

Online supporting information

**One-Step Fabrication of RGO/HNBR Composites via Selective Hydrogenation of
NBR with Graphene-Based Catalyst**

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Experimental

Materials

High-purity graphite powder ($\geq 99.99\%$) was purchased from Aldrich Chemistry. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Shanghai Jiulin Chemical Co., Ltd. Nitrile rubber (Nancar1052M30) was obtained from Taiwan Nantex Chemical Industry Company, Limited. H_2SO_4 (≥ 98 wt%), NaNO_3 (≥ 99.9 wt%) and $\text{K}_2\text{Cr}_2\text{O}_7$ (≥ 99.0 wt%) were obtained from Tianjin Guangfu Research Institute of Fine Chemicals. Chlorobenzene (AR), anhydrous ethanol (AR), acetone (AR), hydrazine (80 wt%) and ammonia (25 wt%) were all obtained from Beijing Chemical Factory. Triphenylphosphine and deuterated chloroform were obtained from National Chemical Reagent Co., Ltd. Nitrogen (research grade; $\text{N}_2 > 99.99\%$) and hydrogen (research grade; $\text{H}_2 > 99.99\%$) were donated by Beijing Beifen Gas Industries Co., Ltd.

Synthesis of Rh/RGO nanoparticles

In the experiments, GO was prepared by the oxidation of high purity graphite powder ($\geq 99.99\%$, Aldrich Chemistry) with $\text{H}_2\text{SO}_4/\text{KMnO}_4$ according to the method of Hummers and Offeman.¹ After repeated washing of the resulting yellowish-brown cake with plenty of deionized water, the sediment was dried at 70 °C in a vacuum

oven overnight. Then, the GO dissolved in deionized water to form a solution of GO of 6 g/L for next step.

For the preparation of Rh/RGO, 25 mL of GO solution and 4 mL of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ solution (2 g/L) were sonicated in 450 mL deionized water until a homogeneous yellow dispersion was obtained, and 2 mL ammonia (25 wt%) was added; after 15 min ultrasonication, reducing agent (hydrazine or sodium borohydride) was added to the mixture. The ultrasonication was continued for 30 min, and then the three-neck flask was heated at 100 °C with mechanical stirring. After 6~8 h of reduction, the black product was centrifuged at 6000 rpm for 20 min for 3 times, washed with deionized water until the pH reached 7 and dried overnight under vacuum.

General procedure for preparation of RGO/HNBR composites

The hydrogenation reaction was carried out in a 1000-mL high pressure reactor. The NBR chlorobenzene solution and catalyst of Rh/RGO were placed into the reactor. Before being heated to the reaction temperature, the reactor was degassed with N_2 for 3 times to remove air. Then the reactor was heated to the desired temperature, and the reaction was initiated by flushing H_2 to 430 psi and adjusted the agitation rate to 480 rpm. The hydrogen pressure and reaction temperature were kept constant throughout the reaction. The conversion of the double bonds, also called the degree of hydrogenation (HD), was calculated as:

$$\text{HD} = (1 - [\text{C}=\text{C}]_t / [\text{C}=\text{C}]_0) \times 100\% \quad (1)$$

where $[\text{C}=\text{C}]_t$ is the concentration of C=C bonds at reaction time t and $[\text{C}=\text{C}]_0$ is the initial double bond concentration. The hydrogenated NBR sample was analyzed by ^1H NMR.² After hydrogenation, the RGO remained in the substance of HNBR to form RGO/HNBR composite.

