

Supporting Information

Growing Vertical ZnO Nanorod Arrays within Graphite: Efficient Isolation of Large Size and High Quality Single-Layer Graphene

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Experimental Section

Preparation of single-layer graphene sheets

ZnO colloidal nanoparticles were prepared according to the method of Meulenkamp.¹ The final concentration of ZnO nanoparticles was 0.7 mg/mL in ethanol. Graphite flakes (0.1 g) and ZnO colloidal solution (10 mL) were mixed together and treated by ultrasound (50 W) for 30 min. Kept the mixture standing for a day, then took out and dripped the upper part of the suspension on a glass wafer to form a uniform film. The wafer containing the film was suspended in an aqueous solution of zinc nitrate hydrate (0.01 M) and methenamine (0.01 M) at 95 °C for 3 h,² and was removed from the solution, rinsed with deionized water and dried naturally in the air. The film on the wafer was dispersed in the mixture of concentrated hydrochloric acid and DMF with a volume ratio of 1:9 by weak ultrasound for 0.5 min to remove ZnO nanorods, which was followed by centrifuging at high rotate speed at 14000 rpm to get precipitate on the bottom of the centrifuge tube. The redundant hydrochloric acid and ZnCl₂ were further removed by washing the precipitate with DMF and strong centrifugation for several times, Finally, the homogeneous and stable single-layer graphene DMF dispersions was obtained by dispersing the resulting precipitate with mild centrifugation (2000 rpm) and taking out the supernatant.

The yield of the single layer graphenes was determined by analysing the weight percentage of all the exfoliated flakes and unexfoliated graphite after separating by centrifugation.

Preparation of ZnO nanoparticle (NPs) ethanol colloidal solution

1.10 g (5 mmol) Zn(Ac)₂·2H₂O was dissolved in 50 mL of boiling ethanol at atmospheric pressure, refluxed for 10 minutes and then cooled to 0 °C. 0.29 g (7 mmol) LiOH·H₂O was dissolved in 50 mL of ethanol at room temperature in an ultrasonic bath and cooled to 0 °C. The LiOH-containing solution was added dropwise to the Zn(Ac)₂ suspension under vigorous stirring at 0°C and kept for 6 h to obtain ZnO sol. After that, about two volume ratio of hexane was added to ZnO sol to precipitate ZnO and remove reaction products (LiOH and H₂O) from the sol. The supernatant was removed by centrifugation and repeated washing by hexane for several times. Then the ZnO precipitate was re-dispersed in ethanol.

Materials and characterization

High purity graphite flakes were purchased from Shanghai Carbon Co., Ltd (China). Other chemical solvents and reagents were of analytical reagent grade and were used without further purification. All the aqueous solutions used in EIS experiment were prepared with Millipore water having a resistivity of 18.2 M Ω .

The transmission electron microscopy (TEM) and electron diffraction (ED) patterns were taken with a Tecnai F20 transmission electron microscope operating at 200 kV. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 scanning electron microscope. Raman spectra were recorded on a Laser Confocal Micro-Raman Spectroscopy (LabRAM Aramis) with a 633 nm He-Ne laser. The AFM images were taken with MultiMode V SPM (VEECO). X-ray powder diffraction (XRD) patterns were carried out on a PANalytical X'Pert Pro MPD diffractometer with Cu K radiation (40 kV, 40 mA).

Characterization

Photocurrent response characteristics were recorded with a CHI 705 electrochemical workstation (CH Instruments, Inc.) at a bias of 0.2V. A three-electrode cell was applied with the same quality ZnO nanorods/graphenes complexes film and pure ZnO nanorods array film covered ITO with a geometric area of 3 cm² serving as the working electrode. A Pt wire and Ag/AgCl electrode were used as the auxiliary electrode and the reference electrode, respectively. An aqueous solution of 0.1 M KCl was used as the electrolyte. Light from a 150 W Xe lamp passing through a holographic grating to generate UV light ($\lambda=360$ nm) was employed as the light sources.

