

## Supporting Information

Positively Charged Bulk Au Particles as Efficient Catalyst for Aerobic Oxidation of  
Styrene

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*Synthesis of polydivinylbenzene.* Polydivinylbenzene was hydrothermally synthesized by polymerization of divinylbenzene. As a typical run, 12 g of divinylbenzene was added into 120 ml of DMF, followed by addition 0.3 g of azobisisobutyronitrile and 12 mL of water. After stirring at room temperature for 3 h, the mixture was transferred into an autoclave and hydrothermally treated at 100 °C for 48 hours. The polydivinylbenzene sample was collected by evaporation of DMF at room temperature.

*Synthesis of Au/PN.* PN was obtained by nitration and reduction of polydivinylbenzene. As a typical run, 4.0 g of polydivinylbenzene was added into the

mixture of H<sub>2</sub>SO<sub>4</sub> (98 %, 116 g) and HNO<sub>3</sub> (65 %, 30 g). After stirring for 16 h at 0 °C in methanol bath, nitro-modified polydivinylbenzene was formed. Then the mixture was added in 1.5 L of water. nitro-modified polydivinylbenzene was collected by filtration and washing with large amount of water. The obtained nitro-modified polydivinylbenzene was stirred in 60 ml of HCl (10 M) with 6.5 g of SnCl<sub>2</sub>. After stirring for 3 days at 27 °C, PN was formed. Then, the mixture was added in 1.5 L of water. PN sample was collected by filtration and washed with a large amount of 2-aminopropane and ethanol. 1 g of PN was treated in HAuCl<sub>4</sub> solvent (45 mg of HAuCl<sub>4</sub> in 40 ml of water and 5 ml of acetone) at room temperature for 12 h. After washing and filtrating, the Au/PN was finally obtained. The Au content is 2.4 wt%, analyzed by inductively coupled plasma (ICP) technique.

*Synthesis of Au/PN-R.* As a typical run, 1 g of Au/PN was dried at 100 °C under vacuum and then transferred to 50 mL of toluene (dried by P<sub>2</sub>O<sub>5</sub>), followed by the addition of NaBH<sub>4</sub>. After stirring for 10 min, 15 mL of ethanol was added and the mixture was stirred for 6 h. Au/PN-R was finally collected by filtration and washing with a large amount of ethanol and water.

*Synthesis of Au/MCM-N and Au/MCM-N-R.* As a typical run, 1g of MCM-41 was dried at 120 °C under vacuum for 3 h, followed by the addition of 50 mL of pretreated toluene containing 1g of aminopropyltriethoxysilane (KH-550). The mixtures were refluxed overnight and collected by rotary evaporation, followed by washing with a large amount of ethanol. The sample obtained was designated as MCM-N. The experiments above were carried out in anhydrous conditions to avoid the reaction between amine ligands and H<sub>2</sub>O. 1 g of MCM-N was treated in HAuCl<sub>4</sub> solvent (45 mg of HAuCl<sub>4</sub> in 40 ml of water) at room temperature for 12 h. After washing and filtrating, the Au/MCM-N was obtained. Further reduction of Au/MCM-N by NaBH<sub>4</sub> in the mixture of anhydrous toluene and ethanol, Au/MCM-N-R was collected by filtration and washing with a large amount of ethanol and water. The Au content is 2.0 wt% by inductively coupled plasma (ICP) analysis.

*Synthesis of Au/non-porous PN.* Non-porous polydivinylbenzene was synthesized by polymerization of divinylbenzene without addition of any solvent. As a typical run, 0.3 g of azobisisobutyronitrile was added into 12 g of DVB. After stirring at room temperature for 3 h, the mixture was transferred into an autoclave and hydrothermally treated at 100 °C for 48 hours. Non-porous polydivinylbenzene sample was collected. Au/non-porous PN was prepared in the same way as Au/PN, except for non-porous polydivinylbenzene instead of polydivinylbenzene. The Au content of this sample is 1.9 wt% by ICP analysis.

