Room-Temperature Pressure Synthesis of Layered Black Phosphorus-Graphene Composite for Sodium-Ion Battery Anodes

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Graphene oxide (GO) preparation: Graphene oxide (GO) water suspension was purchased from Graphene Supermarket (Graphene Laboratories Inc.), then was further treated according to a modified Hummers method to create more void space between the GO layers through exfoliation.[1] H_2SO_4 and H_3PO_4 were mixed with a volume ratio of 9:1, then 1% wt. GO water suspension was added into the mixed acid solution. The mixture was heated to 50°C and stirred for 10 hours, and then cooled with ice and an appropriate amount of added H_2O_2. After standing for one-hour, the supernatant liquid was removed and the rest of the mixture was diluted with water, repeating the procedure several times. The remaining solid material was then washed with water, HCl and ethanol several times, and then filtered and dried at 60°C in air overnight.

RP/rGO flash-heat-treatment synthesis: RP fine powder with 99% purity (Spectrum Chemical Mfg. Corp.) was dried at 90°C to remove moisture and sieved to pass through a 30 μm mesh. The RP and GO powder precursors were placed in a ceramic boat with a RP/GO/RP three-layer structure with a ceramic cover on the boat. The mass ratio between RP and GO is 5:1. The boat with chemicals was loaded into a tube furnace under argon flow with a mixture of 5% hydrogen (Ar/H_2). The boat was first placed in the location outside the hot zone. After heating the furnace to 500°C, the boat was moved into the hot zone. Once P condensation on the inner surface of the quartz tube downstream of the hot zone was seen (~ 1 minute), the boat was moved back to the original position to cool down. The temperature of the boat was maintained at 290°C overnight to convert potential white P to red P. The resulted RP/rGO composite was transferred into an Ar-filled glovebox, washed with methanol and dried accordingly.

RP/rGO film preparation: the film was prepared through vacuum filtration. A small amount of RP/rGO powder was first added to the filtration equipment to obtain a thin layer of rGO network at the bottom. The RP/rGO composite was mixed with ethanol, and the mixture was added to form the main part of the film. In order to obtain a smooth film with excellent mechanical properties, the power of the vacuum pump and the material loading rate during the filtration process were carefully adjusted. The obtained film was pressed to increase the mechanical stability. The mass of the film electrodes was around 2 mg each. Then the film was transferred onto aluminum foil for the pressure synthesis.

The RP/rGO film and GO powder was also analyzed by X-ray photoelectron spectroscopy (XPS) to study the chemical bonding between phosphorus and rGO sheets at the surface of the composite, as shown in Supplementary Figure S2. In Figure S2a, the spectrum of the pristine GO sample can be fitted with three Gaussian–Lorentzian peaks at 284.6, 286.3, and 287.2 eV, corresponding to C=C/C–C, C–O, and O–C=O bonds, respectively. The spectrum of the RP/rGO composite shows peaks at 284.5, 285.5 and 286.5 eV, corresponding to C=C/C–C, C–O and C=O bonds, respectively. Compared with the GO sample, the intensity of the C–O peak of the

RP/rGO composite is markedly reduced and the O–C=O peak vanishes, indicating that GO was thermally reduced during the heat-treatment in an Ar/H_2 atmosphere. In Figure S2b, the O 1s high-resolution spectra of the two samples also confirm the thermal reduction of GO, as the 531.7 eV signal corresponding to the O=C bond of the GO sample disappeared after the heat treatment, and only the peak of the O–C bond at 533.1 eV was observed for the RP/rGO composite.