Characterization of the catalysts

The physical and chemical properties of the prepared catalysts were measured by several methods. FTIR spectra were obtained by a Bruker Tensor 27 spectrophotometer in the wave-number range of 400-4000 cm^{-1} . The crystal phases of the samples were determined by X-ray diffraction (XRD, Bruker D8 Advance) at a

scanning rate of 0.02 °/s in the 2θ range of 5° to 90°. The morphology of the GO and Rh/RGO sheets were examined by an atomic force microscope (BRUKER MultiMode 8) using tapping mode. The Raman spectra were measured using an excitation wavelength of 514 nm provided by a Renishaw inVia argon ion laser. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 electron microscope operated at 200 kV. Samples for TEM were prepared by placing a droplet of a colloid suspension in ethanol on a carbon-coated, 300-mesh copper grid and allowed to evaporate in air at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific ESCALAB 250 system with monochromatized Al K α radiation at 15 kV.

Supplementary Figures and Tables

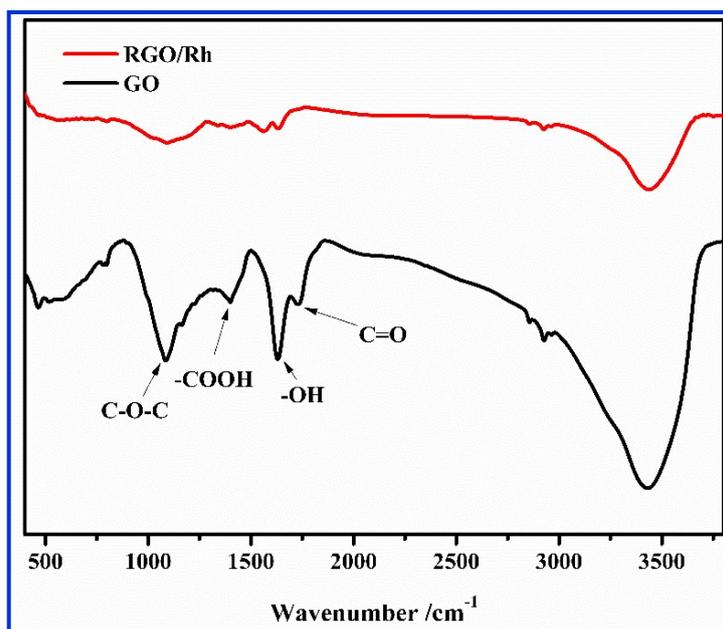


Figure S1 The FTIR spectra of GO and RGO/Rh

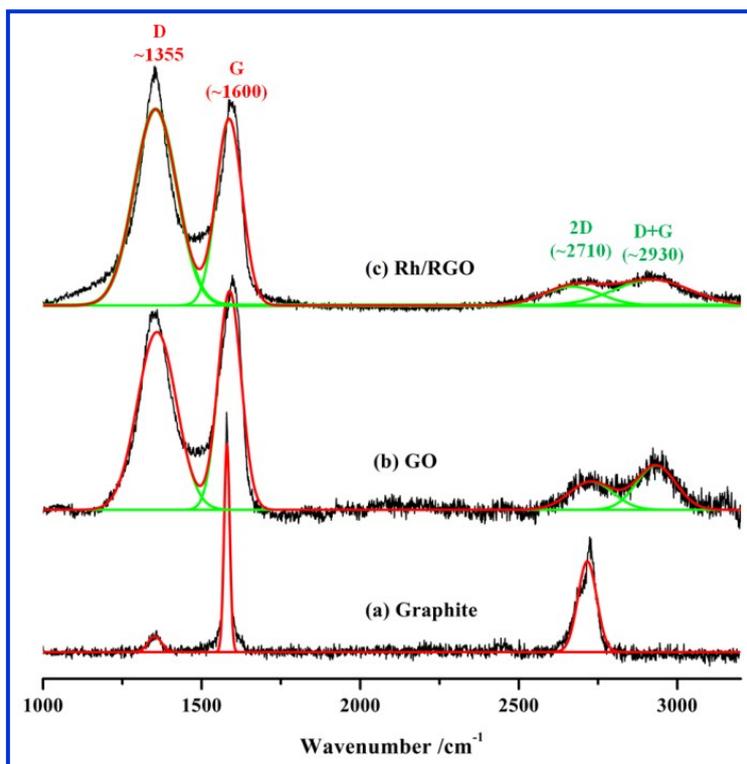


Figure S2 Raman spectra of (a) graphite, (b) GO, and (c) Rh/RGO.

