Electronic Supplementary Information

Porous and Hollow Metal-layer@SiO$_2$ Nanocomposites as Stable Nanoreactors for Hydrocarbon Selective Oxidation

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Experimental

Catalyst Preparation

All chemicals were purchased from Sigma−Aldrich.

Preparation of PS template spheres: The PS colloids were prepared by emulsion polymerization in water-alcohol system. Specifically, 0.1 g sodium lauryl sulfate and 0.11 g potassium pyrosulphate were dissolved into the 70 ml water－alcohol solution (volume ratio is 2:5). Prior to add styrene, the solution was bubbled with N$_2$ for 10 min. After this, 4.0 mL styrene was added under nitrogen atmosphere and rapidly stirred. The emulsion solution was heated to 343K and maintained at this temperature for 8 h. After polymerization reaction, the solution was filtrated and washed with ethanol. The obtained solid was dried under air at room temperature.

Preparation of PS@metal nanocomposites: 0.25 g PS colloids and 10 ml HAuCl$_4$ aqueous solution (0.01 M) were well dissolved and the mixture was constant magnetic stirring at room temperature for 12 h to obtain PS@Au nanocomposites. The PS@Ag and PS@Cu have been simply obtained by exchanging the HAuCl$_4$ aqueous solution to AgNO$_3$ (adding 20 mg ascorbic acid) and Cu(NO$_3$)$_2$ (adding 10 mg NaBH$_4$) aqueous solution, respectively.

Preparation of (PS@metal)@SiO$_2$ nanocomposites: TEOS (2.5 mL) was rapidly added into a mixture containing ethanol (150 mL), ammonium hydroxide (5 mL) and PS@metal nanocomposites dispersed in aqueous solution (20 mL). The resulting mixture was constant magnetic stirring at room temperature for 2 h, and then the obtained samples were washed with ethanol and dried under N$_2$ at 100℃ for 24 h.

Preparation of metal-layer@SiO$_2$ nanoreactor: The as-synthesized (PS@metal)@SiO$_2$ nanocomposites (0.5 g) were mixed with 500 mL of isopropanol and 50 mL of deionized water. The mixture was constant magnetic stirring at room temperature for 24 h, and then the obtained samples were washed with distilled water and dried under N$_2$ at100℃ for 24 h.

Preparation of Au-layer shell: The as-synthesized Au-layer@SiO$_2$ nanocomposites (0.5 g) were mixed with HF(0.5%). After 1 h, the obtained samples were washed with distilled water and dried under N$_2$ at 100℃ for 24 h.

Catalyst Characterization

Scanning electron microscopy (SEM) images were taken on a FEI-quanta 200 scanning electron microscope with acceleration voltage of 20 kV. The Transmission electron microscopy (TEM) image were obtained with a FEI/Philips Tecnai 12 BioTWIN transmission electron microscope operated at 200 kV with EDX analyses. The normal TEM samples were prepared by dropping the solution onto a copper grid covered with carbon film and dried in air. BET specific surface areas and pore size distributions were calculated by plotting the adsorption isotherm of N$_2$ at liquid N$_2$ temperature (77 K). These measurements were made on a

Micromeritics ASAP 2050 porosimeter. The gas chromatography measurements (GC-MS) were performed in a Varian 3400 GC column with a cross-linked 5% PhMe silicone column (25 m × 0.20 mm × 0.33 μm) and a FID detector under the following conditions: carrier gas (N_2) at 140 K; temperature program 60℃, 1 min, 15℃/min, 180℃, 15 min; split ratio,10:1; injector, 300℃; detector, 300℃. The crystal structure of the resultant products was characterized by X-ray powder diffraction (XRD) by using a X'Pert-ProMPD (Holand) D/max-γAX-ray diffractometer with Cu Kα radiation (λ=0.154178 nm).

