

# Physical vapor deposition of metal nanoparticles on chemically modified graphene, and their application for hydrogen sensing

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The properties of graphene are known to be highly dependent on the substrate on which it is supported. It is equally true that the properties of graphene can be influenced by material deposited on top of it, and that additional functionality can be added by combining graphene with other materials. The interaction between metals and graphene are of particular importance; metal contacts are used to probe graphene's transport properties and to inject spin-polarized carriers, metal substrates are used for chemical vapor deposition growth of graphene, and metal nanoparticles are used on graphene for applications such as catalysis, energy storage and generation, and biosensing. Many such applications are likely to involve not graphene, which is still expensive and difficult to fabricate in bulk quantities, but instead chemically modified graphene (CMG).

Oxidation of graphite to graphite oxide and its subsequent exfoliation to water soluble graphene oxide (GO) has proved to be a convenient route to bulk quantities of graphene-like material [1]. Graphene oxide can also be used as the starting point for further functionalization to tailor desirable properties into the graphene-like sheets. Removal of the oxygen to return graphene oxide to graphene is also being heavily investigated. Although complete return to graphene from GO has so far proved impossible, the reduced graphene oxide (rGO) which has been produced has acceptable conductivities of up to  $\sim 10^2$  S/cm [1] and mechanical strength within an order of magnitude of pristine graphene [2]. The comparatively low cost of these CMGs, combined with their ease of processing make them interesting materials for a range of applications. Understanding their properties and their interactions with other materials will be essential for developing and optimizing these applications.

Here we investigate metal-on-CMG, and in particular the growth morphology of metallic nanoparticles formed on CMG by physical vapor deposition (PVD). We have previously shown that single layer CMG support grids can be readily fabricated and enable high-contrast HR-TEM imaging of nanoparticles (e.g. ferritin) [3] and single molecules [4]. Here we use TEM to study the growth morphology of metals-on-CMG. We show that the morphology of the nanoparticles produced by PVD varies for different metals, from a uniform thin film for Ti to a droplet-like growth for Au. These differences in morphology can be understood and predicted by considering the strength of interaction between the CMG and metal adatoms. Fine control over the size (down to  $\sim 1.5$  nm) and coverage (up to  $5 \times 10^4 \mu\text{m}^{-2}$ ) of nanoparticles can be achieved, Figure 1. This control can be used to combine nanoparticles and CMG in rationally designed composite materials. We demonstrate the effectiveness of this approach through the fabrication of selective, highly sensitive (ppm), and practical hydrogen gas sensors, Figure 2.

## References

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## Figures

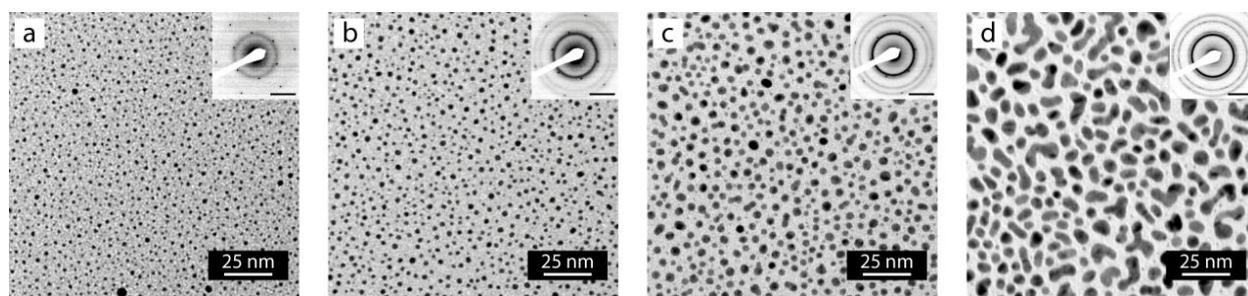


Figure 1. Brightfield TEM images of nominally (a) 0.15 nm, (b) 0.30 nm, (c) 0.75 nm, and (d) 1.5 nm thick Au films on graphene oxide. Inset top right in each image are the corresponding SAED patterns (scale bars correspond to  $3 \text{ nm}^{-1}$ ).

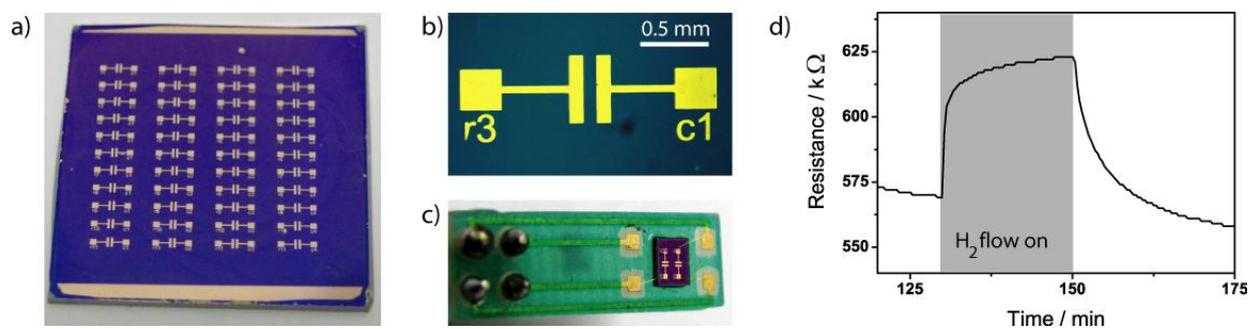


Figure 2. (a) Photograph of array of metal-on-rGO sensor devices, (b) photograph of one device, and (c) photograph of two devices mounted and bonded ready for testing. (d) Example response of one such device to hydrogen gas.