

Supporting Information

Construction of Stable Covalent Bonding in Black Phosphorus/Reduced Graphene Oxide Composite for High-Performance Lithium Ion Battery Anodes

Yang Shi,^{‡a} Zhibin Yi,^{‡a} Yanping Kuang^a, Hanyu Guo^a, Yingzhi Li^a, Chen Liu^{*b}
and Zhouguang Lu^{*a}

^a Department of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen 518055, PR China

^b Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, PR China

[‡] These authors contributed equally to this work

* Email addresses: luzg@sustech.edu.cn (Z.G. Lu); liuchen@szu.edu.cn (C. Liu)

Experimental

Preparation of black phosphorus

Typically, BP was synthesized from the high-energy ball-milling process according to Park's report.¹ Briefly, commercial RP powder (Aladdin, AR, 98.5%) was

purified through a simple hydrothermal reaction in a Teflon liner, followed by heating in a forced air oven at 140 °C for 12 h to remove the surface oxide and other impurities. Purified RP powder was collected through filtration and vacuum drying overnight at 120 °C. Then, 1.04 g purified RP powder was added into a stain steel vial (100 mL 8001) with two 0.5 in. and four 0.25 in. steel balls (ball powder ratio at 20:1). The vial was sealed in an Ar filled glove box (MBRAUN, with oxygen and water concentration lower than 0.1 ppm). Subsequently, HEBM process was conducted using a SPEX-8000M Mixer/Mill for 20 hours (rest 4 h per 10 h to avoid overheating). The as-obtained BP powder was washed several times with CS₂ to remove by-products (mainly white phosphorus) and vacuum dried overnight at 120 °C. The dried BP was stored at the glove box for further use.

Preparation of GO

GO was synthesized according to the typical modified Hummer's method.² First, 3 g graphite (Aladdin, 99.95%, metal basis) was added to a beaker with 70 mL concentrated H₂SO₄ at room temperature. Next, the beaker was transferred to an ice bath and 1.5 g NaNO₃ was added with strong stirring. 9 g KMnO₄ was then slowly added to the solution and further kept at 35 °C for half an hour. Afterwards, 140 mL and 500 mL DI water were introduced into the mixture with 15 min interval. After adding 20 mL 30% H₂O₂ solution to the beaker, a solution in bright yellow color was obtained, which was followed by centrifugations and washing with 250 mL 10% HCl. The solution was washed with DI water for several times until a neutral PH was achieved. Finally, the precipitate was collected and further dispersed in DI water via

ultra-sonication to make a homogeneous solution of 2.5 mg mL⁻¹.

Preparation of BP@irGO composite

Typically, the as-obtained BP powders were mixed with GO in a ball-milling vial with a weight ratio of 7:3. The ball-milling vial was sealed in the glove box and transferred to the SPEX-8000M for ball-milling for 10 hours with the balls to samples weight ratio at 20:1. The produced powder was named as BP@irGO.

Materials characterization

The morphology of the samples was characterized using a field-emission scanning electron microscope (Merlin, ZEISS) equipped with an energy-dispersive X-ray spectrum (EDX, EDAX, Octane Pro) and a field emission TEM (Tecnai G2 F30 U-TWIN). XRD analysis was performed using Bruker-AXS Microdiffractometer (D8 Advance X-ray diffractometer, Cu K α , $\lambda = 1.5046 \text{ \AA}$, 40 kV and 40 mA). Raman spectroscopy was documented on a RENISHAW GL 12 8JR using a laser at 532 nm. XPS was investigated by using a VG scientific ESCALAB 220iXL spectrometer with an Al K α ($h\nu=1486.69 \text{ eV}$) X-ray source. All binding energies were carefully aligned by reference to the C 1s peak (284.6 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon.

