Magnetic and transport properties of graphene@MNPs hybrides

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We have investigated electronic and magnetic properties of the CVD-grown graphene monolayers under interaction with monodisperse magnetic nanoparticles (MNPs). The MNPs, mostly of iron oxide and cobalt ferrite, are used for many different purposes in medicine (MRI contrast agents, drug carriers, smart biosensors, and hyperthermia) and industry (cleaning of water facilities, recording media) [1]. Their magnetic properties, ranging from ordered ferrimagnetism to superparamagnetism can be effectively controlled by variation of their size [1], as is ensured by using smart fabrication procedures providing ensembles of nanoparticles with very narrow size distribution [2]. The huge magnetic response of an individual single-domain MNP is represented by its *superspin*, which is usually in order of 10⁴ Bohr magnetons. Hence tuning of the interaction of the particular electronic states of the graphene monolayers with those of the MNPs opens enormous possibilities to engineer new generation of the hybrid graphene-based nanostructure, as demonstrated recently for few-layer graphene composites with semiconducting NPs and MNPs [4].

The nanostructures, investigated in our work constitute of a CVD-grown graphene sheet(s) and $CoFe_2O_4$ nanoparticles with a size distribution below 0.5 nm, prepared by modification of the hydrothermal method, in the presence of oleic acid [2,3]. The three types of hybrids were fabricated on the SiO₂(top layer)/Si substrate, as schematically shown in Figure 1. The MNPs were either dispersed directly on the graphene layer (1.), or on the substrate, and subsequently the graphene monolayer has been transferred over the fixed MNPs (2.), and finally a sandwich-like structure (3.) has been obtained by combining the two particular steps. Morphology of the samples, with focus on dispersion of the individual MNPs on the substrate (SiO₂ or graphene) was investigated by high-resolution scanning electron microscopy (HR SEM) and atomic force microscopy (AFM). The graphene-MNPs interaction was inspected by Raman spectroscopy and magnetic force microscopy (MFM), and in addition magnetization (M), a.c. susceptibility (χ), electrical resistivity (R) and magnetoresistance (MR) were measured in the temperature range 2 - 400 K and magnetic fields up to 14 T (with orientation parallel and perpendicular to the substrate plane, respectively). Significant electronic and magnetic interactions between the nanoparticles and graphene were detected suggesting charge transfer between the deposited MNPs and the graphene. The results are supported by first principle calculations of the electronic structure and transport properties. The study thus demonstrates significant effects in tailoring the electronic structure of graphene@MNPs hybrids for future applications, e.g. as biosensors and various nanoelectronic biocompatible devices.



Figure 1. Schematic representation of the investigated nanostructures. The MNPs are depicted as the spheres with arrows (representing the superspins), while the graphene layers are illustrated as the solid black lines. The three possible scenarios of application of the external magnetic field ($B_{ext} = 0$, B_{ext} applied perpendicular or parallel to the substrate) are also demonstrated.

References

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