Electronic Supplementary Information for

Designing yolk/shell type porous organic network using phenyl modified template

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Experiment

Materials：

Methanol (AR), tetraethyl orthosilicate (TEOS) (AR) and ammonium hydroxide (28-30 wt% AR) were purchased from Tianjin Kermel Reagent Co. Ltd. All of the materials were used as received without further purification. phenyltriethoxysilane (PTES) (97%) was from Alfa Aesar. Raw material of CHHP was a cyclohexane solution provided by Liaoyang Synthetic Fiber Co. Ltd. (China)

Synthesis of Au NPs:

2 mL of 1 wt% $HAuCl_4$ was added into 50 mL deionized water, followed by 5 mL 38.8 M citrate sodium solution and then the mixture was heated under reflux for 30 min. Finally, the resultant colloid was cooled to room temperature and 13 nm gold nanoparticles were obtained.

Synthesis of core/shell nanoparticle Au@Ph-SiO_2:

A fresh solution of polyvinylpyrrolidone (0.3 mL, 12.8 mg/mL) was added to a previously prepared Au NPs solution. The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the gold surface. Then, the solution was centrifuged (20000 rpm, 20 min) and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 10 mL by dilution with ethanol. The colloid was under ultrasonic for 15 min, followed by addition of ethanol (20 mL) and concentrated ammonia solution (1.65 mL, 28–30 wt% NH_3 in water). Afterwards, a solution of TEOS (1.15 mL), PTES (0.15 mL) in ethanol (1.5 mL) was added. The reaction mixture was then stirred for additional 24 h at room temperature. The resultant colloid was centrifuged and washed with water and ethanol and dried at 353 K.

Synthesis of core/shell nanoparticle Au@SiO_2:

A fresh solution of polyvinylpyrrolidone (0.3 mL, 12.8 mg/mL) was added to a previously prepared Au NPs solution. The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the gold surface. Then, the solution was centrifuged (20000 rpm, 20 min) and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 10 mL by dilution with ethanol. The colloid was under ultrasonic for 15 min, followed by addition of ethanol (20 mL) and concentrated ammonia solution (1.65 mL, 28–30 wt% NH_3 in water). Afterwards, a solution of TEOS (1.3 mL) in ethanol (1.5 mL) was added. The reaction mixture was then stirred for additional 24 h at room temperature. The resultant colloid was centrifuged and washed with water and ethanol and dried at 353 K.

Synthesis of Au@Si-PON:

100 mg of Au@Ph-SiO_2 was dispersed in 0.5 mL for 30 min under ultrasound, then 0.88 mL FDA and 0.54 mL toluene were added into the mixture, then the mixture was ultrasounded for another 30 min. 0.5 g $FeCl_3$ was added, followed by stirred under 80 ^{o}C for 19 h. 5 ml dichloromethane was added after the solid was cooled down. After swollen at room temperature for 10 h, another 1.5 g $FeCl_3$ was added followed by reaction at 80 ^{o}C for 12 h. Then the obtained mixture was washed with methanol and water, then the mixture was under Soxhlet's extractor for 24 h under methanol.

Synthesis of Au/Si-PON:

100 mg of Au@SiO_2 was dispersed in 0.5 mL for 30 min under ultrasound, then 0.88 mL FDA and 0.54 mL toluene were added into the mixture, then the mixture was ultrasounded for another 30 min. 0.5 g $FeCl_3$ was added, followed by stirred under 80 ^{o}C for 19 h. 5 ml dichloromethane was added after the solid was cooled down. After swollen at room temperature for 10 h, another 1.5 g $FeCl_3$ was added followed by reaction at 80 ^{o}C for 12 h. Then the obtained mixture was washed with methanol and water, then the mixture was under Soxhlet's extractor for 24 h under methanol.

Synthesis of yolk/shell type Au@PON:

0.1 g of the obtained Au@Si-PON nanocomposites were dispersed in 20 g methanol for at least 2 h, then 2 g 5 wt% HF solution were added into the turbid liquid. The mixture was stirred vigorously for 25 min at room temperature. The resultant colloid was centrifuged and washed with water and methanol and dried at 353 K.

Synthesis of Au/PON

0.1 g of the obtained Au/Si-PON nanocomposites were dispersed in 20 g methanol for at least 2 h, then 2 g 5 wt% HF solution were added into the turbid liquid. The mixture was stirred vigorously for 25 min at room temperature. The resultant colloid was centrifuged and washed with water and methanol and dried at 353 K.

Catalytic decomposion of CHHP:

The reaction was carried out in a 50 mL stainless steel autoclave under magnetic stirring. In a typical procedure, 0.05 g catalyst and 5 mL of n-heptane solution containing cyclohexyl hydroperoxide (0.309 mmol/mL) were added in the reactor. The reaction was conducted at a certain temperature for 30 min under N_2 atmosphere.

Analysis of products

The products were identified by an Agilent 6890N GC/5973 MS detector and quantitated by an Agilent 7890D GC equipped with a HP-5 column (30 m × 0.25 mm × 0.3 μm) and titration. After transformation of the hydroperoxide into cyclohexanol by adding triphenylphosphine to the reaction mixture, cyclohexanol and cyclohexanone were determined by internal standard method using nonane as an internal standard. The concentration of CHHP was determined by iodometric titration and the acid and ester by acid-base titration. The selectivity of cyclohexanol and cyclohexanone was calculated by combining the result of GC of cyclohexanol or cyclohexanone and the iodometric titration of CHHP.

Characterization:

Fourier transform infrared (FT-IR) spectra were collected between 4000 and 400 cm^{-1} on a Bruker Tensor 27 spectrometer in KBr media. UV-vis spectra were measured on Shimadzu UV-2550. Transmission electron microscope (TEM) was measured on JEM 2000EX. The size distribution of the nanoparticles was measured from the TEM images, and at least one hundred spheres were counted. N_2 adsorption–desorption isomer was performed on Quantachrome Autosorb-1, Water contact angles were performed on contact angle measuring system JC 2000 C1. The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max 2500/PC powder diffractometer with Cu Kα radiation (λ = 0.15418 nm). The nuclear magnetic resonance spectra of ^{29}Si cross polarization/magic-angle spinning nuclear magnetic resonance (^{29}Si CP/MAS NMR) were performed on a Bruker DRX-400 spectrometer at 79.5 MHz with a spinning frequency of 4 kHz. The nuclear magnetic resonance spectra of ^{13}C cross polarization/magic-angle spinning spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) were performed on a Bruker DRX-400 spectrometer at spinning frequency of 6 and 8 kHz.HR-TEMs were performed on JEM-2100. Thermal gravity analysis (TGA) measurements were carried out on a NETZSCH STA 409 PC instrument.

