

Supporting Information

1. Experimental section

1.1. The preparation of metal-graphene core-shell nanostructures.

Here, we take the preparation of Au-graphene core-shell nanostructures for example.

For the calculation of the ratio of graphene to metal salts, we assumed R as a constant by $R = 1 \text{ mg}_{(\text{graphene})}/100 \text{ mmol}_{(\text{metal salt})}$. In our experiments, the ratios of graphene to metal salts were estimated as 4R, 3R and 2R for the preparation of metal-graphene core-shell nanostructures, hollow graphene nanospheres, and a high density of metal nanoparticles supported on graphene, respectively.

The as-synthesized graphene nanosheets were mixed with chloroauric acid (dosage ratio of 4R) to form a homogeneous solution, which was dropped into silicone oil (25 mL) with strong magnetic stirring for 5 h. Then the emulsion droplets with core-shell architecture were formed in the suspension system. Its color turned from transparent to reddish (for the Pt-graphene core-shell nanostructures and Ag-graphene core-shell nanostructures, the color was grey), indicating the formation of Au-graphene core-shell nanostructures. The resulted suspension system was equally transferred into two Petri dishes, and then placed in an oven at 60 °C for 3 days. The colloidal crystallization of the emulsion droplets gradually occurred when water in the droplets was evaporated. The obtained Au-graphene core-shell nanostructures were washed with hexane to remove the silicone oil, and then collected by centrifugation

with 10000 rpm/min for 10 min.

For the preparation of Pt-graphene core-shell nanostructures and Ag-graphene core-shell nanostructures, chloroauric acid was substituted by potassium tetrachloroplatinate (II) and silver nitrate during the synthesis process.

1.2. The preparation of hollow graphene nanospheres.

The as-synthesized GNSs were mixed with chloroauric acid (dosage ratio of 3R) to form a homogeneous solution, which was dropped into silicone oil (25 mL) with strong magnetic stirring for 5 h. Then the emulsion droplets with hollow graphene nanospheres were formed in the suspension system, which was equally transferred into two Petri dishes, and then placed in an oven at 60 °C for 3 days. The colloidal crystallization of the emulsion droplets gradually occurred when water in the droplets was evaporated. The products containing hollow graphene nanospheres and Au nanoparticles were obtained after thoroughly washed with hexane to remove the silicone oil. After that, the products were re-dispersed in hexane to form a homogeneous solution. The Au nanoparticles were collected by centrifugation with 8000 rpm/min for 10 min. The hollow graphene nanospheres were obtained by centrifugation with 12000 rpm/min for 20 min and finally dried under vacuum at 60 °C for 5 h.

The preparation of hollow graphene nanospheres can also be realized by substituting chloroauric acid with potassium tetrachloroplatinate (II) or silver nitrate during the synthesis process.

1.3. The preparation of the high density of Au (Pt or Ag) nanoparticles supported on

graphene.

The as-synthesized GNSs were mixed with chloroauric acid (dosage ratio of 2R) to form a homogeneous solution, which was dropped into silicone oil (25 mL) with strong magnetic stirring for 5 h. Then the emulsion droplets with the high density of Au nanoparticles supported on graphene were formed in the suspension system, which was equally transferred into two Petri dishes, and then the Petri dishes were placed in an oven at 60 °C for 3 days. The colloidal crystallization of the emulsion droplets gradually occurred when water in the droplets was evaporated. The as-prepared high density of Au nanoparticles supported on graphene were washed with hexane to remove the silicone oil, and then collected by centrifugation with 10000 rpm/min for 10 min.

For the preparation of the high density of Pt nanoparticles supported on graphene and the high density of Ag nanoparticles supported on graphene, chloroauric acid was substituted by potassium tetrachloroplatinate (II) and silver nitrate during the synthesis process.

1.4. Catalytic selective oxidation of cyclohexene

Cyclohexene (5 mL) and different metal-graphene complex nanocatalysts (Au-graphene core-shell nanostructures, Pt-graphene core-shell nanostructures, Ag-graphene core-shell nanostructures, hollow graphene nanospheres, and a high density of Au nanoparticles supported on graphene, respectively, 0.05 g) were stirred at 60 °C using air as oxidant for different time. After filtering off the catalysts, the filtrate was analyzed by gas chromatography (GC).