Catalyst Activity

Cyclohexene (15 mL) and as-fabricated catalysts (0.10 g) were stirred at 60℃ using hydrogen peroxide (30 mL) as an oxidizing agent for different times. After filtering off the catalyst, the filtrate was analyzed by GC-MS.
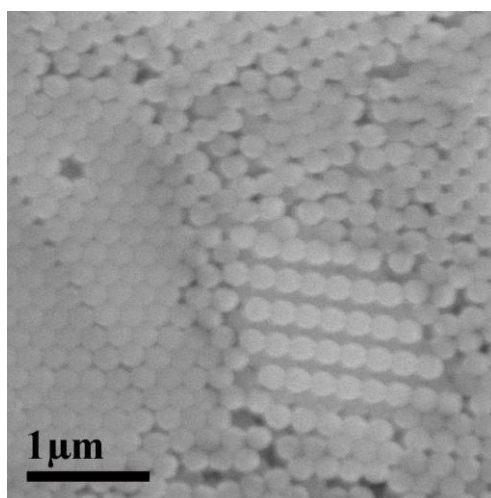
Figure S1. SEM image of PS nanospheres.
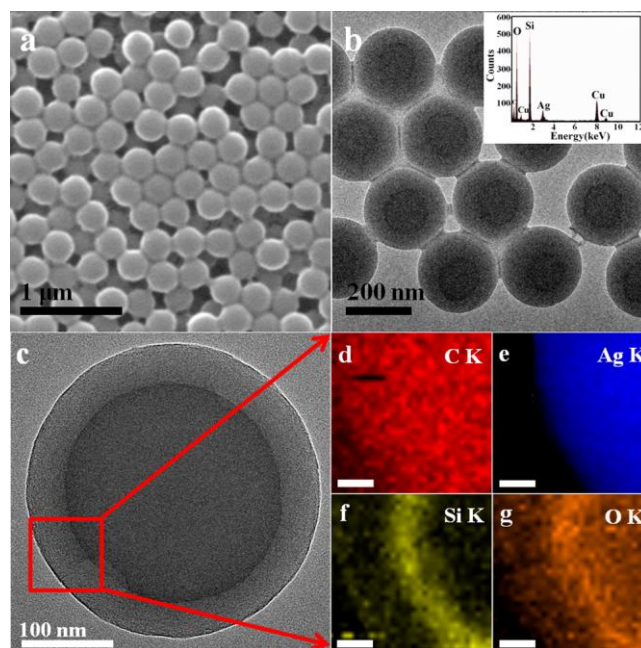
Figure S2. Structure and morphology of porous and hollow Ag-layer@SiO$_2$ nanoreactors. (a) Typical SEM image. (b) TEM image. (Inset: EDX pattern.) (c) TEM image of single porous and

hollow Ag-layer@SiO$_2$ nanoreactor. Corresponding elemental mapping images of (d) C, (e) Ag, (f) Si and (g) O. (Scale bar: 20 nm.)
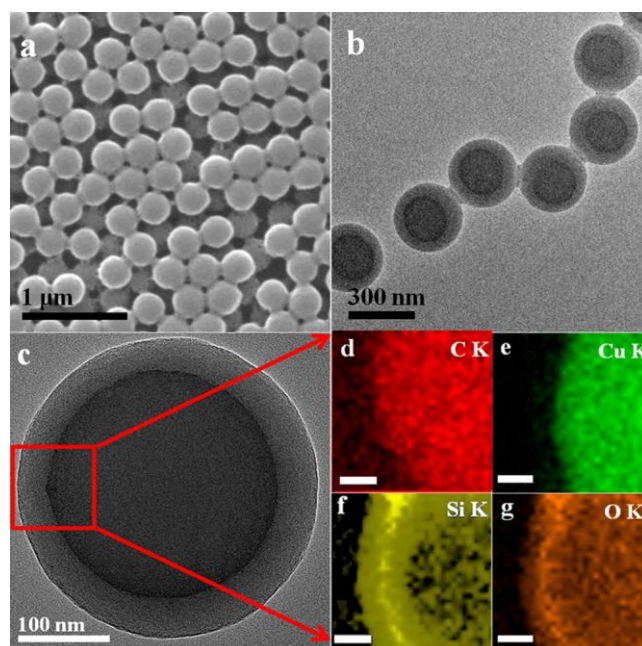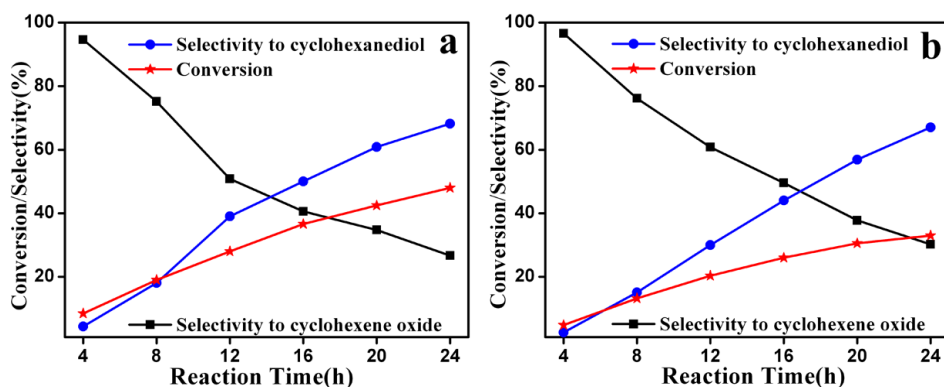

