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Supporting information:

Stable and Accessible Metal Catalysts Confined by Mesoporous Carbon derived from multicomponent Colloidal Spheres.

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1. Materials and Methods.

Chemicals.

Oleic acid (OA, 90%), oleylamine (OAm), 1-octadecene (ODE, 90%), PVP (MW=55000, AR) and tert-Butylamine borane (TBB) were purchased from Alfa Aesar. Sodium oleate, Iron chloride hexahydrate, ethanol, chloroform, 1, 2, 3, 4-Tetrahydronaphthalene, chloroauric acid, Palladium (II) acetylacetonate and hexane was obtained from Shanghai Chemical Reagents, China. All chemicals were used as received without further purification.

Characterization.

The sample was dispersed in ethanol or hexane and dropped to a piece of holey carbon-coated copper grid, then dried in open air. Transmission electron microscopy (TEM) images and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of samples were acquired on a JEOL JEM-2010 LaB6 high-resolution transmission electron microscope operated at 200 kV. The aberration-corrected high-resolution HAADF-STEM images were performed with JEOL JEMARM 200F operated at 200 kV. The energy-dispersive X-ray spectroscopy (EDS) composition measurements were taken on JEOL JSM-6700F equipped with an Oxford INCA x-sight EDS Si (Li) detector, which was operated at 200 kV. The samples were degassed at 60°C for 12h. The obtained adsorption-desorption isotherms were evaluated to give the pore parameters including Brunauer-Emmett-Teller(BET) specific surfacearea and poresize. The pore size distribution was calculated from the HK method. These were all performed on a Micromeritics TristarⅡ3020M. Catalytic performance was analyzed by GC-MS spectrometry (recorded on an Agilent 7890A GC system and 5975C inert XL MDS with Triple-Axis Detector).

Methods.

Synthesis of iron oleate.

In a typical synthesis for the complex, 5.4g of iron chloride ($FeCl_3 \cdot 6H_2O$) and 18g sodium oleate was added to a mixture solvent composed of 40 ml ethanol, 30 ml distilled water and 70 ml hexane in a 500 mL three-necked flask. The resulting mixture was refluxed at 70 °C for 4 h before it was cooled to room temperature. The iron–oleate complex was then extracted in the upper organic layer and washed three times with 15 ml distilled water in a separatory funnel. After washing, hexane was evaporated off at 70°C in a vacuum oven, resulting in iron–oleate complex in a waxy solid form[1].

Synthesis of monodisperse OA-caped Fe_3O_4 NPs

Monodisperse, 10-nm Fe_3O_4 NCs were synthesized by the thermal decomposition of iron oleate. In a typical synthesis for 10-nm Fe_3O_4 NCs, 2.5 g of iron oleate and 300 μL of OA were dissolved in 10 mL of ODE in a three-neck flask, and the resulting solution was heated at 210 °C under a N_2 atmosphere for 45 min. The mixture was then heated to 310 °C and maintained at this temperature for 30 min. After cooling down to room temperature, ethanol were added to precipitate Fe_3O_4 NCs, and the precipitated NPs were re-dispersed in chloroform to form a stable colloidal solution with a concentration of ~ 10 mg/mL.

Fabrication of OMCs-500 °C and OMCs-1000 °C

A 25mL DTAB solution (4 mg mL^{-1}) was thoroughly mixed with the 5mL chloroform solution of 10-nm Fe_3O_4 NPs (10 mg mL^{-1}) by vigorous mechanical stirring in a 100 mL beaker. Afterwards, a bubbling N_2 was introduced to remove the chloroform from the mixture at 40 °C. The mixture was then quickly injected into a 100 mL beaker with 25.0 mL ethylene glycol solution of PVP (550 mg) under vigorous mechanical stirring and stirred for 10 min. As prepared colloidal spheres were separated by centrifuge (5000 rpm, 10 min), and then dried in a vacuum oven at 90 °C for 10 h.[2] The carbonization of colloidal spheres were carried out in N_2 at 500 °C at a heating rate of 2 °C/min and kept at this temperature for 2 h. Fe_3O_4 NPs were then etched by a 12 M HCl solution for 2 h and washed by water and ethanol. The dried OMCs-500 °C powders were then heated to 1000 °C at a heating rate of 10 °C/min.

Synthesis of monodisperse OA-caped Au NPs

The ~6 nm Au NPs was synthesized according to a procedure published elsewhere. 0.2 g of $HAuCl_4•4H_2O$ was dissolved in a mixture composed of 10.0 mL of OAm and 10.0 mL of naphthalene under inert atmosphere in a 50mL three-necked at room temperature. A reducing solution containing TBB (1 mL), 1, 2, 3, 4-Tetrahydronaphthalene (1.0 mL) and OAm (1.0 mL) was then quickly injected into the flask. The mixture was stirred at room temperature for 2 h. Au NPs was precipitated by the addition of acetone and collected by centrifugation (11000 rpm for 8 min) for 3 times. The product was finally re-dispersed in 3.5 mL chloroform.[3]

