Towards Imaging Single Molecules on Graphene Substrate

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Abstract With its two-dimensional geometry, novel electron properties make graphene a promising lab bench for characterizing the low dimensional world. The delocalized electrons of the graphene circulate on the surface only; that is, as a substrate, graphene could significantly reduce the influence of attached molecules. On the other hand, graphene is nearly transparent to electron beams of TEM. All these characteristics of graphene make the imaging of single molecule under TEM possible. We have designed and made a new type of TEM grid as demonstrated in Figure 1. Using this new grid system, we are carrying out single molecular imaging on metallocene@graphene systems, such as ferrocene. Metallocene molecules consist of two cyclopentadienyl rings bound on opposite sides of a central metal atom. These stand vertically on the graphene through π -π interactions[1]. Owing to the relative strong interaction of π -π stacking and to the delocalization of electrons on graphene, we imagine that upper cyclopentadienyl ring of the graphene molecules might rotate in a significantly different manner comparing to the ferrocene crystals.

We have made a set of ferrocene@graphene and Bis(pentamethylcyclopentadienyl) -iron@graphene samples and characterized these using Fourier Transform Infrared spectroscopy (FTIR) and Raman spectra to confirm the formation of the ferrocene@graphene system. Figure 2 shows an example. This ferrocene@graphene system is ideal for the purpose of trying to image single molecules using STEM for the following reasons: 1) Single layer graphene is nearly transparent to electron beams; 2) Ferrocene is a stable system with a heavy (high scattering cross-section) atom defining the centre of the molecule; 3) Due to the symmetrical nature of ferrocene molecules, the dynamics of the ferrocene@graphene is expected to be unusual.

Our ongoing observation to single molecules using the special TEM grid is helpful for revealing the mechanism that connects ferrocene molecules and the graphene sheet, and also might provide direct observation of the clustering trend of ferrocene molecules when they attach to a single layer of graphene. In addition, some information about the rotation of the top cyclopentadienyl ring (for ferrocene@graphene) and pentamethylcyclopentadienyl (for Bis(pentamethylcyclopentadienyl)-iron@graphene) component might be revealed by dynamical imaging. To the best of our knowledge, these experiments should make possible, or at least close to possible, single molecule imaging under TEM.

References

[1] Keqing Deng, Jianhong Zhou, Xiaofang Li, Electrochimica Acta, **95** (2013) 18.

Figures

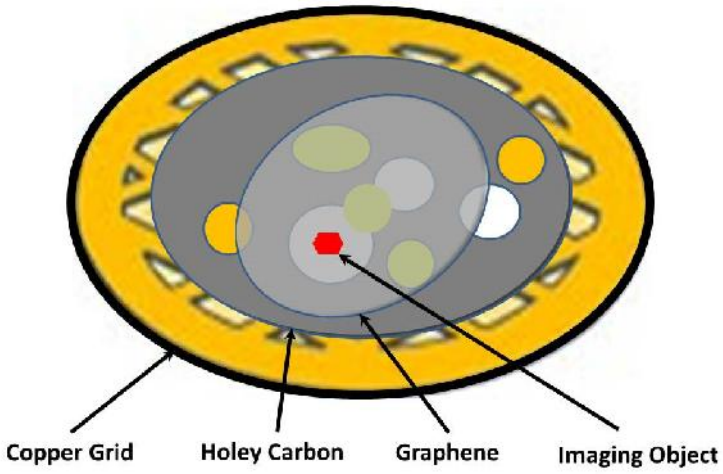

Figure 1. Schematic illustration of the new TEM grid system.

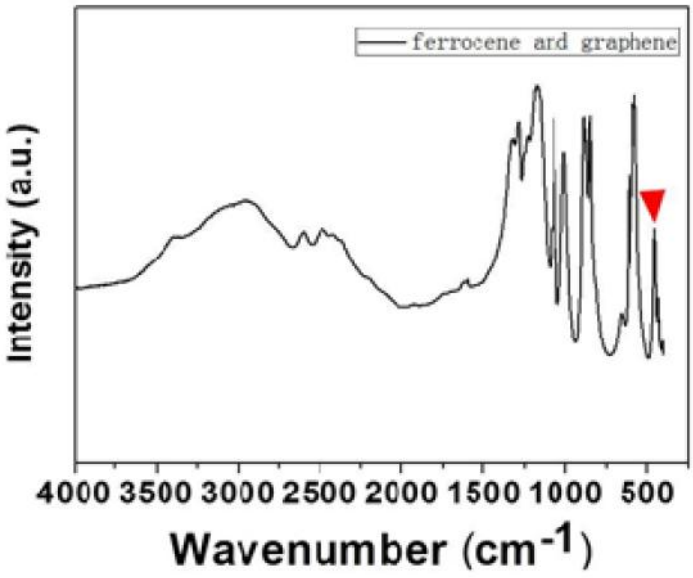

Figure 2. A typical FTIR of the ferrocene@graphene systems we made, the peak (400-500 cm^{-1}) indicated by the red arrow corresponds to ferrocene. The peaks between 500 cm^{-1} to 1200 cm^{-1} are from graphene oxide.