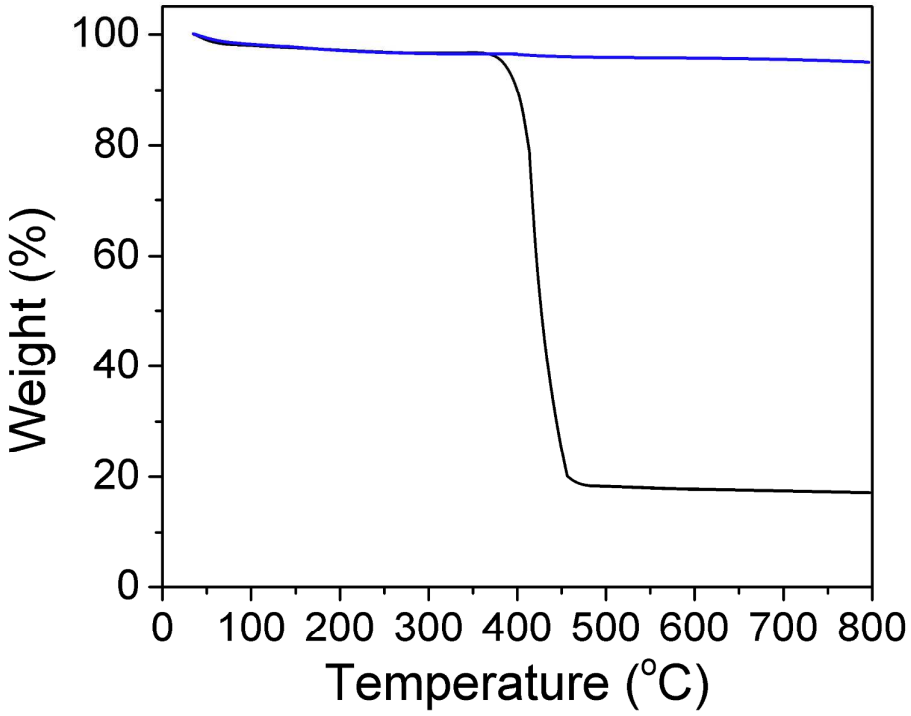

Figure S1. Thermogravimetric analysis (TGA) data of flash-heat-treatment synthesized RP/rGO and thermally reduced rGO with the same heat treatment conditions.

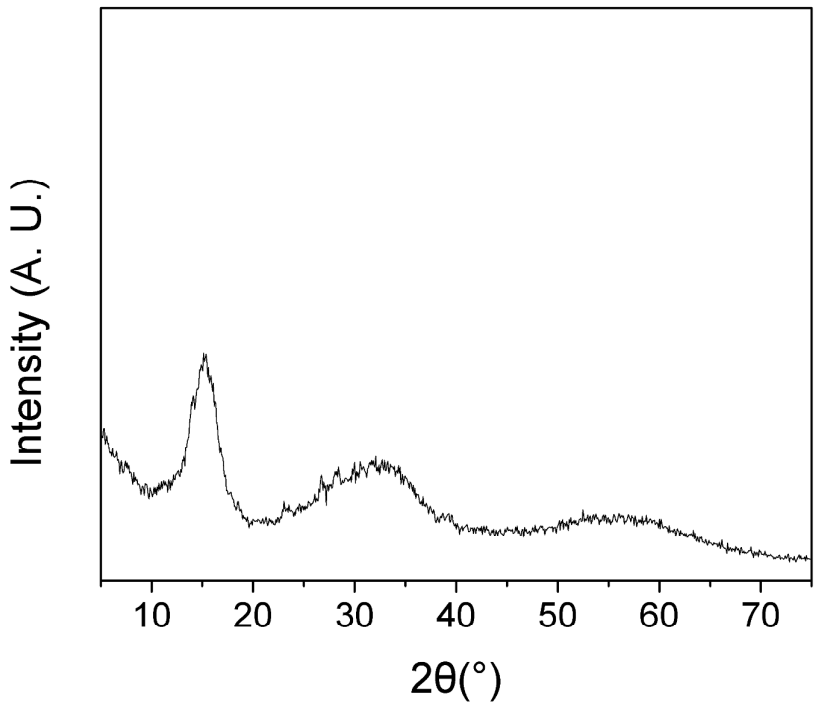

Figure S2. XRD pattern of the commercial red phosphorus.