Synthesis of 5-nm Pd NPs

The 5-nm Pd NPs was synthesized according to the procedure published elsewhere. 78.0 mg of $Pd(acac)_2$ was dissolved in 15.0 mL of OAm under inert atmosphere in a 50 mL three-necked. The mixture was then heated to 60 °C and maintained at this temperature for 10 min. A reducing solution composed of 150 mg of TBB, 3.5mL OAm was then quickly injected into the flask. The temperature was raised to 80 °C and the mixture was allowed to react at this temperature for 60 min before it was cooled down to room temperature. Pd NPs was precipitated by the addition of ethanol and collected by centrifugation (8500 rpm for 8 min) for 3 times. The product was finally re-dispersed in 4 mL chloroform.[3]

Fabrication of Au@OMCs-800 °C

A 25 mL DTAB solution (4 mg mL^{-1}) was thoroughly mixed with the 5 mL chloroform solution of 10-nm Fe_3O_4 NPs (10 mg mL^{-1}) and 90uL chloroform solution of 6-nm Au NPs by vigorous mechanical stirring in a 100mL beaker. Afterwards, a bubbling N_2 was introduced to remove the chloroform from the mixture at 40 °C. The mixture was then quickly injected into a 100mL beaker with 25.0 mL ethylene glycol solution of PVP (550 mg) under vigorous mechanical stirring and stirred for 10 min. As prepared colloidal spheres were separated by centrifuge (5000 rpm, 10 min), and then dried in a vacuum oven at 90 °C for 10 h. The carbonization of colloidal spheres were carried out in N_2 at 500 °C at a heating rate of 2 °C/min and kept at this temperature for 2 h. Fe_3O_4 NPs were then etched by a 12 M HCl solution for 2 h and washed by water and ethanol. The dried Au@OMCs-500 °C powders were then heated to 800 °C at a heating rate of 10 °C/min. The Au content was measured to be 17 wt% based on ICP-AES analysis.

Fabrication of the Pd@OMCs-800 °C

Fabrication of the Pd@OMCs-800 °C uses the same procedure as the Au@OMCs-800 °C except that a 130 μL Pd NPs colloidal solution was added into the Fe_3O_4 NPs colloidal solution to assemble the multi-component colloidal spheres. Fe_3O_4 NPs were then selectively etched by a 12 M HCl solution for 1 h and the left Pd NPs would disperse uniformly in the mesoporous carbon spheres and were confined by the in-situ formed mesoporous carbon. The dried Pd@OMCs-500 °C powders were then heated to 800 °C for 2 h at a heating rate of 10 °C/min. The Pd content was measured to be 24 wt% based on ICP-AES analysis.

Synthesis of Au/AC (19 wt% loading) from ~6-nm Au NPs

2.5 mL of Au NPs colloidal solution were dissolved in 10 mL hexane in a 15 mL vial and 30mg active carbon support was carefully added to it. The mixture was then sonicated for 1 hour. After evaporation of hexane, 20 mL of acetic acid was added to the Au/AC dispersion and heated for 10 hours at 70 °C. The reaction mixture was cooled down to room temperature. 30 mL of ethanol was added and the mixture was centrifuged at 11000 rpm for 5 mins. This procedure was repeated twice. The Au/AC NPs were recovered by adding acetone. Acetone was evaporated and the resultant Au/AC NPs were weighed. Some of as prepared Au/AC catalyst was heated for 2 hours at 800 °C (Au/AC-800 °C) to investigate the catalytic activity for liquid-phase homocoupling reaction of phenylacetylene and hydrogenation reaction of p-nitrobenzene.

Synthesis of Pd/AC (21 wt% loading) from 5-nm Pd NPs

3 mL of Pd NPs colloidal solution were dissolved in 10 mL hexane in a 15 mL vial and 30mg active carbon support was carefully added to it. The mixture was then sonicated for 1 hour. After evaporation of hexane, 20 mL of acetic acid was added to the Pd/AC dispersion and heated for 10 hours at 70 °C. The reaction mixture was cooled down to room temperature. 30 mL of ethanol was added and the mixture was centrifuged at 8000 rpm for 8 mins. This procedure was repeated twice. The Pd/AC NPs were recovered by adding acetone. Acetone was evaporated and the resultant Pd/AC NPs were weighed. A measured amount of de-ionized water was added, resulting in a 2 mg/mL solution. This mixture was sonicated for 1 hour to ensure uniform distribution. Some of as prepared Pd/AC catalyst was heated for 2 hours at 800 °C (Pd/AC-800 °C) to investigate the catalytic activity for formic acid oxidation.

Catalytic evaluation

All the organic catalytic reaction were conducted with 25 mL Schlenk glass vessel tubes. For liquid-phase homocoupling of phenylacetylene, phenylacetylene (15 μL) and catalyst (500 μg) were reacted under 1 atm air at 140 °C. For hydrogenation reaction of p-nitrobenzene, p-nitrobenzene (15μL), formic acid (15μL) and catalyst (500μg) were reacted under 1atm N_2 at 140 °C. All the catalytic reaction were conducted with

Dimethyl Formamide as the solvent and samples were taken to monitor the catalytic activity and detected the conversions by gas chromatography-mass spectrometer (GC-MS) and gas chromatography (GC) (toluene as the internal label for hydrogenation reaction of p-nitrobenzene).

Electrochemical measurements: They were performed on a Electrochemical Analyzer, Model CHI760E, by typical cyclic voltammetry technique. Ag/AgCl and Pt wire were used as reference and counter electrodes respectively.

