# GRAPHENE ENCAPSULATED GOLD NANOPARTICLES AND THEIR CHARACTERIZATION

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## ABSTRACT

Applications of gold nanoparticles under stringent conditions (e.g. low pH) are limited by improper surface passivation and inherent instability or tendency to aggregate. These limitations can be overcome by encapsulating a gold nanoparticle inside a strong and multi-functional cage or a shell. Here, a robust batch-production method to synthesize graphene encapsulated gold nanoparticles is developed. Patterned gold nanoparticles on a silicon substrate were utilized as catalysts for the growth of graphene shells in a hydrocarbon-based chemical vapor deposition (CVD) process. The gold nanoparticles and graphene encapsulated gold nanoparticles are characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As a first step towards understanding the growth mechanism of graphene shells, XPS studies were performed in order to observe the formation of gold oxide shell on gold nanoparticles. Further oxidation of the graphene shells resulted in carboxylic (-COOH) functionalities that can be very useful for developing multi-functional sensors. Finally, the post-fabrication process involving plasma oxidation/etching of graphene shells resulted in reduction of the graphene shell thickness as well as the damage to the shell by the oxidation process.

## INTRODUCTION

There have been reports on the synthesis of polymer or organic molecule encapsulated nanoparticles to prevent aggregation of nanoparticles.[1,2] In most of these cases, the nanoparticle is difficult to stabilize and is incompletely protected.[3] Carbon-based encapsulation of nanoparticles, especially after the discovery of fullerenes,[4] is attracting significant interests due to the unique properties of carbon[5,6,7] and the encapsulated nanoparticle.[8,9,10,11] The carbon shell can also be a robust protective layer for the encapsulated nanoparticle.[9,12,13,14] Such nanoparticles have been prepared by arc, laser, electron irradiation, and chemical methods.[15,16,17,18] It has been observed that transition metal nanoparticles not only catalyze graphene shell growth but also carbon nanotubes (CNTs) and amorphous carbon.[19,20,21,22] In addition, for many envisioned applications, it is important that the encapsulated nanoparticle should not react with the graphene/carbon shell to form carbides.[23] Thus, formation of stable and multi-functional carbon encapsulated nanoparticles requires two major criteria that have not yet been addressed properly. First, the nanoparticle material should be both chemically inert and act as a catalyst/selective substrate for the growth of graphene or carbon shell. Second, the synthesis of such encapsulated nanoparticles should be economical even for large yields, with minimal aggregation. Critical to the graphene shell thickness, crystallinity (or extent of graphitization), and the yield, is the type of the catalyst nanoparticles.[22] To address these issues and the above listed criteria, encapsulating gold nanoparticles with graphene is very promising. Size-dependent properties of gold nanoparticles make them useful for many applications such as optical devices and chemical sensors.[24] Fabrication of a continuous and non-porous graphene shell represents a unique way to stabilize these nanoparticles and provide a robust surface passivation. Additionally, rich surface chemistry of graphene can also be utilized making such nanoparticles multi-functional and useful for novel chemical and biological sensors, analytical platforms for high throughput screening, and advanced spectroscopic tools.[20]

## EXPERIMENTAL

Si wafers (B doped, <100>, International Wafer Service, Colfax, CA) were cleaned using acetone in an ultrasonication process for 25 min. Gold nanoparticles (10 nm colloidal gold, 0.01% as $HAuCl_4$, Aldrich) were dispersed on dried Si wafers by immersing the wafers in gold nanoparticle solution for 48 h. After the dispersion process, the substrates were dried and stored in a vacuum desiccator at room temperature. The substrates with dispersed gold nanoparticles were plasma oxidized using a plasma etcher in an oxygen environment. The oxidation was done in a two-step exposure to $O_2$-plasma, where each step is 15 min. The experiment is stopped in between the steps for 15 min to lower the temperature of the plasma chamber. The gas pressure and the forward power of the plasma system were maintained at 1200 mTorr and 170 W. The oxidized gold nanoparticles were characterized in Field Emission SEM, JEOL 7000 and X-ray Photoelectron Spectroscopy (XPS, Kratos Axis 165 XPS) to observe the presence of gold oxide. For XPS characterization, the pass energy and the current were set at 160 eV and 15 mA, respectively. The curves have been smoothed by "Quadratic Savitzky-Golay" method (kernel width of 1 and 0.5 is used).

