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# Low-energy electron holographic imaging of gold nanorods supported by ultraclean graphene

Jean-Nicolas Longchamp*, Conrad Escher, Tatiana Latychevskaia, Hans-Werner Fink

*Physics Institute, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland*

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ABSTRACT

An ideal support for an electron microscopy should be as thin as possible and be able to interact as little as possible with the primary electrons. Since graphene is atomically thin and made up of carbon atoms arranged in a honeycomb lattice, the potential to use graphene as a substrate in electron microscopy is enormous. Until now graphene has hardly ever been used for this purpose because the cleanliness of freestanding graphene before or after deposition of the objects of interest was insufficient. We demonstrate here by means of low-energy electron holographic imaging that freestanding graphene prepared with a platinum-metal catalysis method remains ultraclean even after re-exposure to ambient conditions and deposition of gold nanorods from the liquid phase. In the holographic reconstruction of gold particles the organic shell surrounding the objects is apparent while it is not detectable in SEM images of the very same sample, demonstrating the tremendous potential of low-energy electron holography for imaging of graphene-supported single biomolecules.



## 1. Introduction

To image an object by means of electron microscopy, it is normally placed onto a substrate. The signal from the object support, arising from the scattering of the impinging primary electrons in transmission electron microscopy, or from the creation of secondary electrons in a scanning electron microscope, is spurious and efforts to reduce these signals have been accomplished since the development and implementation of the first electron microscopes. Ideally, for maximal contrast and resolution, one would like to have the thinnest substrate possible, made up of a low-atomic-number material, in order to reduce the interaction volume and the scattering cross-section of the incoming electrons [1,2]. The idea of using freestanding single-layer graphene as such ultimate microscopic sample carrier in electron microscopy [3–10] has been around since the isolation of single-layer graphene was achieved in 2004 by Geim and Novoselov [11,12].

Significant efforts have been undertaken in the past few years to develop techniques for preparing either exfoliated or CVD grown graphene in a freestanding form [9,13–16]. Unfortunately, the cleanliness of the prepared graphene sheets has never been satisfactory with regards to their use as a sample carrier [9,10,15,17]. Only recently, it has become possible to prepare ultraclean freestanding graphene by platinum-metal catalysis [18]. Compared to the previous methods, the one applied here leads to large regions, extending up to several square microns of atomically clean freestanding graphene suitable for use in electron microscopy [18–20].

Here, we show that freestanding graphene prepared by the platinum-metal catalysis method remains clean, even after re-exposure to ambient pressure and subsequent wet deposition of nanometre-sized gold rods. We present low-energy electron holograms of gold nanorods on graphene and cross-validate the presence of the nanorods by scanning electron imaging of the very same sample. Moreover, we compare the appearance of the rods when either imaged with low-energy electron holography or by means of a scanning electron microscope (SEM).

## 2. Materials and methods

Ultraclean freestanding graphene, covering holes of 500 nm in diameter milled in a silicon nitride membrane, is prepared by the platinum-metal catalysis method, described in detail recently elsewhere [18]. Thereafter, the cleanliness of the as-prepared graphene is inspected in a low-energy electron point source microscope operated under UHV conditions (Fig. 1). In this holographic setup, inspired by the Gabor's original idea of inline holography [21–23], a sharp (111)-oriented tungsten tip acts as a source of a divergent beam of highly coherent electrons[24–27]. The electron emitter can be brought as close as 200 nm to the sample with the help of a 3-axis nanopositioner. Part of the electron wave impinging onto the sample is elastically scattered and represents the object wave, while the un-scattered part of the wave represents the so-called reference wave [28]. At a distant

* Corresponding author.
*E-mail address:* longchamp@physik.uzh.ch (J.-N. Longchamp).

