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Covalently binding atomically designed Au₉ clusters to chemically modified graphene

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Abstract: Atomic resolution transmission electron microscopy was used to identify individual Au₉ clusters on a sulfur functionalized graphene surface. The clusters were pre-formed in solution and covalently attached to the surface without any dispersion or aggregation. Comparison of the experimental images with simulations allowed the rotational motion of individual clusters to be discerned, without lateral displacement, demonstrating a robust covalent attachment of intact clusters to the graphene surface.

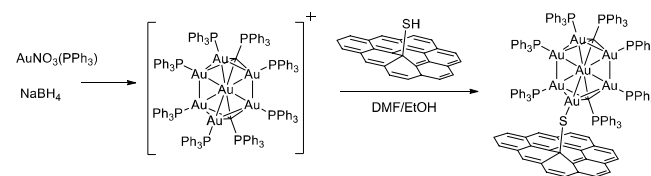
Gold nanoparticles (Au-NPs) have structure and size dependent optical and electronic properties,^{1–4} and their catalytic activity increases when the particle size drops down to around 1 nm.⁵ To achieve this size, an accurate design of ligand protected gold nanoclusters (Au-NCs) is required. A family of phosphine-coordinated Au-NCs ([Au_nL_m]^{z+}; *n* = 1–11, *z* = 1–4; L = PPh₃ or PPh₂(CH₂)₃PPh₂) having well defined nuclearity and geometrical structures have been synthesized^{6,7} and shown to exhibit clearly distinguishable optical and electronic properties.^{7–10} However, immobilization of Au-NCs onto a support is an important step towards their implementation into practical devices, so far yet to be satisfactorily realised.^{1,2,11,12} Therefore, the challenge is to develop a strategy to chemically bind pre-designed Au-NCs onto the surface of solid conductors/semiconductors, allowing direct correlation between property and structural features.

Graphene (G), as a two-dimensional system with outstanding electronic properties and a high surface area,¹³ offers the ideal platform for the deposition of NPs.¹⁴ In addition, the diversity of carbon chemistry offers many routes to producing chemically modified graphene (CMG).^{13,15,16} Both G and CMGs have already been employed to stably attach nanoparticles for a plethora of different applications.¹⁷ In particular, different routes for the hybridization between Au-NPs and G have been studied,^{18–23} but surprisingly, fabrication of atomically precise Au-NCs supported on G remains unexplored. Recently, we have described an easy way to chemically modify graphene with sulfur functionalities,²⁴ and now, by taking advantage of the affinity between gold and

sulfur, we describe the stable attachment of preformed [Au₉(PPh₃)₈](NO₃) clusters²⁵ to our CMG. Aberration-corrected transmission electron microscopy (ac-TEM) is employed to directly identify individual covalently attached Au₉ clusters, and to track their relative orientation.

Chemically modified graphene with sulfur functionalities was synthesized by treatment of graphene oxide (GO) with potassium thioacetate, followed by an aqueous work-up.²⁴ This route is easy and scalable, giving a single layer material with reactive thiol groups that offer anchoring points for further functionalisation, and is referred to as GOSH. Moreover, the synthetic route results in a partial reduction of the GO when the sulfur functionalities are introduced, giving a more graphene-like substance; this is particularly relevant for applications in which a semiconducting/conducting behavior is required as the reduction of GO results in a partial restoration of the sp² structure of G.²⁶

The [Au₉(PPh₃)₈](NO₃) cluster (abbreviated as Au₉) was selected as the target cluster.^{10,25} The D_{2h} symmetric cluster is composed of nine gold atoms arranged such that one central gold atom is surrounded by the remaining eight gold atoms, each of which is coordinated by a mono-dentate phosphine ligand (fig SI.1 and SI.2). The average metal-metal distance is around 0.27 nm, resulting in a cluster diameter between 0.45 nm and 0.54 nm,¹⁰ far below that typically exhibited by Au-NPs (particle size > 3 nm).¹¹ The binding between Au₉ and GOSH was achieved by simply stirring Au₉ with a dispersion of GOSH (Scheme 1). A covalent bond is formed between sulfur and gold, which is accompanied by displacement of a phosphine ligand. As a result a neutral GOSH@Au₉ hybrid is formed.



Scheme 1. Reaction route to GOSH@Au₉.