1. CV measurements (to check for hydrogen absorption & electrochemically active surface area, ECASA) in 0.1M $HClO_4$ under nitrogen, in the range of -250 mV to 1000 mV (scan rate 50 mV/s).

2. Formic acid oxidation in 2 M formic acid and 0.1 M $HClO_4$ with a scan rate 10 mV/s.

The calculation of ECSA based on the following equations:

$$Charge[C] = \int_{t0}^{t1} Idt = \int_{E0}^{E1} \frac{I[A] \times dE[V]}{v[V/s]}$$

$$ECSA[cm^2 Pd] = \frac{charge[\mu C]}{Q[\mu C / cm^2 Pd]}$$

Where C is charge, I the current, E the potential, v the scan rate, and Q the charge density passed during the hydrogen adsorption. The value of Q used for ECSA calculation was experimentally determined to be 210μC/cm.[4]

2. Supporting Figures

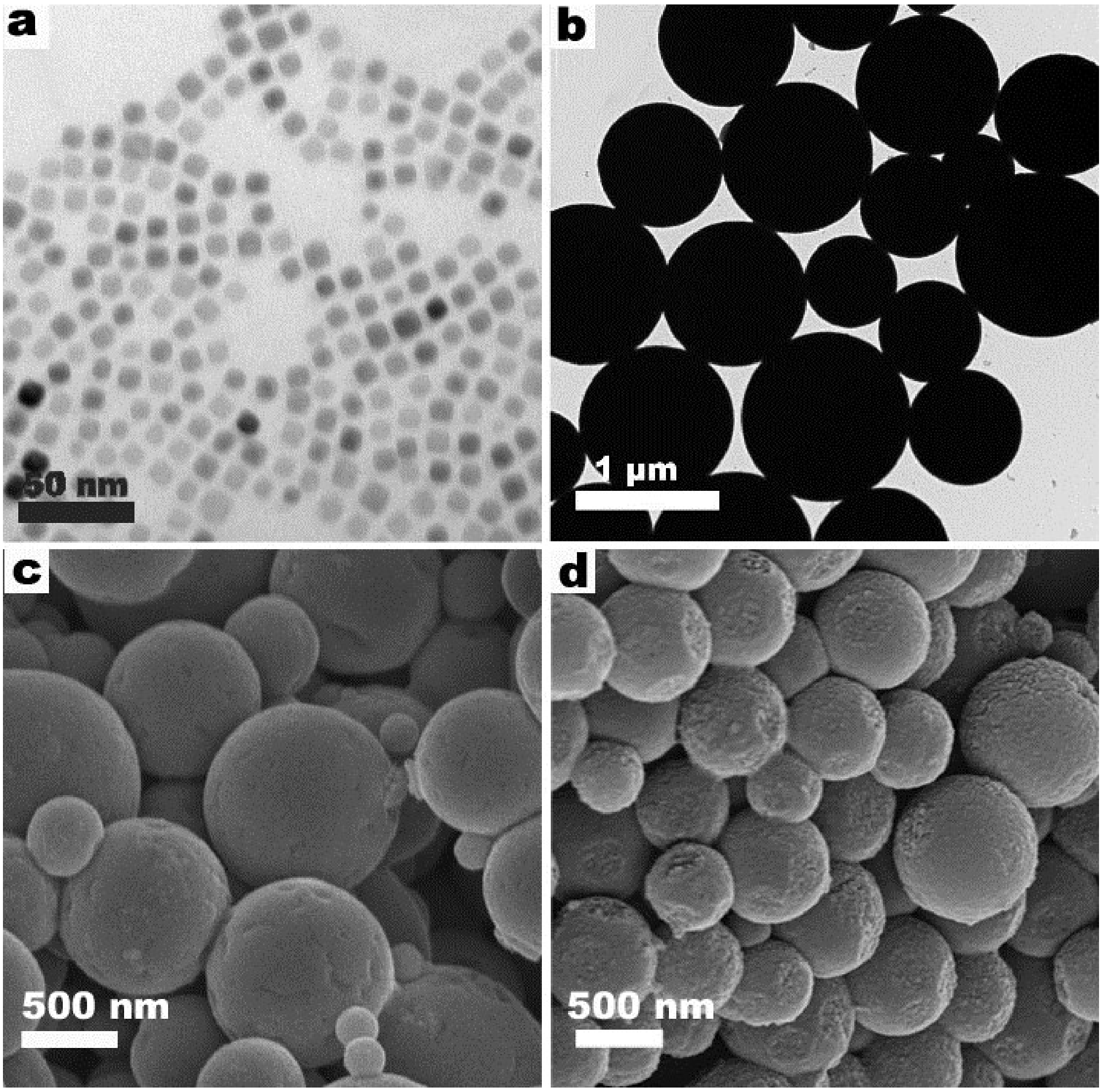

Figure S1. (a) Representative TEM images of pristine 10-nm Fe_3O_4 NPs. (b, c) TEM and SEM images of 3D Fe_3O_4 colloidal spheres self-assembly from 10-nm Fe_3O_4 NPs, respectively. (d) SEM image of ordered mesoporous carbons derived from 3D Fe_3O_4 colloidal spheres(figure S1 (b, c)) hearted for 2 h under N_2 atmosphere at 500 °C.