*Styrene or toluene adsorption capacity.* The adsorption capacity of styrene or toluene over Au/PN and Au/non-porous PN was measured with the weight change of the samples before and after the adsorption test. The samples were evacuated at 60 °C before the adsorption. As a typical run, 1.0 g of Au/PN catalyst was added into 10 g of styrene under vigorous stirring at room temperature for 5 min, then the solid sample was separated by centrifugation, weighted to the weight change. The content of styrene adsorption was defined as follows:

*Content of styrene (g/g) = (weight of sample after adsorption - weight of sample before adsorption) / weight of sample before adsorption*

*Characterization.* FEI Tecnai G2 F20 microscope equipped with an EDAX detector was employed to acquire TEM, HAADF-STEM images, and energy dispersive X-ray spectrum (EDS) elemental maps. The microscope was operated at an accelerating voltage of 200 kV. The samples were ultrasonically dispersed in ethanol, and then a drop of the solution was deposited on a holey C/Cu TEM grid to be used for TEM characterization and elemental mapping. Powder X-ray diffraction patterns (XRD) were obtained with a Rigaku D/MAX 2550 diffractometer with CuK $\alpha$  radiation ( $\lambda=0.1542$  nm). XPS spectra were performed by a Thermo ESCALAB 250, and the binding energy was calibrated by C1s peak (284.9 eV). FTIR spectra were recorded using a Bruker 66V FTIR spectrometer. The electron paramagnetic resonance (EPR)

spectra were obtained on a JES-FA 200 EPR spectrometer at 25 °C. The UV-Visible spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. Nitrogen isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP Tristar. The samples were outgassed for 10 h at 150 °C before the measurement. Pore-size distribution was calculated using Barrett-Joyner-Halenda (BJH) model. The content of Au was determined from inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer.

**Table S1.** The textural parameters of various samples.

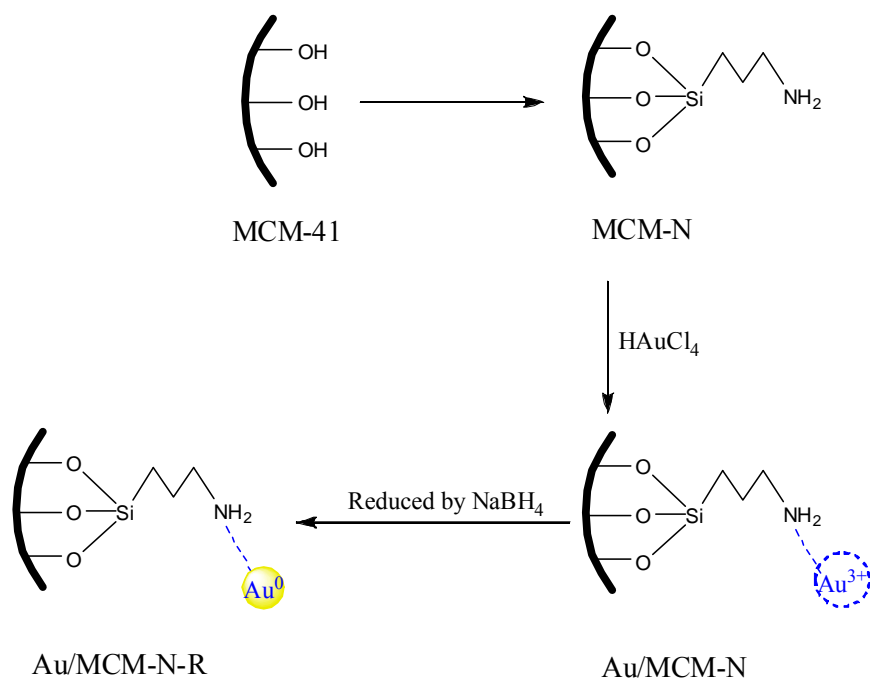
	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore size ( $\text{nm}$ ) <sup>a</sup>	Au content ( $\text{wt}\%$ ) <sup>b</sup>	Au particle size (nm)	Au composition	Ratio of $\text{Au}^{3+}/\text{Au}^+$ [c]
Au/PN	247	17.5	2.4	20-150	$\text{Au}^0, \text{Au}^+, \text{Au}^{3+}$	2.31
Au/PN-R	240	17.0	2.4	20-150	$\text{Au}^0, \text{Au}^+, \text{Au}^{3+}$	2.22
Au/non-porous PN	<5		1.9	25-150	$\text{Au}^0, \text{Au}^+, \text{Au}^{3+}$	2.43
Au/MCM-N	425	3.2	2.1		$\text{Au}^{3+}$	
Au/MCM-R	425	3.2	2.0	2.0-3.4	$\text{Au}^0$	

<sup>a</sup> Average pore size calculated using BJH model; <sup>b</sup> By ICP analysis. <sup>c</sup> By Au4f XPS analysis.