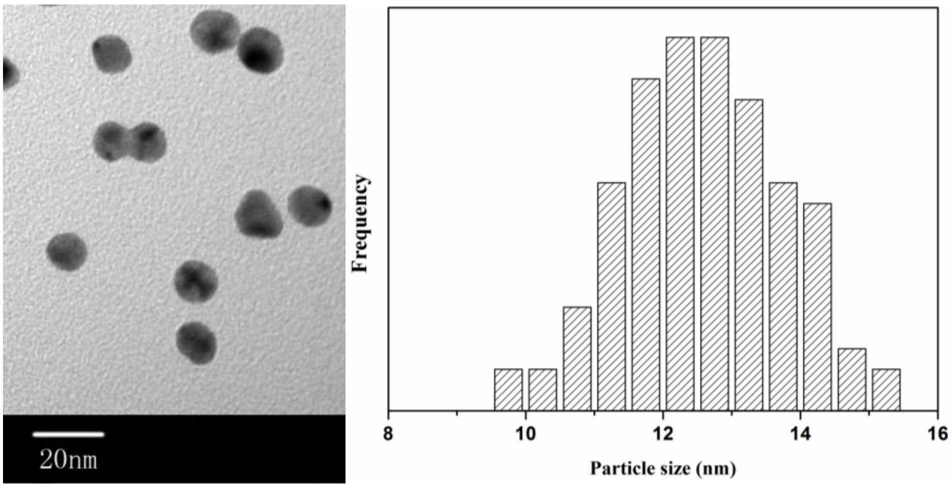

Fig. S1 TEM image and size distribution of the fresh prepared Au NPs

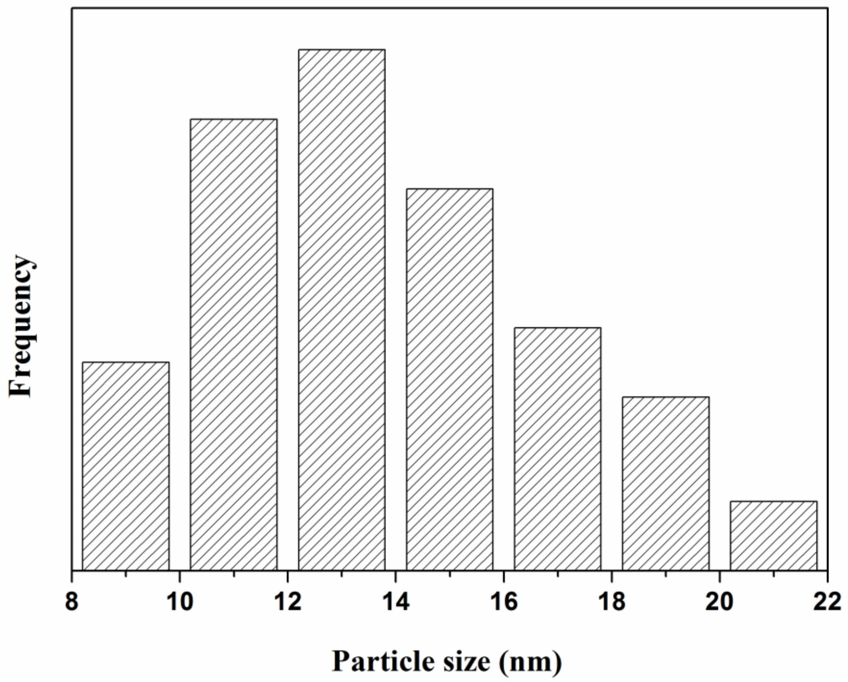

Fig. S2 Size distribution of the Au cores in Au@Ph-SiO_2

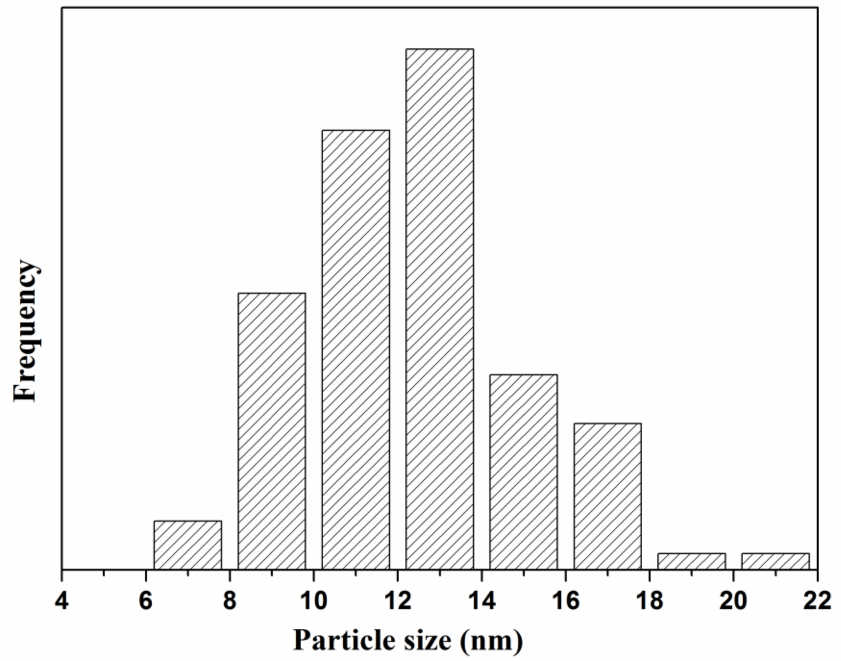

Fig. S3 Size distribution of the Au cores in Au@Si-PON

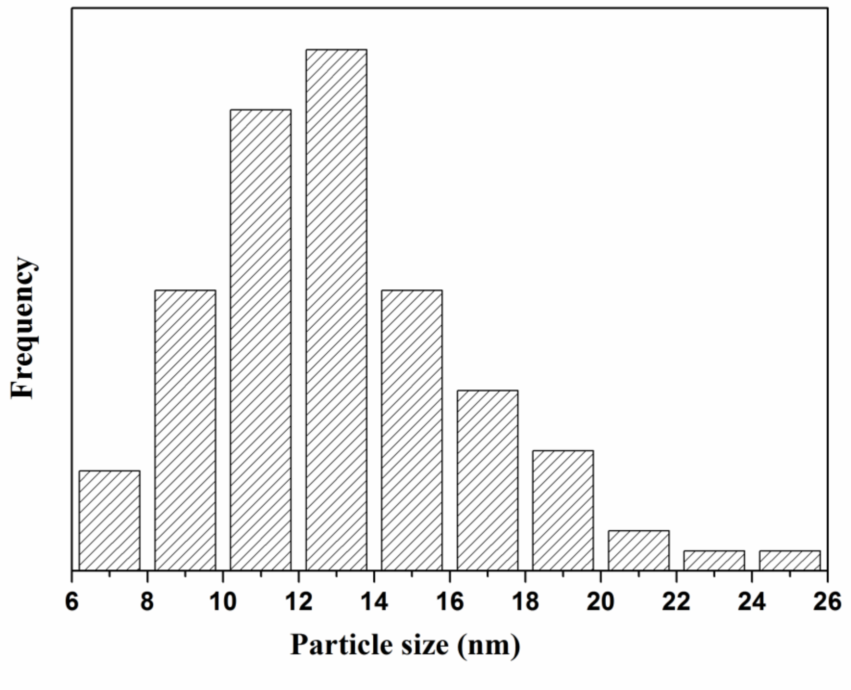

Fig. S4 Size distribution of the Au cores in Au@PON