Electrochemical impedance experiment was performed with a potentiostat/frequency analyzer (EG&G 2273) in 10 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ (1:1) with 0.1 M KCl at +0.25 V when an AC signal (amplitude 5 mV) was applied in the frequency range 10⁵ to 0.1 Hz. Glassy carbon electrode (GCE) was polished with 0.05 μ m alumina powder, then rinsed with copious amounts of water and finally dried under a nitrogen stream. Graphene/GCE was prepared by dropping 5 μ L graphene dispersion (1 mg/mL in DMF) to a pretreated bare GCE and dried under an infrared lamp. Graphite oxide (GO) was synthesized by a modified Hummer's method as reported by Kovtyukhova et al. GO/GCE was also prepared likewise by dropping 5 μ L GO dispersion (1mg/mL in water) to a pretreated bare GCE and dried under infrared lamp. ERGO/GCE was obtained by electrochemically reduction of GO/GCE at a constant potential (-1.3V vs SCE) for 10 min in 10 mmol/L pH 5.0 PBS (K₂HPO₄/KH₂PO₄)

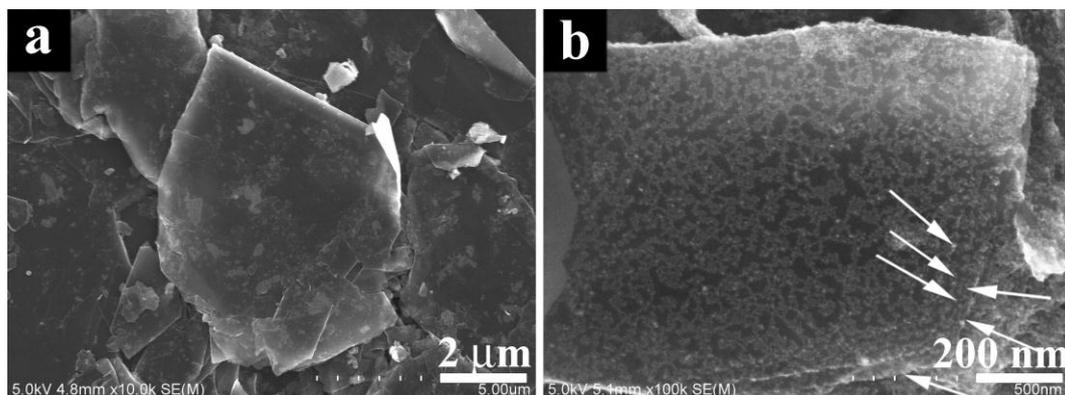


Fig. S1 SEM images of (a) graphite, (b) graphite intercalated by ZnO nanoparticles, the arrows point to the edge of ZnO nanoparticles intercalated graphite layers.