A comparison between the thermogravimetric analysis (TGA) of GOSH and GOSH@Au₉ gives the first evidence of hybrid formation (Fig SI.7). In both cases a first weight loss appears around 130 °C and corresponds to the desorption of water, while the major mass loss is above 500 °C and comes from the decomposition of graphene-like sheets. The main difference appears at higher temperatures where a mass of 10.5 % remains for GOSH@Au₉, pointing to the presence of metallic centers at a level of order 1 atomic %. To further confirm the presence of gold

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Supporting information for this article is given via a link at the end of the document.

in the hybrid, EDX elemental analysis was performed and showed atomic gold and phosphorus contents of around 1 atomic % for each element. Additional, and more accurate, corroboration came from XPS (Fig SI.4,5,6), in which, in addition to the signals corresponding to C, S and O, typical of GOSH,²⁴ signals for Au and P were found, consistent with the presence of Au₉.⁶ Moreover, the ratio between the atomic content determined by XPS (1.6 % Au : 1.3 % P) is consistent with the presence of Au₉P₇ clusters. A control experiment treating GO, instead of GOSH, with Au₉ was performed. With GO, no gold was detected by either EDX or by XPS (Fig SI.5, thus ruling out the possibility of interaction between Au₉ and any remaining oxygen functionalities across GOSH, thus confirming that Au₉ attachment is via the sulfur functionalities. Determining where the Au₉ is attached and whether the clusters remain intact requires direct imaging of the GOSH@Au₉ hybrid at atomic resolution. This was achieved by ac-TEM. Atomically thin 2D materials such as graphene or graphene oxide have been employed as supports for imaging molecular species;^{27,28} at one atom thickness of carbon, they are almost transparent under the electron beam so that individual molecules can be resolved at atomic resolution, whilst their well-defined crystal lattice enables accurate calibration for quantitative measurements. TEM grids were prepared by adding 1 drop of a well dispersed 0.08 mg/mL solution of GOSH@Au₉ in DMSO to a lacey carbon support and allowing it to dry under ambient conditions.

An ac-TEM image of a typical area of GOSH@Au₉ is shown in Figure 1a. As is characteristic for graphene oxide derived samples,²⁹ the image shows ordered regions where the graphene like lattice is visible, regions of higher contrast that are apparently disordered which can be attributed to oxidation debris^{30,31} or other carbonaceous material adhered to the surface, defects and small holes. A single hexagon of spots can be seen in the inset diffraction pattern which shows that the long range crystalline order of graphene is retained, and that this region consists of a single monolayer of chemically modified graphene (see also Fig SI.8).²⁷ Additional features are seen, not observed on GO or GOSH. Clusters of dark spots indicative of high atomic number atoms are apparent, dispersed across the GOSH surface. There is clear structure within the clusters and, as discussed below, this can be used to unambiguously identify these features as Au₉ clusters. No aggregation of the clusters was observed, with isolated clusters distributed uniformly across the sheets (Fig SI.9b), suggesting that they are attached to the GOSH and hence unable to diffuse and coalesce.

Counting the Au₉ clusters gives an estimate of the extent of functionalization. From analysis of images such as Figure 1 a), the estimated concentration of Au₉ clusters is 7 ± 2 per 100 nm² which corresponds to just under 0.2 % of the carbon atoms in GOSH being functionalized with the sulfur to Au₉ linkage. Note that this is only an estimate of the Au₉ cluster density as the image contrast of the Au₉ clusters varies considerably depending on their orientation (as discussed below) which complicates their identification. However, this functionalization density would correspond to an atomic content of 1.6 ± 0.4 % Au which is in close agreement with the TGA, XPS and EDX measurements. More detailed analysis requires comparison between the experimental images and image simulations of the Au₉ clusters on GOSH. Using the known crystal structure of Au₉, a tableau of multi-slice image simulations was constructed by rotating the

molecule about two orthogonal symmetry axes (Fig SI.10). For Au₉ the contrast is dominated by the gold atoms ($Z=79$) which scatter the electrons to a greater extent than phosphorus ($Z=15$) or carbon ($Z=6$). However, for accurate comparison all atoms were contained in the image simulation, including the coordination sphere of ligands and a section of graphene lattice.³² Figure 1b shows three different regions on the GOSH@Au₉, each from an ac-TEM image acquired with 0.3 s exposure. The region in Figure 1 b1 is marked by the box in Figure 1a. Comparison with the simulations, Figure 1c facilitates identification of the orientation of the Au₉ clusters, Figure 1d.

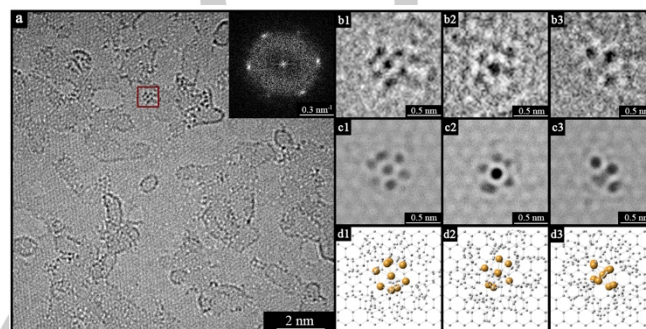


Figure 1. a) General ac-TEM of GOSH@Au₉. The inset, FFT shows the typical hexagonal pattern of a graphene monolayer. b) Three different ac-TEM images with high resolution for Au₉ imaged over GOSH showing three different orientations. b1 corresponds with the molecular cluster highlighted with a red square in (a). c) ac-TEM image simulation produced from the crystal structure model depicted in (d).