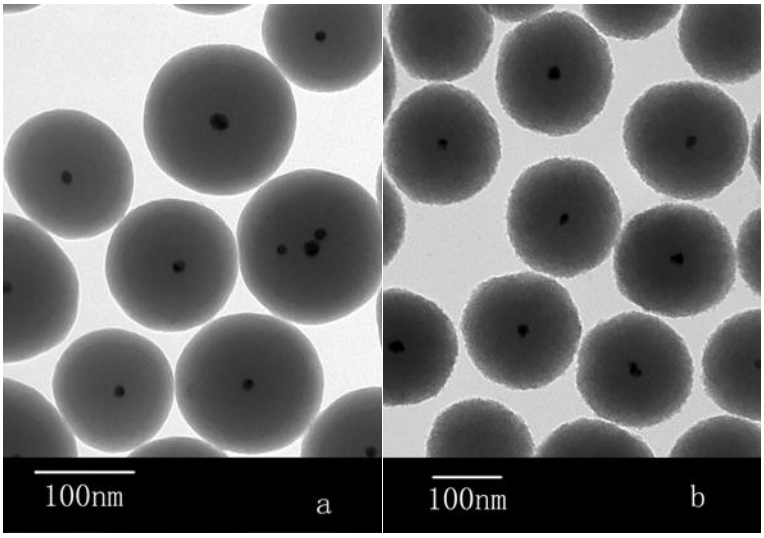

Fig. S5 TEM images of a) Au@SiO_2 and b) Au@Ph-SiO_2

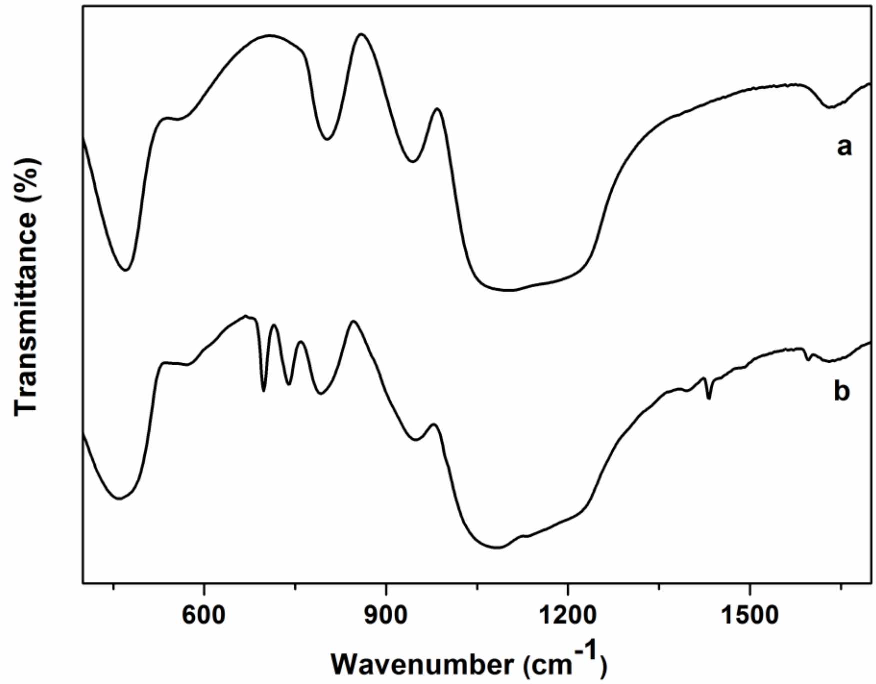

Fig. S6 FT-IR spectra of a) Au@SiO_2 and b) Au@Ph-SiO_2

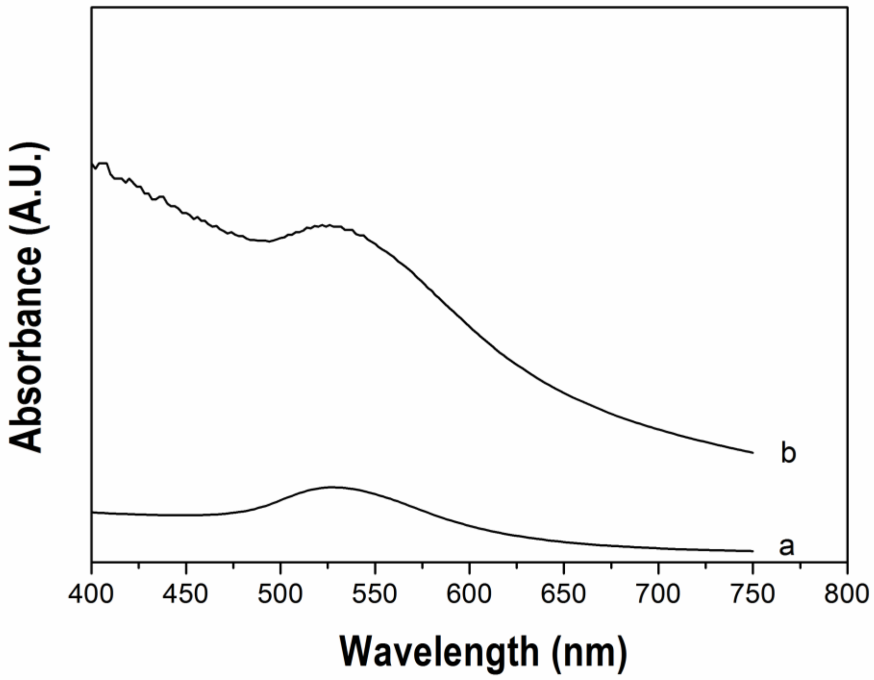

Fig. S7 UV-Vis spectra of the a) Au NPs and b) Au@Ph-SiO_2

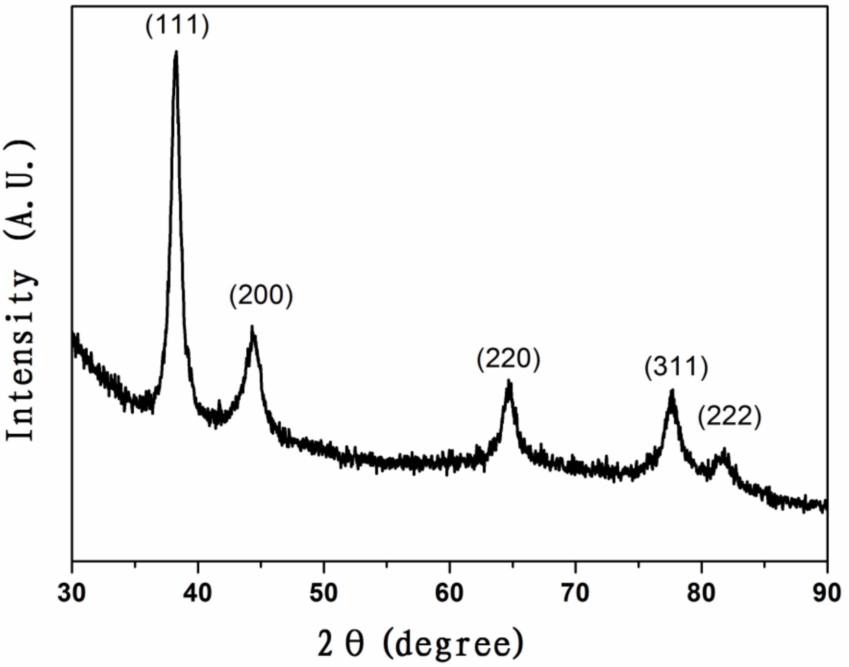

Fig. S8 XRD pattern of Au@Ph-SiO_2