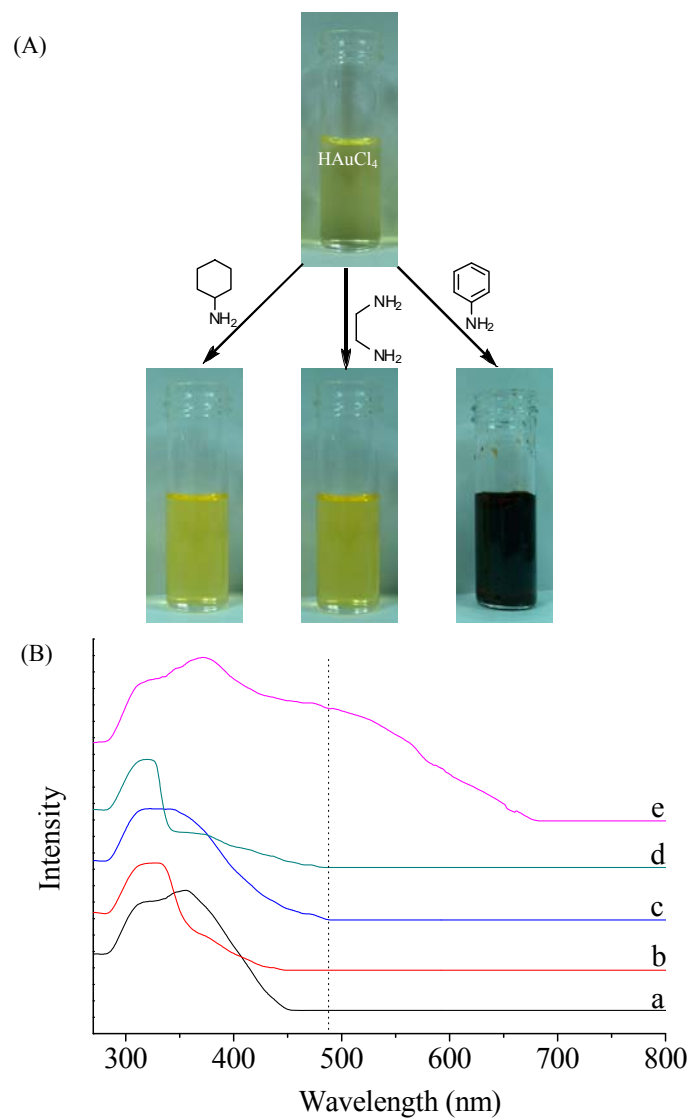
**Table S2.** The adsorption capacity of Au/PN and Au/non-porous PN catalysts for styrene or toluene.

Catalyst	Adsorption capacity for styrene (g/g)	Adsorption capacity for toluene (g/g)
Au/PN	3.9	4.7
Au/non-porous PN	<0.1	<0.1

The PN with porous structure could adsorb the styrene during the reaction. For example, 1 g of Au/PN catalyst could adsorb 3.9 g of styrene or 4.7 g of toluene, while 1 g of Au/non-porous PN catalyst could only adsorb very little styrene or toluene (<0.1 g/g). The high adsorption capacity of Au/PN catalyst could increase the reactant concentration in the catalyst, leading to an enhancement of the styrene conversion, which is well consistent with those reported in the literature (F. J. Liu, L. Wang, Q. Sun, L. Zhu, X. Meng, F.-S. Xiao, *J. Am. Chem. Soc.*, 2012, **134**, 16948). As a result, Au/PN catalyst shows the styrene conversion at 27.0%. In contrast, the Au/non-porous PN catalyst gives relatively low styrene conversion at 14.2%.