On the other hand, similarly oxidized gold nanoparticles on a cleaned Si substrate were inserted in a CVD chamber in the presence of xylene/hydrogen/argon.[19,25,26] This resulted in the production of graphene encapsulated gold nanoparticles uniformly dispersed on a Si substrate. The dispersed graphene encapsulated gold nanoparticles were characterized by TEM. They were further plasma oxidized to observe the effects of plasma damage to the graphene shell.[25]

## RESULTS AND DISCUSSION

A series of characterization and growth steps were employed to fabricate graphene encapsulated gold nanoparticles as well as to understand the oxidation of gold nanoparticles. The latter is the first step in understanding the growth mechanism of graphene encapsulated gold nanoparticles. These hybrid nanoparticles can be multi-functional, versatile platforms for fabricating advanced sensors and devices.[25] The gold nanoparticles (~10 nm diameter) were successfully dispersed on a silicon wafer as indicated in figure 1.

Successful oxidation in an oxygen plasma process formed a very thin gold oxide shell on the surface of the gold nanoparticle. Although this shell was not observed in TEM but the XPS showed a clear evidence of formation of gold oxide (Figure 2). The surface of oxidized and non-oxidized gold nanoparticle samples were examined by XPS and the comparison of the spectra indicate the formation of gold oxide. Pure element gold peaks are visible at Au-Au$^1$ (Au $4f_{7/2}$):

84.2 eV and Au-Au$^2$ (Au 4f$_{5/2}$): 87.6 eV. While extra peaks are developed in oxidized samples corresponding to Au-O$^1$: 85.0 eV and Au-O$^2$: 88.6 eV confirming that gold oxide shell is present on these nanoparticles. These peaks correspond to the chemical shift of Au-4f levels that have been strong indicators of $Au_2O_3$[28] in case of surface oxidized gold nanoparticles. The heat of formation for $Au_2O_3$ is reported to be +19.3 kJ/mol.[27]

Figure 1. SEM image of gold nanoparticles dispersed on silicon substrates.

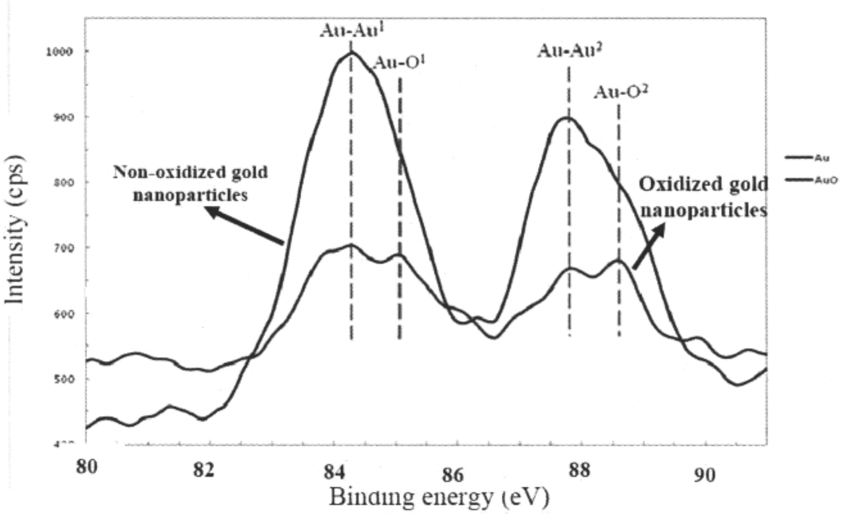

Figure 2. XPS spectra for non-oxidized (black) gold nanoparticles and oxidized (blue) gold nanoparticles. Also indicated by arrows.

