Discrete $Au_1(0)$ Stabilized by 15-Crown-5 for High-Efficiency Catalytic Reduction of Nitrophenol and Nitroaniline

Xing Shen,[a],[b] Kairui Liu,[a]*

(a) State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.

(b) University of Chinese Academy of Sciences, Beijing 100049, China.

* Correspondence: liukairui@163.com

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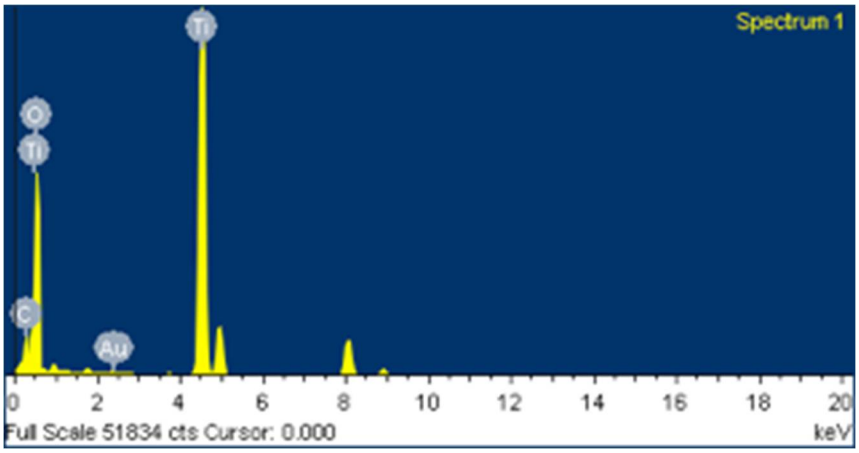


Element	Weight%	Atomic%
C K	6.35	13.93
O K	31.77	52.34
Ti K	61.12	33.63
Au L	0.76	0.10
Totals	100.00	

Figure S1. Energy Dispersive X-ray analysis

Spectrum processing:

Peaks possibly omitted: 0.931, 3.691, 5.415, 6.409, 6.949 keV

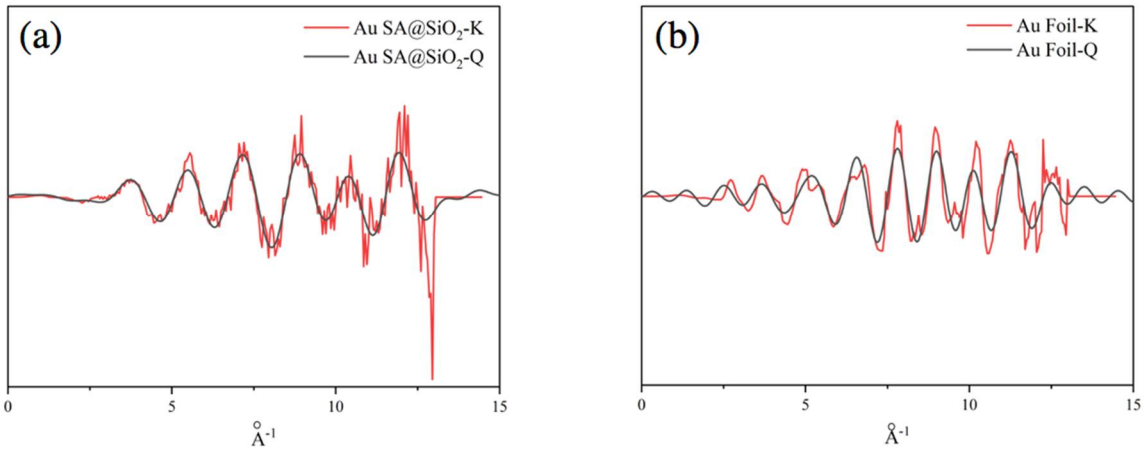
Quantitation method: Cliff Lorimer thin ratio section.

Processing option: All elements analyzed (Normalised)

