation reaction.

# Thanks!!!

## Questions?