

Electronic Supplementary Information for

Graphene Buffered Galvanic Synthesis of Graphene-Metal Hybrids

Zhen Li,¹ Peng Zhang¹, Kunlin Wang,¹ Zhiping Xu,² Jinquan Wei,¹ Lili Fan,¹ Dehai Wu,¹
Hongwei Zhu,^{1,2*}

¹Key Laboratory for Advanced Manufacturing by Materials Processing Technology, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China

²Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, P. R. China

* Corresponding author: hongweizhu@tsinghua.edu.cn.

This file includes:

Simulation method: Binding between Ag atoms and graphene sheets

Fig. S1. SEM images of Ag nanostructures on graphene/PET substrate after primary battery induced deposition: (a) nanoparticles, (b) triangular nanoplates.

Fig. S2. SEM images of Ag nanoplates grown near defects on graphene. (a) Large and irregular Ag nanoplates grown along the boundary of copper and graphene. The growth direction indicated by arrow is perpendicular to the boundary line. (b) Ag nanoparticle deposition along the cracks. The cracks were intentionally made by bending the graphene/copper substrate before Ag deposition. (c) Close-up view of Ag nanoplates deposited along cracks. (d) Ag nanoplate with a dent next to it, copper was etched away by the galvanic reaction of Ag^+ and Cu.

Fig. S3. SEM images of Ag deposited on graphene in solutions of (a) high Ag^+ concentration (10 mM, 10s) and (b) low Ag^+ concentration (0.01 mM, 100min).

Fig. S4. TEM images and selected area electron diffractions (SAED) of three typical Ag nanoplates. Superimposed SAED patterns with blue grids for Ag *fcc* lattice and red grids for graphene hexagonal lattice give the misaligned angles between two lattices.

Fig. S5. Ag clusters deposited on rGO by copper induced galvanic reaction (a) under dark condition; (b) under 635 nm laser illumination.

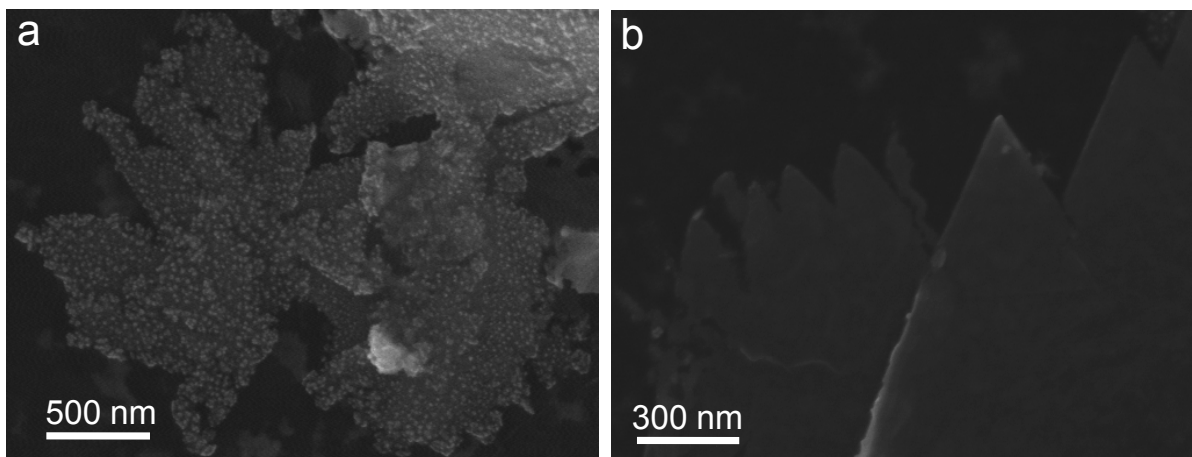
Fig. S6. (a) SEM and (b) TEM images of flower-like Au dendrites deposited on graphene by copper-substrate-induced galvanic displacement. (c) SEM image of CuO nanocubes deposited on graphene by nickel-substrate-induced galvanic displacement. (d) SEM image of CuO octahedral nanocrystals deposited on graphene.

