

## Electronic Supplementary Information

# Recyclable Catalyst for Catalytic Hydrogenation of Phenylacetylene by Coupling Pd nanoparticles with Highly Compressible Graphene Aerogels

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**Synthesis of graphene oxide (GO):** GO was prepared by a modified Hummers' method reported elsewhere.<sup>1, 2</sup> Typically, 5 g of graphite powder, 25 mL of 98 % H<sub>2</sub>SO<sub>4</sub>, 5 g of P<sub>2</sub>O<sub>5</sub> and 5 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was mixed at 80 °C for 4.5 h under constant stirring, yielding pre-oxidized graphite powder after washing with water and dried at 80 °C for 12 h. The pre-oxidized graphite powder was dispersed in 360 mL of 98 % H<sub>2</sub>SO<sub>4</sub>, followed by adding 25 g of KMnO<sub>4</sub> under vigorous stirring. After stirring in ice-water bath for 2 h, 350 mL of deionized water was carefully added into the mixture under continually stirring at 35 °C for 2 h. Then 500 mL of water and 20 mL of H<sub>2</sub>O<sub>2</sub> solution (30 wt. %) was subsequently added in to the mixture solution, resulting in a golden suspension that was centrifuged to remove the residual ions to get aqueous suspension of GO with a concentration of 3.5 mg mL<sup>-1</sup>.

**Synthesis of 3D graphene aerogels:** 10 mL of GO suspension was mixed with the equal amount of the HI at 90 °C for 12 h, followed by washing with deionized water to reach neutral. The resultant graphene hydrogels were treated by freeze drying to remove the absorbed water, eventually yielding 3D graphene aerogels (GAs).

**Synthesis of Pd/GAs catalyst:** the as-made GAs were immersed into 10 mL ethanol solution of Na<sub>2</sub>PdCl<sub>4</sub> (0.1 mM) under constant stirring for 24 h. After drying at 100 °C for 12 h, the samples were annealed in H<sub>2</sub> with a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup> at 100 °C for 2 h, yielding Pd/GAs catalyst.

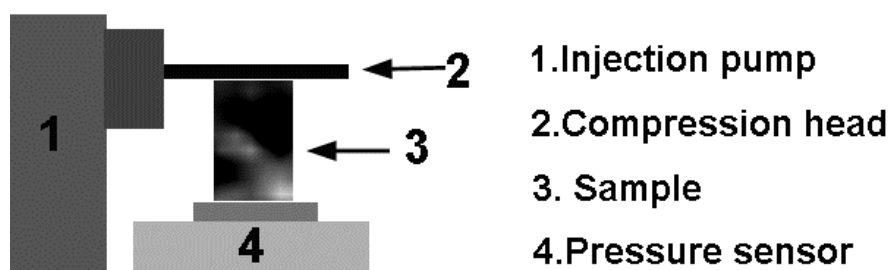
**Catalytic reactions:** the selective semi-hydrogenation of phenylacetylene was performed in a glass reactor equipped with a magnetic stirrer, in which H<sub>2</sub> flow was bubbled through a quartz fritted disk. For the test, 20 mg of as-made Pd/GAs catalyst

were immersed into the ethanol solution of phenylacetylene (10 mL, 0.1 M). The reaction was performed at 50 °C for 1 h. The resultant solution was analyzed by gas chromatography (GC) using a capillary column. Prior to catalytic reaction, the catalyst was throughoutly washed with ethanol and then was immersed in ethanol for 12 h to remove residues. After the reaction, the Pd/GAs catalyst was separated from the liquid phase by the tweezers for reusing. The residual products adsorbed in the catalyst are removed by squeezing the GAs and subsequent washing with ethanol for several cycles. Then the catalyst was employed for the same reaction while other conditions remain unchanged. For the next several runs, the reusing step of the catalyst follows the same procedure.

