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Solution-Processable Black Phosphorus Nanosheets Covalently Modified With Polyacrylonitrile for Nonvolatile Resistive Random Access Memory

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Experimental Section

General

All reactions were carried out under dry nitrogen atmosphere by using standard Schlenk techniques. The black phosphorus (BP) crystals (99.98%) were purchased from Xian Feng Nano Company (China) and kept in a glove box filled with Ar before use. 4-nitrobenzenediazonium tetrafluoroborate was purchased from TCI (Shanghai) development Co., Ltd. BP-C6H4-NO2, BP-C6H4-NH2 and DDAT were synthesized according to the literatures.[1-3] The other analytically pure chemicals were purchased from Aladdin and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen.

Ultraviolet/visible (UV/Vis) absorption spectra were measured on a Shimadzu UV-2540 spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded by Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). Raman spectra were recorded on an Invia/ReflrIx Laser Micro-Raman spectrometer (Renishaw, England) with excitation laser beam wavelength of 514 nm. Atomic force microscopy (AFM) and conductive atomic force microscopy (C-AFM) measurements were performed on a Solver P47-PRO (NT-MDT Co., Moscow, Russia) microscope, and a Bruker Dimension Icon scanning probe microscope, respectively. Transmission electron microscopy (TEM) images were recorded on a JEOL-2100 (JEOL Ltd., Japan) TEM system operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA, respectively. The pressure in the analysis chamber was maintained at 5×10^{-8} Torr or lower.
during each measurement. The number-average \( (M_n) \) and weight-average \( (M_w) \) molecular weights of the polymers were determined with a Waters 2690 gel permeation chromatography (GPC) using a polystyrene standards eluting with DMF.

**Device fabrication**

The ITO glass substrate was carefully precleaned sequentially with deionized water, acetone, and 2-propanol in an ultrasonic bath for 15 min, and then treated with oxygen plasma. A 100 \( \mu L \) of the sample solution (10 mg·mL\(^{-1}\)) in NMP was spin-coated on the pre-cleaned ITO sheet at a spinning speed of 800 rpm for 20 s and then 1500 rpm for 45 s, followed by the removal of the solvent under vacuum at 80°C overnight. Al top electrodes were deposited on the surface of active layer through a shadow mask at 10\(^{-7}\) Torr via E-beam evaporation. All electrical measurements were performed on a Keithley 4200 semiconductor parameter analyzer in ambient condition without any device encapsulation.

**Materials synthesis**

**Preparation of few-layer BP:** By using liquid exfoliation technique that has been widely used to exfoliate various layered-materials producing single- and/or few-layer nanosheets, we prepared few-layer BP nanosheets with very regular and uniform structural feature. In a typical procedure, 50 mg of BP powder, which was obtained by grinding the BP crystals in the glove box, was added to 100 mL of anhydrous NMP, and then was sonicated for 5 hours in a water bath of 10-15°C until a homogeneous suspension was formed. After being centrifuged at 5000 rpm for 120 minutes, the superstratum dispersions were collected and kept in a dark bottle in nitrogen atmosphere. Before use, the above dispersions were centrifuged at high speed of 12000 rpm for 20 minutes. The collected solid few layer BP was directly used for the synthesis of BP-DDAT.

**Synthesis of BP-DDAT:** To the solution of BP-C\(_6\)H\(_4\)-NH\(_2\) (20 mg) in dry dichloromethane (20 mL) was added a mixture of DDAT (1.0 g, 2.75 mmol) and \(N, N'\)-dimethylaminopyridine (DMAP, 25 mg, 0.20 mmol) under dry nitrogen atmosphere. After stirring at 0°C for 1h, 1,3-dicyclohexylcarbodiimide (DCC, 950 mg, 4.60 mmol) was added to the above soluton, followed by reaction for an additional 48h at room temperature. Then the reaction mixture was poured into 300 mL of dry methanol and vacuum-filtered through a polycarbonate film (\(\phi\)0.22 \(\mu\)m). The collected product was washed with ethanol, deionized water and THF, respectively, to remove any adsorbed unreacted DDAT. 29 mg of BP-DDAT after dryness under vacuum at 40°C for 24h was obtained.
Synthesis of BP-PAN: Polymerization reaction was carried out under highly purified dry nitrogen by the use of a standard Schlenk tube. A degassed mixture of BP-DDAT (20 mg) as the RAFT agent, acrylonitrile (AN, 0.5 ml, before use, it was purified by vacuum distillation, dried by MgSO₄, and stored in the dark), and AIBN (2 mg, 0.012 mmol) as the initiator was heated in a water bath of 70 °C in a ultrasonic generator for 4 h under ultrasonic irradiation. After completion of the reaction, the mixture was allowed to cool to room temperature. The crude product was dissolved in THF and dropped into 50 mL of methanol, followed by vacuum-filtering through a polycarbonate film (φ0.22 μm). The collected solid product was washed with a large amount of CH₂Cl₂ to remove any possible unreacted monomer and soluble free PAN polymer (if any) trapped in the resultant product. The product was further purified by Soxhlet extraction with acetone. After drying in a vacuum at 60 °C for 24 hours, 143 mg of BP-PAN powder was obtained.

Preparation of PAN via RAFT polymerization: Polymerization reaction was carried out under highly purified dry nitrogen by the use of a standard Schlenk tube. A degassed mixture of DDAT (10 mg) as the RAFT agent, acrylonitrile (AN, 0.5 ml, before use, it was purified by vacuum distillation, dried by MgSO₄, and stored in the dark), and AIBN (2 mg, 0.012 mmol) as the initiator was heated in a water bath of 70 °C in a ultrasonic generator for 4 h under ultrasonic irradiation. After completion of the reaction, the mixture was allowed to cool to room temperature. The crude product was dissolved in CHCl₃ and dropped into 120 mL of methanol. This process repeated for at least three times to remove any possible unreacted monomer and initiator. The product was further purified by Soxhlet extraction with acetone. After drying in a vacuum at 50 °C for 24 hours, 211 mg of PAN powder was obtained.

**Figure S1.** Cyclic voltammograms for the sample films coated on Pt at ambient temperature. a) BP-PAN and b) pyro-BP-PAN. Scan rate: 100 mV s⁻¹. Reference electrode: Ag/AgCl. Electrolyte: Bu₄NClO₄ (0.1 M) in deaerated acetonitrile.
**Figure S2.** Current-voltage ($I$–$V$) characteristics of the Al/BP-PAN/ITO device kept in the air for more than 2 weeks.

**References**