Simulation method

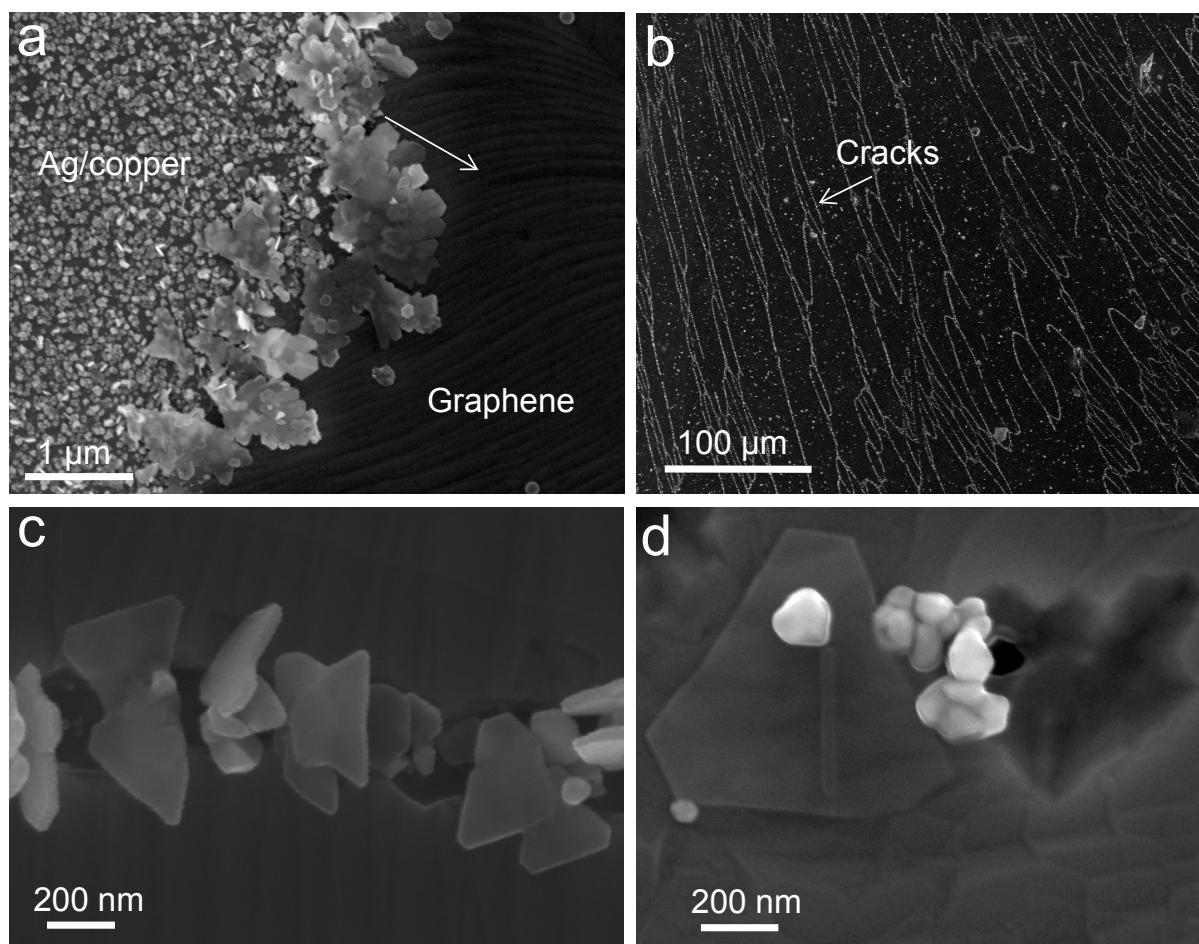
First-principles calculations are performed to obtain the binding energy between one silver atom and pristine or defected graphene sheets. The interface is investigated through a rectangular super-cell of 0.85 nm×0.93 nm. A vacuum layer of 2 nm is used in the direction normal to interface, representing the isolated boundary condition for the graphene sheet. For the binding site at the edge of graphene, the periodic boundary condition is removed and the extended graphene sheet becomes an isolated flake.

The structure and properties of this hybrid system are studied using plane-wave basis sets based density functional theory (DFT) methods. Local density approximation (LDA) is used for the exchange-correlation functional and projector augmented wave (PAW) potentials are used for ion-electron interaction. We use the Vienna Ab-initio Simulation Package (VASP) for the calculations. For all results presented, an energy cut-off of 300 eV is used for plane-wave basis sets. Monkhorst-Pack 4×4×1 grid points and the gamma point are used for Brillouin zone sampling for periodic and non-periodic system respectively. These settings have been verified to achieve a total energy convergence less than 1 meV/atom. For geometry relaxation, the force on atoms is converged below 0.01 eV/Å. All structures are initially optimized using a conjugated gradient method.