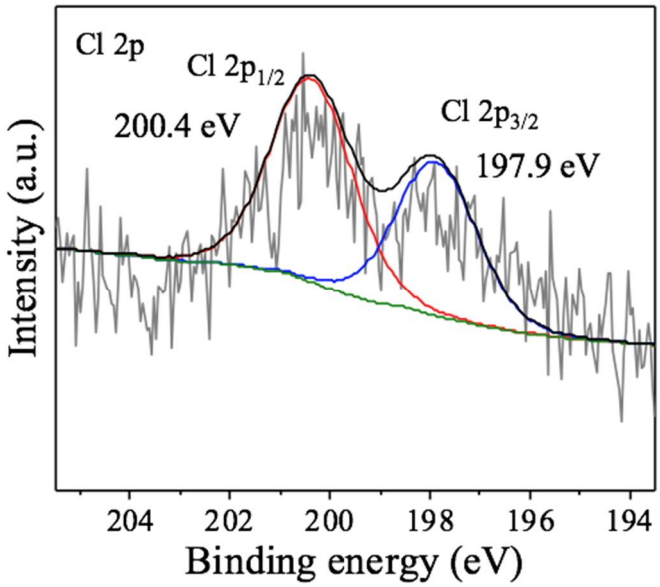
Number of iterations = 3

Standardless

Comparing the peak patterns of K space and Q space spectra, if the peak patterns are similar, it can be confirmed that the range of K space selected by Fourier transform to R space is reasonable (Figure S3). Figure S2 shows that the K space and Q space of Au@15-crown-5/SiO_2 and Au foil have good matching degree.



Firure S2. Comparison of K space and Q space of Au@15-crown-5/SiO_2 and Au foil: (a) Au@15-crown-5/SiO_2; (b) Au foil



Firure S3. XPS-Cl_{2p} spectra of 0.5 wt% Au_1@15-crown-5 catalyst

Table S1. Curve fit Parameters for Au K-edge EXAFS for Au@15-crown-5/SiO_2 Standard

Sample	Path	CN	$\sigma^2(10^{-3}Å)$	ΔE_0(eV)	R (Å)	*R*-factor
	Au-H	1.786 (±0.4)	-0.0105		1.544(±0.0092)	
Au SA@SiO_2	Au-O	2.000	0.0404	6.942	2.137(±0.1260)	0.02012
	Au-Cl	2.050(±1.3)	0.0018		2.261(±0.0048)	

S_0 was fixed as 0.71-0.82, ΔE_0 was refined as a global fit parameter. returning a value of (6.942 ± 0.0873) eV. Data ranges: $1.0 \le k \le 13$ Å^{-1}, $1.0 < R \le 3.0$ Å .The number of variable parameters is 9, out of a total of 11 independent data points. The distances for Au-O are from the crystal structure of Au_2O_3. The distances for Au-Cl are from the crystal structure of AuCl.

Table S2. Comparing catalytic activities to the 4-NP reduction by several catalysts

Catalyst	State of catalyst	Substrate	Catalyst	k/s^{-1}	K_{nor}/M($s^{-1}g^{-1}$)	TOF or TON /h^{-1}	conversion	Refs
Au–Pd/TiO_2	Bio-metal NPs	5×10^{-6} M	1.0 wt% catalyst Au 50% Pd 50 %	0.006a	Not mention	TOF: 366	30 ℃ 80%; Over 4 cycle 75%	[15]
eHA[a]@α-$Ni(OH)_2$-B	nanotubes	0.074 mM	0.0092 mg·mL^{-1}	1.458×10^{-2}	583.27	TOF: 4743	RT 6 min 100% Almost 100% After 11 cycle	[26]
eHA@α-$Ni(OH)_2$-B-1.5	nanotubes	0.074 mM	0.0092 mg·mL^{-1}	1.512×10^{-2}	604.67		RT 6 min 100% Almost 100% After 11 cycle	[26]
RGO[b]@AC/Pd	SACs	4-NP	Wt %=0. 292%			Up to TOF:602	RT 99 s	[29]
Pd_1/GDY[c]/G-1	SACs	10^{-4} M	2 mg Pd:0.151 wt %	3.45×10^{-3}		1762	RT 100% over 7 cyle	[30]

Pd_1/GDY/G	SACs	10^{-4}M	2mg Pd:0.855 wt %	0.016		Not mentioned	RT 100% over 7 cyle	[30]
Au/CB[d]	NPs	4-NP 50 mL, 0.5 mM	Au/CB 1.2% wt	0.0138		TOF 492.48	RT 5 min,99.9 % over 10cycle 89%	[31]
Au/CB	NPs	2-NP 50 mL, 0.5 mM	Au/CB 1.2% wt	0.0077		TOF 492.48	RT 5.5 min,90%	[31]
Au/CB	NPs	3-NP 50 mL, 0.5 mM	Au/CB 1.2% wt	0.0074	not mentioned	not mentioned	RT 4 min,90%	[31]
Ni-Pd/NrGO[e]	NPs	0.05 mM	0.000045 mmol	0.017	not mentioned	416.58	2.67 min 99.5%	[32]
Au/Cu-MgO	NCs	0.06 mM		Up to 0.33×10^{-3}	4.47	not mentioned		[33]
Ru/CNT[f]	Mixture of SACs and NPs(20:1)	4-NP 0.3 g/L 0.7 g/L 1 g/L	20 mg Ru:1 at %	0.031 0.037 0.046	2959.59 1791.3 1479.8	not mentioned	78 s,100%	[34]
Ru/CNT	Mixture of	4-NA	20 mg	0.064	6059.2	not	78 s,100%	[34]

