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Black phosphorus-based cathode for aqueous Na-ion batteries operating under ambient conditions

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. SUPPLEMENTARY INFORMATION

1 Methodology

1.1 Experimental procedure

Films of PANI and BP-PANI were prepared through the liquid/liquid (L/L) interfacial method, as previously described.[1] Summarizing, BP exfoliation was conducted for 5h and in the following, aniline (10 μL) was polymerized in the dispersion of BP (0.025 mg mL^{-1}, deaerated acetonitrile) and, after the solvent exchange to a biphasic system (aqueous HCl solution/toluene), a freestanding thin film of BP covered by the conducting polymer polyaniline (PANI) was observed at the L/L interface, which could be easily deposited over any desired substrate. PANI films followed the analogous process without the presence of BP.

It was not possible to obtain thin films of pure BP through this methodology. Then, this sample was prepared through drop casting from BP dispersion. For all electrochemical measurements and characterization described in this work, films were deposited over Fluorine doped Tin Oxide (FTO).

The mass of the thin films was determined by weighing three layers deposited onto the same substrate with an area of 1 cm^2. After each deposition the substrates were dried at 100 °C for 30 minutes under vacuum. The mass found was 42.5 μg cm^{-2} for PANI and 25 μg cm^{-2} for BP-PANI. Samples of pure BP were prepared with 800 μL of a 0.025 mg mL^{-1} BP dispersion in acetonitrile dropped and dried at 60°C.

1.2 Electrochemical evaluation

Cyclic voltammetry (CV), charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) measurements were carried out in a Autolab potentiostat, operated by GPS and NOVA 1.11 softwares, in a conventional three-electrode cell. Films deposited over FTO were used as working electrodes with a 0.75 cm^2 of electroactive area for PANI and BP-PANI and 0.25 cm^{-2} for BP. An Ag/AgCl (3 mol L^{-1} KCl) was used as the reference electrode and a platinum wire as the counter electrode. The analyses were performed in 0.5 mol L^{-1} NaCl pH 3 (adjusted with a 1 mmol L^{-1} solution of HCl). VC was carried out at 10 mV s^{-1}. CD and EIS were performed after a pretreatment of the films of 15 voltammetric cycles.

The specific capacity (C) of the thin films was calculated using the equation bellow:

$$C = \frac{I \times t}{m}$$

where I is the charge-discharge current (A), t is the time of discharge (h) and m is the mass of material on the electrode (g).

EIS involved the frequency range of 0.01 Hz to 10 kHz under 0.4 V, applying 10 mV.

1.3 Characterization

Images of scanning electron microscopy (SEM) were obtained in a Mira FEG-SEM (Tescan) coupled to an EDS detector (OXFORD Instruments) for elemental analysis. Raman spectra were collected in a confocal Raman spectrometer (WITec Alpha 300 R) using a 532 nm laser line and 100× objective lens. The optical power was kept at 1 mW in order to avoid laser-induced thermal effects. X-ray diffraction (XRD) measurements were recorded on a Shimadzu XRD-6000 diffractometer using CuKα radiation (1.5418Å), at 40 kV and 30 mA, both with a step of 5s per point and at 0.02 scan rate.

1.3.2. Post characterization of the materials:

(i) Raman spectroscopy and SEM analysis: substrates used in the electrochemical evaluations were dried at 70^{o}C under vacuum for 1h and taken for analysis.

(ii) XRD analysis: substrates used in the electrochemical evaluations were washed with deionized water, in order to avoid the interference of adsorbed NaCl. In the following, substrates were dried at 70^{o}C under vacuum for 1h and analyzed.

