Peculiar Plasmon Peak Position in Electron Energy Loss Spectrum of Hexagonal Boron Nitride/Graphene Double Layer

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Van der Waals (vdW) heterostructures of two-dimensional materials have attracted considerable research interest [1]. We report the observation of a large blue shift in the $\pi+\sigma$ plasmon peak of the electron energy loss spectrum of a hexagonal boron nitride (h-BN)/graphene vdW heterostructure with regard to those of single-layer graphene, single-layer h-BN, and bilayer h-BN.

Samples for this study have been grown by an atmospheric-pressure chemical vapor deposition process modified from previous work [2]. First, graphene is grown on a copper foil substrate, followed by a hydrogen etch step that result in fresh zigzag-oriented edges of graphene islands and holes in the islands. Ammonia borane (NH_3-BH_3) is then used as the precursor to grow h-BN. In contrast to previous work, where the precursor charge was controlled to ensure the synthesis of strictly in-plane heterojunctions of graphene and h-BN, the precursor charge is significantly increased to result in the formation of bilayer h-BN and h-BN/graphene double layer regions, along with areas of single-layer graphene and single-layer h-BN on the same sample. Atomic-resolution imaging and electron energy loss spectroscopy (EELS) of the samples is accomplished using a state-of-the-art fifth order aberration-corrected scanning transmission electron microscope (STEM) Nion UltraSTEM100, with the capability to obtain high-angle annular dark field (HAADF) images that can distinguish intensity differences between low-Z elements (e.g. N, B, and C). Images are acquired with an accelerating voltage of 60 kV, and EELS performed with an energy dispersion of 0.3 eV/channel and an energy resolution of 0.6 eV.

Figures 1A, B, C, and D show typical HAADF images of single-layer graphene, single-layer h-BN, bilayer h-BN, and an h-BN/graphene double layer, along with their respective electron energy loss spectra. The spectra are fit with both Lorenztian and Gaussian distributions to obtain a noise-free representation of the spectra and give confident peak positions and widths. Table 1 shows that the π plasmon peaks of the h-BN/graphene double layer are within 0.1 eV from those of graphene, single-layer h-BN, and bilayer h-BN. While the $\pi+\sigma$ plasmon peaks of graphene, single- and bilayer h-BN are consistent with those reported in the literature [3,4], the $\pi+\sigma$ plasmon peak of the h-BN/graphene double layer, a vdW heterostructure, is appreciably blue shifted with regard to *each* of graphene, single- and bilayer h-BN. This suggests that the in-plane σ bonds of the two two-dimensional sheets interact, resulting in alteration of the electronic structure.
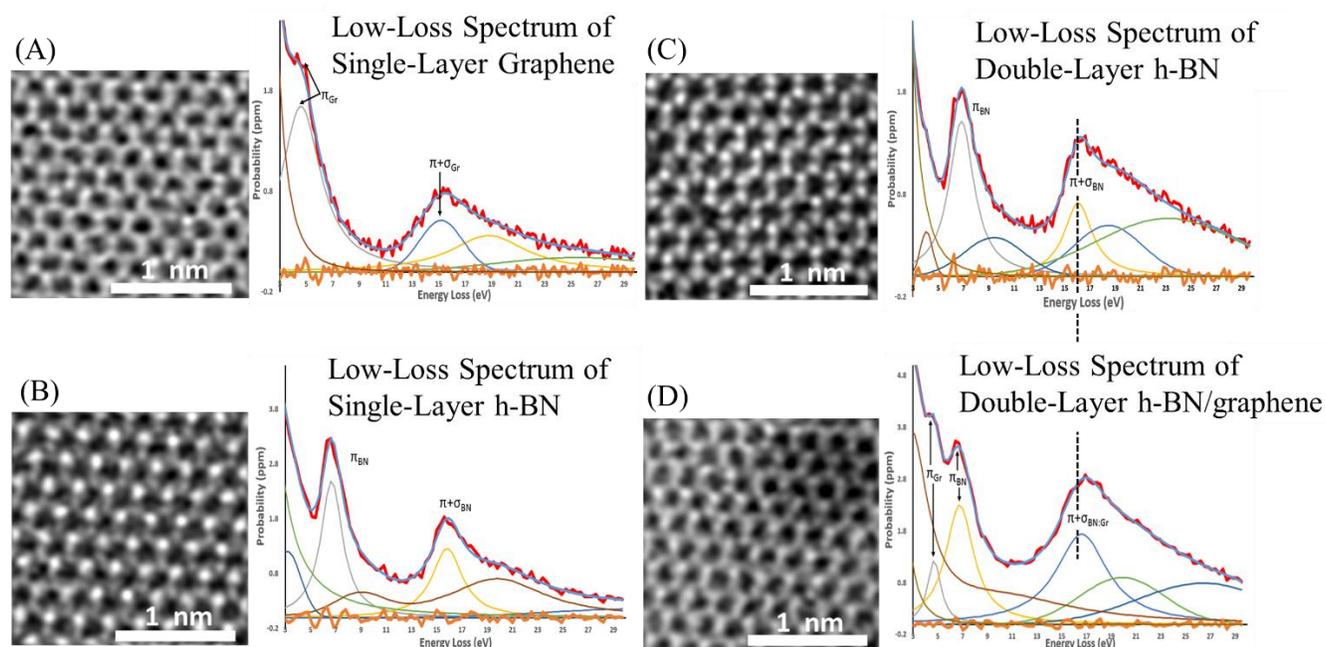
Figure 1. HAADF images (2 nm × 2 nm) and EELS of (A) graphene, (B) single-layer h-BN, (C) double-layer h-BN (C), and (D) h-BN/graphene double-layer. EELS plots graph the experimental data (red lines/fluctuating spectrum), model data (blue lines/ smooth spectrum) (summation of all of the Lorenztian and Gaussian peaks used to fit experimental data) and the noise (orange line/fluctuates around the x-axis) (difference between experimental and model data). The dashed line is an indicator to aid in recognizing peak shift.

	π (eV)	π+σ (eV)
1L Gr	4.60	15.19
1L h-BN	6.67	15.83
2L h-BN	6.84	16.08
h-BN/graphene	4.70 ; 6.76	16.62

Table 1. Peak positions of π and π+σ surface plasmons for all four types of regions in Fig. 1.

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