2. Characterization

The particle size and shape were analysed with TEM using a Philips/FEI Tecnai 12 BioTWIN TEM operating at 200 kV. The TEM samples were prepared by dropping the sample solution onto a copper grid covered with carbon and dried in air. The EDX and EELS spectra were obtained with an FEI/Philips Tecnai 12 BioTWIN TEM operating at 200 kV. Raman spectra of samples were measured using a LabRAM HR800 microspectrometer using an excitation wavelength of 514 nm. All samples were deposited on a sheet of copper in powder form without using any solvent. The products of the selective oxidation reactions were analyzed using GC. The GC measurements 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 (N₂) at 140 K; temperature program 60°C, 1 min, 15°C/min, 180°C, 15 min; split ratio, 10:1; injector, 300°C; detector, 300°C. The Brunauer-Emmett-Teller (BET) specific surface areas and pore size distributions were calculated by plotting the adsorption isotherm of N₂. The measurements were made on a Micromeritics ASAP 2050 porosimeter. The XPS spectra were obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg K_α X-ray (hν = 1283.3 eV). XPS samples were prepared by drying a dispersion of different products on a piece of Cu wafer.

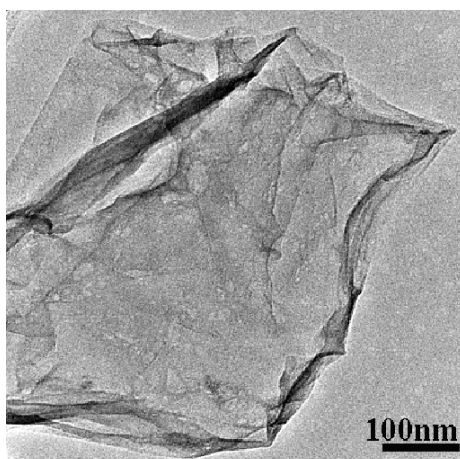


Figure S1. TEM image of graphene nanosheets.

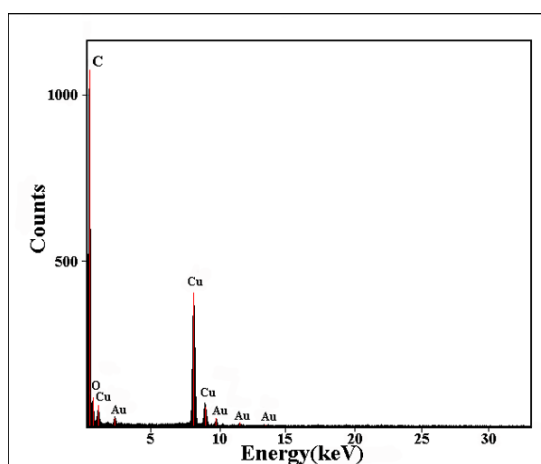


Figure S2. EDX spectrum of Au-graphene core-shell nanostructures.

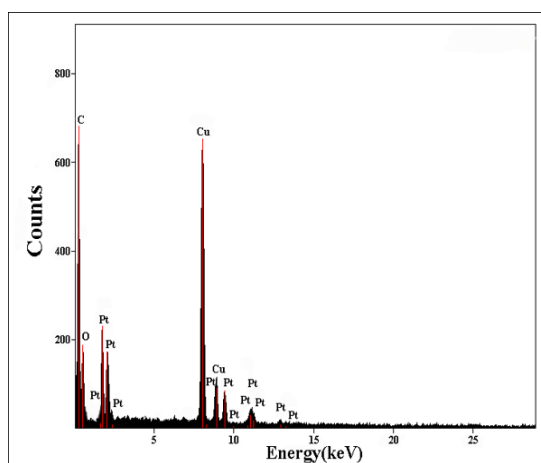


Figure S3. EDX spectrum of Pt-graphene core-shell nanostructures.

