Tuning Magnetism and Novel Electronic Wave Interference Patterns in Nanographite Materials

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Introduction

Nanographite systems, where graphene sheets of the orders of the nanometer size are stacked, show novel magnetic properties, such as, spin-glass like behaviors [1], and the change of ESR line widths while gas adsorptions [2]. Recently, it has been found [3] that magnetic moments decrease with the decrease of the interlayer distance while water molecules are attached physically. Such the phenomena indicate the tunable magnetism in nanometer size systems.

First, antiferromagnetism in the stacked nanographite is investigated with using the Hubbard-type models taking into account of the hopping interactions of π-electrons and the strong onsite repulsions at carbon atoms [4]. The A-B stacking or the stacking near to that of A-B type is favorable for the hexagonal nanographite with zigzag edges, in order that magnetism appears. We find [5] that the open shell electronic structure can be an origin of the decreasing magnetic moment with the decrease of the inter-graphene distance, as experiments on adsorption of molecules suggest [3].

Next, superperiodic patterns with a long distance in a nanographene sheet observed by STM are discussed in terms of the interference of electronic wave functions [6]. The period and the amplitude of the oscillations decrease spatially in one direction. We explain the superperiodic patterns with a static linear potential theoretically. In the k·p model, the oscillation period decreases, and agrees with experiments. The spatial difference of the static potential is estimated as 1.3 eV for 200 nm in distance, and this value seems to be reasonable in order that the potential difference remains against perturbations, for example, by phonon fluctuations and impurity scatterings. It turns out that the long-distance oscillations come from the band structure of the two-dimensional graphene sheet.

Tuning Magnetism in Stacked Nanographite

First, we report the total magnetic moment per layer for the A-B stacked hexagonal nanographite. In each layer, the nearest neighbor hopping t is considered. Each layer has *closed shell electron systems* when the layers do not interact mutually, because the number of electrons is equal to the number of sites. The interlayer hopping t_1 is assigned at the nearest interlayer sites. The model is solved numerically, and antiferromagnetic solutions are obtained. The magnetic moment increases as the interlayer interaction becomes stronger. This behavior does not accord with the experiments.

Next, we consider systems with *open shell electronic structures* when a nanographene layer is isolated. One case is the effects of additional charges coming from functional side groups with introducing a site potential E_s at edge sites. We take a negative E_s, and one additional electron per layer is taken account. We find that the total magnetization is a decreasing function, and this agrees with the decease of magnetization by the magnitude 30-40% with the water molecule attachment [3]. The other origin, i.e., the geometrical effects can give rise to the decrease of the magnetic moment with increasing interlayer hopping interactions, too. Therefore, we conclude that the *open shell nature of electronic states* in a single graphene layer plays an important role in controlling the magnetism in nanographite materials.

Electronic Wave Interference and Theoretical Characterization

In Fig. 1, an STM image of the graphene sheet with a necktie shape is shown. The observation has been done with the following condition: bias voltage V = 200 mV and current I = 0.7 nA. The distance between the graphene necktie and the substrate is over 0.8 nm, suggesting that it consists of a stacking of two graphene layers, which interact weekly with the HOPG substrate. Interestingly, the period and the amplitude of the oscillations decrease from the top to the bottom along the graphene necktie. The oscillation period is one order of magnitude larger than that of the Moiré pattern due to stacking, which has been reported elsewhere, and therefore this possibility may be weak. We can assume effects of long-distance periodic-structural deformations in the graphene surface or interference effects of electronic wave functions. We have also observed [6] that the oscillation period becomes longer by placing a nanographene flake on the graphene necktie. The oscillations period seems to be double in the upper region of the necktie after addition of one flake. The oscillation below the flake seems to be only slightly modified by the flake. Such effect on the oscillations cannot be explained by some structural modulations. Therefore, the oscillation patterns could be the effect of interference of the electronic wave functions in the graphene surface.

In order to analyze the interference patterns, we give comparison with the calculation of the model for the graphene plane. Here, we use the continuum k·p model [6]. The electron density is calculated with including a static potential which has a functional form of the linear decrease from top to the bottom along the surface of the graphene necktie. The peak positions of the electron density in the long direction of the graphene necktie of Fig. 1 are plotted in Fig. 2, and comparison with the theoretical results is given. The decrease of the oscillation period fairly agrees with the experiments. However, the slight decrease of the experimental corrugation cannot be reproduced by the theoretical result because of neglecting an effect of a tip-apex shape of STM on the observed corrugatrion amplitude. The fitting gives the parameter of the potential gradient 6.49×10^{-3} eV/nm. The total potential variation over the distance 200 nm becomes 1.3 eV. Such magnitude of the potential change would survive thermal lattice fluctuations and can really exist in experiments. The present result by no means implies that the wave functions observed with superperiodic amplitudes are of the electrons which have energy levels of the graphene plane.
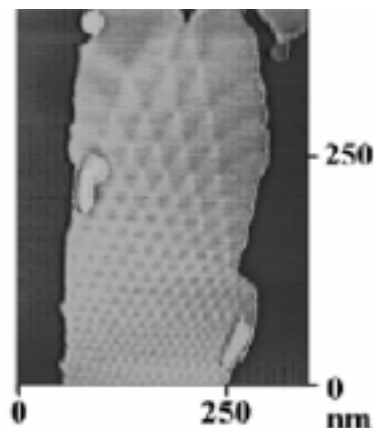

Fig. 1. STM image of the superperiodic pattern on a necktie shaped graphene plate on HOPG substrate.
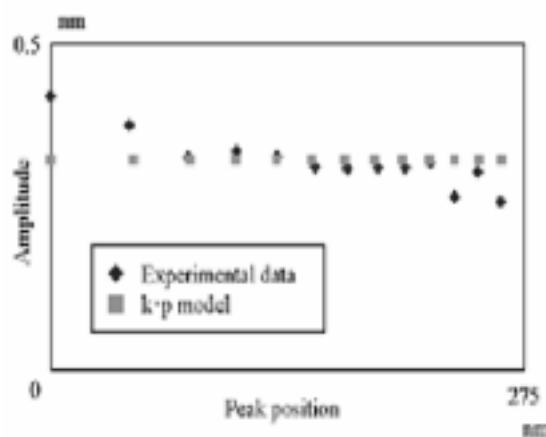

Fig. 2. Comparison for the electron wave patterns by STM and the k·p model. Experimental peak positions along the perpendicular direction of Fig. 1 are plotted by diamonds. The results of the fitting by the long distance envelope functional form derived from the k·p model are shown by squares.

References

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