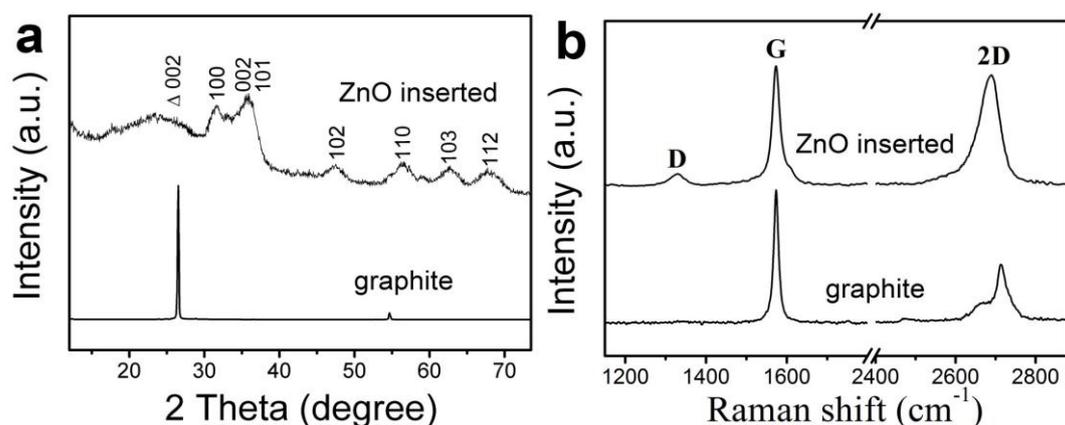


Fig. S2 (a) XRD pattern of ZnO nanoparticles inserted graphite and (b) Raman spectra of bulk graphite and ZnO nanoparticles inserted graphite. It can be seen from (a) that after intercalation of ZnO nanoparticle, the (002) reflection characteristic of the π - π stacked layers was noticeably weakened (as indicated with ' Δ '), suggesting that ZnO NPs readily intercalate into graphite interlayers. From (b), it is clearly seen that the 2D band of graphites is asymmetric and consists of two components, while the 2D band of graphites inserted by ZnO nanoparticles is symmetric. On the basis of peak profile and position, it can be concluded that the thickness of flake between ZnO nanoparticle layers is 1-4 layers (Reference 4c and 5)

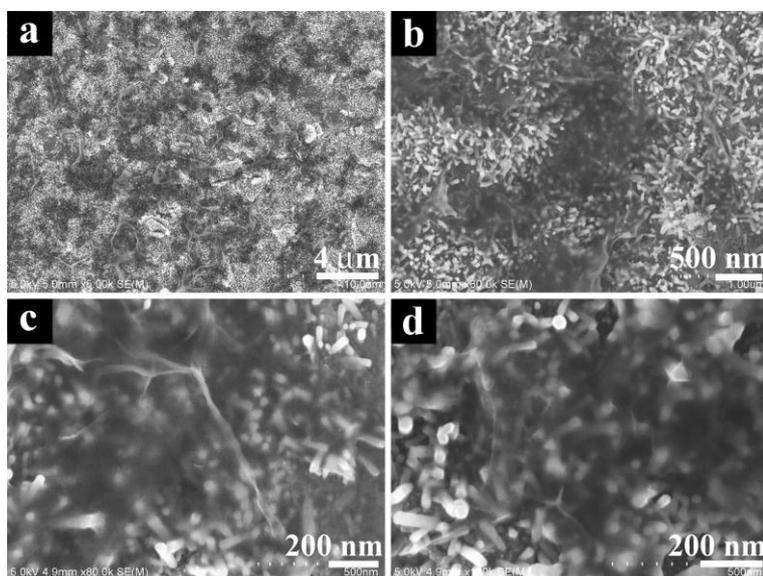


Fig. S3 Typical top view SEM images of graphene layers separated by ZnO nanorods array at different magnification.

