FABRICATION AND INVESTIGATION OF GRAPHENE-NANOPARTICLE HYBRID STRUCTURES BY SCANNING PROBE METHODS

PhD thesis booklet

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Introduction and motivation

Graphene, the archetypal two-dimensional material, was first isolated by Konstantin Novoselov and Andre Geim in 2004 [Novoselov, 2004], who demonstrated the intriguing and novel physical phenomena in this one-atom-thick crystal. Highlighting just a few of the properties of graphene, like the unprecedented mechanical strength and flexibility [Lee, 2008], the high charge carrier mobility [Bolotin, 2008], or its unique linear band structure near the Fermi energy [Reich, 2002], we can understand why it has been of great interest in the last 15 years.

On the other hand, metal or semiconducting nanoparticles (NPs) have also been in the focus of considerable interest, as they may have special properties which are different from their bulk material. For instance, due to the local plasmon resonance and the resulting special optical properties, noble metal nanoparticles can provide an enormous enhancement of the electromagnetic radiation (order of 10^9–10^{11}), which could open the possibility of engineering sensors with single-molecule detection capabilities [Nie, 1997]. Metal nanoparticles can be used in various fields, such as medical applications [Abadeer, 2016], as catalyst material [Guo, 2013], or even as optical tweezers [Jones, 2015].

In graphene, all atoms are on the surface, therefore the interaction with its environment, the substrate and contacting nanostructures can play a dominant role. For example, by evaporating plasmonic or superconducting nanoparticles onto graphene, these properties can be inherited into the graphene layer, which can thus be used as a sensor [Fang, 2012] or made superconducting [Allain, 2012], respectively. Hybrid materials made of various metal or metal oxide nanoparticles and graphene can be used either in solar cells or as electrode materials for Li-ion batteries. Graphene plays a role in these systems as an electrically conductive matrix material [Wang, 2011], a corrosion-inhibiting layer [Gergely, 2018], or a mechanically stabilizing coating [Shao, 2017]. Investigating the interaction between graphene and different nanoparticles, as well as the elaboration of hybrid nanomaterials with designed properties is a highly promising area for potential applications.

Objectives

The aim of my doctoral research is to fabricate and investigate hybrid structures consisting of graphene and various metallic nanoparticles.

- In order to use graphene in electronic devices in the future, it is important to understand the effects of different contact metals and supporting materials on the properties of graphene. My goal is to map the electrostatic doping and the mechanical strain emerging in graphene when transferred onto metallic nanoparticles. Corrugated graphene stretched onto nanoparticles may be of interest in sensing applications.

- Graphene, as an atomically thin cover layer, can fix the nanoparticles on the surface, at the same time protecting them from corrosion. Therefore, my objective, equally to the above, is to investigate the role of graphene overlayer in the case of tin nanoparticles, i.e., whether they remain electrically conductive in air.

- Furthermore, I investigate how the constructed hybrid systems respond to different external influences (eg. annealing, laser irradiation) and how these affect the graphene-nanoparticle interaction.

Experimental methods

During my PhD work, I have most frequently used different Scanning Probe Microscopes (SPMs) for characterization. Using instruments belonging to this microscope family, we can study the properties of different surfaces in the size ranges of a few hundreds of microns down to a few tens of picometers. The topography of conductive surfaces can be investigated with a scanning tunneling microscope (STM), even with atomic resolution. Local measurements can also be performed at different points of the surface, measuring the local density of states by scanning tunneling spectroscopy (STS). The morphology of both conductive and insulating samples can be mapped using an atomic force microscope (AFM) by scanning and detecting the atomic forces between a sharp tip and the sample.

I studied the phonon modes of the samples using Raman spectroscopy, a method based on the inelastic scattering of light. By this technique, we can identify the material of the sample, and in addition, also measure the distribution of mechanical stress or electrostatic doping in it.

Using the above techniques, not only we can characterize but also modify the samples. For example, we can mechanically indent the sample with an SPM probe, or we can heat it with the laser of the Raman equipment. In my dissertation, I present examples for both of these modifications. I show the SPM probe-induced modifications (both in AFM and STM) on suspended graphene samples, giving an estimate for the magnitude of the mechanical forces between the STM tip and the sample, while the modifying effect of local heating with a laser beam is demonstrated on graphene supported by gold nanoparticles.

New scientific results

[1] Graphene nanobubbles (height of 20–40 nm, diameter of few hundred nm) formed on gold nanoislands, and graphene samples suspended on gold nanovoids (diameter around 100 nm) were indented by both AFM and STM. Comparing the STM results with the quantitative PeakForce AFM measurements, I showed that repulsive forces of the order of 10^{-8} N occur between the STM tip and the graphene under ambient imaging conditions and typical tunneling parameters (bias voltages of 250 mV or less, and tunneling currents of 1 nA).