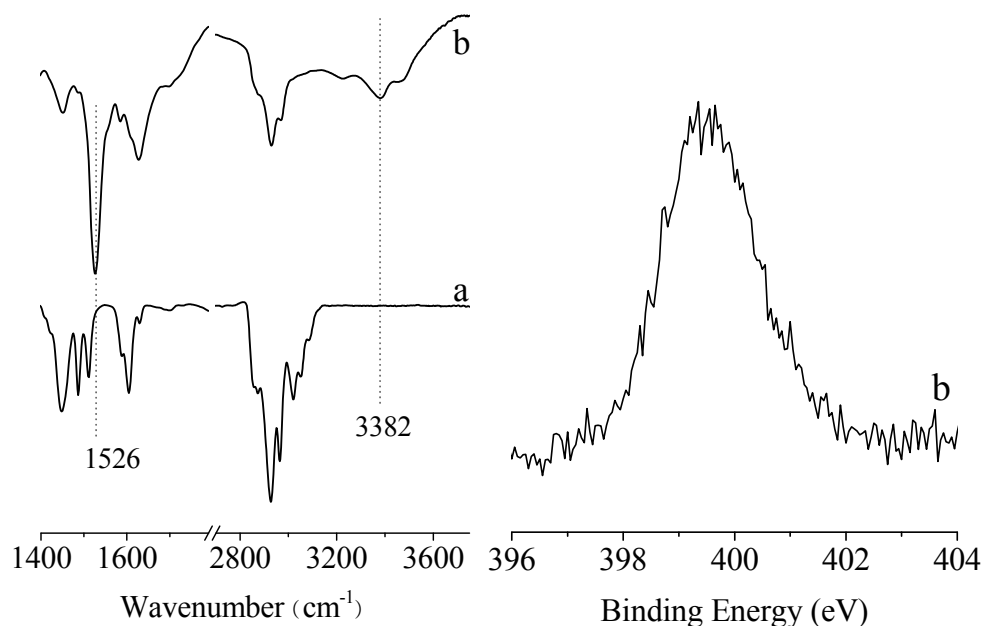


**Scheme S1.** The synthesis of Au/MCM-N and Au/MCM-N-R.

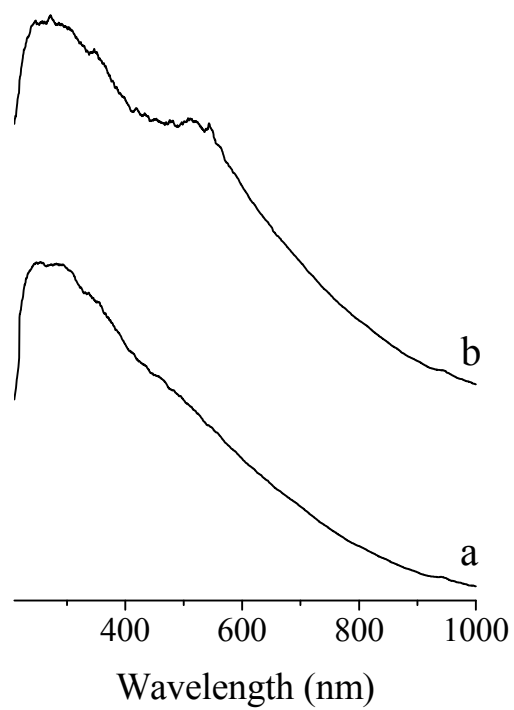


**Figure S1.** (A) Photographs of H[AuCl<sub>4</sub>] solution and the addition of various amines to H[AuCl<sub>4</sub>] solution; (B) UV-Vis spectra of (a) H[AuCl<sub>4</sub>] solution, (b) cyclohexylamine, (c) mixture of H[AuCl<sub>4</sub>] and cyclohexylamine, (d) aniline, and (e) mixture of H[AuCl<sub>4</sub>] and aniline.

