

## Supporting Information

### Molecular Manipulation of Microenvironment of Au Active Sites on Mesoporous Silica for Enhanced Catalytic Reduction of 4- Nitrophenol

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## Experiment section

### Materials

Cetyltrimethylammonium tosylate (CTATos) was purchased from MERK. Triethanolamine (TEAH<sub>3</sub>), tetraethylorthosilicate (TEOS), (3-aminopropyl) trimethoxysilane (APTMS, 97%) were purchased from Aladdin., hydrochloric acid (HCl, 36%~38%), sodium hydroxide (NaOH, AR), sodium borohydride (NaBH<sub>4</sub>, AR), ethanol (EtOH, AR), Sodium chloride (NaCl, AR), Potassium chloride (KCl, AR), Rubidium chloride (RbCl, SP), Cesium chloride (CsCl, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium borodeuteride (NaBD<sub>4</sub>), Deuterium oxide (D<sub>2</sub>O, 99% D), Lithium Bromide (LiBr, 99%), Lithium iodide (LiI, 99%) were achieved from Shanghai Macklin Biochemical. Chloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O, 47.8wt% Au) was purchased from Shanghai Chemical Reagent Co. Ltd. Lithium chloride (LiCl, AR) was purchased from Shanghai Jufeng Chemical Technology Co. Ltd. Lithium hydroxide (LiOH, >98.0%) was purchased from TCI.

### Techniques

The X-ray diffraction (XRD) patterns were required using a Rigaku Ultima Discover X-Ray Diffractometer at a wavelength of Cu K $\alpha$  (1.5405 Å). TEM analyses were performed by using a JEOL 2010F microscope equipped with a field-emission gun and operating at 200 kV. FTIR spectra were recorded on a Nicolet FTIR spectrometer (NEXUS 670) by diluting the sample with fine KBr powder and pressing into a pellet. Fluorescence was measured by using a FluorMax-4 fluorimeter (Horiba, Japan). Ultraviolet visible (UV-vis) spectroscopy was conducted with a Shimadzu UV-2700 UV-vis spectrophotometer and the BaSO<sub>4</sub> was used as reference. Fluorescence was measured by using a RF-6000 fluorimeter.

### Synthesis of dendritic mesoporous silica nanospheres (DMSNs) supports

DMSNs were synthesized according to the literature report [1]. The DMSNs were treated by HCl(1M) and then functionalized by aminopropyl before grafting metal nanoparticles. In a typical process, 5 g of DMSNs, 8.4 mL of 1 M HCl and 200 mL of EtOH were added into a round-bottom flask, the mixture stirred at 60 °C for 1 h. The solid was dried at 80°C overnight after filtered and washed by deionized water and EtOH three times. Then, 3.250 g DMSNs washed by HCl, 5.655 g of APTMS and 130 mL EtOH were introduced into a round-bottom flask at 80°C for 12 h with stirring under reflux condition. The solution was filtered and washed by deionized water and EtOH. Then the solid was dried at 80°C overnight.

### Synthesis of DMSNs supported gold nanoparticles (Au@DMSNs) catalysts.

In a 200 mL beaker, 1.0 g of amino-functionalized DMSNs was suspended in 80 mL EtOH, subsequently added 20.8 ml of 4.85 mM HAuCl<sub>4</sub>·4H<sub>2</sub>O EtOH solution. After being stirred at room temperature for 12 h in dark, 76 mg NaBH<sub>4</sub> was added at once and stirred for another 30min. The obtained product was filtered and washed repeatedly with deionized water and dried overnight at 80°C. The loading weigh of gold on DMSNs support was about 2%. As-obtained sample was denoted as Au@DMSNs.[2]