2. Stability study

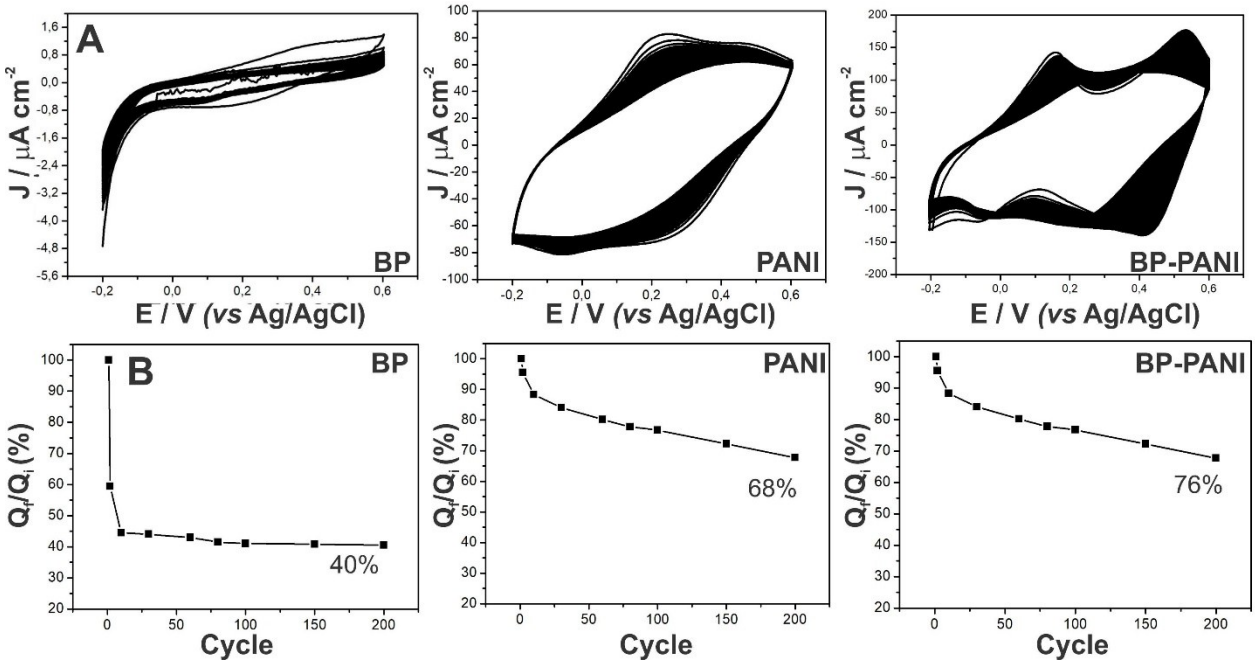

Figure S1. (A) 200 cyclic voltammograms of BP, PANI and BP-PANI samples, (B) curves of ratio percentage between the final (200th) and the initial (1st) cycle of the voltammograms.

3. Charge/discharge measurements of control samples

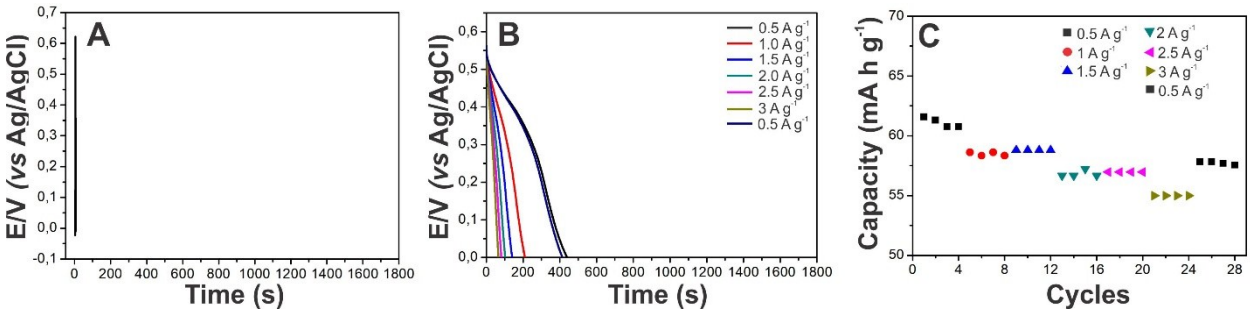

Figure S2. CD curves of (A) BP at 0.5 A $g^{-1}$and (B) PANI and (C) capacities of PANI at different applied current densities. All measurements in NaCl 0.5 mol L^{-1} pH 3.

4. Characterization post CD measurements

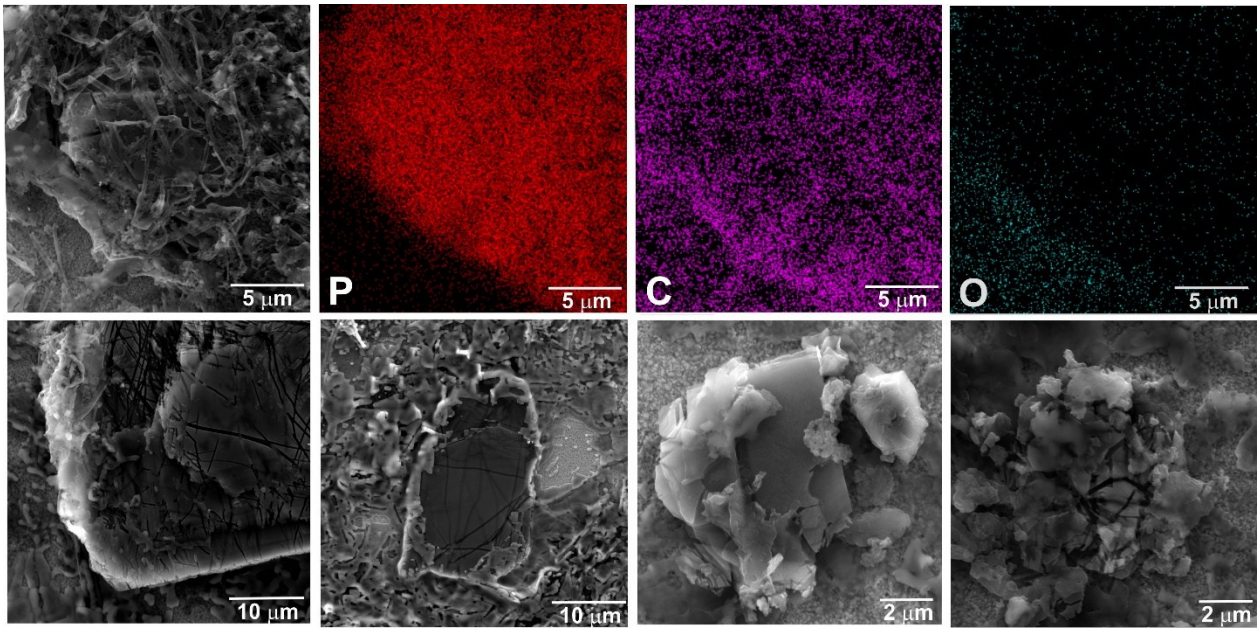

Figure S3. SEM images and EDS elemental mapping of BP-PANI.

References

1. J. E. Fonsaca, S. H. Domingues, E. S. Orth and A. J. Zarbin, *Sci. Rep.*, 2017, 7, 10165**.**