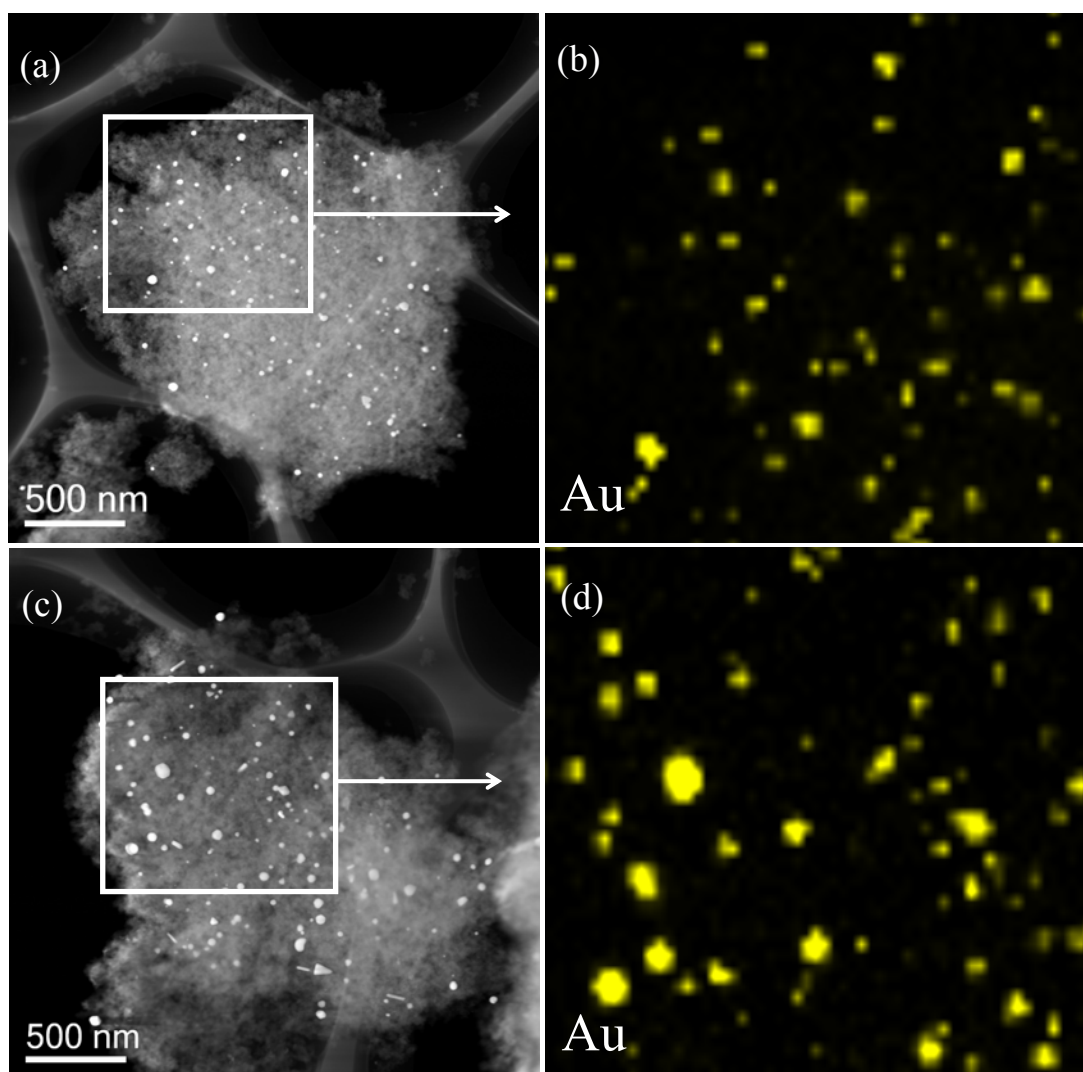




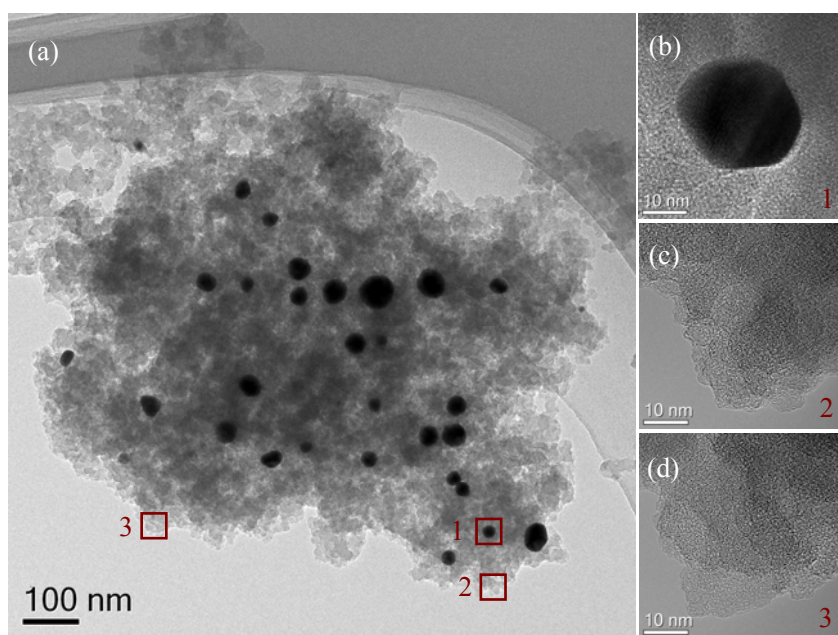
**Figure S2.** (Left) IR and (right) N1s XPS spectra of (a) polydivinylbenzene and (b) PN. Compared with polydivinylbenzene, PN shows additional peaks at 1526 and 3382 cm<sup>-1</sup> in the IR spectrum, which are assigned to C-N and N-H bonds, respectively. The N1s XPS spectra of both PN and Au/PN exhibit peak at 399.5 eV, associated with the presence of amino groups. These results indicate the successful modification of amino groups on polydivinylbenzene.



