Facile Hydrothermal Preparation of Graphene Oxide

Nanoribbons from Graphene Oxide

Supplementary Information

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Experimental Part

Materials

The graphite flakes were provided by Sigma-Aldrich. In all preparation, deionized water was used. All reagents were analytical grad and used as received.

Method for the preparation of graphene nanoribbons

Preparation of graphene oxide (GO)

GO was made by a modified Hummers' method^{1, 2}. 1g expandable graphite was grounded, washed and dried, and it was then added to a 250 mL round bottom flask containing 23 mL concentrated sulfuric. The mixture was stirred for 24 hours at room temperature (25 °C). Next, the flask was placed in an oil bath at 40 °C, to which 0.1 g NaNO₃ and 0.5 g KMnO₄ were added for oxidation. The reaction was

gradually terminated by adding 140 mL water and 10 mL 30% H_2O_2 solution. This suspension was centrifuged and washed twice with 5% HCl and water. The precipitate was dispersed in 150 mL water and sonicated for 20 minutes. The suspension was centrifuged at 5000 rpm for 5 minutes twice. The brown homogeneous supernatant was diluted 50-fold for following experiment.

Preparation of graphene oxide nanoribbons (GONR)

In the first step, 2.4 mL GO aqueous solution of NaVO₃ (0.4 mol/L) was added dropwise to 2.4 mL GO aqueous solution containing La(NO₃)₃ (0.4 mol/L) under constant magnetic stirring at room temperature. After stirring for 20 minutes, 6.8 mL GO aqueous solution and 0.4 mL ethanol were added to the system. The suspension was then transferred into 20 mL Teflon-lined stainless autoclave and heated at 180 °C for 48 h. The reaction system was cooled down to room temperature naturally, which afforded well-crystallized GONR@m-LaVO₄ nanobelts settled on the bottom of autoclave. A small amount of m-LaVO₄ nanocrystallites might be mixed among the nanoribbons. A certain amount of GONR was obtained after dissolving m-LaVO₄ by using 5% HCl. If one-dimensional structure of LaVO₄ was preserved, GONR@m-LaVO₄ nanobelts would be obtained.

Characterization

AFM image of GONR was obtained with a Nanoscope IIIa multimode instrument in tapping mode. The sample for AFM imaging was prepared by drying droplets of the GONR@*m*-LaVO₄ nanoribbons suspension onto a piece of Si substrate. The substrate was immersed in 5% HCl solution for 15 minutes, then taken out, rinsed with water for 3 times, dried at room temperature for 20 minutes and additional 1 h at 50 $\$ in oven.

Individual nanoribbon was examined by Raman spectroscopy using the same specimen for AFM analysis. Raman spectroscopy of individual nanoribbon was collected with Horiba Jobin Yvon LabRAM Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2013

Aramis Raman microscope with 633 nm He-Ne laser excitation (spot size ~0.86 μ m and power ~6.8

mW).

The GONR were observed by a FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. The TEM sample was prepared using the same procedures as that for AFM analysis except that C grid were used instead of Si substrate.

Additional Figures



Figure S1. TEM image of GO.



Figure S2. AFM image of GO. The height of the GO is 2.0 nm indicating that GO is bi-layered.

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Figure S3. The XRD patterns of GONR@m-LaVO₄ nanobelts and m-LaVO₄ nanocrystallites.

XRD analyses of GONR @*m*-LaVO₄ nanobelts and m-LaVO₄ nanocrystallites indicated the monoclinic symmetry of LaVO₄ (JCPDF: 50-0367) with lattice constants a = 7.043 Å, b = 7.279 Å, c = 6.721 Å, $\alpha = \gamma = 90^{\circ}$ and $\beta = 104.861^{\circ}$. The peak indicated by arrow might belong to GORN.



Figure S4. C_{1s} XPS spectra of GO and GONR@*m*-LaVO₄ nanobelts.

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Figure S5. SEM image of GONR.



Figure S6. AFM image of GONR. The height of the GONR is about 2.0 nm indicating that GONR is bi-layered.

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Figure S7. a) and b) SEM images of GONR @*m*-LaVO₄ nanobelts from reaction systems containing 5-fold diluted GO aqueous solution, c) and d) SEM images of product without ethanol.



Figure S8. Reaction device.

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Note that this pressure might lead to explosion and therefore the catalytic reaction should be conducted

in a high pressure reactor with an explosion-proof pressure sensor.

References

- 1 W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339-1339.
- 2. H. L. Wang, L. F Cui, Y. Yang, H. S. Casalongue, J. T. Robinson, Y. Y. Liang, Y. Cui and H. J.

Dai, J. Am. Chem. Soc., 2010, 132. 13978-13980.