Figure S3. Structure and morphology of porous and hollow Cu-layer@SiO$_2$ nanoreactors. (a) Typical SEM image. (b) TEM image. (c) TEM image of single porous and hollow Cu-layer@SiO$_2$ nanoreactor. Corresponding elemental mapping images of (d) C, (e) Cu, (f) Si and (g) O. (Scale bar: 20 nm.)

Figure S4. The relationship between the conversion of cyclohexene/selectivity of different products and reaction time with (a) porous and hollow Ag-layer@SiO$_2$ and (b) porous and hollow Cu-layer@SiO$_2$ as catalysts.
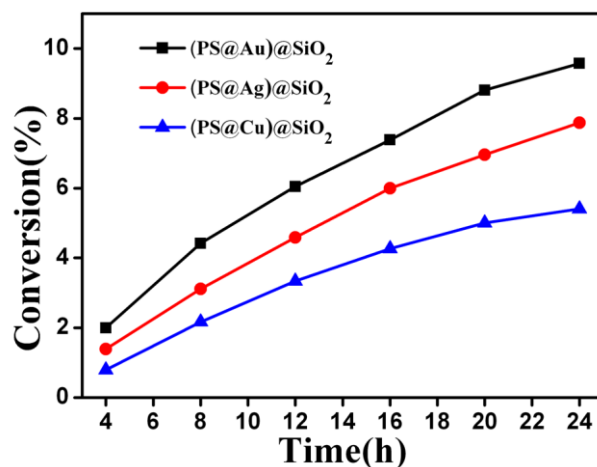
Figure S5. The relationship between the conversion of cyclohexene and reaction time with different (PS@metal)@SiO_2 (metal=Au, Ag, Cu) nanoparticles as catalysts.
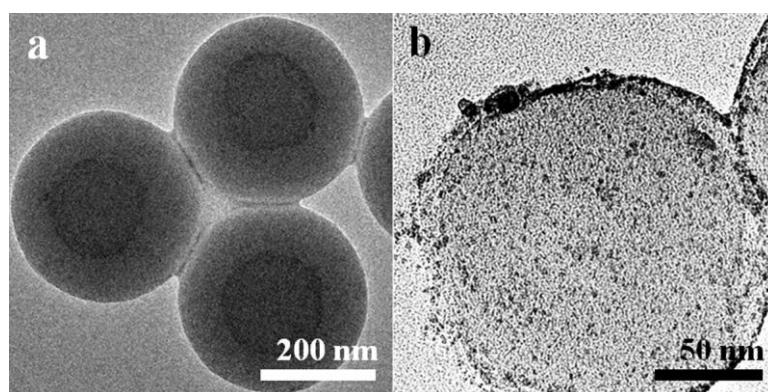
Figure S6. TEM images of (a) porous and hollow Au-layer@SiO_2 nanoreactors and (b) porous and hollow Au-layer shell after removal the SiO_2 of Au-layer@SiO_2 nanoreactors
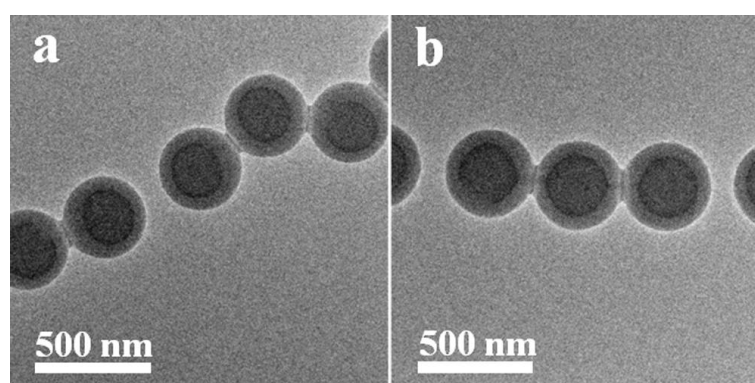