### Reduction of 4-Nitrophenol

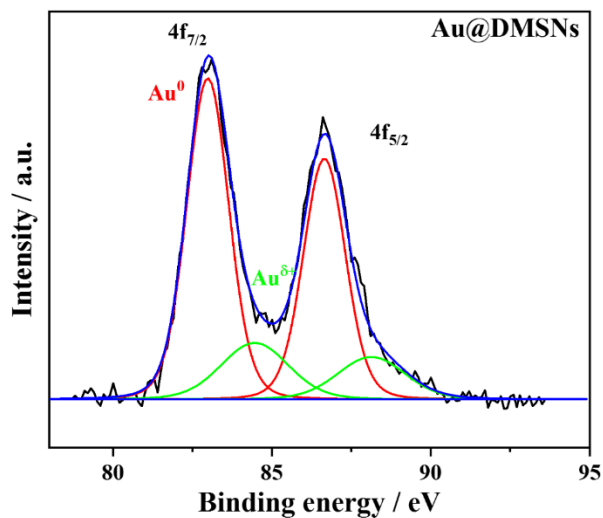
H<sub>2</sub>O (2.5 mL), 4-NP (0.2 mL, 2.5 mM aqueous solution) and NaBH<sub>4</sub> (0.4 mL, 250 mM aqueous

solution) were added into a quartz cuvette. The solution turned yellow. Subsequently, a certain amount (30  $\mu$ L) of aqueous solution of catalyst (5 mg/mL) was added. As the reaction progressed, the bright yellow solution gradually faded. The reaction was scanned by UV-vis spectrum repeatedly from 500 nm to 250 nm over the whole course to record the changes. To test the effect of cations/anions additives on the reaction activity, 2.5 mL H<sub>2</sub>O was replaced by the aqueous solution with different concentration of AMCl (AM = Li, Na, K, Rb, Cs) and LiX (X = OH, Br, I, NO<sub>3</sub>, 1/2SO<sub>4</sub>). In the deuterium isotopic experiments, the reduction was conducted under the same conditions except for the use of NaBD<sub>4</sub> and/or D<sub>2</sub>O.

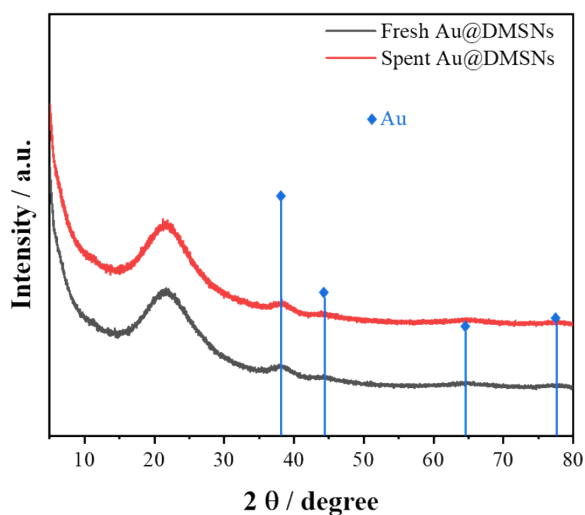
#### **Large Scale Reduction of 4-NP.**

To obtain more reduction products of 4-NP for spectroscopic measurements, large scale synthesis was carried out according to the literature<sup>[3]</sup>. First, 15 mg of 4-NP was dissolved in 3 mL of H<sub>2</sub>O under magnetic stirring in reaction bottle, followed by addition of a 1 mL 5 mg/mL catalysts. Then, 30.0 mg of NaBH<sub>4</sub> was dissolved in 1 mL H<sub>2</sub>O and the solution was immediately added into the bottle. When the reaction completed. The completed reduction was confirmed by UV-vis absorption spectroscopic measurement, in which the peak of 4-NP at about 400 nm disappeared. Afterward, the solution was extracted with 5 ml ethyl acetate three times and the products in the organic phase were collected and dried over anhydrous sodium sulfate (NaSO<sub>4</sub>). Finally, the reduction products were obtained after evaporating the solvent under reduced pressure.

