Supplementary Information: Hybrid Nanocomposites of 2D Black Phosphorus Nanosheets Encapsulated in PMMA Polymer Material: New Platforms for Advanced Device Fabrication

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21 March 2018

Keywords: black phosphorus, two-dimensional materials, organic-inorganic hybrid compounds, polymers, nanotechnology

Submitted to: Nanotechnology
1. Time stability of the spin-coated hybrid film

A nanocomposite film, obtained from the solution in anisole, was spin-coated and annealed in the same conditions as the ones used for device fabrication (5000 revolutions per minutes for 1 minute, 5 minutes annealing at 120 °C).

We measured Raman spectra on selected bP nanosheets, found on the freshly prepared sample, and on the same nanosheets after 3 months of storage in a vacuum desiccator in darkness. Figure S1 shows one such Raman spectrum. It clearly displays all three peaks of the bP Raman signature, both as prepared and after three months, without a significant decrease in the intensity. All analyzed nanosheets preserved their Raman activity after 3 months.

![Figure S1: Raman activity of a bP nanosheet embedded in the PMMA matrix as prepared (black curve) and after 3 months (red curve).]
2. EDX characterization of the nanocomposite thin film

On the same sample, on some of the nanosheets, EDX was performed. One example is shown in Fig. S2. The EDX spectrum (Fig. S2 (a)) shows a large contribution from the SiO$_2$ substrate, but in the zoomed-in panel (inset of Fig. S2 (a)) carbon and phosphorus peaks are clearly visible. Figure S2 (b) shows the SEM image of the nanosheet where the spectrum was taken. An EDX map from the same region was also acquired, and the results are shown in panels (c) and (d) of Fig. S2: the phosphorus nanosheet covers only the upper left part, while the bright region in the SEM image is carbon–rich. This is a further evidence of the fact that bP nanosheets can act as seeds for PMMA polymerization, as suggested also by the increase of molecular weight of PMMA in the nanocomposite discussed in the main text.

![Figure S2](image_url)

*Figure S2.* (a) EDX spectrum acquired in the dark region of the nanosheet shown in (b). In the inset, a zoom-in clearly shows carbon and phosphorus peaks. (b) Secondary electron SEM image of the nanosheet, acquired with 10 kV acceleration voltage. (c) Phosphorus map on this nanosheet and (d) carbon map in the same area. Scale bar is 200 nm both for the secondary electron SEM image and for the phosphorus and carbon maps.
3. Further morphological characterization.

Figure S3 (a) and (b) shows SEM and AFM images carried out on a different device after the removal of the MMA(8.5)MAA copolymer/PMMA bilayer [1]. Inspection of the AFM line profile shown in Fig. 4 (c) clearly shows that the central part of the flake, not clamped by gold, was accidentally removed during the cleaning with acetone. The upper and lower parts of the structure show height values around 50 nm (Fig. 4 (d)). This, together with morphological information collected on similar materials discussed in Passaglia et al. [2] suggests that this nanosheet is indeed an aggregate of smaller bP flakes, held together by thin polymer layers. It can be expected that any improvement in preparation conditions, which could decrease aggregation effects and provide better shaped single flake nanosheets, will lead to even better transport properties, especially in terms of mobility.

![Figure S3](image-url)

Figure S3. (a) SEM image of another device. The scale bar is 1 µm (Image acquired at 5 kV acceleration voltage.). (b) AFM image of the same device, with two cross-sections (c) and (d). The scale bar of the AFM image is 440 nm (Image size 2.2 µm × 3.8 µm). The top layer of PMMA was removed in acetone and caused the accidental removal of the part of the device not clamped by the gold contacts, as shown in the central cross-section (c).

References

[1] MMA(8.5)MAA copolymer/PMMA bilayer would be exposed in case of SEM imaging and would not allow the height determination by AFM.