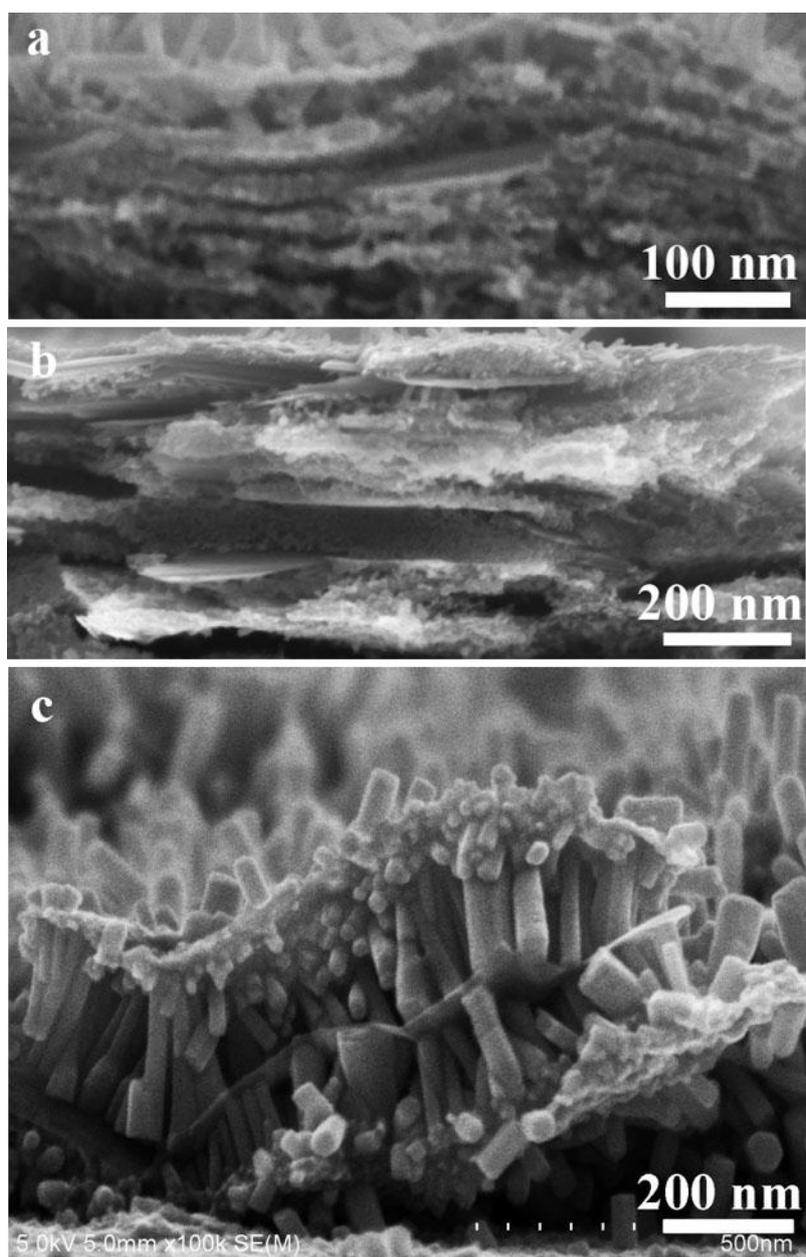


Fig. S4 Lateral view SEM images of graphene layers separated by ZnO nanorods.

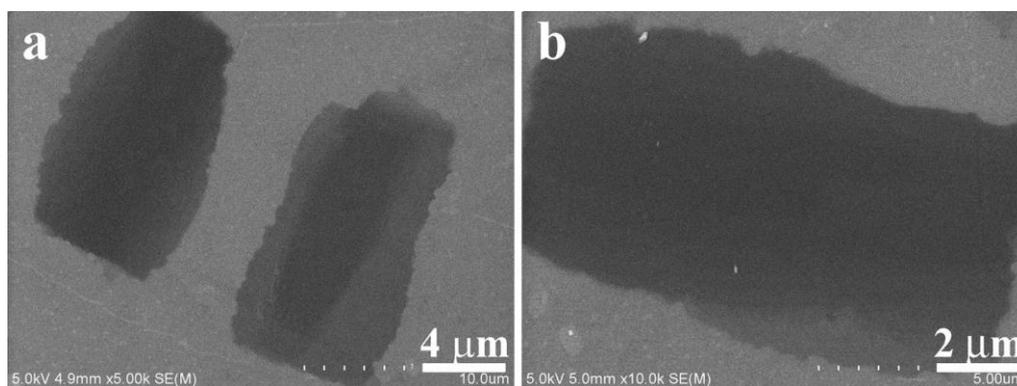


Fig. S5 SEM images of higher magnification of large-size graphene sheet.