Battery assembly and testing

The anodes were prepared by mixing 70 wt% active material (BP, BP@irGO composite) with 15 wt% super P and 15 wt% PVDF in NMP solution. The mixed homogenous slurry was further coated on the Cu foil surface with a coating thickness

of 0.2 mm. The coated foils were vacuum dried at 120 °C overnight and further pressed into disks with a diameter of 16 mm. Typically, the active materials loading is ~0.7 mg cm⁻². Coin cells (CR2016) were assembled in a glove box using lithium foils as the counter electrodes. The commercial electrolyte (1 M LiPF₆ dissolved in the mixture of EC: DMC: DEC=1:1:1) was purchased from the CAPCHEM Co. Ltd. CV and EIS measurements were performed by electrochemical workstation (Bio-logic VMP3) with a voltage window ranging from 0.01 to 2.5 V at a rate of 0.1 mV s⁻¹ and an amplitude of 10 mV. The cycling and rate performance of the assembled batteries were measured via Arbin battery cycler (BT-2000) at 25 °C.

References

- 1 C.-M. Park and H.-J. Sohn, *Adv. Mater.*, 2007, **19**, 2465–2468.
- 2 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

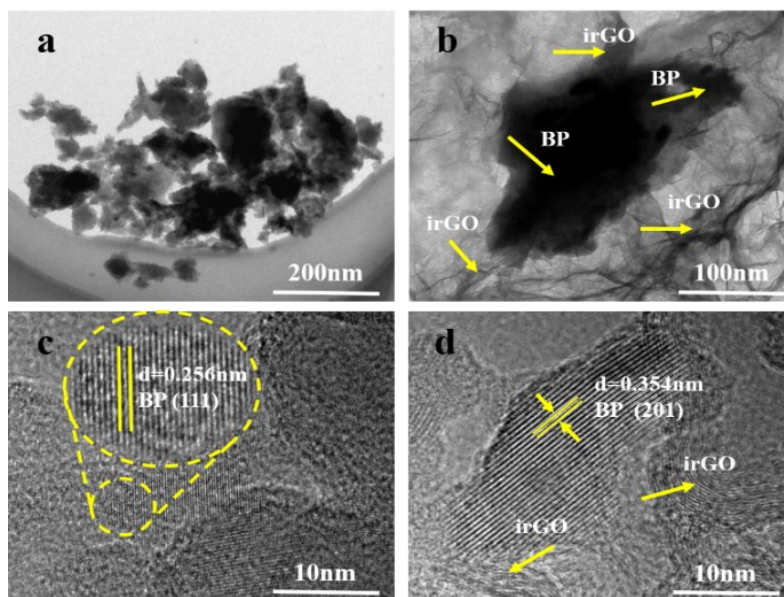


Fig. S1. TEM images of (a) the high energy ball-milling (HEBM) black phosphorus (BP) and (b) BP@irGO nanocomposite; High resolution TEM images of (c) HEBM BP and (d) BP@irGO nanocomposite.

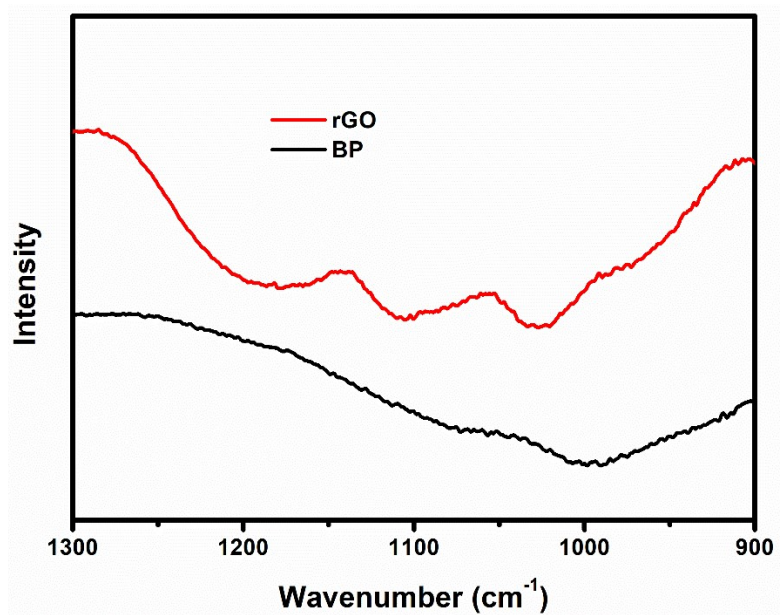


Fig. S2. FTIR spectra of the BP and rGO.