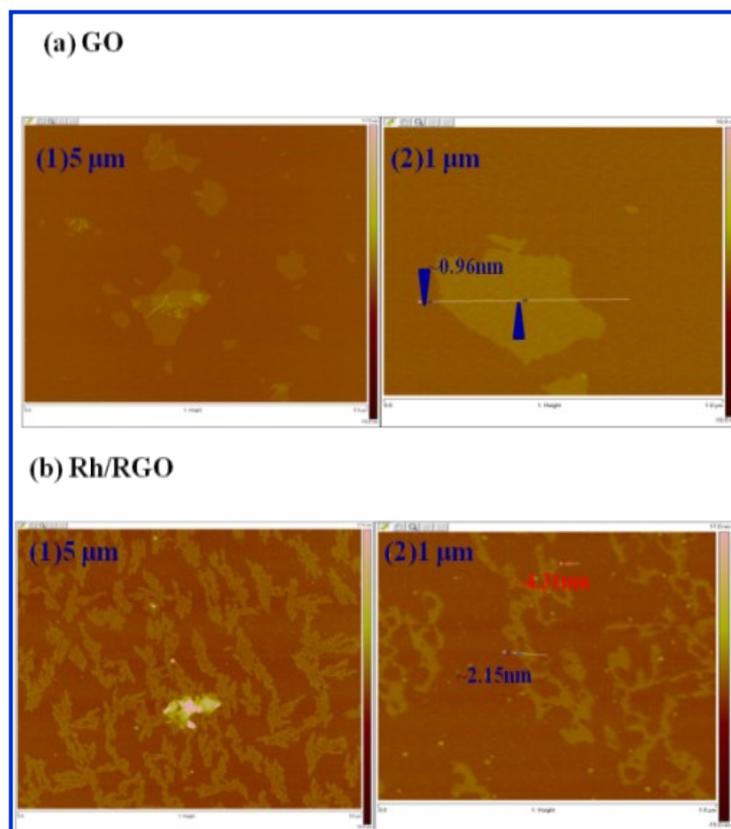


Figure S3 AFM images and section analyses of (a) GO and (b) Rh/RGO.

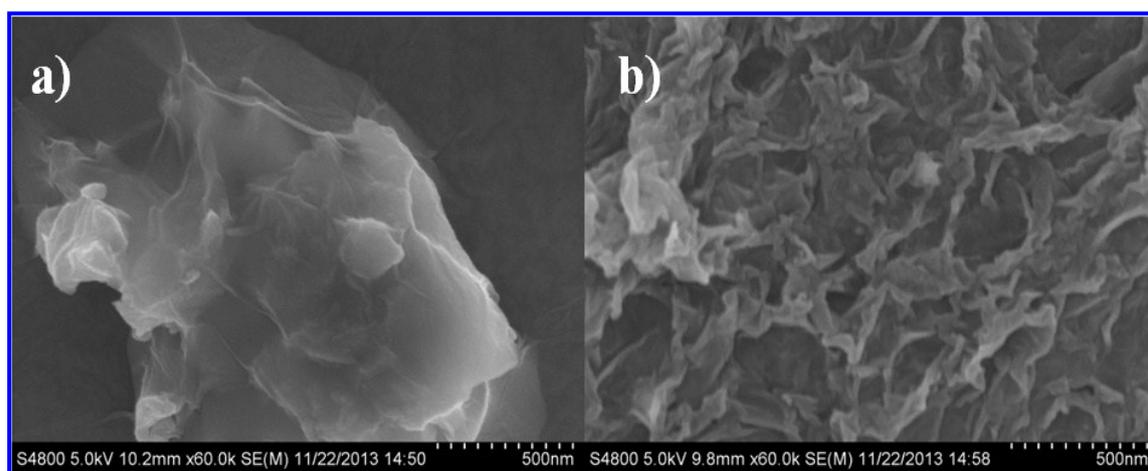


Figure S4 SEM image of (a) GO and (b) Rh/RGO.

