

Supporting information

## Catalytic hydrogenation of graphene films†

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### 1) The preparation of conditioning catalyst Ni(8%wt)/Al<sub>2</sub>O<sub>3</sub>.

The Ni(8%wt)/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by an impregnation method. Al<sub>2</sub>O<sub>3</sub> powder was used as the catalyst support and the strong metal-support interaction can prevent the aggregation of nano-sized Ni into bigger clusters at high reaction temperature, so all nano-sized nickel particles clung to the Al<sub>2</sub>O<sub>3</sub> powder increase the reaction surface and thus improve the catalyst efficiency. The nickel nitrate hydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) solution with Al<sub>2</sub>O<sub>3</sub> powder (BET 270 m<sup>2</sup>/g) was ultrasonicated and dried at 110 °C, ground to a fine powder, and then calcined at 500 °C for 2 hours.

### 2) Hydrogenation of graphene coating films using the conditioning catalyst Ni(8%wt)/Al<sub>2</sub>O<sub>3</sub>.

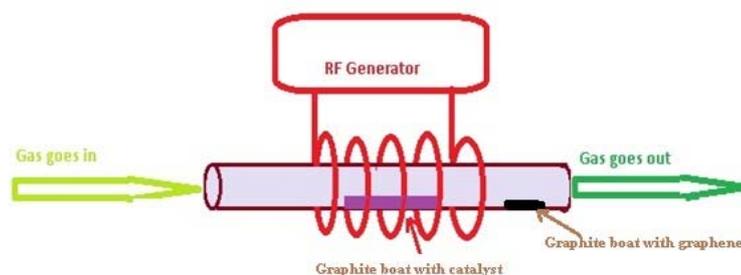


Figure S1. The schematic diagram of the rf-cVD system.

Graphene powder (Angstrom Materials LLC, N002, 1 g) was dispersed in 50 mL of dimethylformamide (DMF). The appropriate amount of as-obtained graphene solution was air-brushed onto glass slides, which were heated at 150 °C in order to remove DMF solvent from the coatings. Around 300 mg of the catalyst was uniformly spread into a thin layer under argon flow at 200 mL/min on a graphite susceptor and placed at the center of a quartz tube positioned horizontally (Figure S1). Graphene coating films were put in another graphite susceptor at the downstream of the catalyst

susceptor and there were about 2 inches apart between these two susceptors. After the carrier gas argon (flow rate 100 mL/min) was introduced to purge the system, the pretreatment was performed. First the conditioning catalyst (moved to the center of the coil) was reduced at 600 °C for 30 min with hydrogen flow rate of 20 mL/min until the catalyst color became black. It means that  $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$  was decomposed and reduced into metallic state. And then radio frequency (RF) heating at 350 kHz was applied to heat the graphite susceptor (moved to the center of the coil) with the graphene film only under argon atmosphere at 400 °C for 10 min in order to remove any possible contaminants. The whole system was cooled down naturally to room temperature to finish up the pretreatment. Next, the susceptor with conditioning catalyst Ni(8%wt)/Al<sub>2</sub>O<sub>3</sub> was moved back to the center of the coil, and heated at 820 °C under hydrogen flow (20 mL/min) for 240 minutes. The susceptor containing graphene sample was outside of the coil and 2 inches apart were still kept between these two susceptors. The reason for doing this is that only the dissociation of hydrogen molecules needs quite high temperature, while the hydrogenated graphene would dehydrogenate above 450 °C. Finally the whole system was cooled down to room temperature under H<sub>2</sub> flow. In this approach, the major advantage of utilizing the conditioning catalyst is that it can efficiently dissociate molecular hydrogen into highly active atomic hydrogen radicals, which greatly facilitates the hydrogenation of graphene.

### 3. Characterization

Raman scattering studies of the graphene films were performed using Horiba Jobin Yvon LabRam HR800 equipped with a charge-coupled detector and He-Ne laser (632.8 nm) as excitation source. The laser beam intensity measured at the sample was kept at 0.5 mW. Raman shifts were calibrated with a silicon wafer at the peak of 521 cm<sup>-1</sup>. The Fourier transform Infrared (FTIR) spectra were collected on Nicolet MAGNA-IR 550 Series 2 Spectrometer with resolution of 8 cm<sup>-1</sup>, the reported spectra were average of 32 scans. The water contact angles of the graphene films were measured on VCA-Optima system. The morphology of the graphenes was monitored with a JEOL 7000F high resolution scanning electron microscope. The high resolution TEM images were obtained on JEOL JEM 2100F at 200 kV accelerating voltage. For this analysis, hydrogenated graphene flakes were dispersed in 2-propanol and ultrasonicated for 10 min. A few drops of the suspension were deposited on the TEM grid, and dried before analysis. AFM images were obtained on Veeco Dimension 3100 AFM system.

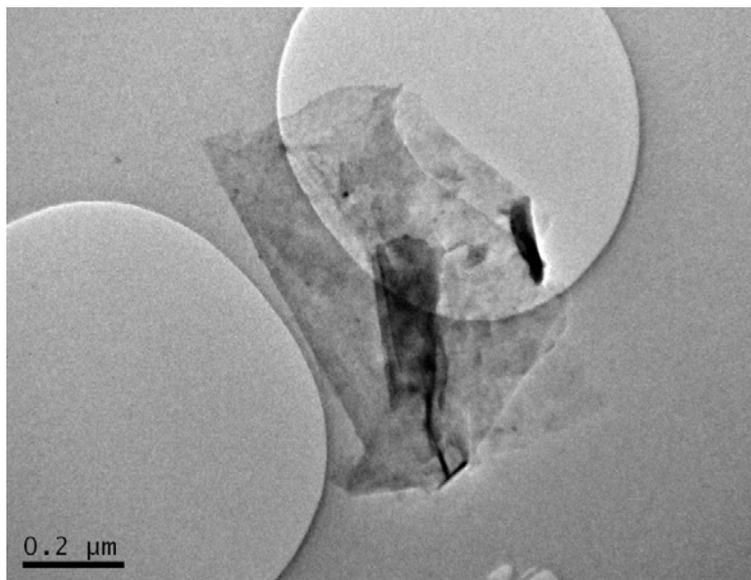


Figure S2. TEM image for the hydrogenated graphene flakes



Figure S3. The reciprocal lattice peaks, which were obtained from 2D Fourier transform of the lattice resolved TEM image for the hydrogenated graphene sample

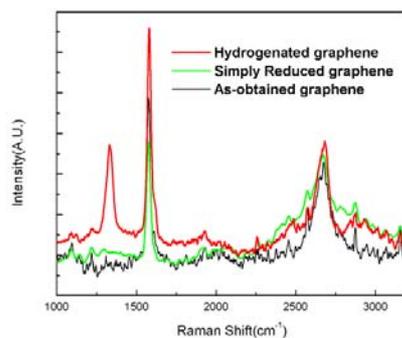


Figure S4. The Raman spectra for the hydrogenated, simply reduced and untreated graphene films.

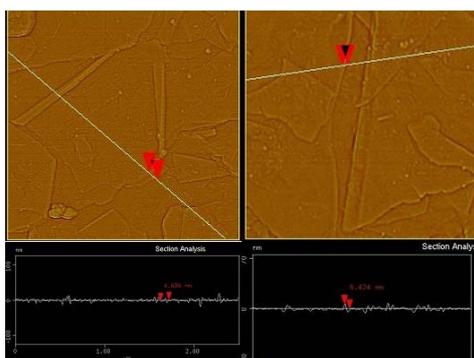


Figure S5. The AFM images for the simply reduced graphene films (left) and the hydrogenated films (right).