	SACs and NPs(20:1)	0.3 g/L 0.7 g/L 1 g/L	Ru:1 at %	0.188 0.239	8987.53 7061.24	mentioned	30 s,100% 30 s,100%*	
Ru/CNT	Mixture of SACs and NPs(20:1)	2-NP 0.3 g/L 0.7 g/L 1 g/L	20 mg Ru:1 at %	0.027 0.052 0.102	2585.67 4962.56 5797.68	not mentioned	60 s,100% 30 s,100% 30 s,100%	[34]
BNNF$_g$-Cu	SACs	80 mL 10 ppm	10 mg	0.011	Not mentioned	690 mmol $g^{-1}h^{-1}$	100%, 5 min over 5 cycle	[35]
Au/MOF^h	SACs	1 mM	1.4 mg/mL Surface Au:1.0% wt	0.0415		TOF 34860	RT,2 min > 90%	[27]
Au/MOF	NPs	1 mM	1.4 mg/mL	0.0106		TOF 9780		[27]
Pt_1 /NMCW^i	SACs	3 mM	50 mg Catalyst Pt: 2.5 wt%	Up to 1.73×10^{-3}		TOF: 315	RT, 40 min ≈100%	[36]
Fe/PMS^j	SACs	50 mL 20 mg/L	0.05 g/L Fe	5.03×10^{-3}		TOF:362.4	Ph=6.0 RT 6 min, 99%	[37]
Pd-CP^k	nanoparticle	2 mL 20 mM	Pd: 0.000032 mmol	0.025	0.17 $min^{-1}mg^{-1}$	TOF: 6232.8	12 min:99.9 %	[38]

Pd-CNSP[k]	nanoparticle	2 mL 20 mM	Pd: 0.000047 mmol	0.072-0.054(8th cycle)	2.17 $min^{-1}mg^{-1}$	TOF: 50880	60 s:99.9% After 8 cycle conversion can still reach 98%	[38]
$CoMn_2O_4$/APTPOSS@FPS[l]	NPs	2-NA 0.2 μmol/mL	1.0 mg	not mentioned	not mentioned	not mentioned	RT 100 s,95%; 10th cycle conversion can still reach 90%	[14]
$CoMn_2O_4$/APTPOSS@FPS[l]	NPs	4-NP 0.2 μmol/mL	1.0 mg	1.83×10^{-2}	not mentioned	not mentioned	RT 100 s,95% 10th cycle conversion can still reach 80%	[14]
Ag/TP[m]	NPs	2-NP		1.23×10^{-3}		TOF 3974.4 TON 63720	16 min ≈93%	[39]
Ag/TP	NPs	4-NP		5.27×10^{-3}		TOF 230.76 TON 1152	6 min ≈98%	[39]

a: eHAs: etched halloysite nanotubes.

b: RGO: reduced graphene oxide; AC: amorphous carbon.

c: GDY/G: graphdiyne/graphene.

d: CB: carbon black

e: NrGO: nitrogen-doped reduced graphene oxide

f: CNT: carbon nano tube
g: BNNF: boron nitride nanofibers
h: MOF: Metal-OrganicFrameworks
i: NMCW: N-doped mesoporous carbon nanowires
j: PMS: peroxymonosulfate
k: CP: acid polymer; CNSP: phytic acid/thiourea polymer.
l: APTPOSS: octakis [3-(3-aminopropyltriethoxysilane) propyl] octasilsesquioxane; FPS: fibrous phosphosilicate
m: TP: taro powder

We calculated TOF based on the number of reaction substrates (e.g., 4-nitrophenol) converted by each gold atom per unit time.
TOF calculation process:

Figure 6b: TOF = $\frac{\mathbf{25\ ml\times(2\times10^{-4}\ mol/L)}}{\mathbf{2.265\times10^{-4}mol/L\times(2\times10^{-3})\ ml}}\times\frac{60}{30}$=22075;

25ml: The amount of 4-nitrophenol added;
2×10^{-4} mol/L: The concentration of 4-nitrophenol.
2.265×10^{-4} mol/L: The concentration of the catalyst.
2×10^{-3} ml: The amount of catalyst added.
30min: Reaction time

Figure 6c: $TON_{(Max)}$: $\frac{150ml\times(2\times10^{-4}mol/L)\times31\%}{2.265\times10^{-4}mol/L\times0.2\times10^{-3}}$ = 205298

150 ml: The amount of 4-nitrophenol added;
2×10^{-4}mol/L: The concentration of 4-nitrophenol.
2.265×10^{-4}mol/L: The concentration of the catalyst.
0.2×10^{-3}ml: The amount of catalyst added.
Figure 7:

TOF = $\frac{\mathbf{25\ ml\times(2\times10^{-4}\ mol/L)}}{\mathbf{2.265\times10^{-4}mol/L\times(2\times10^{-3})\ ml}}\times\frac{60}{50}$=13245;

TOF = $\frac{\mathbf{25\ ml\times(2\times10^{-4}\ mol/L)}}{\mathbf{2.265\times10^{-4}mol/L\times(2\times10^{-3})\ ml}}\times\frac{60}{60}$=11038;

TOF = $\frac{\mathbf{25\ ml\times(2\times10^{-4}\ mol/L)}}{\mathbf{2.265\times10^{-4}mol/L\times(2\times10^{-3})\ ml}}\times\frac{60}{65}$=10348;

50, 60, 65 are reaction times.