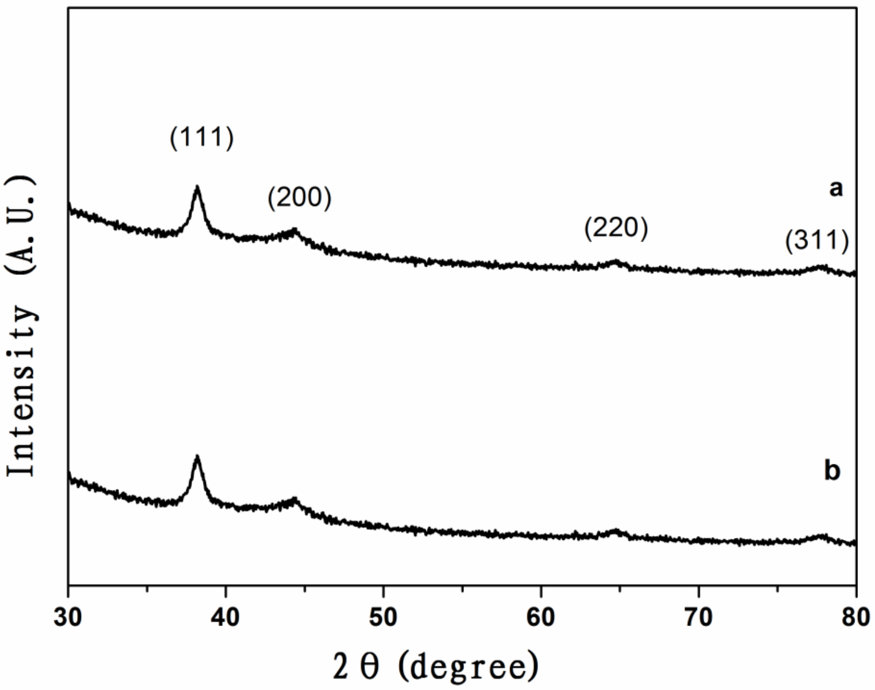

Fig. S9 XRD pattern of a) Au@Si-PON and b) Au@PON

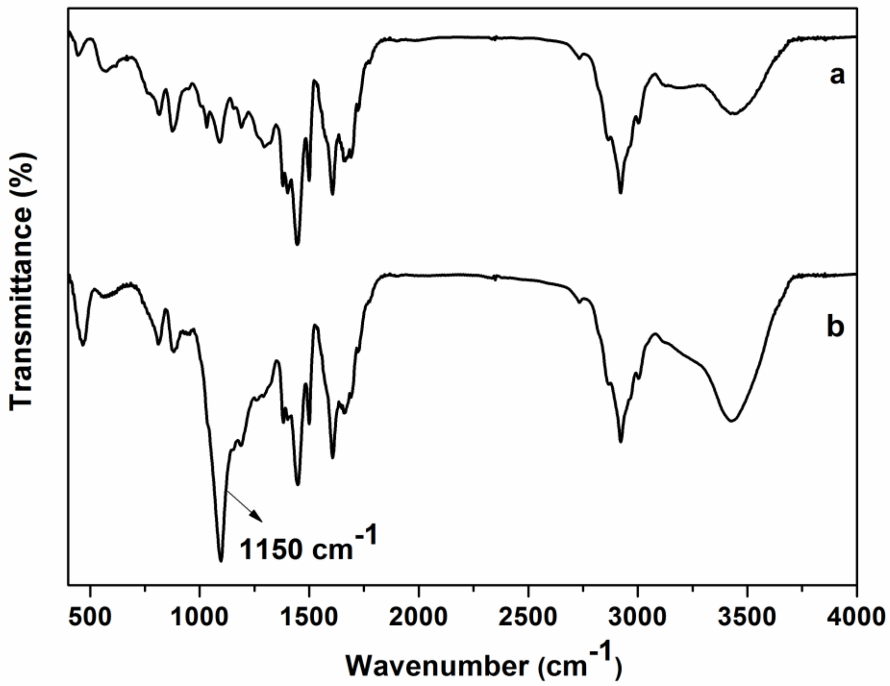

Fig. S10 FT-IR spectra of a) Au@PON and b) Au@Si-PON

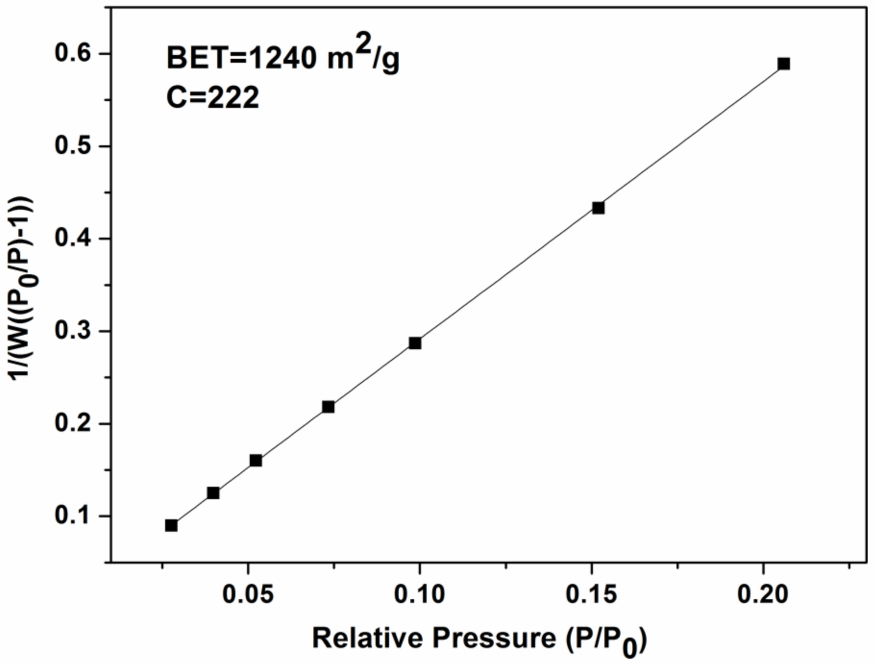

Fig. S11 BET plot of the Au@Si-PON

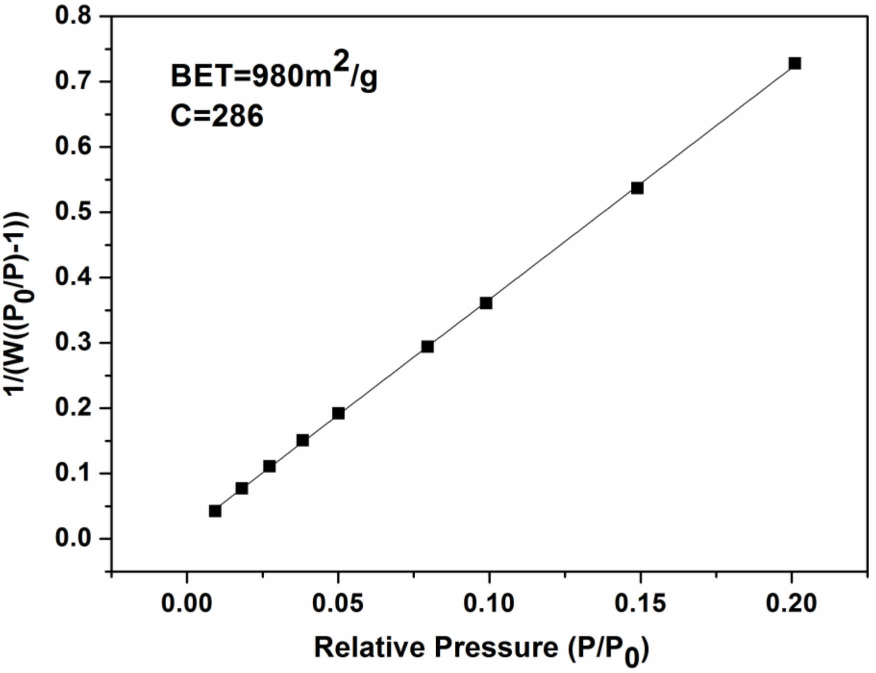

Fig. S12 BET plot of the Au@PON

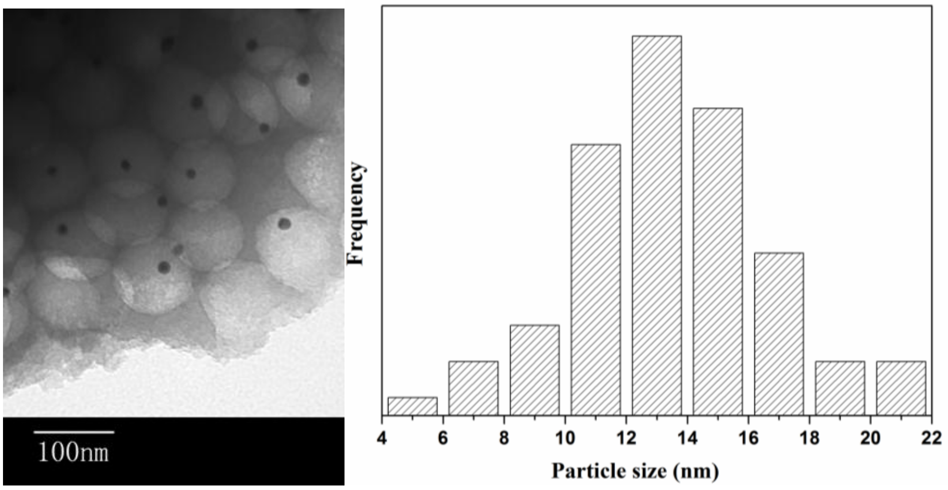

