Synthesis and characterization of graphene-covered silver nanoparticles

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INTRODUCTION

Nanostructured Ag is the best material for plasmonics due to the absence of interband absorptions and low optical loss at optical frequencies. However, silver has poor stability under ambient conditions, forming Ag_2S on its surface. This leads to morphological changes of the Ag nanoparticles (NPs), and significant diminishing of the optical properties.

Covering Ag nanoparticles with graphene provides not only a unique platform to study the silver–graphene interaction at nanoscale, but also a way for preserving the high surface plasmon resonance intensity of the nanoparticles, which is of key importance in potential applications. Combining Ag nanoparticles with graphene can yield hybrid materials with enhanced light-matter interaction. Here we report a simple method for the synthesis of graphene-silver nanoparticle hybrids on highly oriented pyrolytic graphite (HOPG) and SiO_2 substrates.

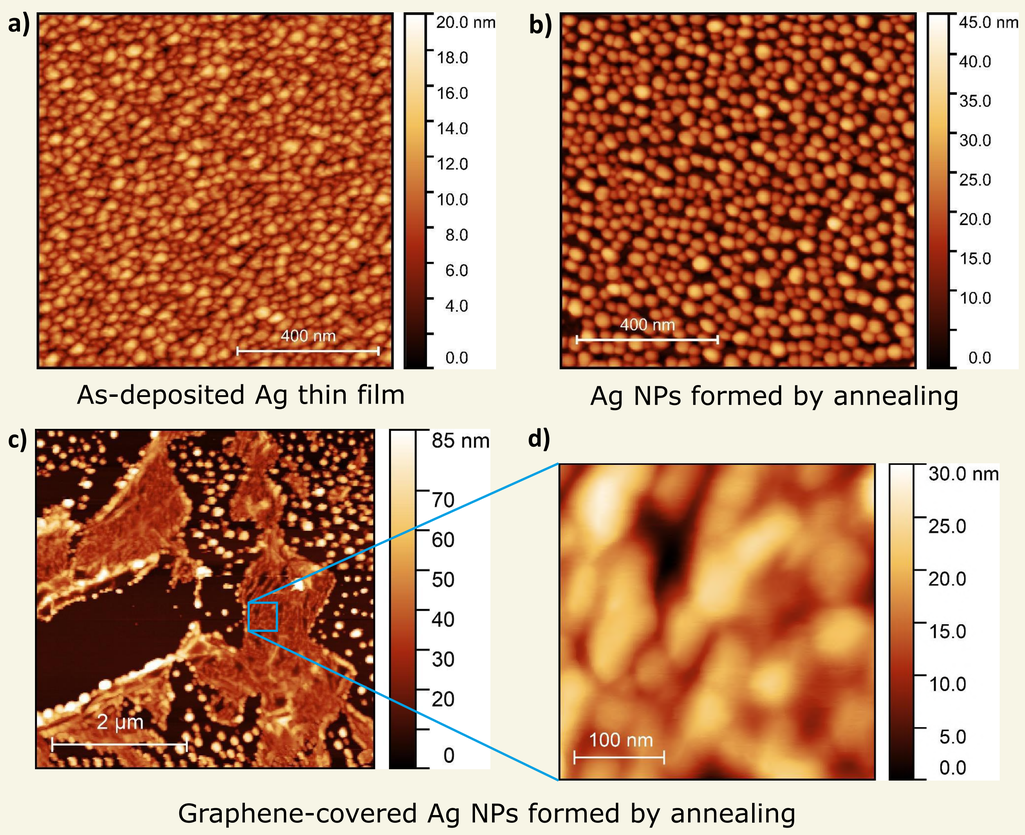
EXPERIMENTAL DETAILS

Thin silver films (7 nm) were evaporated onto SiO_2 and HOPG substrates. and annealed at 400 °C in argon atmosphere to form silver nanoparticles. Immediately after silver deposition and opening of the vacuum chamber, the thin silver films were covered with CVD graphene using thermal release tape. Subsequent annealing of both bare and graphene-covered thin silver films was performed at 400 °C under Ar atmosphere for 90 minutes, which resulted in the formation of Ag nanoparticles.

The Ag NPs and graphene/Ag NP hybrid structures were investigated by tapping mode AFM measurements performed on a MultiMode 8 (Bruker), and STM/STS measurements using a DI Nanoscope E operating under ambient conditions. The STM measurements were performed in constant current mode. Optical reflectance spectra were recorded using an Avantes AvaSpec-HS1024x122TEC fibre optic spectrometer (Avantes BV, Apeldoorn, Netherlands).