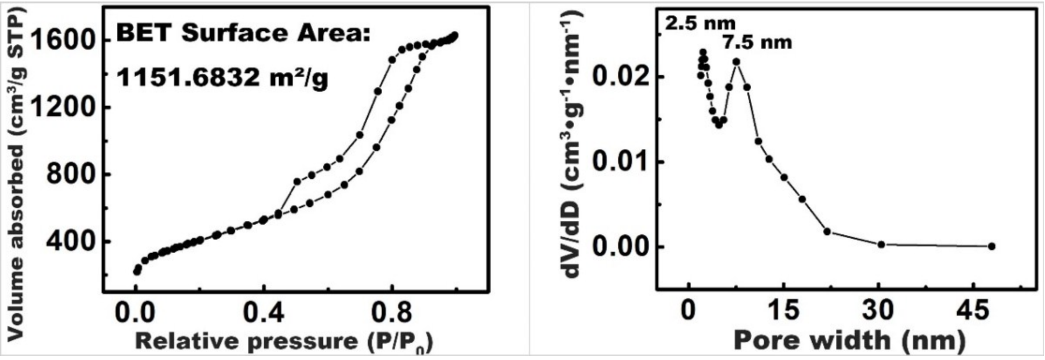

Figure S2. N_2-adsorption-desorption isotherms and pore width distribution of OMCs-1000 °C, respectively.

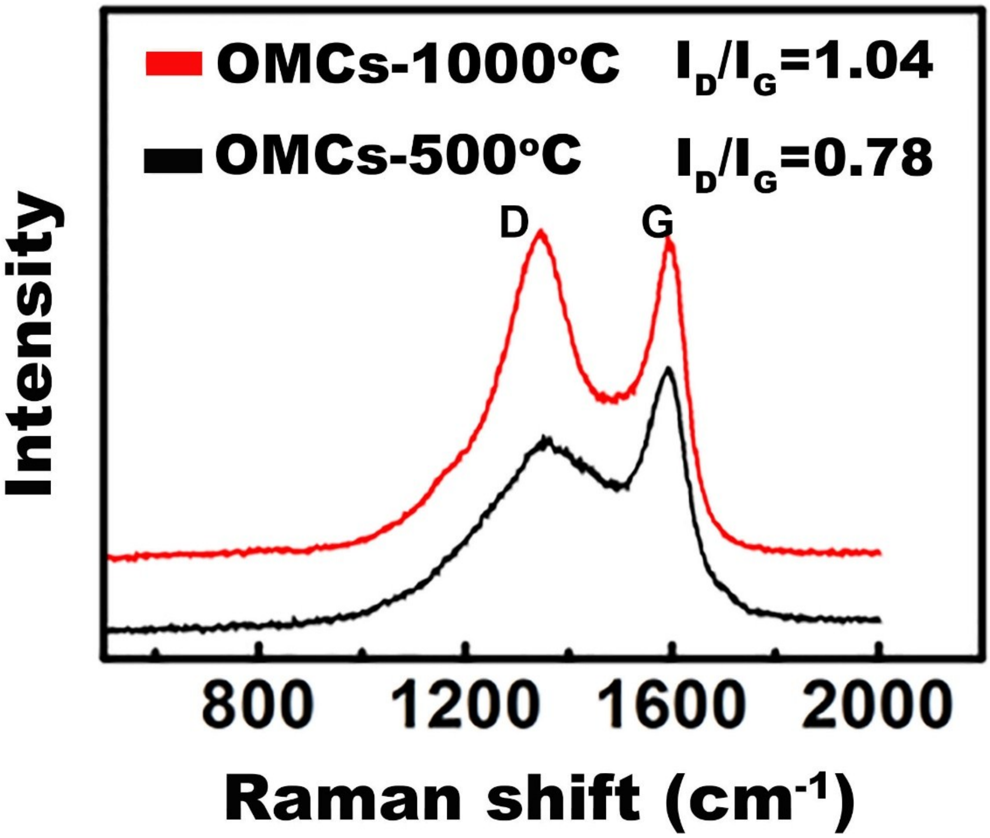

Figure S3. Representative Raman spectrum of Fe_3O_4-NPs-derived OMCs-500 °C and OMCs-1000 °C.

