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MS-2-P-5999 Counting the number of layer of graphene flakes embedded in polymer by STEM-EELS

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Polymers of intrinsic microporosity (PIMs) exhibit molecular sieve behaviour as a consequence of their rigid, contorted macromolecular backbones.[1]The archetypal membrane-forming PIM shows exceptional promise for membrane processes such as organophilic pervaporation, solvent-resistant nanofiltration and gas and vapour separations. PIM-1 defines the 2008 upper bound of performance for important gas pairs such as CO2/N2.[2] Nanocomposite or “mixed matrix” membranes comprising PIMs with suitable nanofillers offer the potential for even better combinations of selectivity and permeability, together with resistance to ageing effects over the period of use. The incorporation of graphene or functionalized graphene platelets may modify membrane performance in a number of ways, depending on their size, distribution and functionality.

PIM-graphene composite solutions have been used to prepare thin composite membrane films by spin coating onto glass substrates. The films have been characterized using Transmission electron microscope (TEM) imaging, Raman spectroscopy and X-rays Photoelectron Spectrosocopy. TEM imaging was performed using a FEI Tecnai F30 S/TEM at 300 kV and a probe-corrected FEI Titan 80-200 G2 ChemiSTEM at 200 kV fitted with a GIF Quantum for electron energy loss spectroscopy (EELS) spectral imaging. TEM specimens have been prepared by transferring the spin-coated membranes onto a holey carbon grid.

Fig. 1 shows a scanning TEM (STEM) images acquired using a low angle annular dark field (ADF) detector. Optimisation of the specimen preparation and imaging conditions allows imaging of the PIMs nanoporous structureat high resolution as well as revealing the distribution of the graphene flakes within the PIM matirx at low magnification, as shown in Fig. 1a and b, respectively.

It is interesting to determine the number of graphene layers for flakes within the PIM but diffraction analysis is complicated by the strong amorphous background generated by the PIM matrix. Here we show that EELS provides an alternative method with which to characterize the thickness of graphene flakes within a polymeric matrix. Due to the anisotropy of the bonds in graphene and the isotropy of the bonds in the polymer, the sensitivity of EELS to the anisotropy of carbon[3] provides insight in the number of layer of the graphene flakes embedded in the polymer (Fig. 2d). Fig. 2b and c show the π* and σ* map of the graphene flake displayed in Fig. 2a. Thicker graphene flakes provide a higher σ*/π* bond ratio enabling EELS to quantify the number of graphene layers for an individual flake.

[1] McKeown and Budd, Macromolecules 43 (2010), p. 5163.
[2] L M Robeson, J. Membr. Sci. 320 (2008), p. 390.
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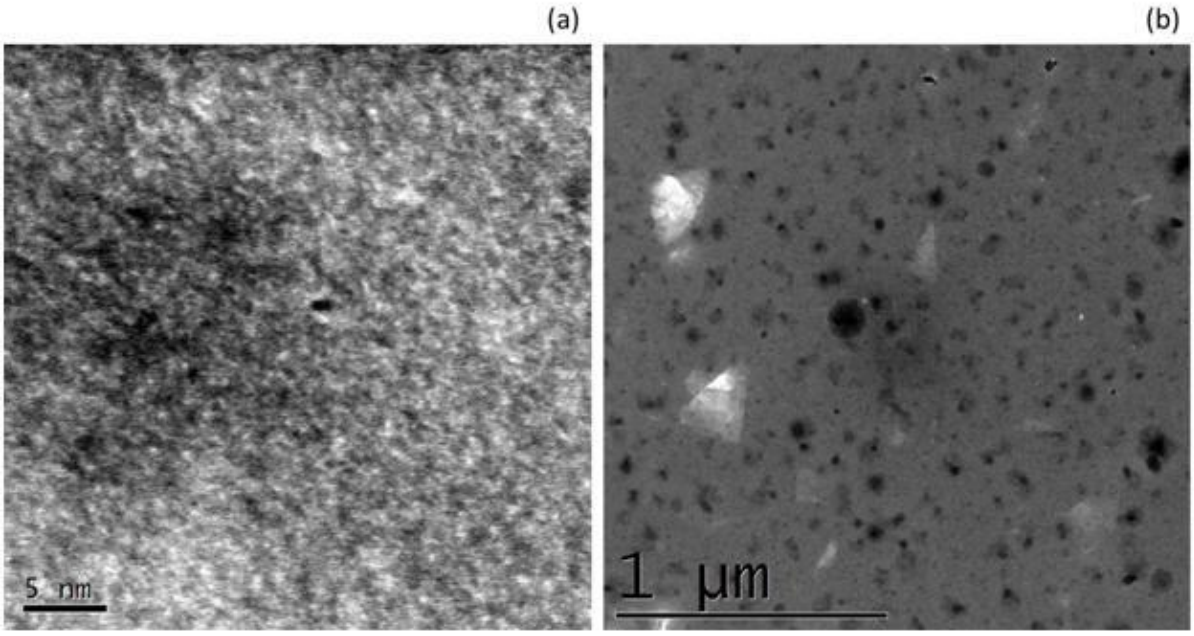