AFM measurements

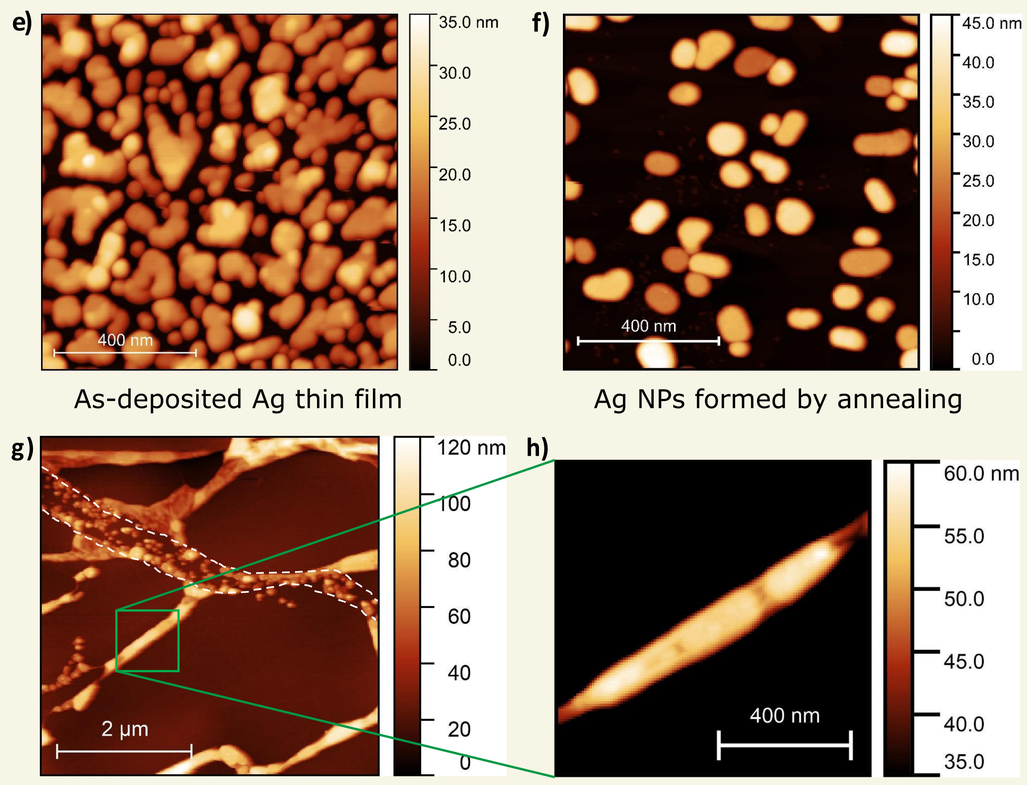
SiO_2 substrate:



As-deposited Ag thin film | Ag NPs formed by annealing

Graphene-covered Ag NPs formed by annealing

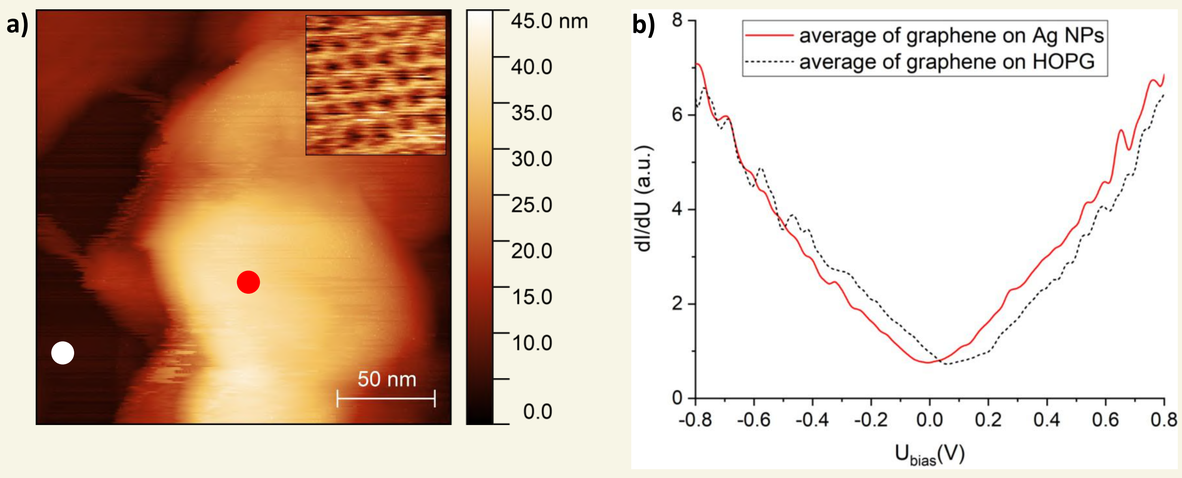
HOPG substrate:



As-deposited Ag thin film | Ag NPs formed by annealing

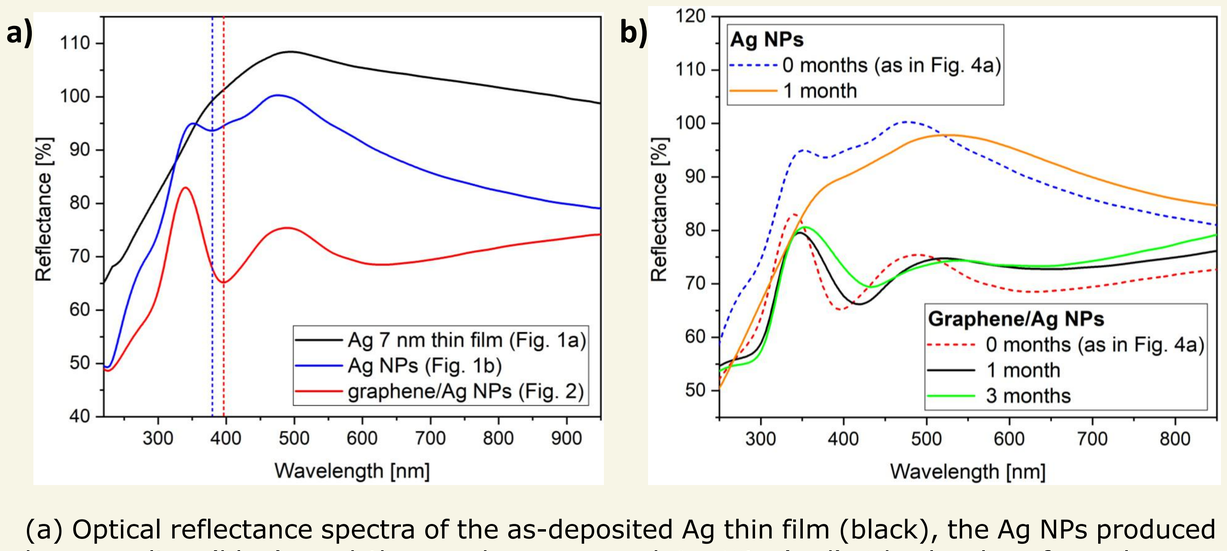
Graphene-covered Ag NPs formed by annealing

STM and STS measurements



Scanning tunneling microscopy (a) and spectroscopy (b) of graphene-silver hybrid nanostructures. (a) Dark-coloured regions correspond to graphene on HOPG substrate. Tunneling parameters: I=0.4 nA, U=0.8 V. Atomic resolution STM image of silver-supported graphene is shown in the inset. (b) dI/dU spectra measured on graphene/HOPG (dashed line) and graphene/Ag (red line). The STS measurements were performed at the graphene/HOPG and graphene/Ag positions marked in a) with white and red symbols, respectively.

Optical spectroscopy measurements



(a) Optical reflectance spectra of the as-deposited Ag thin film (black), the Ag NPs produced by annealing (blue), and the graphene-covered Ag NPs (red). The local surface plasmon resonance (LSPR) of Ag NPs (blue dashed line) is redshifted when covered with graphene (red dashed line). (b) Optical spectra measured after one month on bare Ag NPs (orange) and on graphene/Ag NPs (black). For better comparison, the initial spectra from a) are also shown (blue dashed and red dashed lines, respectively). The spectrum of graphene/Ag NPs measured after 3 months is also plotted (green).

CONCLUSIONS

- Dome-like Ag NPs form on SiO_2 substrates, while flat Ag nanoislnads form on HOPG substrates.
- A graphene overlayer encapsulates the Ag nanoislands and forms elongated hybrid structures.
- STM/STS measurements on graphene/Ag NPs revealed electron transfer from silver to graphene, i.e. silver induces n-type doping of graphene.
- We revealed by optical reflectance investigations that a graphene overlayer preserves the LSPR of Ag NPs for at least three months, although the LSPR is gradually decreased and redshifted due to the spontaneous sulphurization of Ag NPs.

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