

Carbon nanotubes as nanodispensers for metals onto graphene

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1. INTRODUCTION

The astonishing physical properties of graphene and carbon nanotubes (CNTs) recommend them as promising candidates for the fabrication of nanodevices with applications in several fields. In addition, the prospects of delivering mass onto predefined spots in the femtogramme regime or of generating nanowires in a tube plead for developing adapted approaches for the investigation of mass transport in or out of carbon nanotubes [1,2]. Today, however, only little is known on the mechanisms, conditions and constraints governing the process of materials transfer from one support, i.e. CNT, to another, i.e. graphene, when an electrical potential difference is applied between them.

The present experiments have been performed using CNTs filled with metal nanoparticles as a “pen” and a few-layer graphene (FLG) flake as a “paper board”. In an approach that combines high-resolution transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) via a specific sample holder (Nanofactory) we were able to carry out the real-time observation of a nanoparticle (NP) transfer from the inner channel of a CNT onto FLG flakes. The approach proposed herein takes advantage of the electron energy loss spectroscopy (EELS) technique for monitoring the chemical changes that occur during nanoparticles transfer while the use of in-situ TEM-STM allows for the observation of the NPs transfer process from a mechanistic perspective and the monitoring of the NPs motion into the CNT on the FLG surface and vice-versa.

2. RESULTS

2.1 Experimental methods

The filling of commercial multi-wall CNTs (MW-CNTs) with Fe_{3-x}O₄ NPs was performed using the thermal decomposition of iron stearate [3]. The graphene samples were synthesized from expanded graphite by surfactant-assisted high power ultra-sonication. An electrochemical etching method was used to prepare Au tips, which were used as contact bridges. The filled CNTs and graphene samples were dispersed in ethanol and subsequently deposited on the movable Au tip and the fixed Au wire, respectively. The two Au contacts were fixed in the Nanofactory TEM-STM holder, which permits a sub-nanometer precision in sample positioning during the experiment. The real-time observation and the HR-TEM imaging were performed using a JEOL 2100F microscope EEL spectra were recorded using a GATAN Tridiem imaging filter.

2.2 CNT to FLG nanoparticle transfer by electro-migration

After a Joule activation of the nanotubes conductivity, the NPs/CNT system is converted to an Ohmic device. In the same time the encapsulated NPs undergo a fast thermal and/or electrochemical reduction followed by a coalescence phenomenon, induced by the large thermal energy injected into the CNT via the Joule heating. After the activation step a bias voltage is applied in such a way that the electrons do flow through the nanotube in the direction of the FLG sheet (Figure 1). Under such conditions the nanoparticles in the CNT start to migrate along the tube channel towards the FLG substrate. The evolution of the system during the subsequent mass transfer from the CNT to the FLG edge versus time is presented in Figure 1b-d here below. More precisely, the initial NPs inside the CNT are ripped out atom by atom and then are reassembled at the FLG edge, in a mechanism similar to Ostwald ripening. From a phenomenological point of view, an electro-migration force appears along the CNT under the application of the electrical field; this force is responsible for the dragging of the iron nanoparticles from the nanotube center to the nanotube exit end. It is created by the interaction of the scattering electrons in the electric current that flows along the CNT and the metal atoms localized on the CNT inner surface and it imposes a global movement to the metal atoms along the electron flow direction [4].

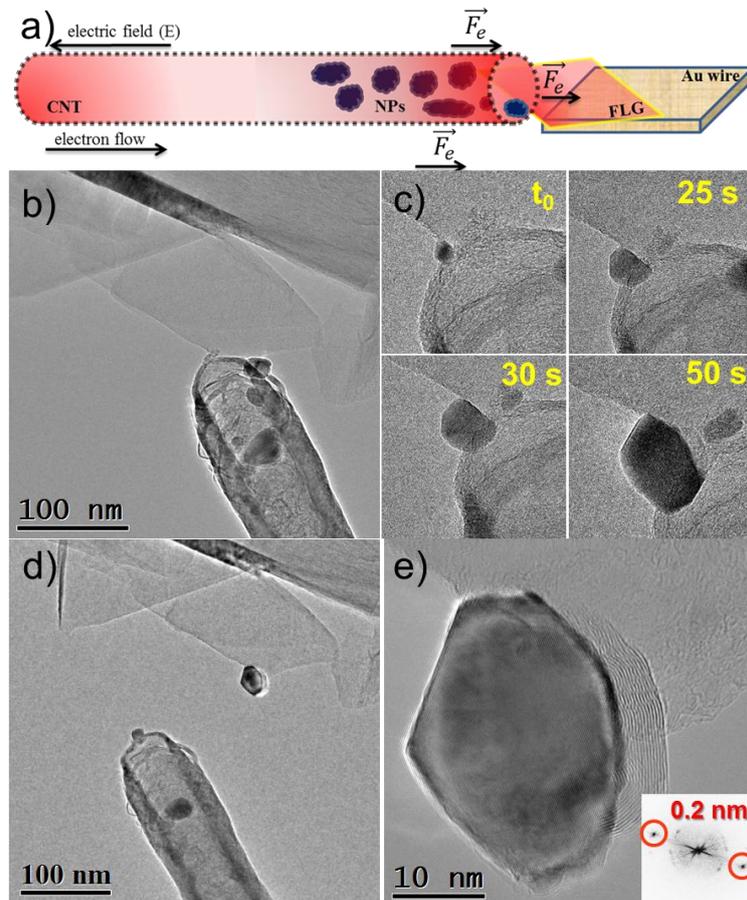


Figure 3. Controlled deposition of a metallic Fe nanoparticle on the edge of a FLG flake. a) Schematic representation of the experiment showing the forces acting in the system upon application of a bias voltage; b) The CNT/FLG system before the NP deposition; c) Time series of the NP growing (time resolution 0.33 s); d) The CNT/FLG system after the NP deposition on the FLG edge; e) HR-TEM image of the final NP grown at the FLG edge. The FFT inset identifies a lattice spacing of about ~ 0.2 nm, characteristic to ϕ and γ metallic Fe.

2.3 Opposite configuration: FLG to CNT nanoparticle transfer under inversed voltage polarity.

Removing nanoparticles deposited close to the contact point between a CNT and a FLG sheet can be simply achieved by reversing the polarity of the applied voltage. In this case the electromigration force transports the metal atoms inside the nanotube where they will recombine forming new nanoparticles. However, a stronger electromigration force (and thus a higher bias voltage) is needed for their transfer, if the NPs have to be collected from regions far away from the CNT/FLG contact point.

3. CONCLUSION

Using a combined HRTEM - STM technique associated to electron spectroscopy, we were able to define conditions under which a reliable electrically controlled transfer of NPs from the inner part of a CNT onto a FLG sheet can be performed. From a general point of view, the mass transfer requires four individual steps: the annealing of the tube, the chemical transformation or the reduction of the original particles, the particle transfer through the tube and the dispensing of the metal atoms on the graphene sheet. The erasing of already deposited NPs can also be achieved by reversing the applied electrical voltage. The printing process described in this work mimics the process used in a “dye sublimation printer” and we therefore consider that this study is the proof-of-concept for the design of printing devices at the nanoscale. Devices can now be imagined that could directly print nanowires and electronic components at the nanoscale for both fundamental understanding and potential industrial applications.

References

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