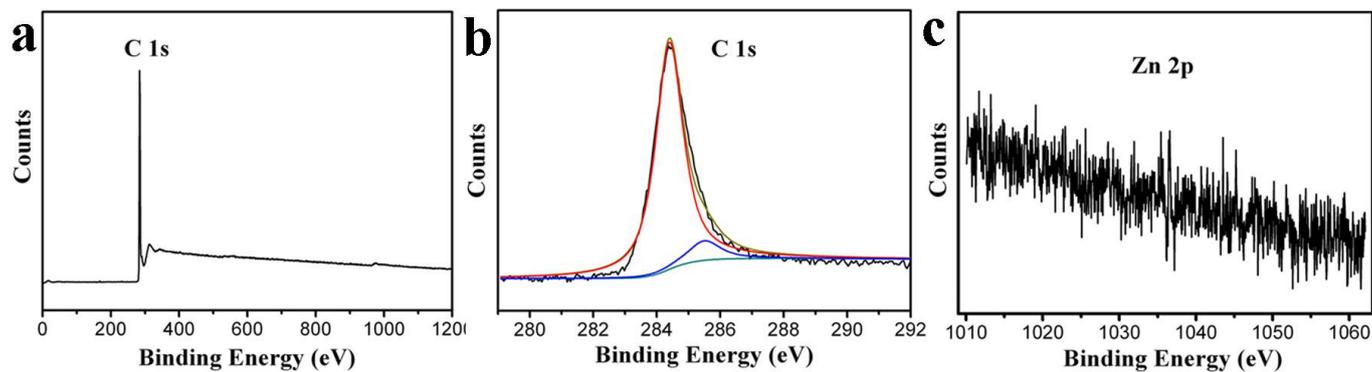


Fig. S6 XPS analysis of the exfoliated graphene. The C 1s peak is mainly consisted of sp^2 C=C at binding energy of 284.4 eV, a little sp^3 C-C or C-H at binding energy of 285.5 eV also appears. From Zn 2p peak, no Zn species was observed in the exfoliated graphene.

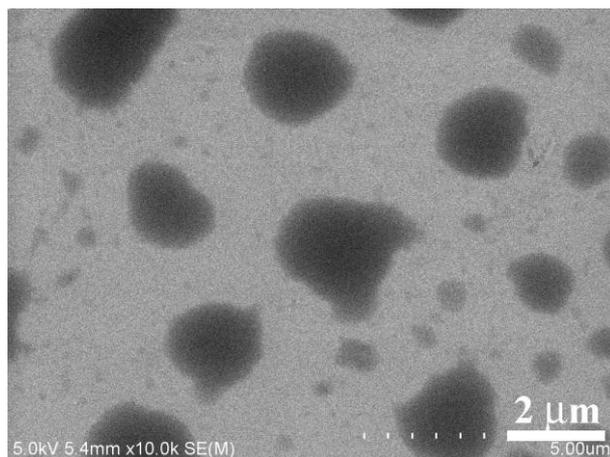


Fig. S7 SEM image of graphene sheets drop from ethanol dispersion to silicon substrate.

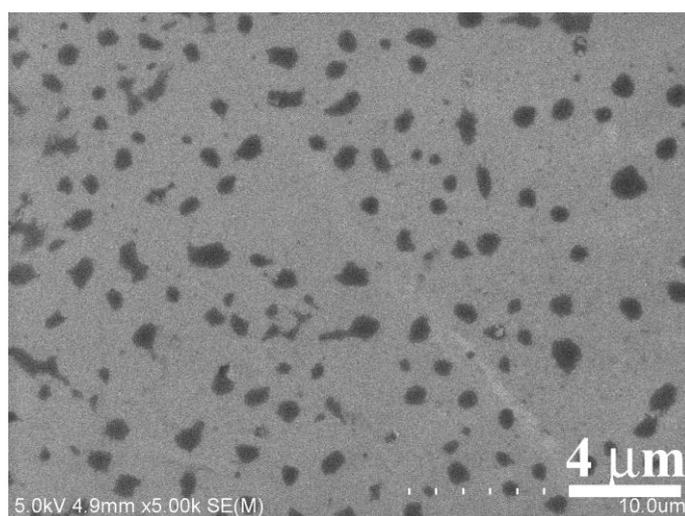


Fig. S8 SEM image of graphene sheets with the follow-up exfoliation of precipitate.