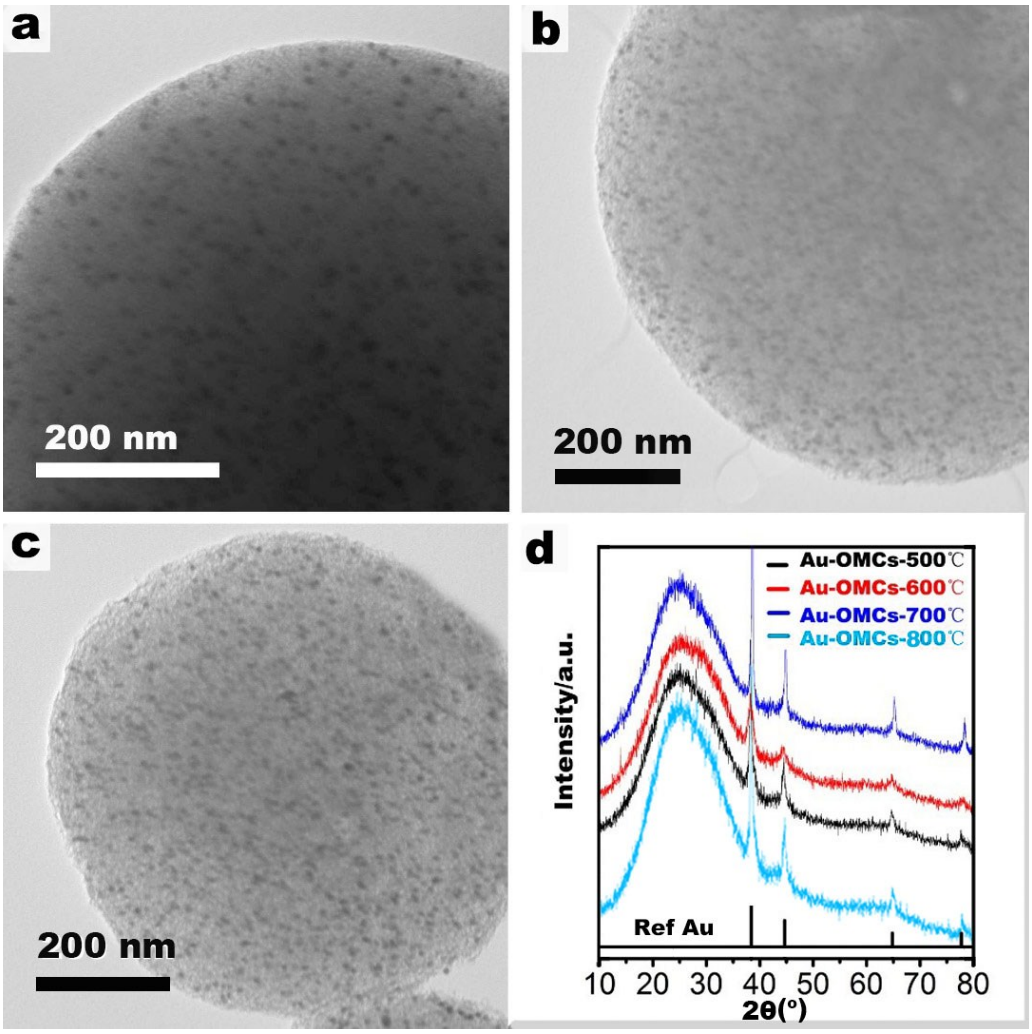

Figure S4. (a, b, c) Representative TEM images of Au@OMCs subjected to heat treatment at 500 °C, 600 °C and 700 °C, respectively. (d) Powder XRD patterns of Au@OMCs subjected to heat treatment at 500 °C, 600 °C and 700 °C, respectively.