Fig. S13 TEM image of Au@PON after thermal treatment and the size distribution of the Au cores in Au@PON

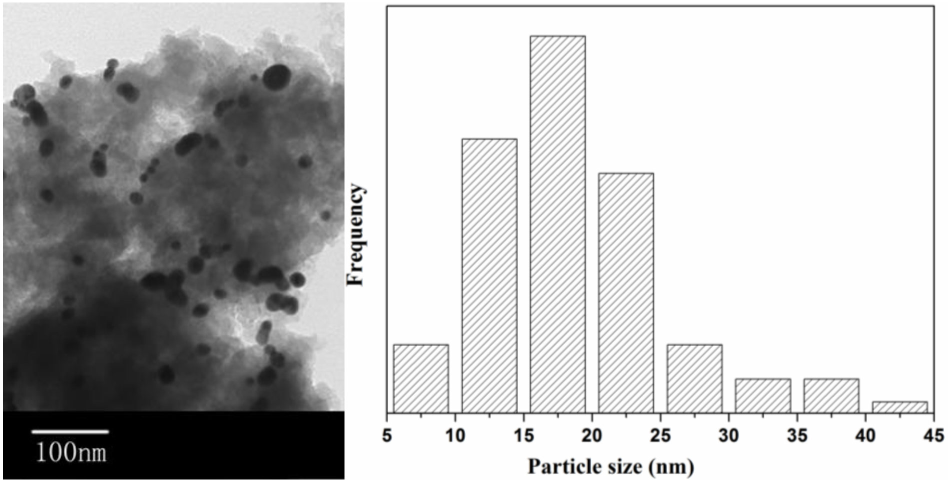

Fig. S14 TEM image of Au/PON after thermal treatment and the size distribution of the Au cores in Au/PON

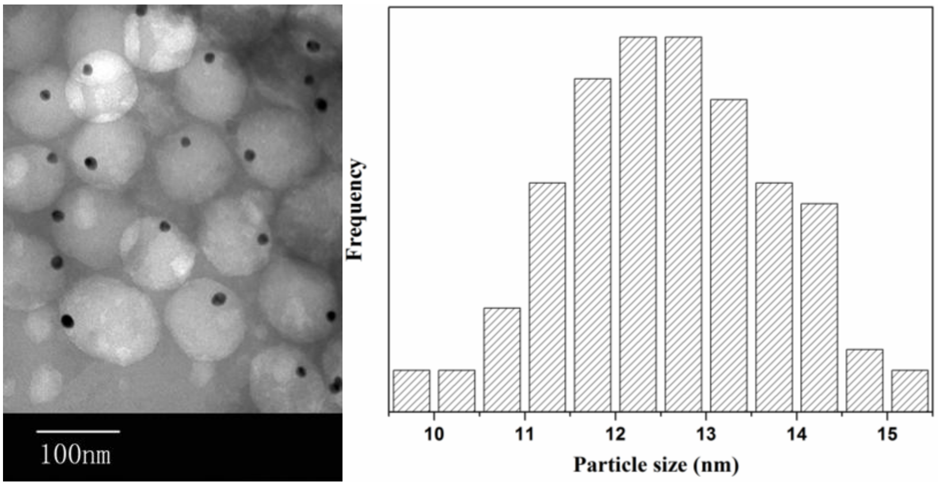

Fig. S15 TEM image of Au@PON after reaction and the size distribution of the Au cores in Au@PON