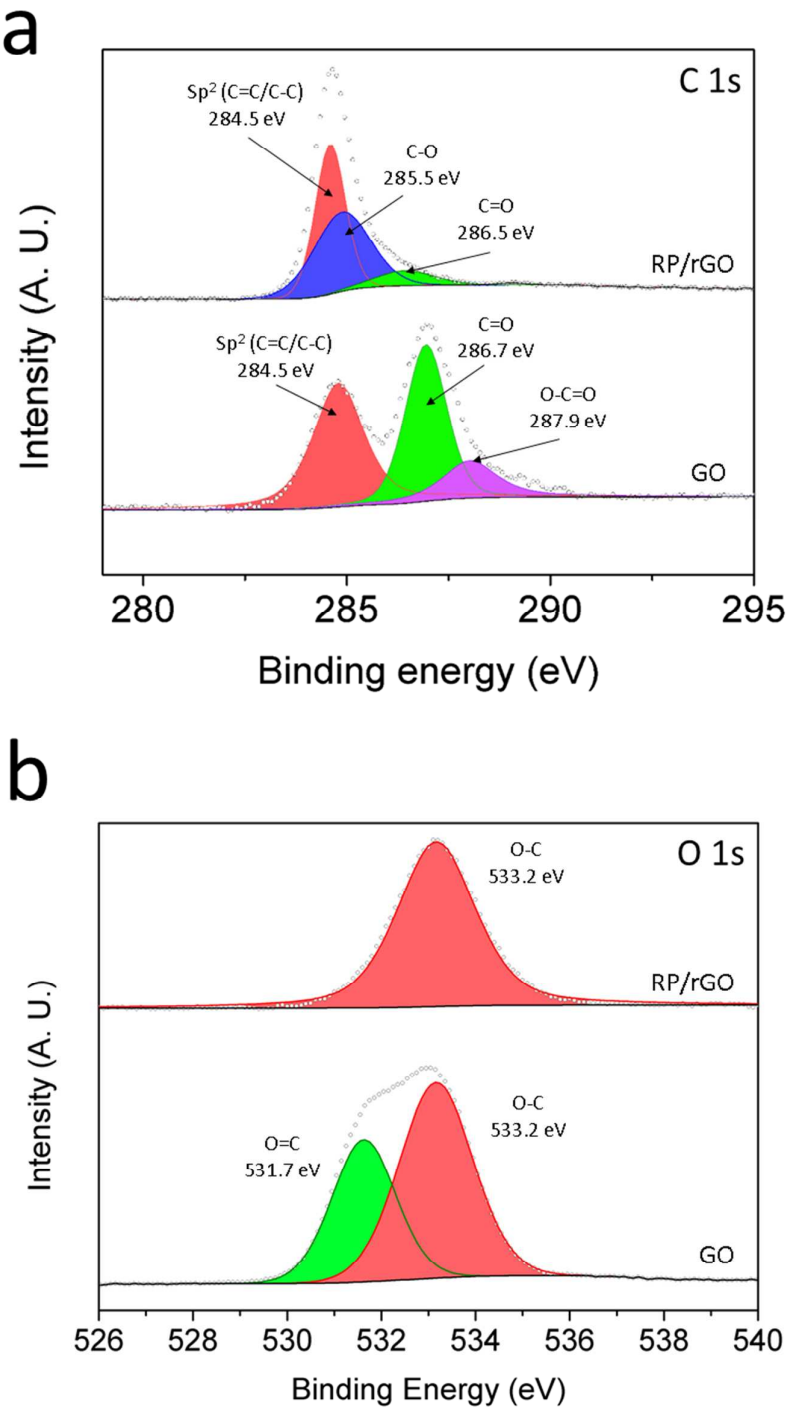

Figure S3. High-resolution (a) C 1s and (b) O 1s XPS spectrum of the flash-heat-treatment synthesized RP/rGO composite and the GO sample.

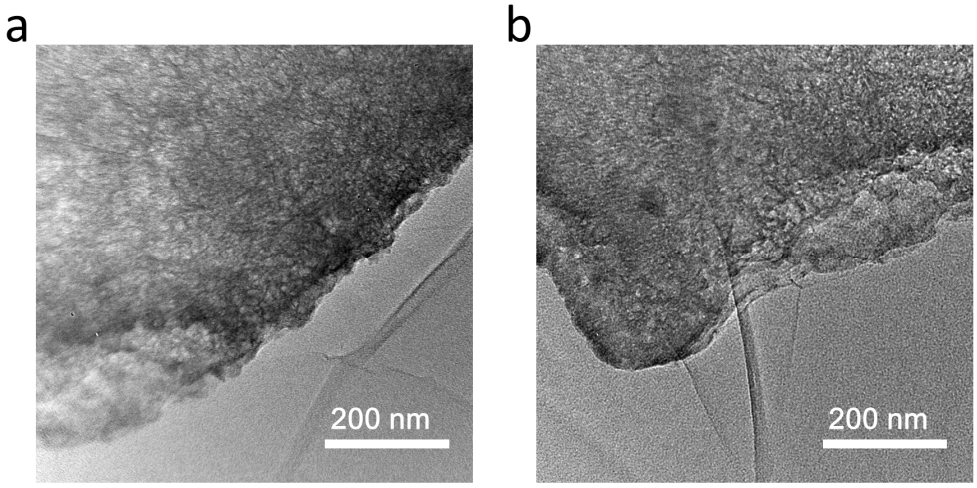

Figure S4. TEM images of post-cycling BP/rGO anode.

Reference

1. Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. *ACS Nano* **2010**, *4*, 4806−4814