Figure S7. TEM images of porous and hollow Au-layer@SiO_2 nanoreactors as catalysts after

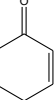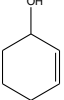recycling experiments (a) 1time, (b) 2 times. (60℃ and 24 h)
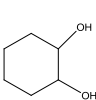
Catalyst	Selectivity (%)				Conversion (%)	$\Sigma_{sel}C_6^§$	TOF [s^{-1}]
Au-layer@SiO$_2$	22.63	70.20	1.05	5.10	58.41	99	0.0008
Ag-layer@SiO$_2$	26.69	68.20	0.70	4.40	48.03	100	0.0007
Cu-layer@SiO$_2$	30.21	67.02	trace	2.77	32.99	100	0.0005
(PS@Au)@SiO$_2$	12.54	85.21	trace	1.21	9.57	99	0.00016
(PS@Ag)@SiO$_2$	16.25	80.98	trace	0.96	7.87	98	0.00014
(PS@Cu)@SiO$_2$	18.98	78.20	trace	0.61	5.40	98	0.0001

Table S1. As-synthesized catalysts on selective oxidation of cyclohexene at 60℃ after 24 h. §Total selectivity to C$_6$ partial oxidation products.
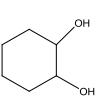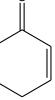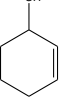
Reaction time (h)	Selectivity (%)				Conversion (%)	$\Sigma_{sel}C_6^§$
0	0	0	0	0	0	0
4	91.61	6.39	trace	0.90	12.18	99
8	77.16	21.06	trace	0.92	26.95	99.1
12	52.42	45.01	0.28	1.49	36.89	99.2
16	37.58	59.04	0.58	2.00	45.05	99.2
20	30.44	64.61	0.85	3.12	53.74	99
24	22.63	70.20	1.05	5.10	58.41	99

Table S2. Effect of variety of reaction time on selective oxidation of cyclohexene using porous and hollow Au-layer@SiO$_2$ as catalyst. §Total selectivity to C$_6$ partial oxidation products.
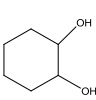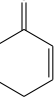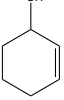
Times	Selectivity (%)				Conversion (%)	$\Sigma_{sel}C_6^§$
1	22.63	70.20	1.05	5.10	58.41	99
2	16.31	75.12	0.92	6.70	60.01	99
3	24.56	68.79	0.61	4.77	54.13	99
4	20.11	72.63	0.81	5.15	53.79	99
5	15.28	79.15	0.48	4.05	50.93	99

Table S3. Porous and hollow Au-layer@SiO$_2$ as catalyst on repeat experiments of selective oxidation of cyclohexene at 60℃ after 24 h. §Total selectivity to C6 partial oxidation products.