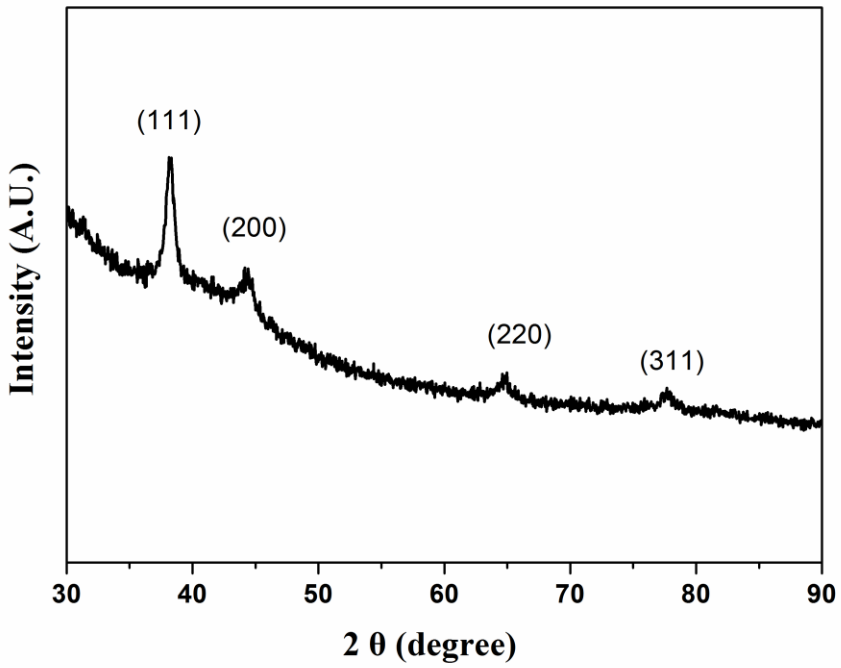

Fig. S16 XRD pattern of Au@PON after reaction

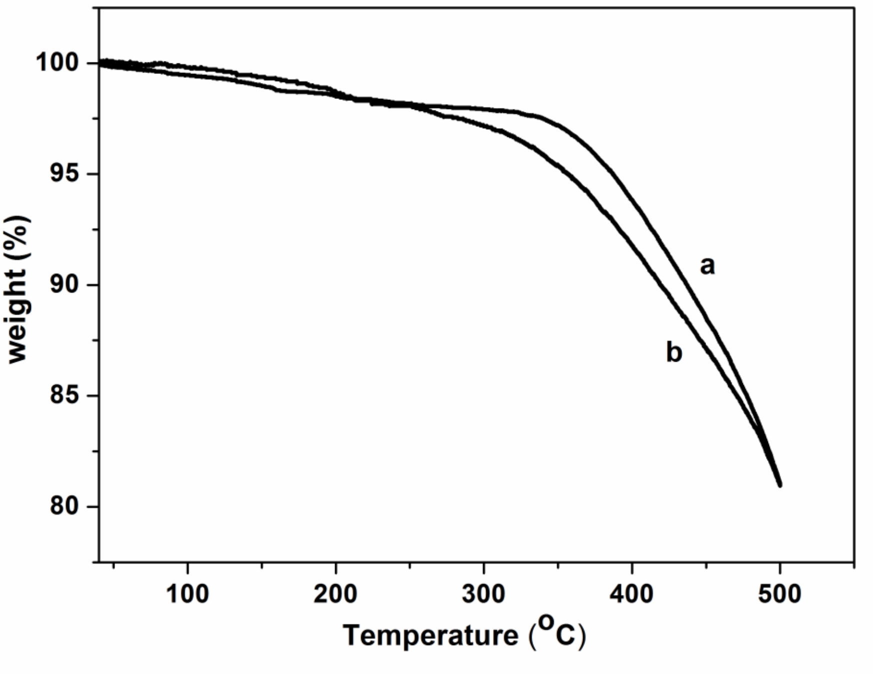

Fig. S17 TGA curves of a) Au@Si-PON and b) Au@PON

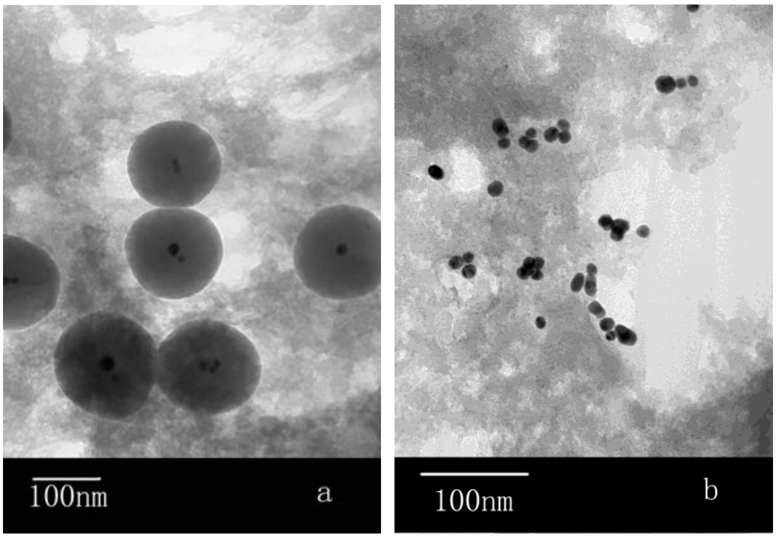

Fig. S18 TEM images for a) Au@SiO_2 dispersed on the PON and b) Au/PON

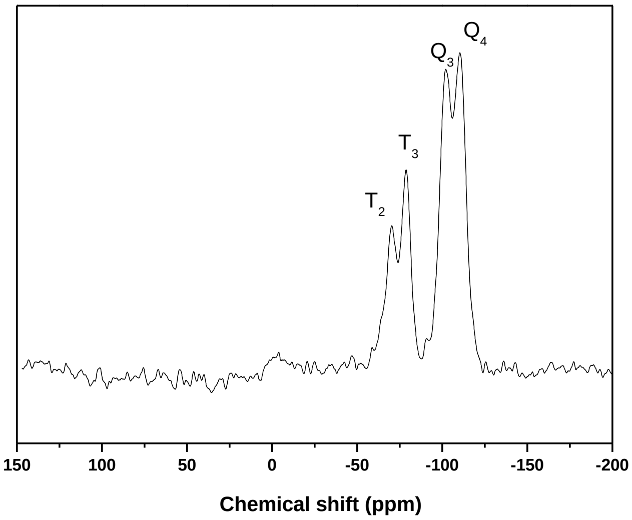