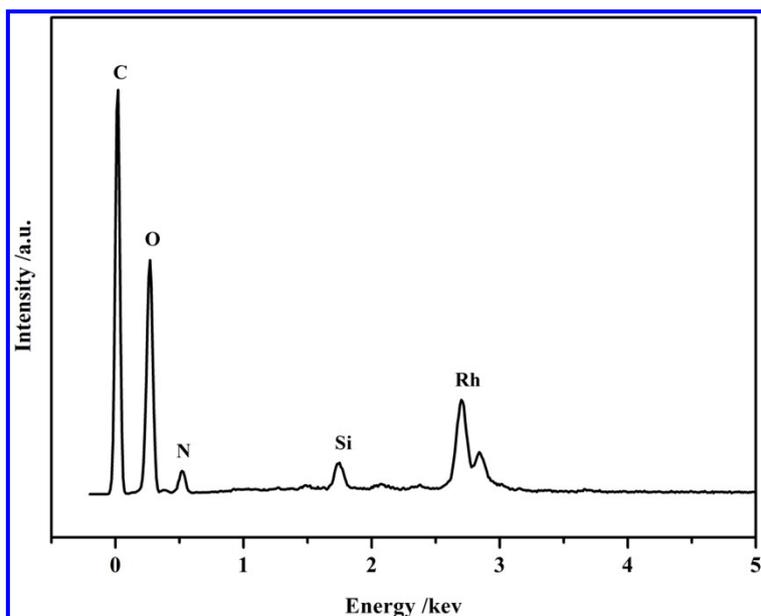


Figure S5 EDS analysis of Rh/RGO.

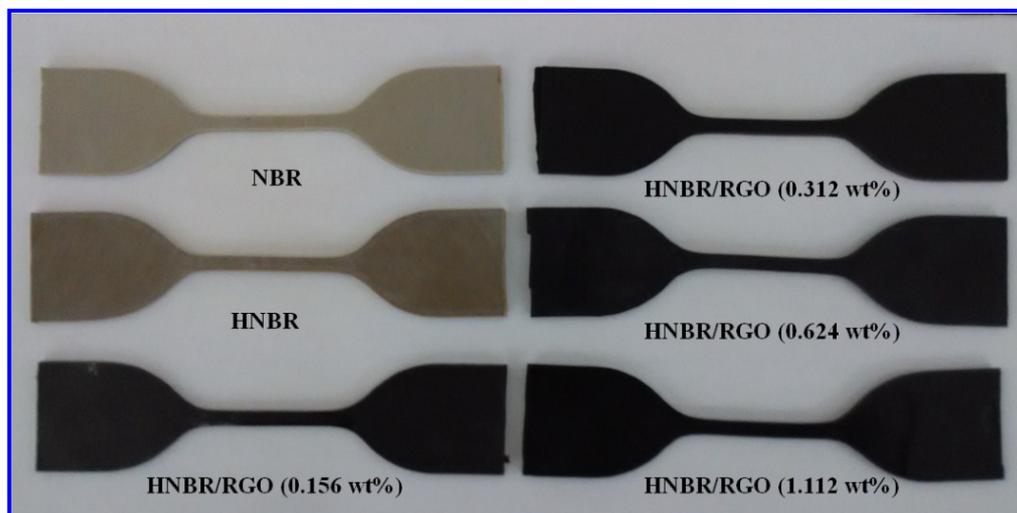


Figure S6 The image of tested samples.

