

π -Plasmon Dispersion in Free-Standing Monolayer Graphene Investigated by Momentum-Resolved Electron Energy-Loss Spectroscopy

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Graphene is a single layer of carbon atoms densely packed in a honeycomb lattice with each carbon atom accommodating four valence electrons: one π electron and three σ electrons [1]. The lone unpaired π electron in the half-filled p_z orbital would form a π bond with the neighboring carbon atoms leading to delocalized π bands. Three σ electrons, sp^2 -hybridized with neighboring three carbon atoms, form stronger σ bonds within the graphene layer. The π electrons play a predominant role in the electronic excitations below 10 eV while the σ electrons have important contributions at energies above 10 eV [1]. Furthermore, graphene is characterized by the signature linear dispersion of the π electrons near K , K' points of the Brillouin zone (Dirac cone) [1].

Recently, the electronic excitations in monolayer graphene have been widely studied using electron energy loss spectroscopy (EELS) [2-3], which could be separated into three distinct spectral regime: the low-energy excitations at 0 ~ 3 eV [2], the spectral features at ~ 4.5 ~ 5 eV (π plasmon) and ~ 14.5 ~ 15 eV ($\pi+\sigma$ plasmon) [3]. The low-energy excitations at 0 ~ 3 eV has been demonstrated with the characteristic square root of momentum (q) dependence of 2D plasmons [2], while the dispersion of π plasmon has been reported to exhibit either linear dependence [3] or quadratic dependence [4], in contrast to the square root of q dependence predicted by theoretical prediction in literature [5]. Furthermore, the π plasmon dispersion exhibits a classical in-plane anisotropy in the parent graphite, while that in monolayer graphene remains largely unexplored. Here, we report our studies to address the aforementioned issues concerning the π plasmon in monolayer graphene using momentum-resolved EELS (ω - q maps) with q spanning from 0 to Brillouin zone boundary (~1.5 \AA^{-1}).

Figure 1(a) displays the momentum resolved ω - q maps in monolayer graphene along the ΓM direction with the momentum resolution of $\sim 1.4 \times 10^{-4} \text{\AA}^{-1}$, clearly showing two spectral branches: a lower-energy branch with stronger intensity at ~ 4.5 eV and a higher-energy branch with much weaker intensity. Figure 1(b) shows the EELS spectra at different q values extracted and integrated with window of 0.002\AA^{-1} and over the full q range (see the bottom gray curve). This integrated spectrum faithfully reflects the π and $\pi+\sigma$ plasmons in monolayer graphene at 4.5 and 15 eV, respectively [3,4]. The individual q -dependent spectrum in Figure 1(b) reveals the respective dispersions of the two plasmon branches from 4 and ~13 eV at $q \rightarrow 0$ (see also the enlarged inset). In addition, the initial spectral energy of 4 eV in monolayer graphene at $q \rightarrow 0$ coincides with the energies of the well-known $\pi \rightarrow \pi^*$ interband transitions in graphene [1]. In accordance with the further q -dependent experimental results to be described below (see Figure 2), we consider the spectral feature at 4(4.5) eV to be simply π plasmon mode in this study.

Figure 2(a) shows the momentum resolved ω - q maps extension of Figure 1(a) to the ΓM zone boundary and Figure 2(b) exhibits the corresponding q -dependent spectra derived at each individual q . It clearly reveals that the π ($\pi+\sigma$) plasmon disperses from 4 eV (~13 eV) to ~12 eV (~30 eV) at $q = 1.4 \text{\AA}^{-1}$, respectively. Furthermore, an additional spectral feature at 4.5 eV becomes visible from $q \geq 0.5 \text{\AA}^{-1}$ and

continuously disperses upward to ~ 7 eV at $q = 1.4 \text{ \AA}^{-1}$. Moreover, this spectral feature exhibits a linear dispersion and an energy of ~ 4 eV when extrapolated to $q=0$, coinciding with the $\pi \rightarrow \pi^*$ interband transition in graphene [1]. It strongly suggests that this linearly dispersive feature is due to direct nonvertical interband transitions, giving rise to the in-plane anisotropy in monolayer graphene. This is the first experimental observation for the low-energy dispersive spectral feature in monolayer graphene, and has never been documented in literature.

References:

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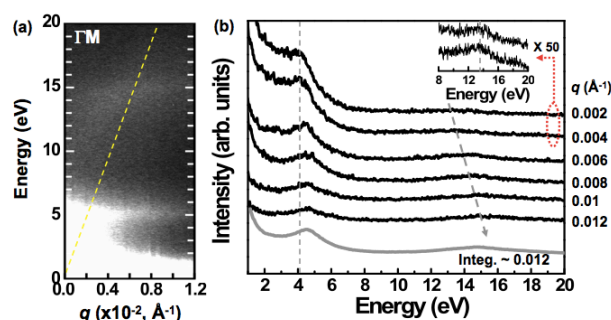


Figure 1. (a) Momentum-resolved ω - q map of the monolayer graphene along the Γ M direction. The yellow line indicates the light line, (b) The EELS spectra at different q values, extracted from (a) using the q -integration window of 0.002 \AA^{-1} in width. Inset is the EELS spectra at $q=0.002 \text{ \AA}^{-1}$ is the blow-ups of those in (b).

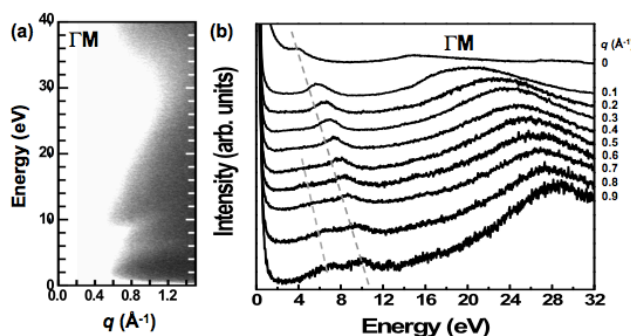


Figure 2. (a) Momentum-resolved ω - q map of the monolayer graphene obtained along the Γ M direction, (b) The EELS spectra at different q values, extracted from (a) using the q -integration window of 0.06 \AA^{-1} in width. The gray line was plotted for ease of guidance.