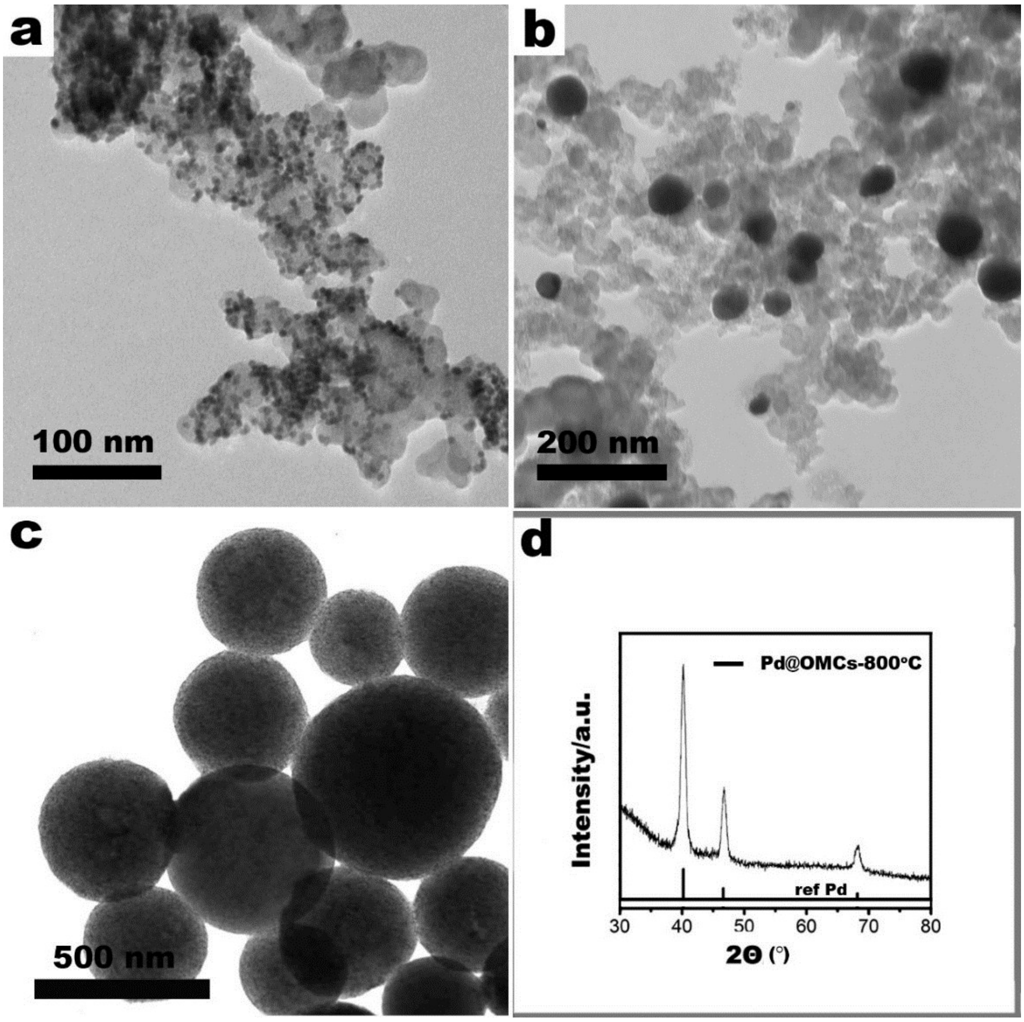

Figure S5. (a, b, c) Representative TEM images of Pd/AC, Pd/AC-800 °C and Pd@OMCs-800 °C, respectively. (d) Powder XRD patterns of Pd@OMCs-800 °C.

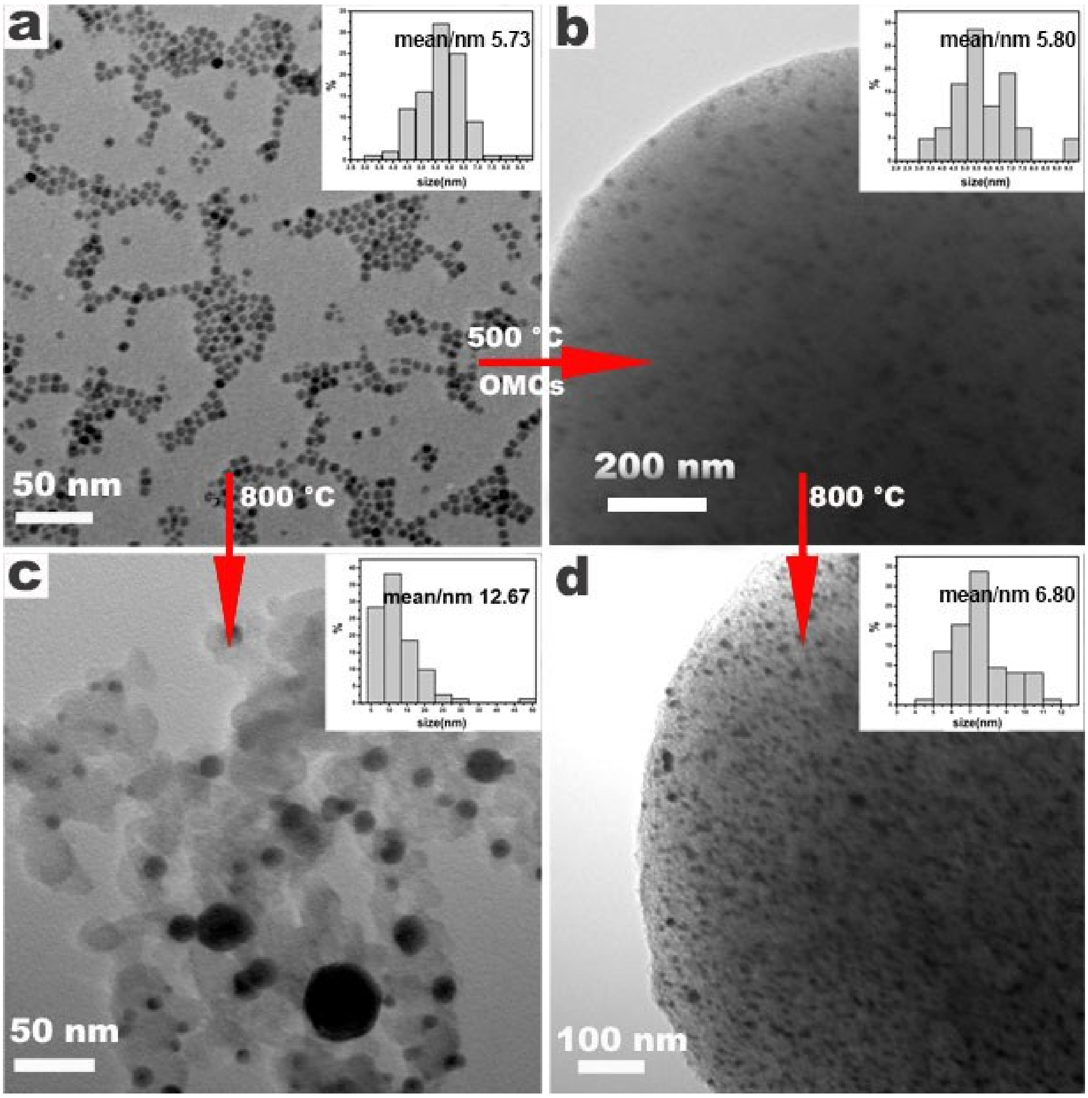

Figure S6. (a) TEM image of pristine Au NPs. (b, d) TEM images of Au@OMCs subjected to heat treatment at 500 °C and 800 °C for 2 h, respectively. (c) TEM image of Au/AC subjected to heat treatment at 800 °C for 2 h (Au/AC-800 °C).

