

Polybromide formation in carbons

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Bromination of carbon materials is the effective route to control work function and to enhance conductivity of carbon materials because bromine acts as a *p*-dopant to graphite and carbon nanotubes. Intercalation of bromine into carbon material is successfully investigated by Raman spectroscopy. The most pronounced low-frequency bromine feature is the strong broad peak at ~230-240 cm⁻¹ which is significantly downshifted from its position in gaseous and solid bromine (~305 cm⁻¹). The spectrum in the vicinity of this peak is broad and complicated, therefore, interpretation of Raman bands for intercalation compounds of graphite and carbon nanotubes with bromine will be helpful in understanding bromine intercalation process.

In the present work, we synthesized bromine-intercalated natural graphite, graphite fluorides with different fluorination content and double-walled carbon nanotubes. Vibrational properties of bromine intercalated in carbon nanomaterials has been investigated by Raman spectroscopy accompanied with density-functional theory (DFT) calculations. The calculations were performed within the local density approximation using the AIMPRO software package [1-3]. This software contains basis sets of atomic orbitals in the form of localized Gaussian based functions (22 and 50 independent functions for carbon, fluoride and bromine, respectively) with angular momenta up to *l* = 3.

The spectra of pristine graphite and highly fluorinated graphites were found to be featureless in the region 100-550 cm⁻¹. For other carbon samples, the presence of bromine causes distinct features in Raman spectrum dominated by two main peaks around 154-161 cm⁻¹ and 229-237 cm⁻¹. In order to gain insight into the origin of peaks observed in the Raman spectra, we calculated normal vibration frequencies of bromides adsorbed on graphene and graphene fluoride. Our results suggest preferable formation of polybromides on graphene and fluorinated graphene surface. Nudged elastic band calculations show that this reaction could be exothermic with small energetic barrier.

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