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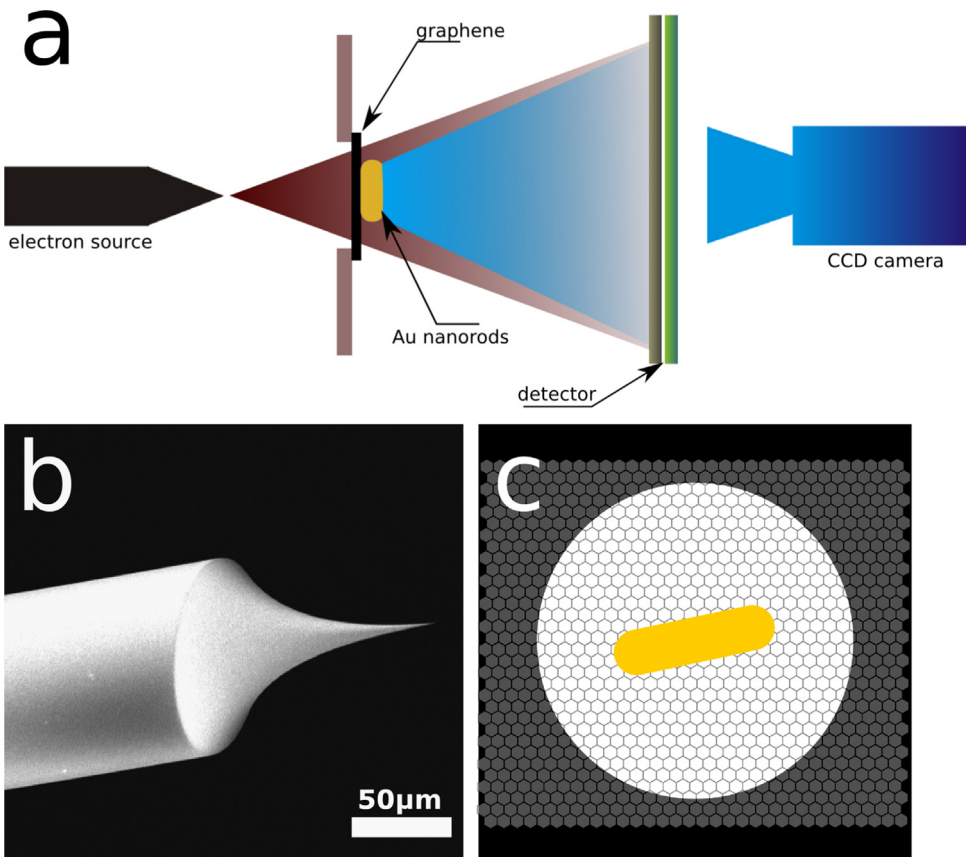


**Fig. 1.** (a) Scheme of the experimental setup of low-energy electron holography. The source-sample distance amounts to typically 100–1000 nm which leads to kinetic electron energies in the range of 50–250 eV and the sample to detector distance is 68 mm. The electron detector is 75 mm in diameter, which represents an acceptance angle of 29°. (b) SEM image of an electrochemically etched W(1 1 1) tip acting as field-emitter of a divergent coherent low-energy electron beam. (c) Schematic illustration of the sample geometry with a gold nanorod lying on ultraclean freestanding graphene suspended over a round hole.

detector, the interference pattern between object wave and reference wave — the hologram —is recorded. The magnification in the image is given by the ratio of detector-tip-distance to sample-tip-distance and is typically of the order of $10^6$.

## 3. Results and discussion

Fig. 2(a) shows an example of a hole of 500 nm in diameter covered by a single layer of ultraclean graphene, imaged by low-energy electrons. Only the observation of interference fringes, arising due to the presence of a few hydrocarbons less than 1 nm in size, reveals the existence of graphene covering the hole [18]. The cleanliness of the as-prepared graphene has also been investigated by means of high-resolution transmission electron microscopy (TEM) at 80 kV in order to give the reader the possibility to compare the quality of the cleanliness with former TEM results. Fig. 2(b) shows a TEM image of graphene, uniformly covering the entire freestanding region, and it is only by imaging the hexagonal atomic arrangement (Fig. 2(c)) that the presence of graphene can reliably be confirmed.

For the deposition of gold nanorods, a graphene sample prepared as described above is taken out of the low-energy electron microscope. Under ambient conditions, a drop of 0.5 nM gold nanorod aqueous solution [29] is subsequently applied onto the graphene (Fig. 3(b)). A few seconds were given for the rods to sediment before the excess water was removed by using a filter paper (Fig. 3(c)). Prior to the re-introduction of the sample into the electron microscope, the sample is kept at 200 °C for 30 min.

Fig. 4(a) shows an electron hologram of gold nanorods on freestanding graphene recorded with 93 eV kinetic energy electrons. The graphene surrounding the rods remained clean even after the re-exposition to ambient pressure and the deposition of the gold particles from the liquid phase. In Fig. 4(b) a SEM image (7 kV) of the very same sample is presented. The nanorods can be associated one-to-one with the objects observed in the holographic image presented in Fig. 4(a). The yield of secondary electrons produced by the graphene substrate is so low that the rods, shown in Fig. 4(b), seem to levitate, demonstrating the utility of graphene as a substrate for scanning electron microscopy. A high-magnification hologram (58 eV) of a gold nanorod is presented in Fig. 4(c) along with its reconstruction, see Fig. 4(d), obtained as described in [30,31]. The object presented in these two images is the very same gold nanorod observed in Fig. 4(a) in the low right corner. The remaining interference fringes that can be observed around the object in the reconstruction (Fig. 4(d)) are due to the presence of the out-of-focus twin image [32]. The size of the rod in Fig. 4(d) accounts for a width of 30 nm and a length of 72 nm. While the length in the holographic reconstruction image matches perfectly with the length that can be measured in the SEM image; a discrepancy opens up when one compares the width measured in the two images (30 nm in the holographic reconstruction and 21 nm in the SEM image). We associate this discrepancy with the fact that the gold rods feature an organic coat in order to be soluble in aqueous solution [29]. This organic layer, however, is only present along the rods but not at the face sides. The several-nanometre thick methyl-shell cannot be imaged in an SEM because of the low contrast that it produces and because of the radiation damage provoked by the high-energy

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