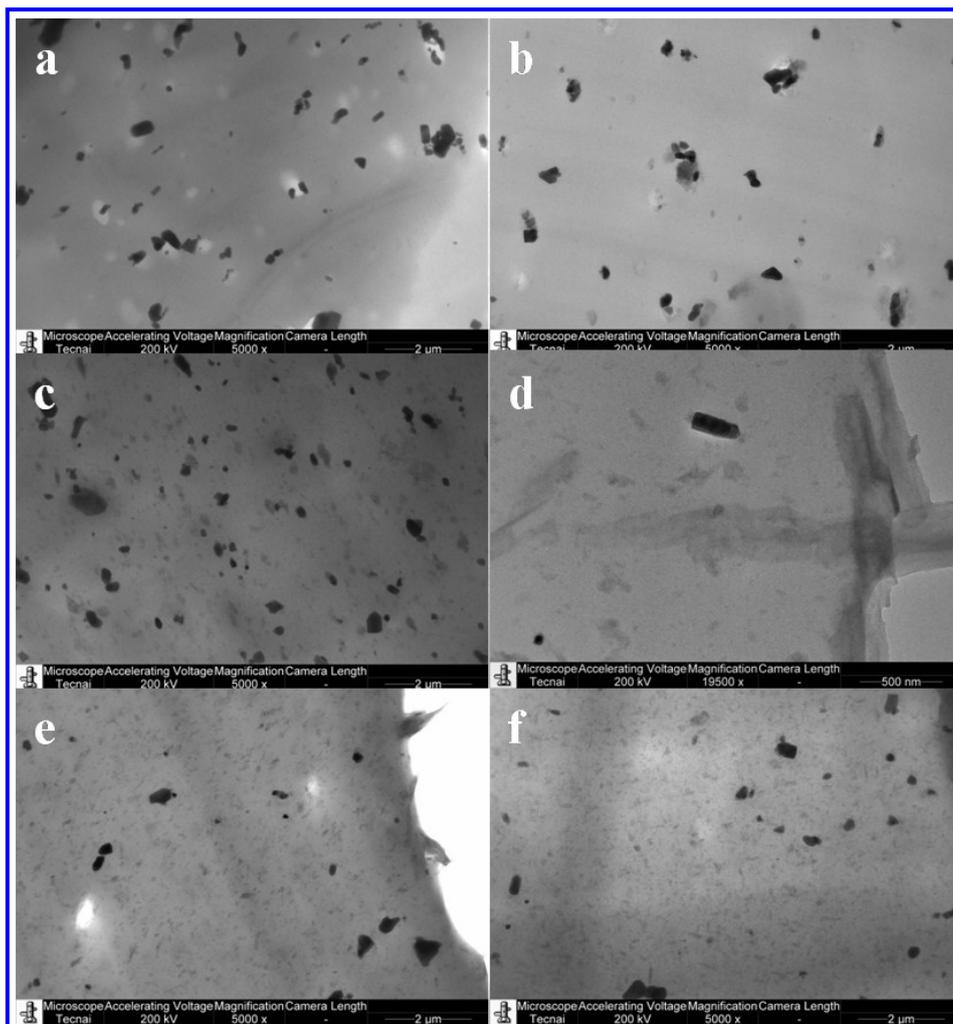


Figure S7 The TEM of (a) NBR, (b) HNBR and RGO/HNBR with different content of RGO: (c) 0.156 wt%, (d) 0.312 wt%, (e) 0.624 wt% and (f) 1.112 wt%