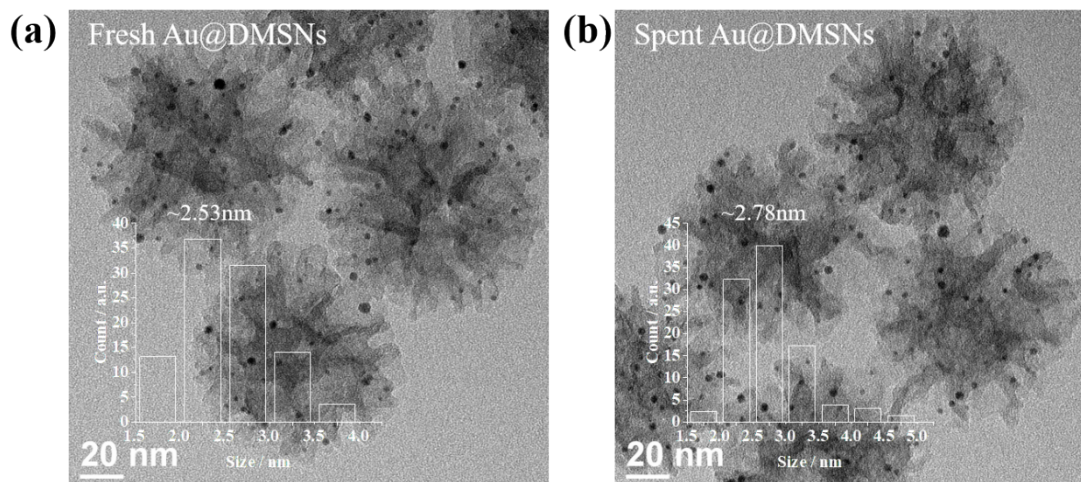
## Experiment results



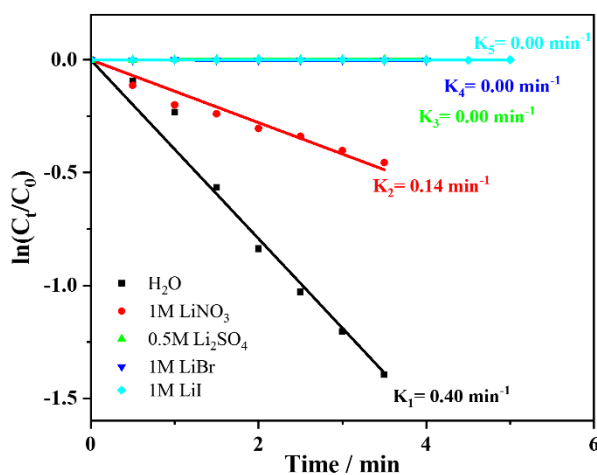
**Figure S1.** XPS spectra of Au 4f of Au@DMSNs catalysts.



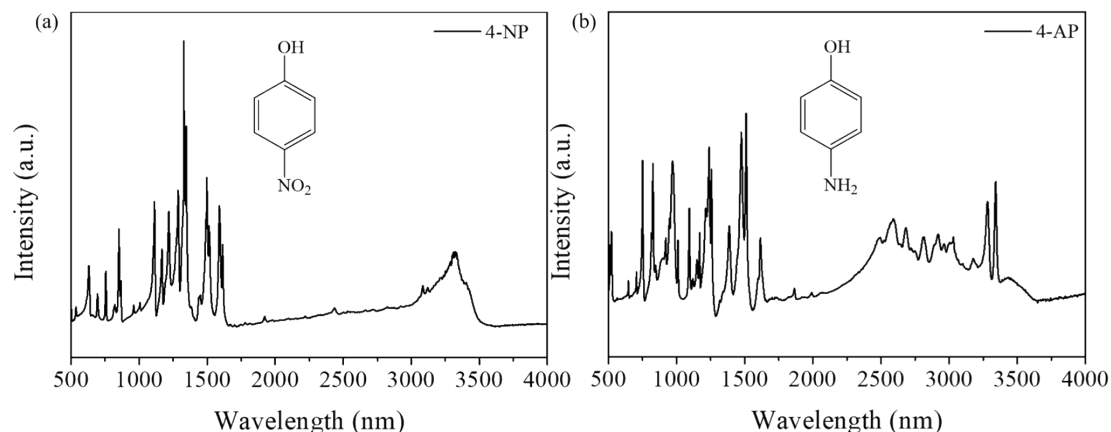
**Figure S2.** XRD patterns of fresh Au@DMSNs (black line) and spent Au@DMSNs catalysts (red line) compared to the standard crystalline gold (vertical blue line, JCPDS No. 99-0056).