Large size, high quality, and excellent dispersion in organic solvent of the single-layer graphene sheets make them an ideal candidate for device applications as has been proposed for quite some times. This, coupled with no obvious crinkles after evaporation of solvents (see Fig. 2d, S5), promotes us to demonstrate their direct usage for the photoelectric materials. ZnO nanorods/graphenes complexes were further fabricated by the similar solution approach as shown in Fig. 1 but using as-prepared graphene sheets in place of graphite. Fig. S9 shows the typical SEM image of as-prepared ZnO nanorods/graphenes complexes. The SEM image at high magnification (Fig. S9b) clearly shows that the highly oriented ZnO nanorods with a relatively uniform diameter and 500 nm length densely grow on both sides of graphene.

The XRD pattern shown in Fig. S9c confirms the complex formation of ZnO nanorods and single-layer graphene sheets. There are eight main peaks at $2\theta = 31.73^\circ$, 34.40° , 36.21° , 47.50° , 56.55° , 62.81° , 67.90° , and 69.04° , which correspond to the crystal planes of (100), (002), (101), (102), (110), (103), (112) and (201) of ZnO, respectively. All of these peaks are indexed to be hexagonal wurtzite-structured ZnO (JCPDS No. 65-3411). A broad and very weak peak appears at around 26° , indicating graphene sheets do not re-stack or aggregate and ZnO nanorods were grown on individual graphene sheets.

It is tempting to combine the intensively studied wide band gap semiconductor ZnO and the two-dimensional carbon nanomaterial graphenes and explore new optoelectronic properties that may emerge. To this end, the photocurrent response of ZnO nanorods/graphenes complexes was investigated as compared with ZnO nanorods on indium-tin oxide (ITO) substrate (Fig. S9d). Upon the illumination of the UV light ($\lambda=360$ nm), a significant increase of the current was observed. The on/off ratio of ZnO nanorods/graphenes complexes is about 5 times higher than that of ZnO nanorods array. This improved photocurrent response is believed to be attributed to the good light transmittance and conductivity of graphenes.

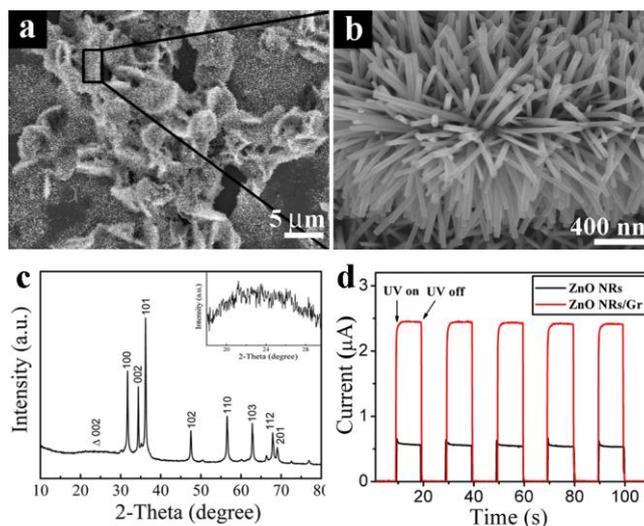


Fig. S9 (a) Overview and (b) high magnification SEM images of ZnO nanorods/graphenes complexes. (c) XRD pattern of the ZnO nanorods/graphenes complexes (the insert shows an amplificatory peak at around 26° as ' Δ ' shown). (d) Photocurrent response curves of ZnO nanorods (black line) and ZnO nanorods/graphenes complexes (red line) in 0.1 M KCl at a bias of 0.2 V, under 360 nm UV light irradiation.

References:

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2. X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang and D. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 62.
3. (a) X. Wang, L. Zhi, N. Tsao, Ž. Tomović, J. Li and K. Müllen, *Angew. Chem., Int. Ed.*, 2008, **47**, 2990; (b) X. Wang, L. Zhi and K. Mullen, *Nano Lett.*, 2008, **8**, 323.