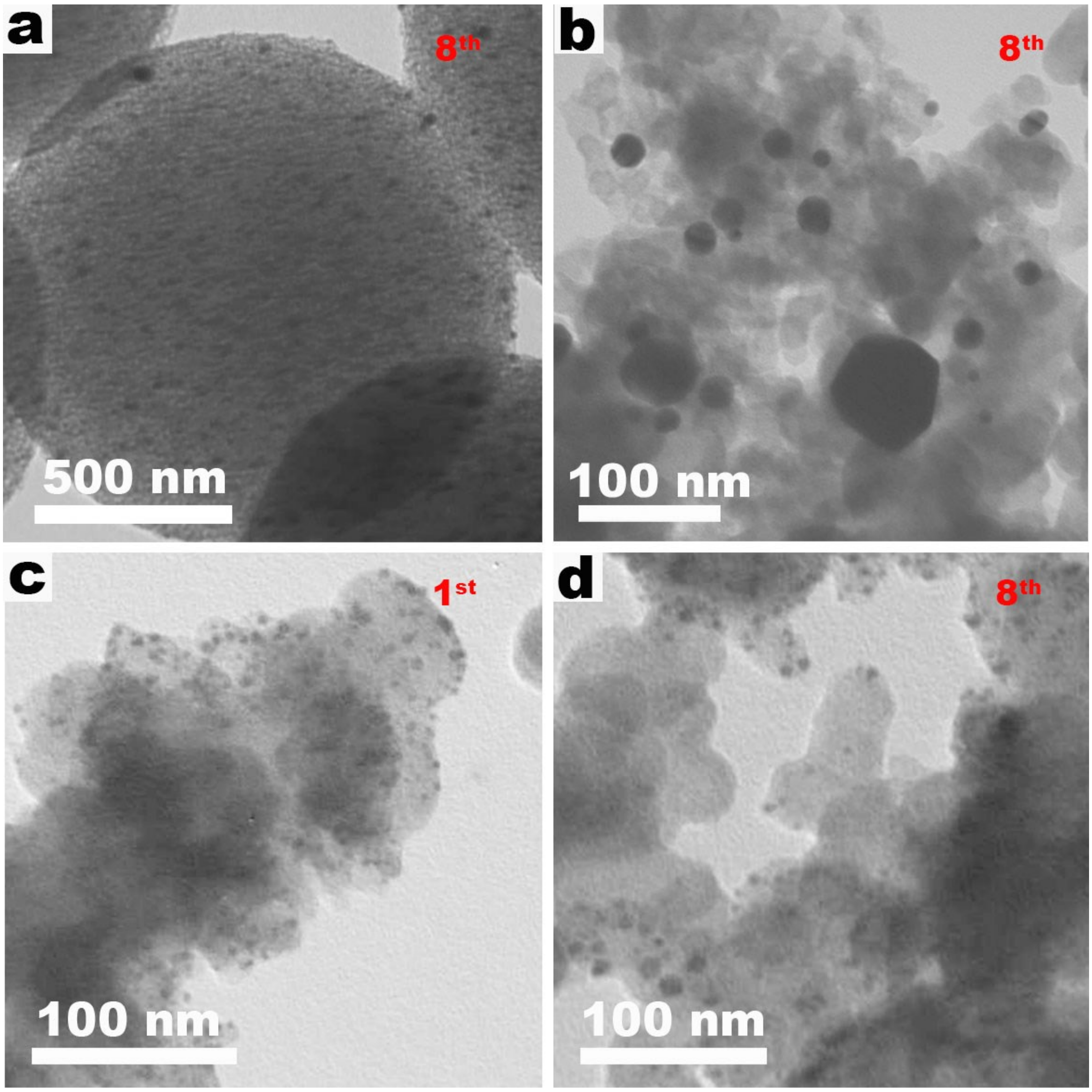

Figure S7. (a, b) TEM images of Au@OMCs-800 °C and Au/AC-800 °C when they are tested in the eighth circle for hydrogenation reaction of p-nitrobenzene; (c, d) TEM images of pristine Au/AC and Au/AC tested in the eighth circle for hydrogenation reaction of p-nitrobenzene.