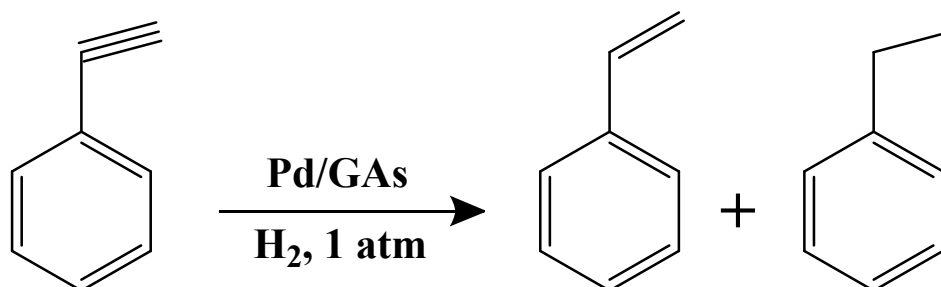
**Characterization and measurements:** the samples were characterized by scanning electronmicroscope (SEM, QUANTA 450, FEI, America), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) , transmission electron microscope (TEM, TF 30, FEI, America) and X-ray diffraction (X'Pert Philips Materials Research Diffractometer, Cu K $\alpha$ ). Raman spectra were recorded from 1000-3000 cm<sup>-1</sup> on a DRX Raman Microprobe (Thermo Fisher Scientific, America) using a 532 nm He-Ar ion laser. An oxford X-MAX 20 energy dispersive spectrometer (EDS) was used to get the elemental mapping data. The specific surface areas of the samples were obtained on a Micromeritics ASAP 2020 nitrogen adsorption equipment. The Pd contents in the catalysts were determined using Inductive Coupled Plasma Spectrometry (ICP, Optima 2000 DV, Perkin Elmer, America) The products of the catalytic reactions were analyzed by HP 6890 gas chromatography (GC) using a HP-5 capillary column. The compressive test was performed on a home-made equipment shown in Scheme S1. The injection pump (TJ-3A/W0109-1B, Baoding Longer Precision Pump Co., Ltd.) drives the compression head up and down at a rate of 60 mm min<sup>-1</sup>. The load on the sample was recorded using a pressure.

## References

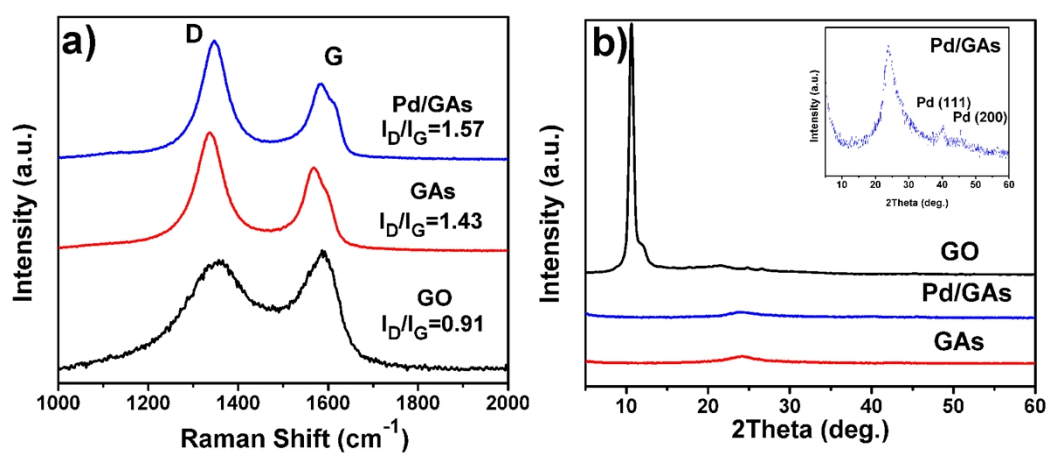
1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, 80, 1339-1339.
2. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, *et al.*, *Chem. Mater.*, 1999, 11, 771-778.



**Scheme S1** Schematic illustration of the home-made device for compressive test of GAs.



**Scheme S2** Chemical formula for the semi-hydrogenation of phenylacetylene over Pd/GAs.



**Fig. S1** (a) Raman spectra and (b) XRD patterns of GO, GAs and Pd/GAs catalyst, in which the enlarged XRD patterns of Pd/GAs catalyst is shown in the inset.

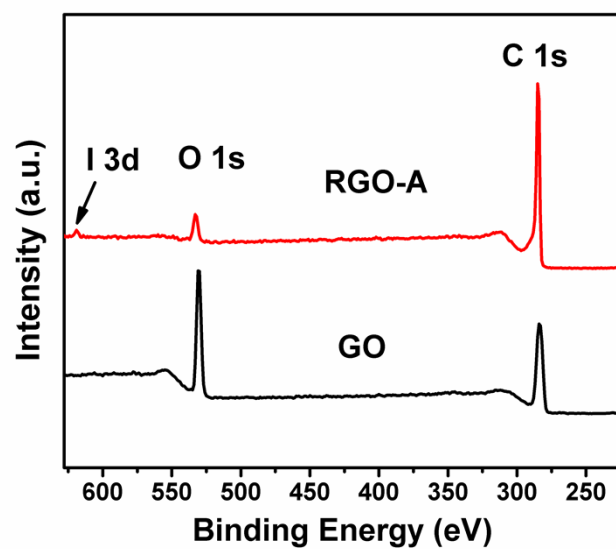


Fig. S2 XPS full scan of (a) GO and (b) GAs.