These results are published in: [T1]

[2a] I revealed by constant current STM measurements performed on graphene-covered gold nanoparticles that a graphene overlayer induces the recrystallization of the polycrystalline Au-surface into the (111) surface texture during annealing at 650 °C. While every graphene-covered gold surface displayed – reconstructed or unreconstructed – (111) texture after annealing, no such order was found on non-covered surfaces.

[2b] I showed by tunneling spectroscopy that the superlattice moiré periodicity between graphene and the underlying Au(111) surface induced secondary Dirac points in the graphene local density of states. I showed that the energy of the observed secondary Dirac points is inversely proportional with the moiré wavelength, which is in agreement with the theory.

[2c] I observed anomalously large wavelength moiré superlattices on graphene-gold hybrid nanostructures annealed at 650 °C, which implied that in these areas the lattice constants of both the graphene and the topmost gold layer were considerably distorted. I revealed that the largest observed moiré superlattice (period of 7.7 nm) induced not only structural corrugation, but also room temperature charge localization on the topographically high graphene areas.

These results are published in: [T2]

[3] I prepared Au nanoparticles by local annealing with a focused laser beam of gold thin films pre-evaporated onto SiO_2 substrates. I revealed by Raman-spectroscopy that dynamic hydrostatic strain could be induced in the graphene transferred onto the formed gold nanoparticles, and the induced strain could be dynamically tuned by the laser power. I demonstrated that while a few seconds of higher intensity (6 mW) laser irradiation increased gradually the *p*-type doping and the defect concentration in SiO_2-supported graphene, similar laser irradiation turned out to be completely reversible, without any noticeable change in doping or strain, when applied on gold nanoparticle-supported graphene. I revealed that the substrate used could play a major role in the resistance of graphene to radiation damage.

These results are published in: [T3]

[4a] I proved by SPM and Raman spectroscopic measurements that a graphene overlayer insulates tin nanoparticles from the ambient oxygen and thus protects them from complete oxidation. The graphene-covered nanoparticles remained in a mixed Sn/SnO phase, while the non-covered nanoparticles oxidized to SnOx phase (where x>1). I showed by STS measurements that charge transfer occurs from Sn nanoparticles, inducing uniform doping of graphene (including the graphene suspended between nanoparticles), which reduces significantly its environmental *p*-type doping.

[4b] I demonstrated that the single-atom thick graphene overlayer could immobilize the wide band gap tin oxide nanoparticles on the graphite (HOPG) substrate, and enabled their STM investigation, even at bias voltages one order of magnitude lower than their band gap. Performing tunneling spectroscopy measurements on these graphene-covered samples, I revealed the electronic band gap of individual SnO_x ($x>1$) nanoparticles, for which I obtained values between 2.7 and 3.2 eV.

These results are published in: [T4]

Publications related to thesis statements

[T1] Pálinkás, A., Molnár, G., Hwang, C., Biró, L. P. & Osváth, Z. Determination of the STM tip-graphene repulsive forces by comparative STM and AFM measurements on suspended graphene. *RSC Adv.* **6**, 86253–86258 (2016).

[T2] Pálinkás, A., Süle, P., Szendrő, M., Molnár, G., Hwang, C., Biró, L. P. & Osváth, Z. Moiré superlattices in strained graphene-gold hybrid nanostructures. *Carbon* **107**, 792–799 (2016).

[T3] Pálinkás, A., Kun, P., Koós, A. A. & Osváth, Z. Dynamic strain in gold nanoparticle supported graphene induced by focused laser irradiation. *Nanoscale* **10**, 13417–13425 (2018).

[T4] Pálinkás, A., Molnár, G., Magda, G. Z., Hwang, C., Tapasztó, L., Samuely, L., Szabó, P. & Osváth, Z. Novel graphene/Sn and graphene/SnO_x hybrid nanostructures: Induced superconductivity and band gaps revealed by scanning probe measurements. *Carbon* **124**, 611–617 (2017).

Other publications

5. Hagymási, I., Vancsó, P., Pálinkás, A., & Osváth, Z. Interaction effects in a chaotic graphene quantum billiard. Phys. Rev. B **95**, 075123 (2017).

6. Szendrő, M., Pálinkás, A., Süle, P. & Osváth, Z. Anisotropic strain effects in small-twist-angle graphene on graphite. Phys. Rev. B **100,** 125404 (2019).

7. Piszter, G., Kertész, K., Molnár, G., Pálinkás, A., Deák, A. & Osváth, Z. Vapour sensing properties of graphene-covered gold nanoparticles. *Nanoscale Adv.* **1**, 2408–2415 (2019).

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