Similarly oxidized gold nanoparticles were further utilized as a catalyst for the growth of graphene shells in a CVD process.[25] In our previous study, we have demonstrated that non-oxidized gold nanoparticles do not result in any graphene shells.[25] Thus, it is proposed here that the formation of graphene shell over the surface oxidized gold nanoparticles involves electron transfer process. Gold oxide being unstable at high temperatures[28], tends to reduce to gold (0) during the CVD process.[28] The electrons needed for this process are provided by the incoming carbon feed, which in turn forms $sp^2$ hybridized graphene shell. In this regard, our XPS studies confirm that gold oxide is present on gold nanoparticles after plasma oxidation process.

Once the graphene shell is formed on the gold nanoparticles, it imparts multi-functionality to the nanoparticles. This can be attributed to rich graphene/carbon chemistry instead of thiol-based gold chemistry that severely limits applications of gold nanoparticles. As a next step, the graphene shell can be further oxidized using plasma oxidation process and results in –COOH derivatization of graphene encapsulated gold nanoparticles.[25] These –COOH groups are readily available for further chemical functionalization and form the basis of developing novel bioanalytical systems based on graphene encapsulated gold nanoparticles. However, it is possible to damage the graphene shells if a prolonged plasma oxidation of shells is performed. In addition, this process can also result in reduction in number of graphene shells encapsulating gold nanoparticles. Thus, in this study, we also report a unique method to etch graphene shells or reduce the number of layers of the graphene shells in the graphene encapsulated gold nanoparticles. This is achieved by performing post-growth plasma etching process. As indicated in the figure 3, it was observed that the graphene shells were etched, damaged, and the number of shells decreased after performing the plasma oxidation. This is a promising approach to control the physical characteristics of these nanoparticles and is an easy handle to tune their properties as well as chemical functionalities. More detailed microscopic analysis of graphene shell is reported recently.[25]

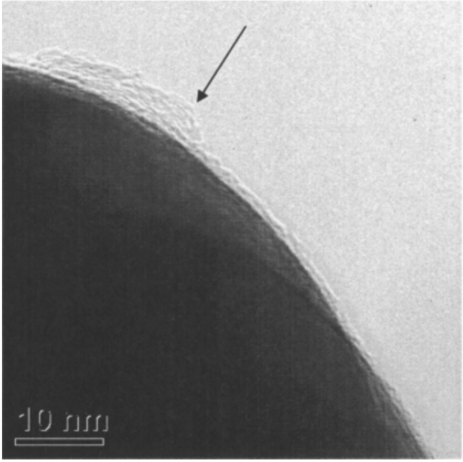

Figure 3. TEM image of a plasma oxidized/etched graphene (marked by an arrow) encapsulated gold nanoparticles. Plasma etching of graphene shells in a graphene encapsulated gold nanoparticles. The shells are damaged, etched, and removed during the process.

## CONCLUSIONS

Graphene encapsulated gold nanoparticles were fabricated and dispersed on a silicon wafer. SEM, TEM, and XPS studies confirmed the chemical composition and physical characteristics of nanoparticles at various stages of the fabrication process. XPS studies reveal the formation of gold oxide after plasma oxidation of gold nanoparticles. A growth mechanism based on electron transfer process during the CVD process is proposed that facilitates the growth of graphene shell on the surface oxidized gold nanoparticles. Finally, post-CVD plasma etching removes and damages graphene shell. This dry processing or etching of graphene shell allows for controlling the characteristics of graphene encapsulated gold nanoparticles. Such multi-component and multi-functional nanoparticles are of immense importance for developing analytical devices and sensors, self-assembly platforms, and optical systems.

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