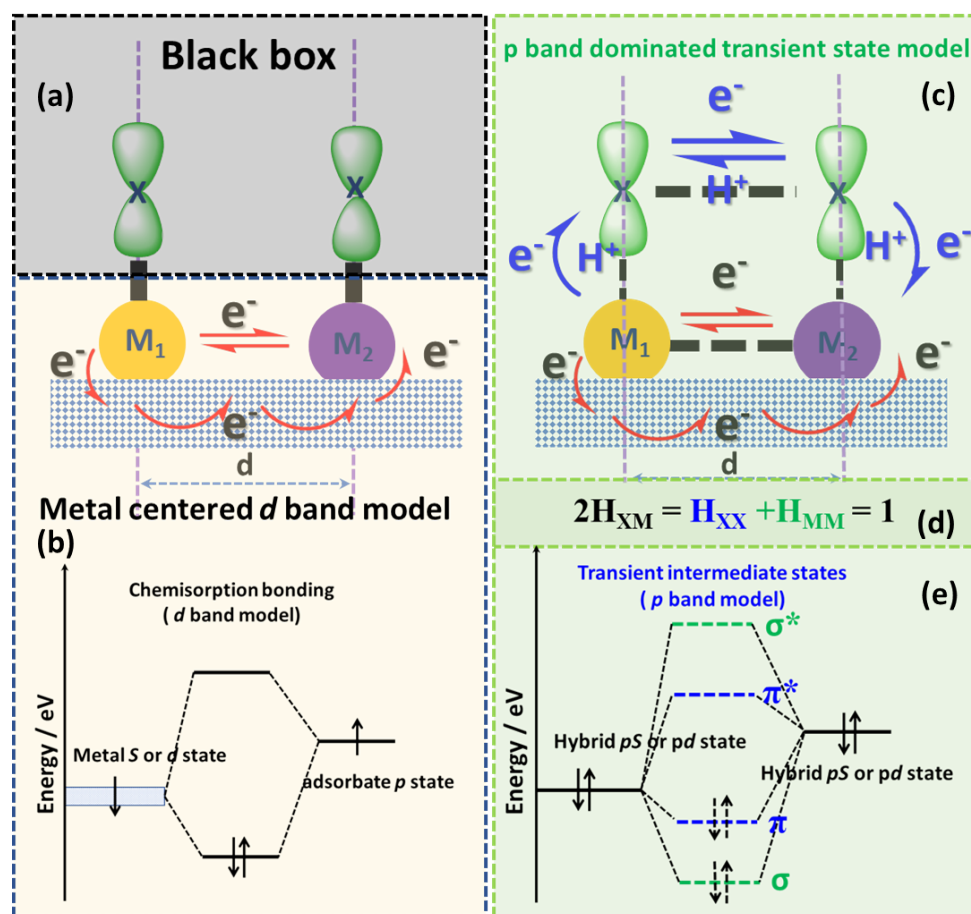
**Figure S3.** TEM image of fresh Au@DMSNs (a) and spent Au@DMSNs (b) catalysts. Insert: Particle size (PS) histograms of gold nanoparticles obtained from the TEM pictures on  $N$  particles are ( $N > 100$  in each case).