Fig. 1: (a) STEM-ADF images of polymer of intrinsic microporosity (PIM) and (b) overview of graphene flakes distribution embedded in PIM.

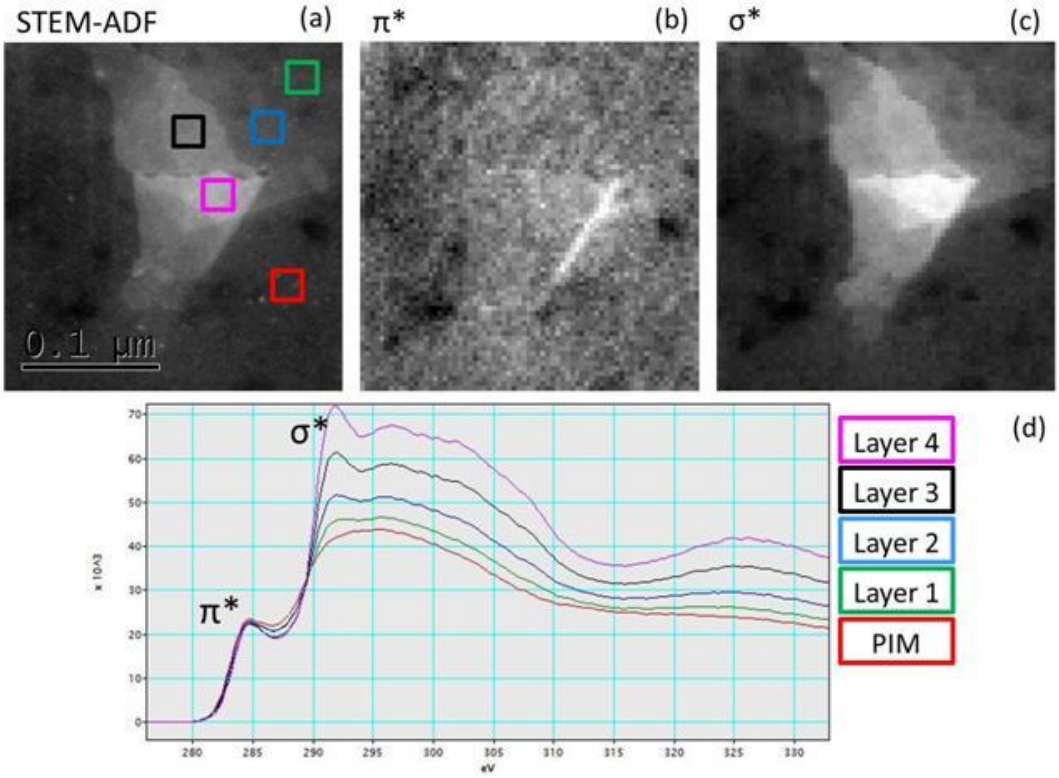

Fig. 2: (a) STEM-ADF image of a multilayer graphene flake embedded in PIM. (b) σ* and (c) π* map obtained from the EELS C-K edge.(d) Background subtracted EEL spectra corresponding to the regions of the flake shown in (a).