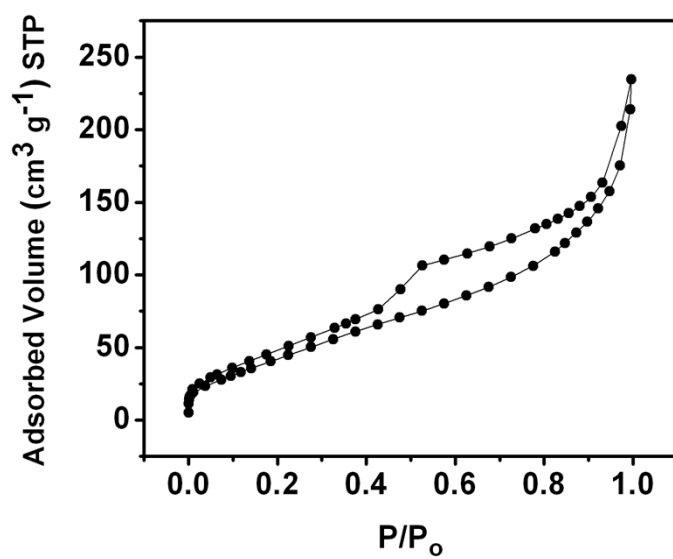
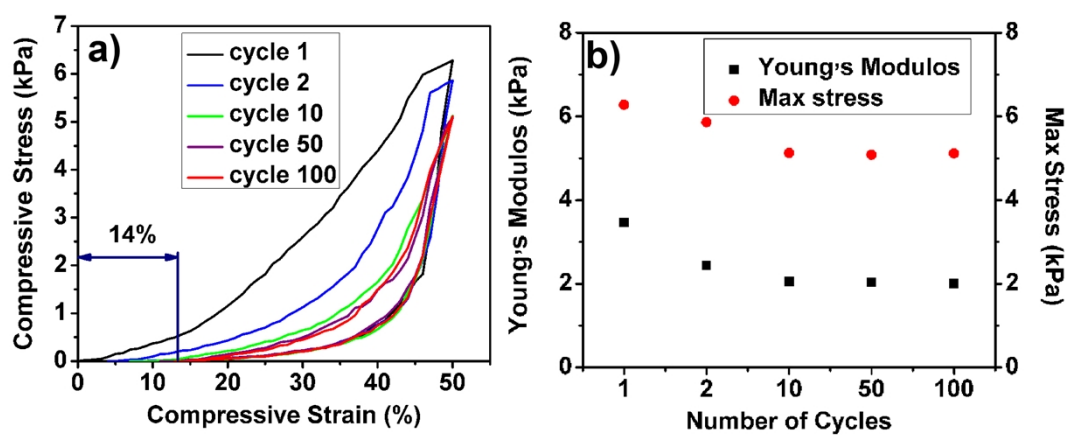
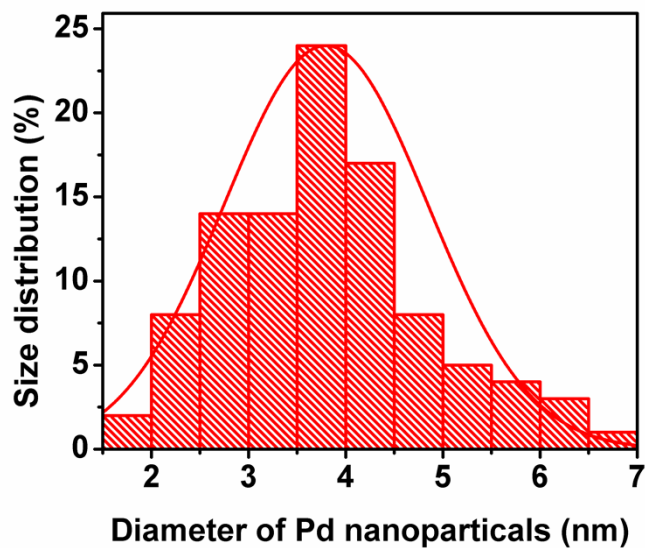


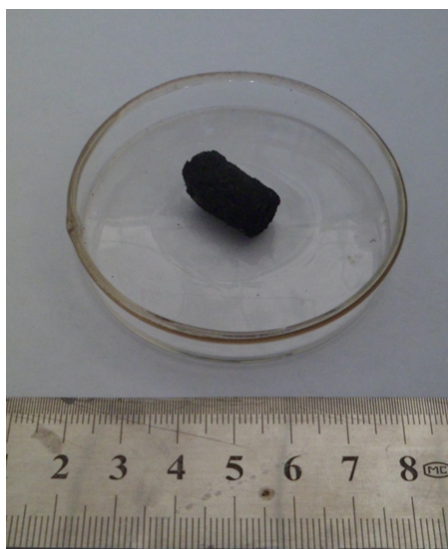
Fig.S3. Nitrogen adsorption isotherms of GAs.



**Fig. S4** (a) The stress-strain curves of GAs at the maximum compressive strain of 50 % for 100 cycles at a loading rate of 60 mm min<sup>-1</sup>; (b) the corresponding Young's modulus and maximum stress for different cycles



**Fig. S5** Size distribution of Pd nanoparticles on GAs.



**Fig. S6** Optical photograph of Pd/GAs catalyst after six runs.