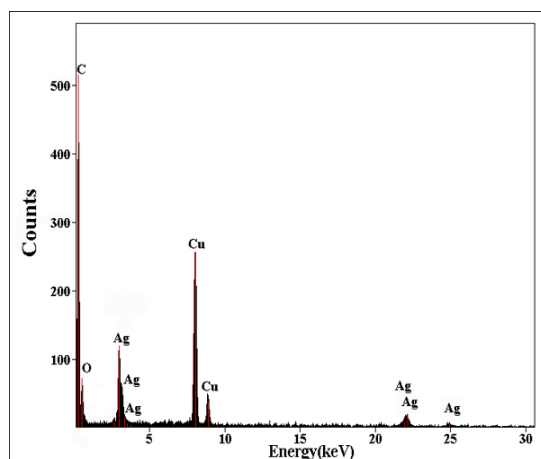


Figure S4. EDX spectrum of Ag-graphene core-shell nanostructures.

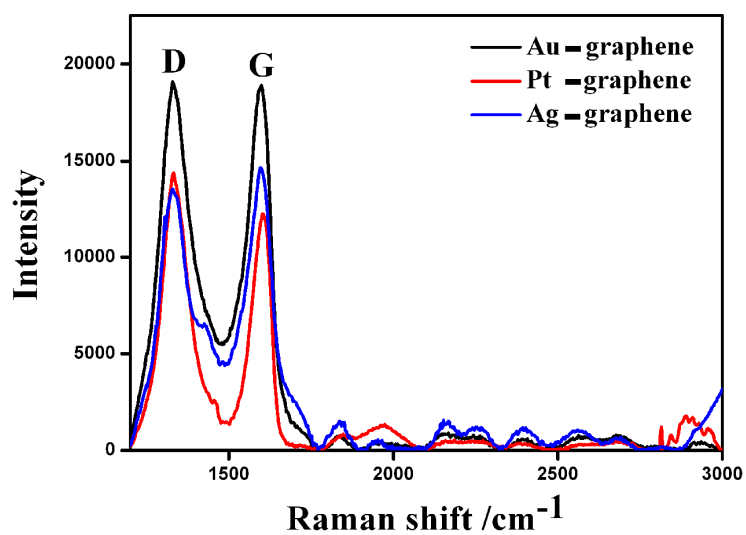


Figure S5. Raman spectra of Au-graphene, Pt-graphene, and Ag-graphene core-shell nanostructures with the exciting laser wavelength of 514 nm.

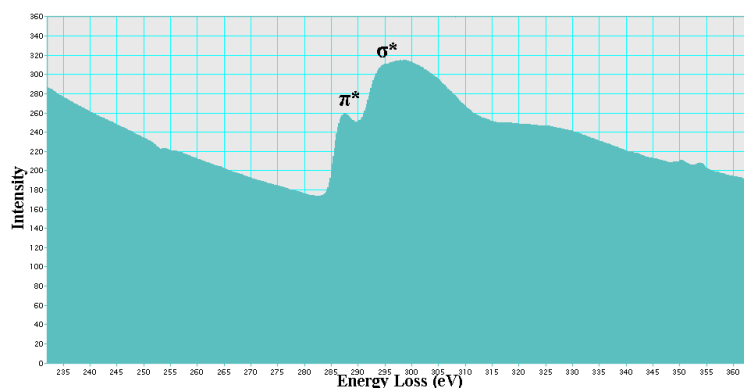


Figure S6. EELS spectrum of C K-edge for Au-graphene core-shell nanostructure.

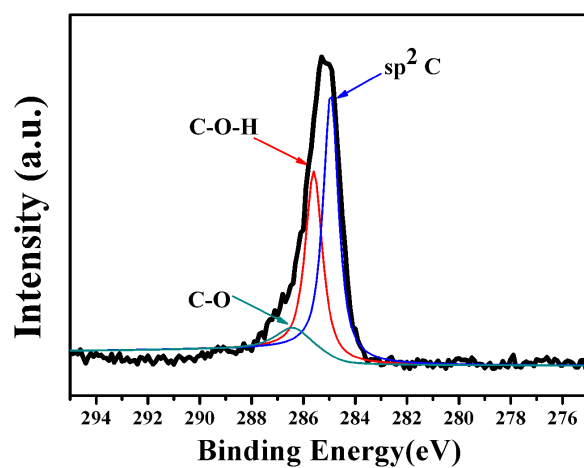


Figure S7. C1s XPS spectra of Au-graphene core-shell nanostructure.