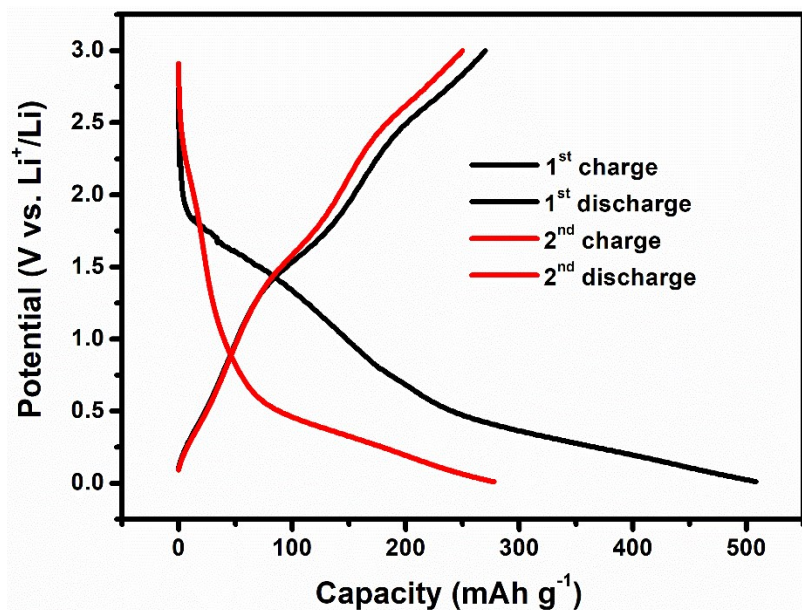


Fig. S3. Galvanostatic charge-discharge profiles of rGO.

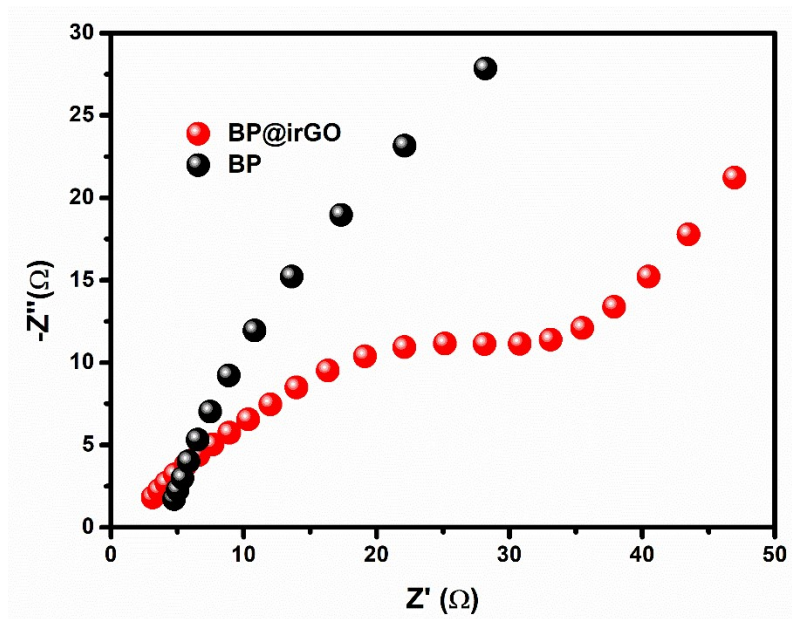


Fig. S4. Enlarged EIS spectra of the BP and BP@irGO.