Fig. S19 ^{29}Si CP/MAS NMR of Au@Ph-SiO_2

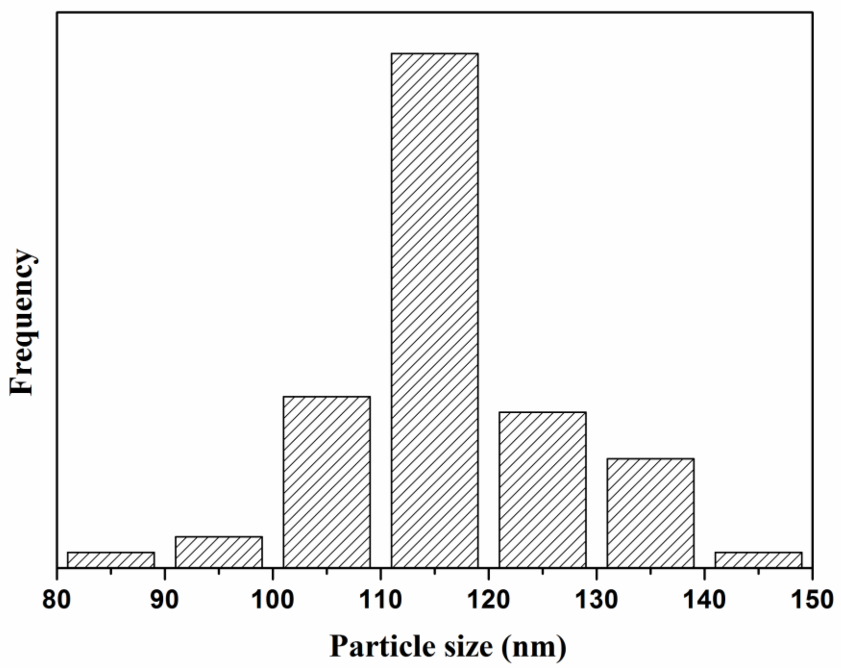

Fig. S20 Size distribution of Au@Ph-SiO$_2$

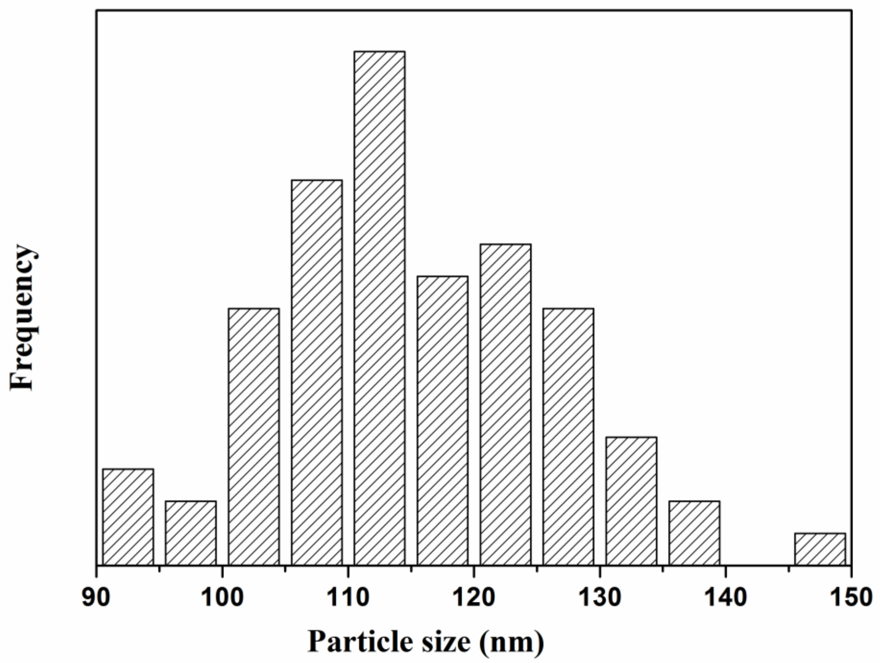

Fig. S21 Size distribution of the caves in Au@PON

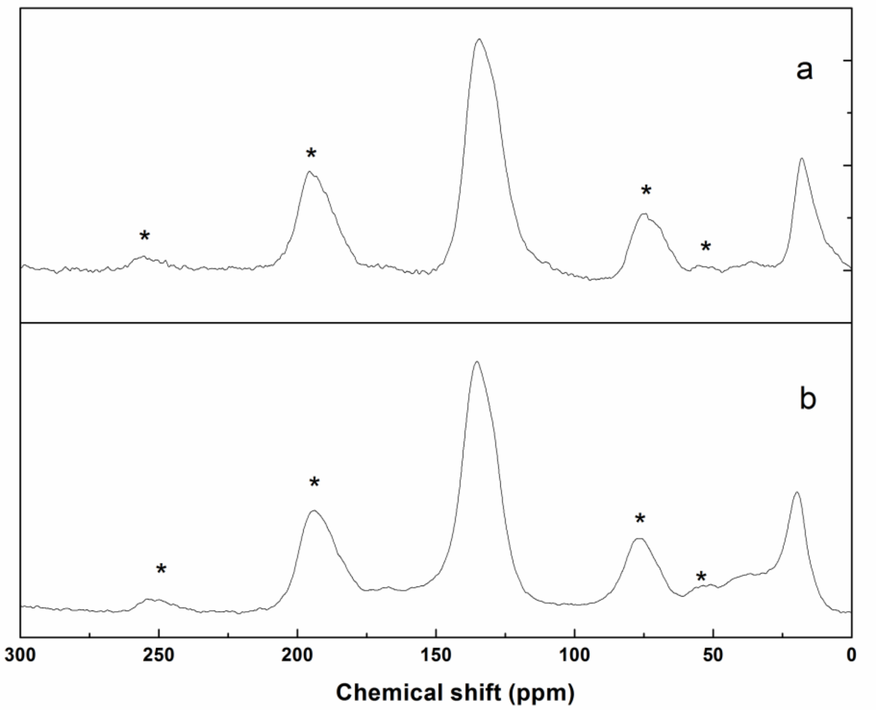

Fig. S22 ^{13}C CP/MAS NMR at the spinning rate of 6 Kz of a; Au@Si-PON; b; Au@PON, * Spinning sidebands