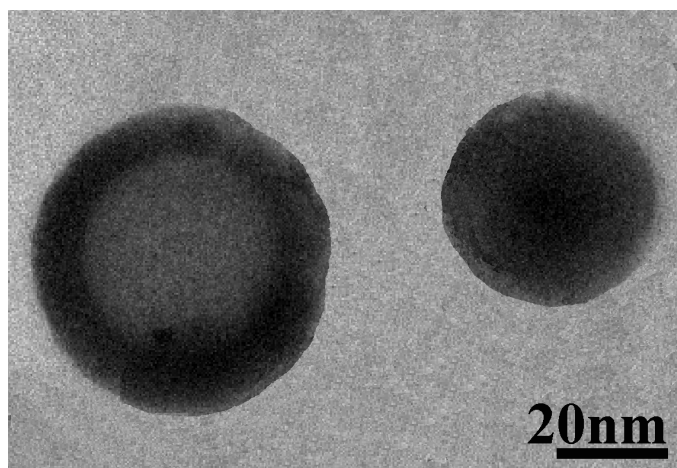


Figure S8. The single hollow graphene nanosphere and the corresponding Au nanoparticle.

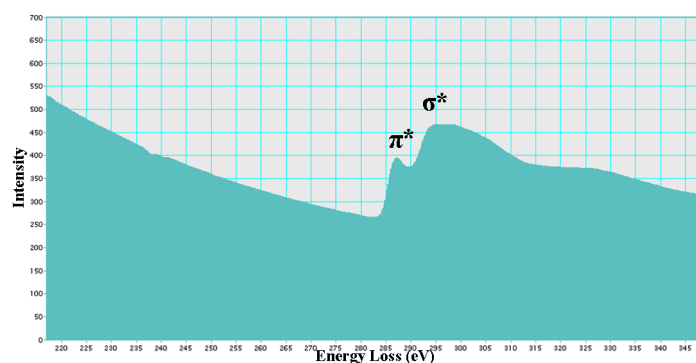


Figure S9. EELS spectrum of C K-edge for hollow graphene nanospheres.

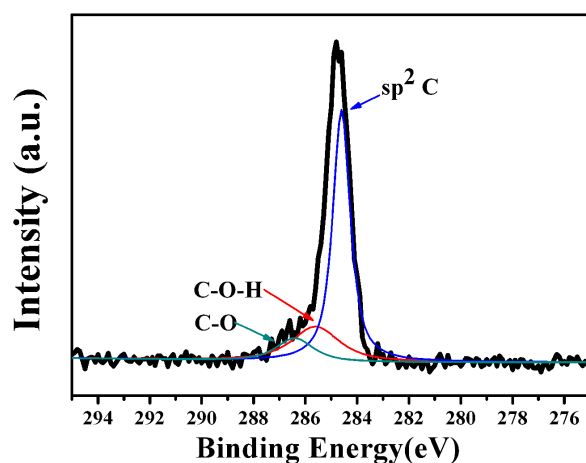


Figure S10. C1s XPS spectra of the hollow graphene nanospheres.

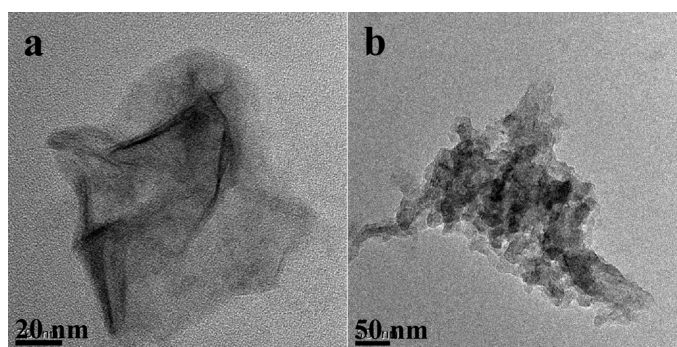


Figure S11. The TEM images of the synthesis of graphene nanostructures without the metal salt.