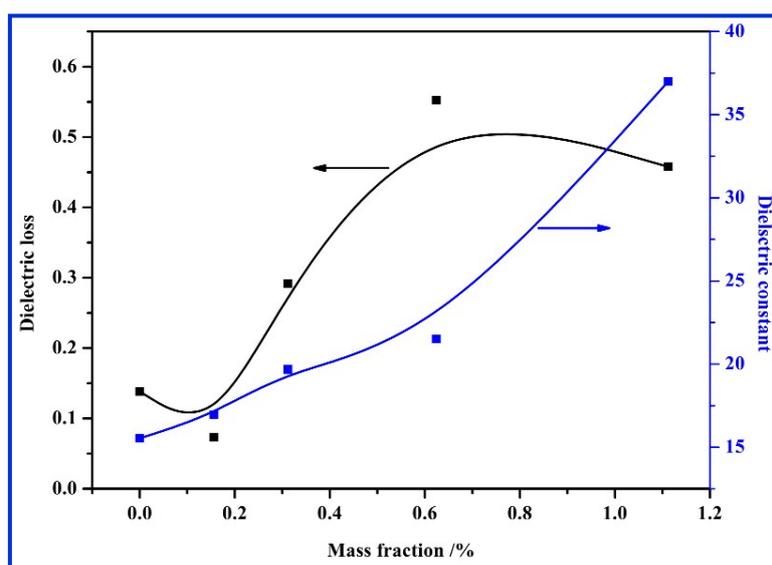


Figure S8 Dielectric constant and dielectric loss of RGO/HNBR composites at 10^3 Hz

Table S1. Raman spectra data of GO and Rh/RGO catalyst

Sample	Band position (cm ⁻¹)				I_D/I_G ^a	I_{2D}/I_{D+G} ^a
	D	G	2D	D+G		
GO	1355	1601	2714	2935	1.367	0.705
Rh/RGO	1356	1599	2706	2934	1.747	1.191

^aDetermined from the relative peak areas in Raman spectra.

Table S2. XPS data of graphite, GO and Rh/RGO catalyst

Sample name	Relative atomic percentage (%)				Heterocarbon component (%)	Relative atomic percentage (%)	
	C=C	C-OH	C=O	O-C=O		Metallic Rh	Rh ³⁺
Graphite	91.09	7.21	0.42	1.28	8.91	-	-
GO	50.35	44.01	5.64	0	49.65	-	-
Rh/RGO _{-NaBH₄}	81.03	15.84	0	3.13	18.97	78.98	21.02
Rh/RGO _{-HH}	71.86	15.98	8.85	3.31	28.14	1.15	98.75

^acalculated by the peak area of Rh 3d XPS analysis of Rh/RGO.

Table S3. The vulcanization recipe

	PHR
Rubber	100
Zinc oxide	5
Stearic acid	1
Sulfur	0.5
Accelerator M	0.5
Accelerator TMTD	2
Antiager D	1
Antiager 4010	1

PHR stands for one gram per a hundred gram of rubber.

Table S4. Mechanical properties of graphene/graphite-based rubber nanocomposites

Matrix	Filler	Synthetic routes	Filler loading	Mechanical properties		Reference
				Tensile strength	Elongation	
				(MPa)	at break (%)	
HXNBR	GO	Solution	0 ^a	14.8±0.8	534±13	Ref. ³
			0.22 ^a	21.7±1.8	485±10	
			0.44 ^a	22.4±1.3	419±18	
			1.3 ^a	10.3±0.5	248±8	
NR	rGO	Solution	0 ^a	17.1	579	Ref. ⁴
			2 ^a	25.2	564	
NR	rGO	Solution	0 ^a	5.15	844	Ref. ⁵
			5 ^a	10.18	319	
NBL	GE	Latex	0 ^a	17.0	1111	Ref. ⁶
			1.78 ^b	23.3	783	
NBR	Graphite	-	0 ^a	3.2	500	Ref. ⁷
		Dry mixing	5 ^a	6.6	630	
		Solution	5 ^a	5.0	600	
		Latex	5 ^a	10.5	180	
NR	Modified GO	Solution	0 ^a	7.35	-	Ref. ⁸
			0.3 ^a	14.7	-	
HNBR	rGO	Solution	0 ^a	18.57	610.90	Our work
			0.156 ^a	20.21	628.56	
			0.312 ^a	22.14	685.34	
			0.624 ^a	23.12	720.71	
			1.112 ^a	26.80	850.62	

Notes: a-wt%, b-vol%.

Reference:

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