Comparison between the image simulations and experimental images clearly shows that the clusters are Au₉, with a close match for the contrast due to the gold atoms and also subtler variations in contrast that are consistent with the ligands still being present. Further confirmation comes from the measurement of the atomic column spacings within the clusters which shows that the Au-Au distances in the experimental images are consistent with those expected for Au₉ (Fig SI.11). This proves that intact, undamaged, Au₉ NCs are present on the GOSH surface.

Study of the dynamics of these Au₉ clusters demonstrates that they are covalently bound to GOSH and not simply adsorbed to the surface. The ac-TEM image shown in Figure 1a was taken with a 0.3 s exposure; the match between experimentally observed contrast and image simulation shows not only that Au₉ is present and intact, but also that those clusters are stationary on the GOSH surface for the period of that exposure. However, inspection of subsequent images shows that clusters are not permanently fixed and their contrast changes over time. Figure 2 shows a sequence of ac-TEM images of a single Au₉ cluster on GOSH; images were acquired at 0.3 s intervals over a period of more than 10 seconds, the full image sequence is shown in supporting information (Fig SI.12) with only selected images shown in Figure 2. The images are from the same region and, through comparison with fixed points in the larger image (Fig SI.9a), show no apparent lateral displacement of the cluster relative to the underlying GOSH. The change in contrast is indicative of rotations of the Au₉ cluster relative to the GOSH

surface, and comparison with the image simulation tableau enables each of the images shown in Figure 2 to be identified as specific Au₉ orientations. From this it is apparent that the Au₉ cluster is rotating, but without lateral displacement. This is consistent with covalent attachment of Au₉ to GOSH through the -S-Au bond.

The inhibited rotation is caused by interaction with the electron beam and is indicative of a set of metastable orientations. Prior work has observed similar electron beam induced molecular motion on graphene oxide,³² on carbon nanotubes^{33,34} and for molecules attached to carbon nanohorns where it was shown that lower acceleration voltages in the TEM resulted in higher frequency of molecular motion due to larger scattering cross-section.^{35,36} An accelerating voltage of 80 kV was used here to minimize damage to the chemically modified graphene by the electron beam. At this acceleration voltage the clusters are fixed in each orientation for timescales of the order of seconds before switching to another orientation. This indicates that each observed orientation is metastable, corresponding to a local energy minimum. As each image shows well defined spots rather than blurred streaks, it is also clear that the transition between orientations must be relatively rapid.

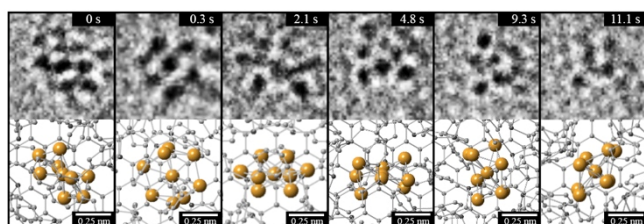


Figure 2 Selected ac-TEM image frames taken from the dynamics of a single Au₉ with their corresponding molecular models. The full ac-TEM sequence representing the motion of a single Au₉ cluster over a period of 11.4 seconds is shown in SI.12.

In conclusion, we have proven that atomically designed clusters can be covalently attached to chemically modified graphene by taking advantage of the affinity between gold and the sulfur functionalities present on the surface. We have demonstrated that the Au₉ clusters are intact and well dispersed over GOSH, showing no obvious aggregation. Dynamic ac-TEM measurements show how a single molecular cluster rotates due to the effect of the electron beam, but without lateral diffusion, indicative of a strong covalent interaction between Au₉ and GOSH. Moreover, the results of the dynamical study suggest the presence of metastable orientations that may appear as a consequence of the steric demands of the ligands.

Our approach is generally applicable to the whole family of gold nanoclusters, and may be extended to other atomically designed clusters. This will allow fine tuning of the graphene-nanocluster properties (e.g. optical or charge transfer properties), thus permitting exploration of the effect that the size and morphology of clusters have in applications ranging from biosensors or biomedicine, to energy storage or heterogeneous catalysis.

Experimental Section

Full experimental details, together with spectroscopic data and a complete set of image simulations and a movie of experimental images, complementary image simulations and corresponding molecular models are available in Supporting Information.

Acknowledgements

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Keywords: graphene · graphene oxide · gold nanoparticles · thiol · nanoclusters

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION

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Covalently binding atomically designed Au₃ clusters to chemically modified graphene

Graphene has been chemically modified and functionalised with atomically designed Au₃ clusters. The individual clusters, and their movement on the surface, has been imaged directly by aberration corrected transmission electron microscopy and correlated to image simulation.