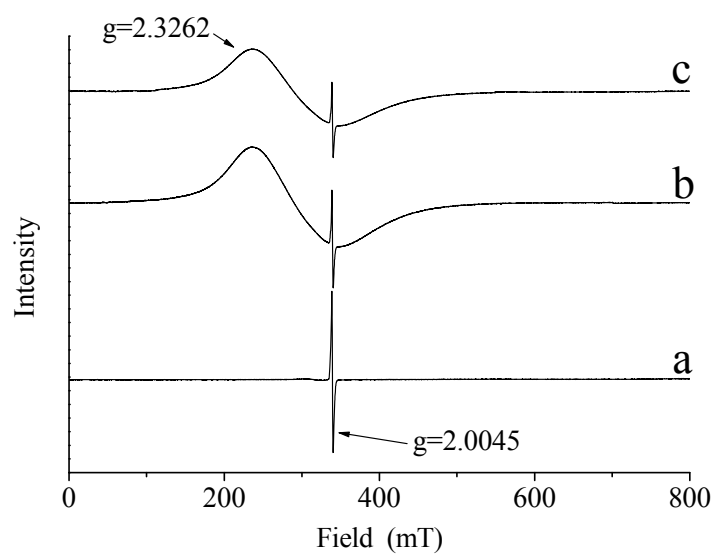
**Figure S3.** The UV-Vis spectra of (a) PN and (b) Au/PN.



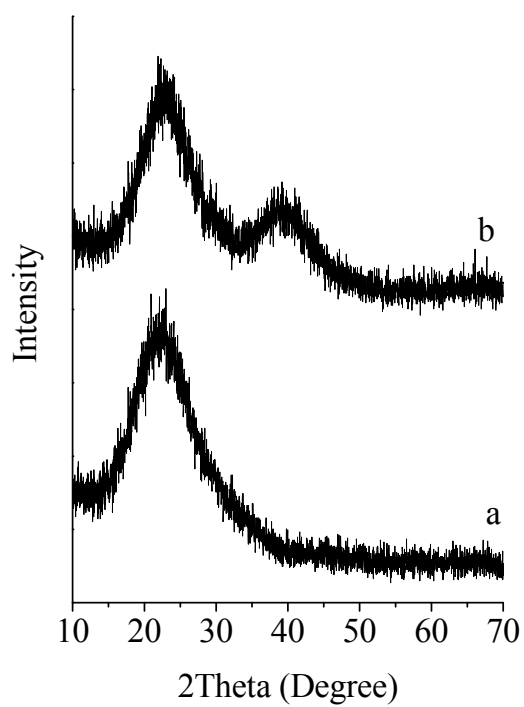
**Figure S4.** (a and c) STEM images and (b and d) the corresponding Au elemental maps of Au/PN.



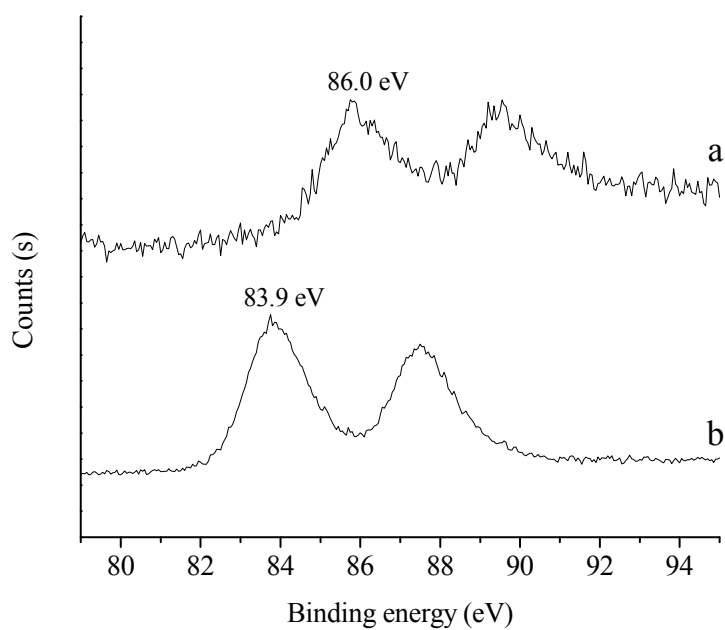
**Figure S5.** (a) TEM image of Au/PN; (b, c and d) HRTEM images of area 1, 2, and 3 in image (a).