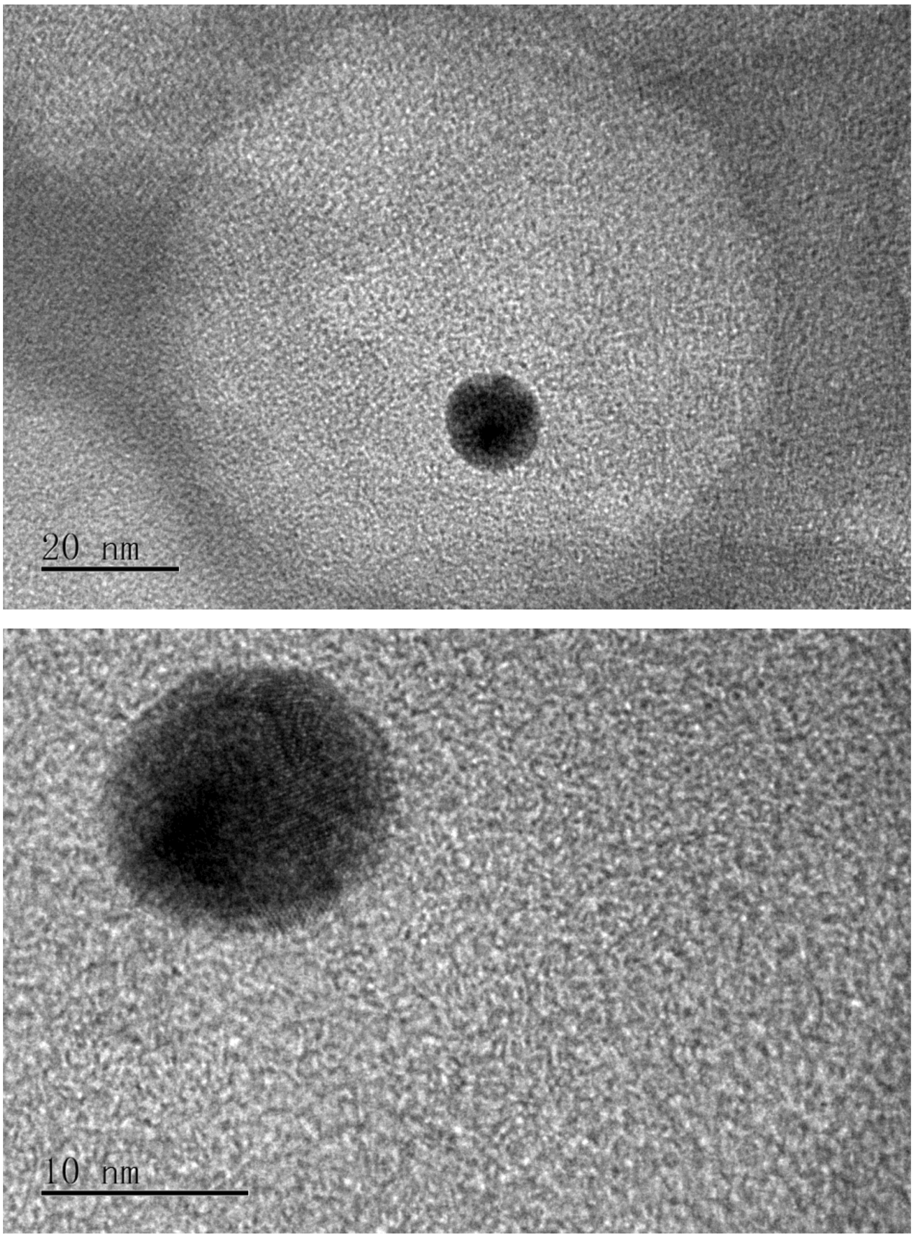

Fig. S23 HR-TEM images of Au@PON

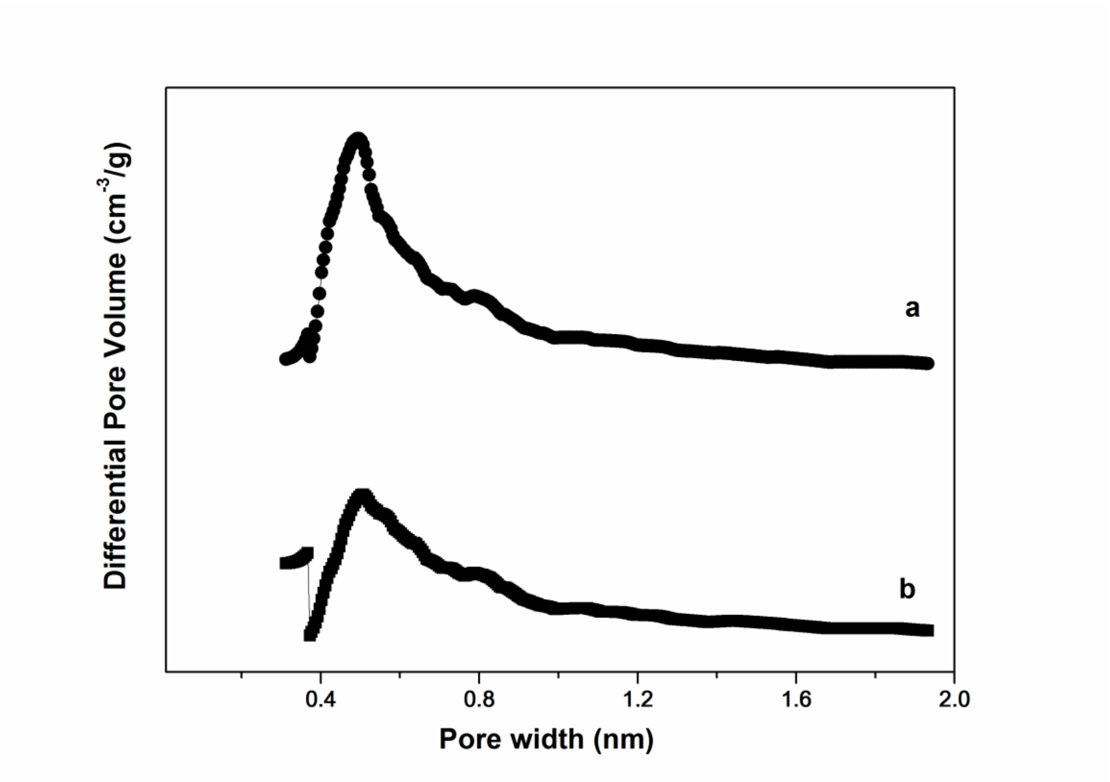

Fig. S24 Pore size distributions calculated using HK methods; a) Au@Si-PON; b) Au@PON

Table S1

	S_{BET} (m^2/g)^a	**Pore Volume (cm^3/g)^b**	**$S_{BET-micro}$ (m^2/g)^c**	**Pore Volume $_{micro}$(cm^3/g)^d**
Au@Si-PON	1240	1.03	404	0.17
Au@PON	980	0.81	384	0.17

a) Surface area calculated from the N_2 adsorption isotherm using the BET method; b) Total pore volume at P/P_0=0.99; c) Micropore surface area calculated from the N_2 adsorption isotherm using t-plot method; d) The micropore volume using the t-plot method based on the Halsey thickness equation.