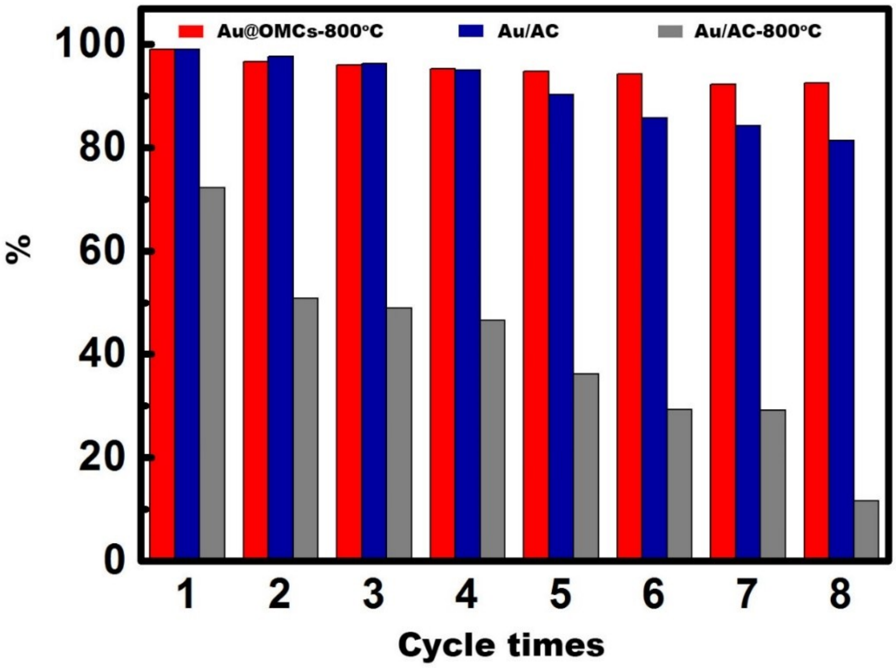

Figure S8. Cycle tests for p-nitrobenzene hydroconversion.

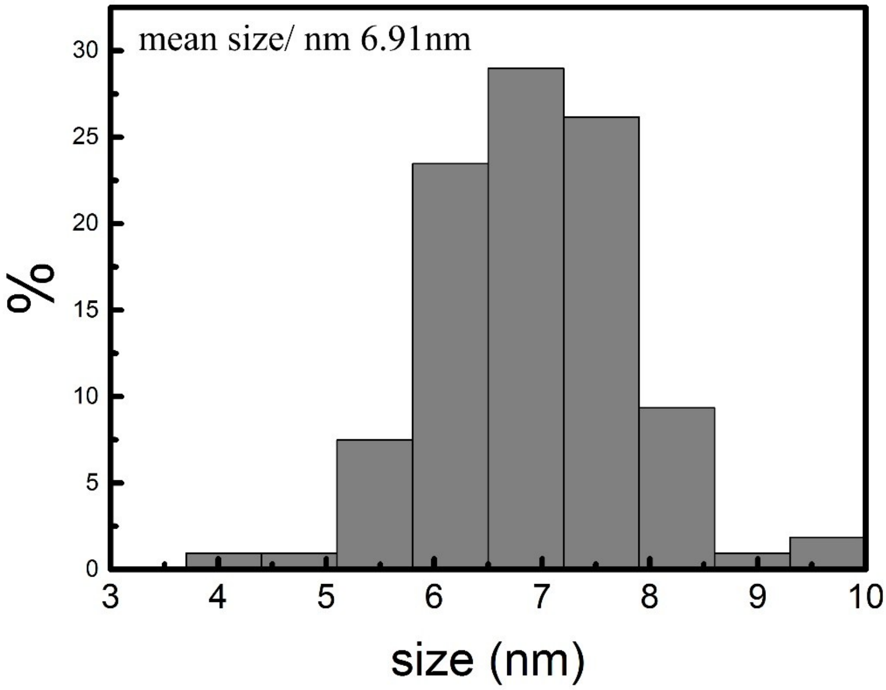

Figure S9. Particle size distribution plot of Au@OMCs-800°C tested in the eighth circle for hydrogenation reaction of p-nitrobenzene.

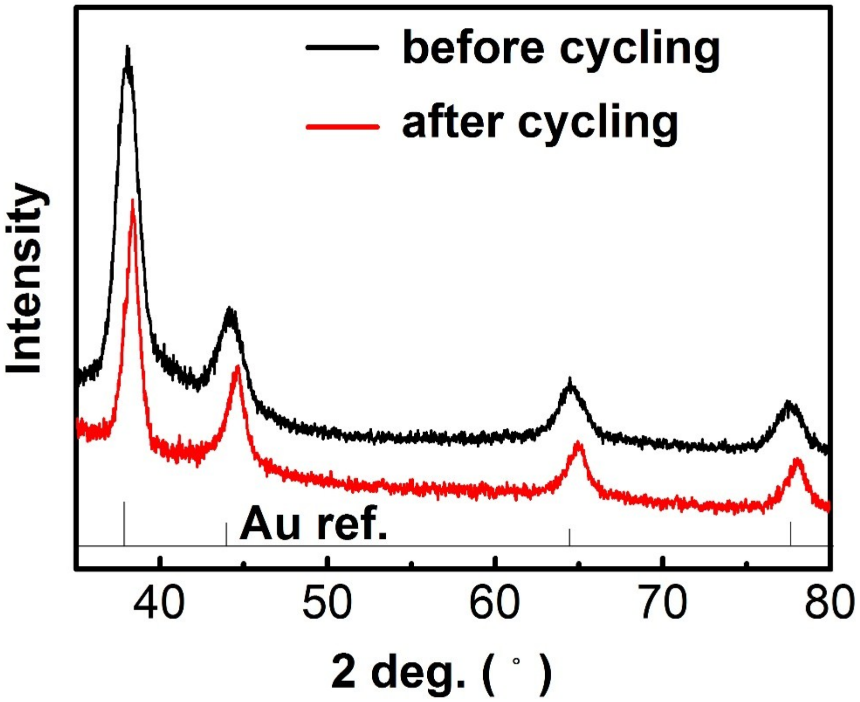

Figure S10. Powder XRD patterns of Au@OMCs-800 °C before and after cycling (8th) of hydrogenation reaction of p-nitrobenzene.

3. References

1. J. Park, K. An, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang and T. Hyeon, *Nat Mater*, 2004, **3**, 891-895.
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