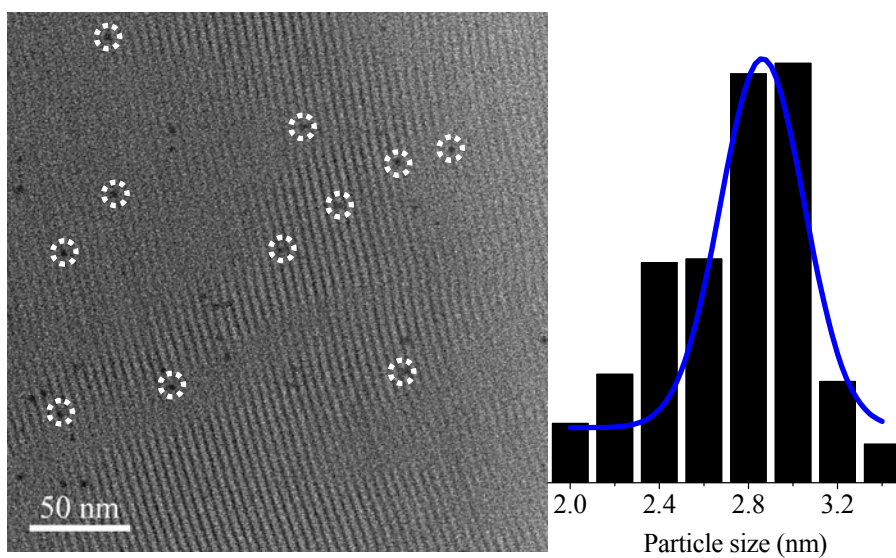
**Figure S6.** Room-temperature EPR spectra of (a) PN, (b) Au/PN, and (c) Au/PN-R.



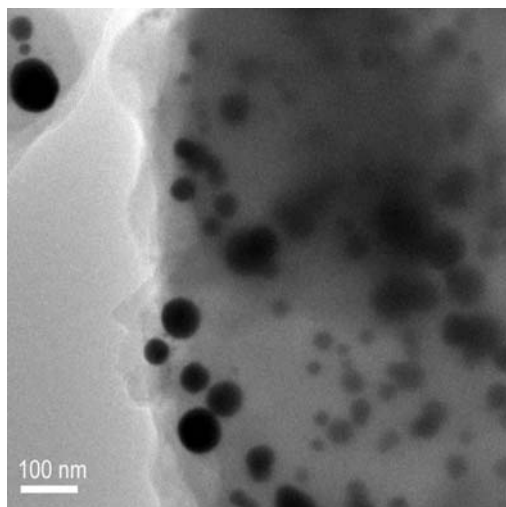
**Figure S7.** XRD pattern of (a) Au/MCM-N and (b) Au/MCM-N-R.



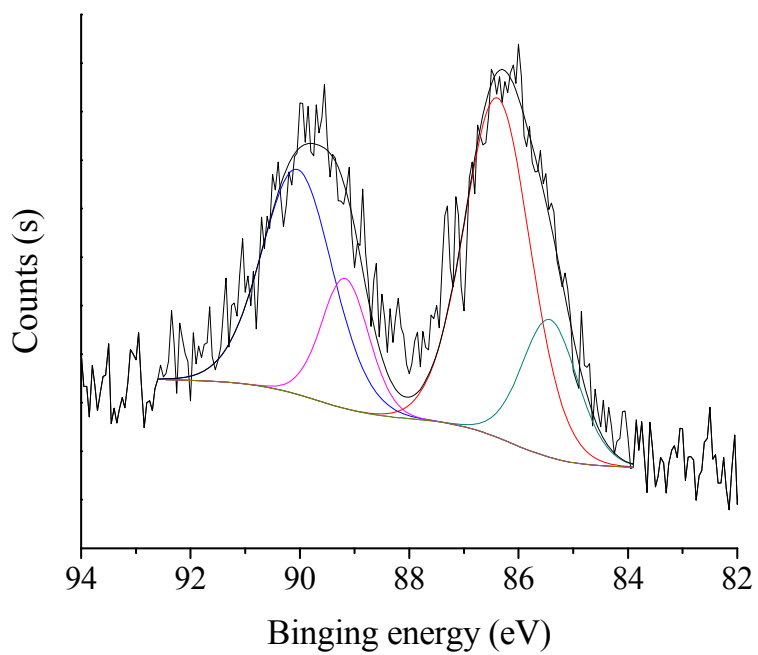
**Figure S8.** Au4f XPS spectra of (a) Au/MCM-N and (b) Au/MCM-N-R samples.