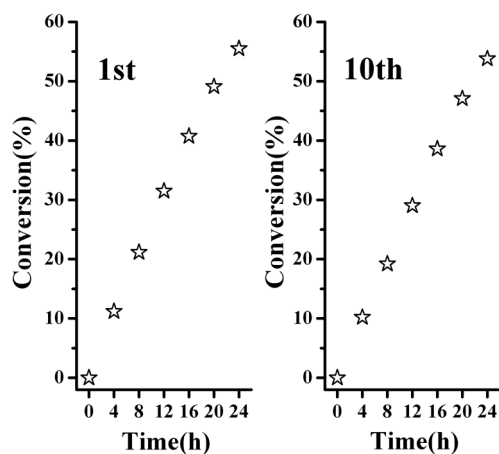


Figure S12. The repeated catalytic experiments of Au-graphene core-shell nanostructures in ten times during selective oxidation of cyclohexene.

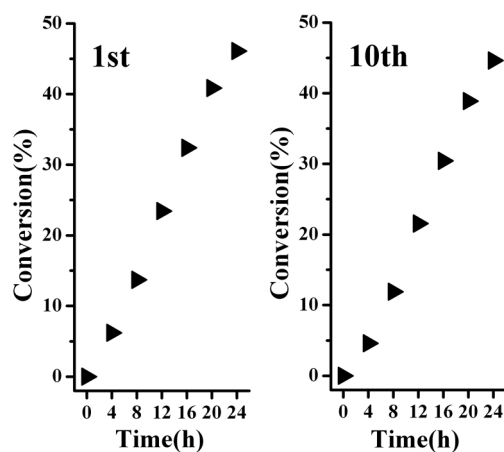


Figure S13. The repeated catalytic experiments of Pt-graphene core-shell nanostructures in ten times during selective oxidation of cyclohexene.

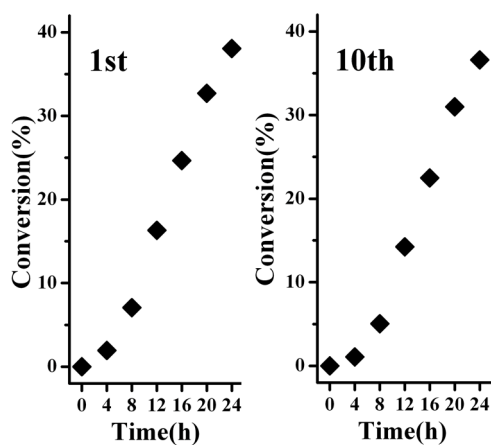


Figure S14. The repeated catalytic experiments of Ag-graphene core-shell nanostructures in ten times during selective oxidation of cyclohexene


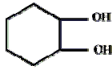
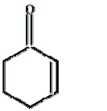
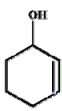
Au-graphene core-shell nanostructures reaction time(h)	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$
						
0	0	0	0	0	0	0
4	0.65	69.14	24.80	5.41	11.20	100
8	0.41	75.20	14.48	9.91	21.15	100
12	0.82	74.23	10.12	14.83	31.50	100
16	0.27	70.29	9.45	19.99	40.75	100
20	0.44	66.05	8.06	25.37	49.10	99.92
24	0.69	61.61	7.24	30.23	55.50	99.77

Table S1. Effect of reaction time on selective oxidation of cyclohexene using Au-graphene core-shell nanostructures as catalyst.

Reaction conditions: 0.05g catalyst, cyclohexene (5 mL), 60 °C.

§Total selectivity to C6 partial oxidation products.

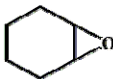
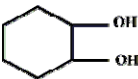

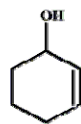
Catalyst	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$	TOF [s ⁻¹]
							
Au-graphene core-shell nanostructures	0.69	61.61	7.24	30.23	55.50	99.77	0.018
Pt-graphene core-shell nanostructures	0.17	72.33	10.87	15.86	46.10	99.23	0.012
Ag-graphene core-shell nanostructures	0.15	48.06	15.73	35.75	38.05	99.69	0.0009
Hollow graphene nanospheres	0.51	70.44	10.68	17.89	15.40	99.52	---
High density of Au nanoparticles supported on graphene	8.40	58.65	14.68	17.96	52.75	99.69	0.015

Table S2. Detailed conversion and selectivity of the selective oxidation of cyclohexene with different metal-graphene complex nanostructures as catalysts.

Reaction conditions: 0.05g catalyst, cyclohexene (5mL), 60 °C, 24 h.

§Total selectivity to C6 partial oxidation products.