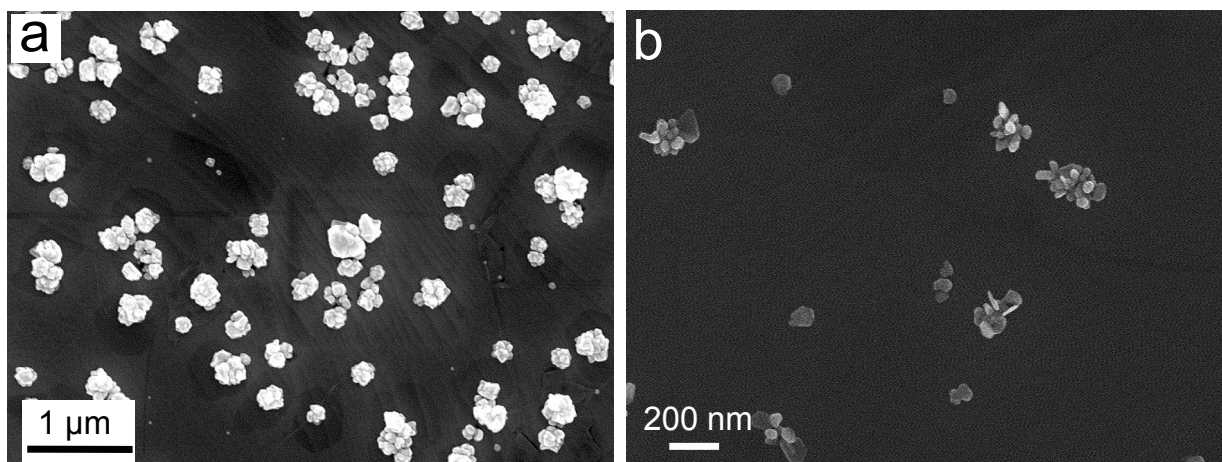
The binding energy between graphene and the silver atom is calculated as $E_b = E_{C_Ag} - E_C - E_{Ag}$, where E_{C_Ag} is the total energy of the silver and graphene system, E_C is the energy of graphene sheet without binding silver atoms. E_{Ag} is the energy of an isolated silver atom.



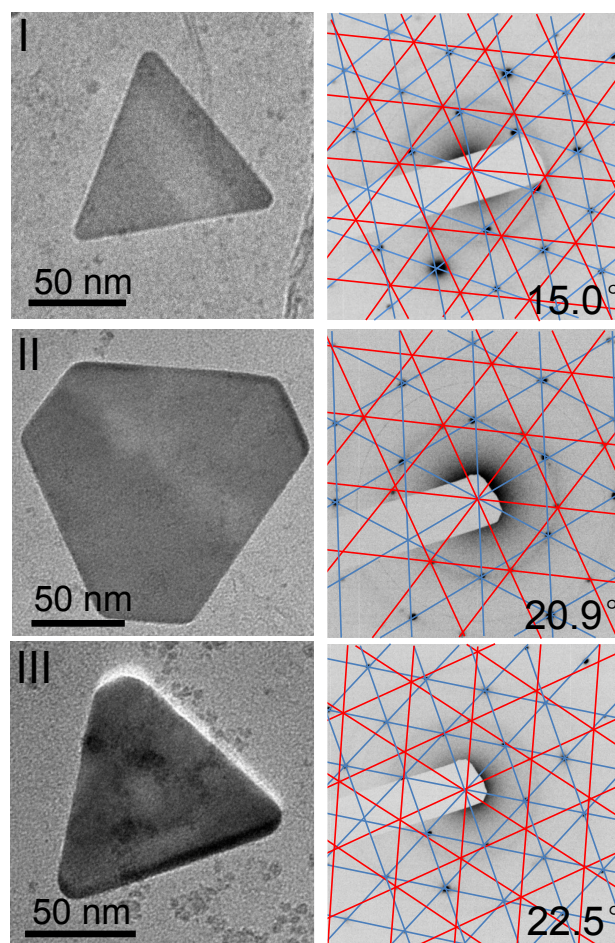
(Fig. S1)