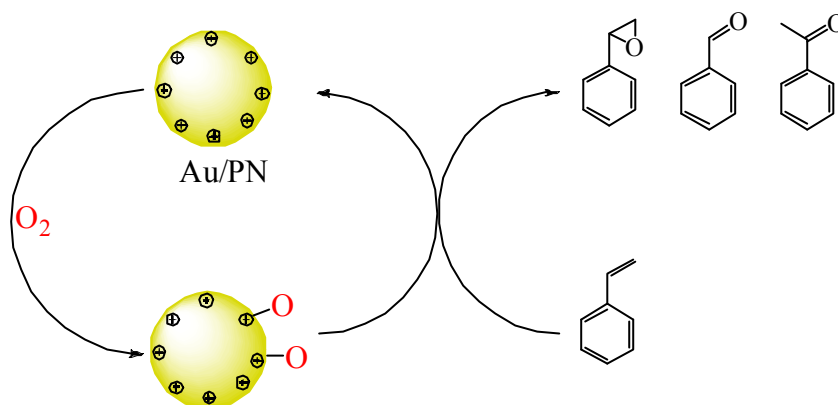
**Figure S9.** TEM image and particle size distribution of Au/MCM-N-R.



**Figure S10.** TEM image of Au/non-porous PN.

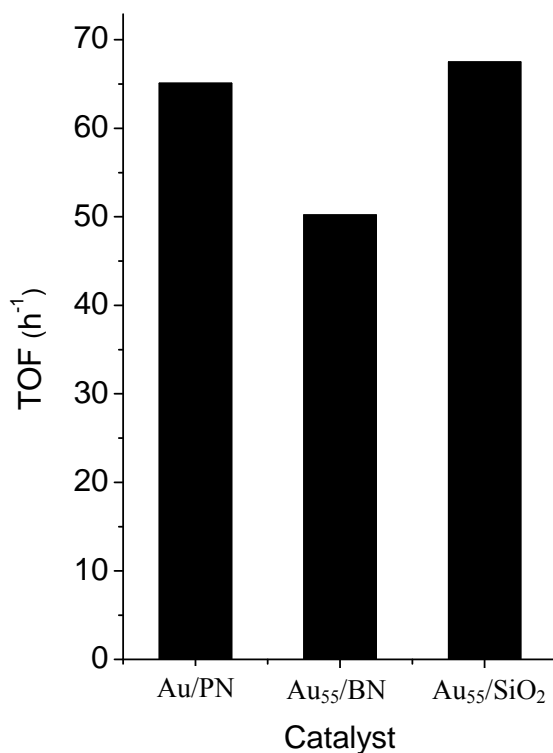


**Figure S11.** Au4f XPS spectrum of Au/non-porous PN.



**Figure S12.** Proposed reaction profile for the oxidation of styrene over Au/PN catalyst. From literature (H. G. Boyen, G. Kastle, F. Weigl, B. Koslowski, C. Dietrich, P. Ziemann, J. P. Spatz, S. Riethmuller, C. Hartmann, M. Moller, G. Schmid, M. G. Garnier, P. Oelhafen, *Science*, 2002, **297**, 1533; M. Turner, V. B. Golovko, O. P. H. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M. S. Tikhov, B. F. G. Johnson, R. M. Lambert, *Nature*, 2008, **454**, 981; X. Deng, C. M. Friend, *J. Am. Chem. Soc.*, 2005, **127**, 17178), it is well known that dissolution of oxygen molecule is a key step for aerobic oxidation of styrene. In our experiments, it is confirm the presence of positively charged bulk Au particles.





**Figure S13.** TOF number of Au/PN, Au<sub>55</sub>/BN and Au<sub>55</sub>/SiO<sub>2</sub> catalysts in the aerobic oxidation of styrene. Reaction conditions: 100 mg of Au<sub>55</sub>/BN or Au<sub>55</sub>/SiO<sub>2</sub>, or 25 mg of Au/PN (the same amount of Au species), 12 mmol of styrene, 20 mL of toluene, 1.5 bar of O<sub>2</sub>, 100 °C, 15 h, dodecane as internal standard. The TOF was calculated over all the Au species in the reaction mixture. The Au/PN catalyst exhibited TOF at 65.1 h<sup>-1</sup>, which is comparable with that (50.2 h<sup>-1</sup>) of Au<sub>55</sub>/BN catalyst and that (67.5 h<sup>-1</sup>) of Au<sub>55</sub>/SiO<sub>2</sub> catalyst, suggesting the superior activity of Au/PN catalyst.