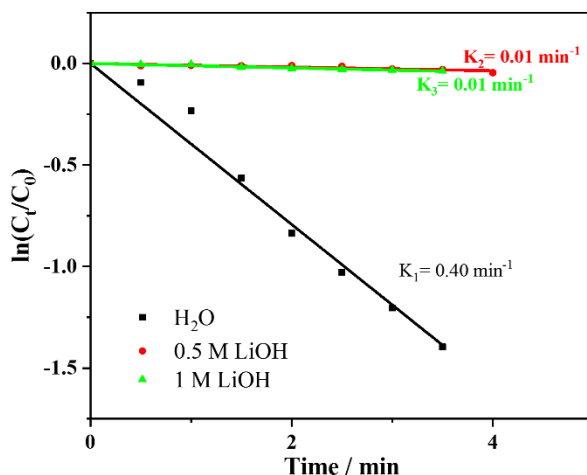
**Figure S4.** Catalytic activity of Au@DMSNs catalysts for the reduction of 4-NP in the different lithium salts ( $\text{LiX}$ ,  $\text{X} = \text{NO}_3$ ,  $1/2\text{SO}_4$ ,  $\text{Br}$ ,  $\text{I}$ , 1 M) aqueous solution.  $K_n$  is the apparent pseudo-first-order rate constant as the molar ratio of  $\text{NaBH}_4/4\text{-NP}$  was about 200 in the reaction.



**Figure S5.** FTIR spectrum of commercial 4-NP (a) and 4-AP (b).



**Figure S6.** Nature of surface bonding and/or state at heterogeneous nanoscale interface. Metal centered  $d$  band model (a and b) and  $p$  band dominated transient state model (c, d and e). X = O, B, C, N, S, P etc.; M= metal or metal ions; H denotes the hybridization of interfacial atomic orbitals, and its subscripts represent the interaction between metal and surface adsorbates (XM, traditional chemisorption), surface adsorbates (XX) and metals (MM) respectively. Importantly note that these surface transient intermediate states formed by spatial interaction have dynamic features, which provides more alternative channels and/or excited states for electron transfer and transition.



**Figure S7.** Catalytic activity of Au@DMSNs catalysts for the reduction of 4-NP in the aqueous solution with different concentration of LiOH.  $K_n$  is the apparent pseudo-first-order rate constant as the molar ratio of  $\text{NaBH}_4/4\text{-NP}$  was about 200 in the reaction.

**Table S1.** The metal contents (wt%) of Au@DMSNs catalysts determined by ICP-OES analysis

Sample	Theoretical value (wt%)	Actual value (wt%)
Au@DMSNs	2.0	1.18

**Table S2.** Surface compositions of catalysts determined by XPS.

Sample	Au Component (%)		Binding energy (eV)	
	$\text{Au}^0$	$\text{Au}^{\delta+}$	$\text{Au}^0$	$\text{Au}^{\delta+}$
Au@DMSNs	78.08	21.92	83.0	84.5

**Table S3.** Comparison of recent reports on noble Au-based catalysts catalyzed reduction of 4-NP by  $\text{NaBH}_4$ . The comparisons for the chemical reactivity were done for the Au metal-based catalysts under the similar reaction conditions.

Catalyst	Catalyst used (mg)	$K^a$ ( $10^{-3} \text{ s}^{-1}$ )	$K/M^b$ ( $\text{s}^{-1} \text{ g}^{-1}$ )	Ref.
AuNPs	0.02	9.00	450	[4]
Resin-AuNPs	100	17.70	0.177	[5]
Au/Au@polythiophene	0.16	0.65	4.06	[6]
Au MPCs	0.03	11.33	377.78	[7]



Au@OMS	2.00	0.97	0.49	[8]
Au@TpPa-1	20	5.35	0.27	[9]
Au@Fe <sub>3</sub> O <sub>4</sub>	0.06	13.00	216.67	[10]
Au@g-C <sub>3</sub> N <sub>4</sub>	2.00	15.5	7.75	[11]
Au@SBA-15	0.15	2.5	16.67	[2]
Au@MCM-41	0.15	3.33	22.22	[2]
Au@DMSNs	0.15	6.67	44.44	This work
Au@DMSNs <sup>c</sup>	0.15	9.17	61.11	This work

<sup>a</sup> The reaction rate constant.

<sup>b</sup> The reaction rate constant per total weight of used catalyst.

<sup>c</sup> The reaction condition is Au@DMSNs in 1M LiCl solution.

## Reference

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