Electronic Supplementary Information for

Rhodium Metal Complex Immobilized on Graphene Oxide as Efficient and Recyclable Catalyst for Hydrogenation of Cyclohexene

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Experimental Section

**Synthesis of NH$_2$–f–GO.** Graphene oxide was prepared and purified by Hummers Method.$^1$ A suspension was obtained by dispersing GO (12.0 mg ml$^{-1}$, 16.7 ml) in 120 ml ethanol with the aid of intensive sonication (100 W, 40 KHz, 0.5 h). NH$_2$–f–GO was processed by stirring the obtained GO suspension with excess 3-aminopropyltrimethoxysilane (680.8 mg, 3.85 mmol) and refluxed for 6 h. The suspension was filtrated and washed with ethanol, water and anhydrous toluene. The resulting solid was dispersed in anhydrous toluene (2.0 mg ml$^{-1}$) and labelled as NH$_2$–f–GO.

**Preparation of Rh–f–GO.** Immobilization of RhCl(PPh$_3$)$_3$ complexes on GO was processed as follows: 200 mg of the as-prepared NH$_2$–f–GO (100 ml) was added to an anhydrous toluene solution of RhCl(PPh$_3$)$_3$ (150 mg, 0.16 mmol). The solution was refluxed under N$_2$ atmosphere for 24 h. After cooling to room temperatures, the mixture was filtrated and washed with toluene, dichloromethane, methanol and water three times, respectively, followed by freeze-drying. The resulting solid powder was labeled as Rh–f–GO and stored under N$_2$ atmosphere.

**Catalytic Activity Reaction.** The catalytic hydrogenation of cyclohexene was carried out with a stainless steel reactor containing 2.5 ml cyclohexene (2.03 g, 24.65 mmol) in 47.5 ml toluene solution. 10$^6$ Pa H$_2$ was pressured in and the reaction was undertaken at 80 °C for 3 h with intense agitation (1000 rpm). Afterward the solid was simply separated from the mixture by simple filtration or centrifugation and could be reused after washed with toluene three times. The recycling experiments were undertaken under the same conditions and 60 mg Rh–f–GO was used in the first run. The resulting solution was analyzed by gas chromatography using a capillary column.

**Characterization**

All chemicals used were commercially purchased from Aladdin Reagent Corporation (Shanghai, China). The samples were characterized by Fourier transform infrared (FTIR) spectra (Thermo Nicolet Nexus FTIR), X-ray photoelectron spectroscopy (XPS) (PerkinElmer, PHI 1600 spectrometer), $^1$H NMR spectra (Varian Inova, 500MHz), Raman spectroscopy (NT-MDT NTEGRA Spectra), UV-Vis spectra (Unico 2802 spectrometer), scanning electron microscopy (SEM) (Hitachi S4800), energy dispersive X-ray spectroscopy (EDS) (Hitachi S4800), high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20), atomic force microscopy (AFM) (CSPM 5000). The hydrogenation results were measured by GC (Agilent 6890N GC-FID system).

**References**

Fig. S1 (a), (b) Full range XPS spectra and (c), (d) C 1s XPS spectra of GO and NH$_2$–f–GO. (e) C 1s and (f) Si 2p XPS spectra of Rh–f–GO.
**Fig. S2** (a), (c) SEM and (b), (d) TEM images of NH$_2$–f–GO and Rh–f–GO. TEM images prove the absence of rhodium nanoparticles.

**Fig. S3** $^1$H NMR (500MHz, in CD$_2$Cl$_2$) spectrum of Rh–f–GO.
**Fig. S4** Typical AFM images of (a) NH$_2$–f–GO and (b) Rh–f–GO, and corresponding cross-section analysis of (c) NH$_2$–f–GO and (d) Rh–f–GO.

**Fig. S5** FTIR spectrum of Rh–f–GO. Due to the weak signal and overlapping of absorption by other groups, hardly evident additional peaks or shifts can be observed in the spectrum of Rh–f–GO. Nevertheless, the weak signal at 534 cm$^{-1}$ which might be one of the characteristic absorptions of triphenylphosphine (PPh$_3$) implies the introduction of RhCl(PPh$_3$)$_3$. 
**Fig. S6** (a) SEM image of the NH$_2$-f-GO and corresponding quantitative EDS element mapping of (b) C, (c) Si and (d) N. The Si and N elements are homogeneously distributed on the whole surface of GO.

**Fig. S7** EDS spectrum of the graphene oxide. The element atom ratios of carbon and oxygen are 75.71% and 24.29%, respectively. This result is in line with the previous XPS analysis. Note that the GO sample was placed on a copper sheet in the testing process. As a result, signals of Cu could also be detected.