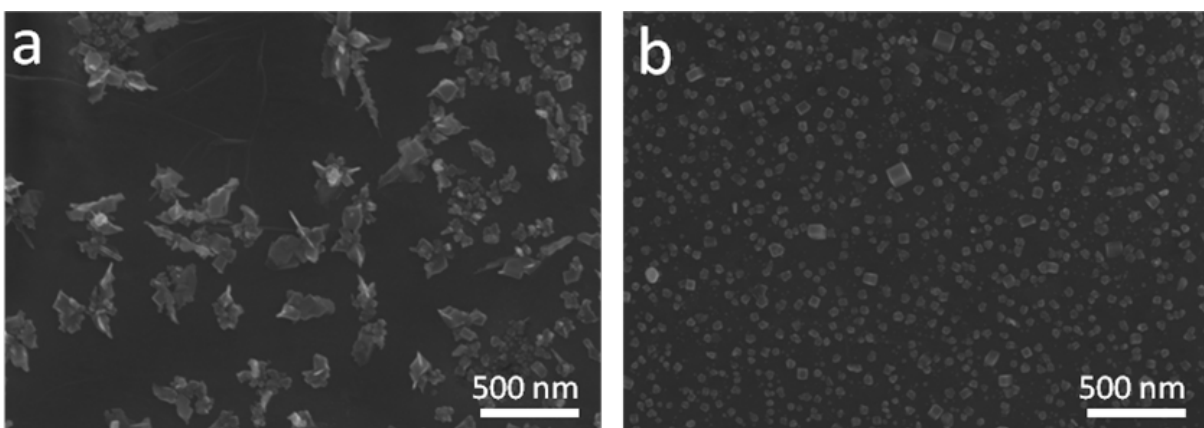
(Fig. S2)



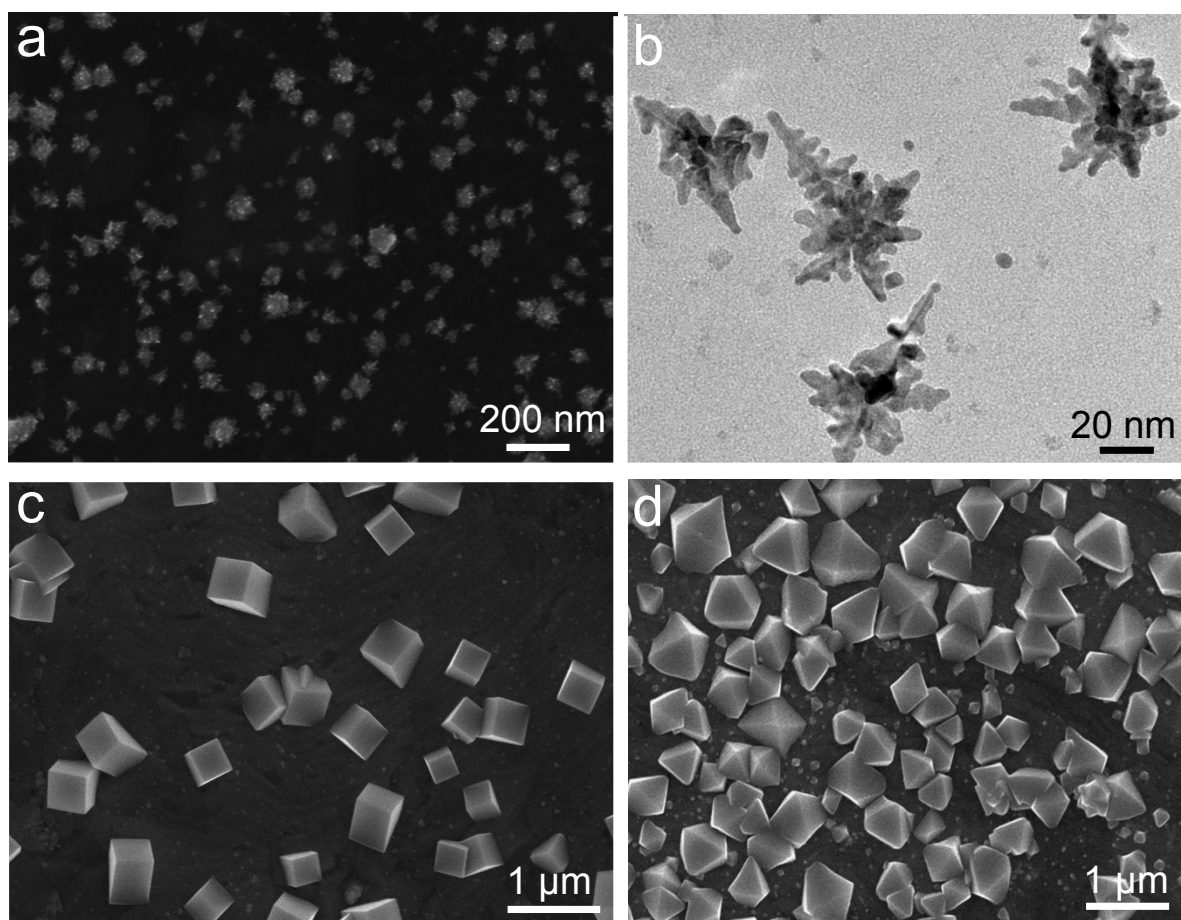
(Fig. S3)



(Fig. S4)



(Fig. S5)



(Fig. S5)