If we increase the quantity of the catalyst, the reaction time can be reduced to less than 4 minutes.

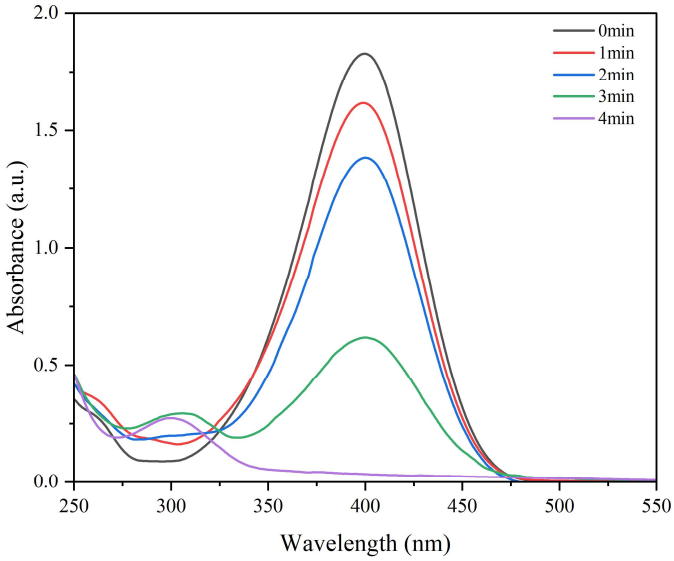


Figure S4. Reduction of 4-NP in 4 minutes

After the p-nitrophenol reduction reaction, the spherical aberration electron microscope is used to detect the state of the catalyst. The results of spherical aberration electron microscopy showed that most of the Au remained in a single-atom state distribution, but some of the Au elements are aggregated into nanoparticles after the reaction.

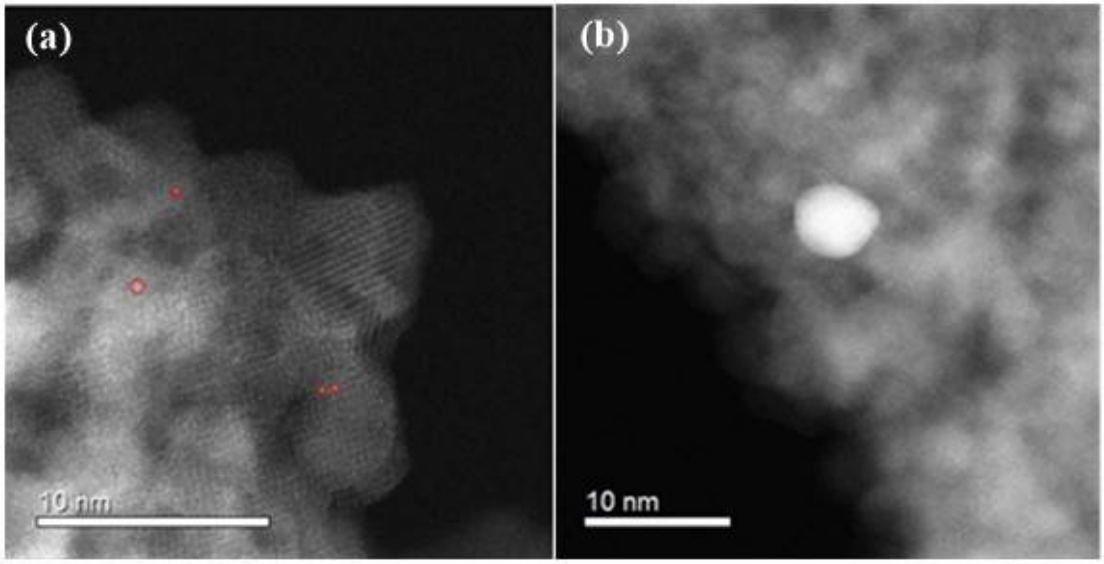


Figure S5. spherical aberration electron microscopic images of Au@15-crown-5 after the reaction: (a) Monodisperse catalyst after reaction. (b) Catalyst agglomerated after reaction.