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Modifying the chemistry of graphene with substrate selection: A study of gold nanoparticle formation

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Graphene and metal nanoparticle composites are a promising class of materials with unique electronic, optical, and chemical properties. In this work, graphene is used as a reducing surface to grow gold nanoparticles out of solution-based metal precursors. The nanoparticle formation is found to strongly depend upon the graphene substrate selection. The studied substrates include diamond, p-type silicon, aluminum oxide, lithium niobate, and copper. Our results indicate that the chemical properties of graphene depend upon this selection. For example, for the same reaction times and concentration, the reduction of gold chloride to gold nanoparticles on graphene/lithium niobate results in 3% nanoparticle coverage compared to 20% coverage on graphene/silicon and 60% on graphene/copper. On insulators, nanoparticles preferentially form on folds and edges. Energy dispersive X-ray analysis is used to confirm the nanoparticle elemental makeup. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4916567]

Graphene and metal nanoparticle composites exhibit unique optical properties[1,2] which have been studied for a range of applications including memory devices, photonic devices,[3] energy storage,[4] catalysis,[5] solar cell enhancement,[6] and sensing.[7]

There are several routes for fabricating graphene-metal nanoparticle hybrid materials. Thin metal films can be patterned with nanospheres[8] or lithographically defined masks. Alternately, a thin film of metal evaporated onto graphene and subsequently heated dewets from the surface to form islands.[1] In this work, we submerge graphene in a gold-chloride solution, and the spontaneous reduction of gold chloride on the surface of graphene results in gold nanoparticles. We find that the reduction of gold chloride on graphene has markedly different features when p-type silicon, diamond, aluminum oxide, copper, or lithium niobate is used as the substrate. These substrates represent several distinct classes of materials: a doped semiconductor, insulators, a ferroelectric insulator, and a conductor. Copper substrates result in the greatest gold coverage and insulating substrates the least.

Solution-based spontaneous reductions are a class of reactions that require no additional catalyst or electrode and consist of a reduction-oxidation pair, also known as redox pair. The well-known copper and zinc galvanic cell is an example of such a redox reaction. The graphene/gold ion system also comprises a redox pair.[9] Given that the work function of graphene is approximately 4.4 eV, the Fermi level is −0.1 V vs the normal hydrogen electrode (NHE). For comparison, the reduction potential of $AuCl_4-$ is +1.002 V. Hence, the spontaneous transfer of electrons from the graphene (oxidation) to the metal ion (reduction) is energetically favorable. The reaction is illustrated in Fig. 1.

To date, the spontaneous reduction of gold chloride has been demonstrated on carbon nanotubes,[10] with the substrate selection also playing a role in which metal ion species can be reduced by electroless deposition,[11] with copper and zinc substrates studied. Another study compared the reduction of gold chloride by carbon nanotubes, carbon encapsulated nanoparticles, activated carbon, and carbon black and found that the nanoparticle formation rate is inversely correlated to the amount of sp^2 carbon.[12] CVD graphene on poly(methyl methacrylate) (PMMA) films,[6] zinc foil, and copper foil[9] have also been separately demonstrated as reducing surfaces for gold chloride. In this work, we replicate the copper foil substrate results and demonstrate the role of other substrates on the electroless deposition of gold nanoparticles. While prior studies have focused on the favorable energetics resulting in electroless deposition, we find that on substrates with similar Fermi energies, depositions do not occur at similar rates, indicating an additional dependence on electron availability, or conductivity.

In this study, we use chemical vapor deposition (CVD) graphene grown on copper foil (Graphene Supermarket). We use the graphene on copper as-is for the copper substrate experiment. For the experiments with other substrates, we transfer graphene onto the target substrate using the poly (methyl methacrylate) (PMMA) method.[13] The PMMA is lifted off in an overnight acetone bath, followed by a 30 min methanol bath and a hydrogen anneal ($5\% H_2$) for 60 min at ∼325 °C. Following transfer to the target substrate, the gold nanoparticles are produced via reduction of gold chloride in aqueous solution (20 mM) for 60 s. The samples are then rinsed in deionized water for 15 s and dried with nitrogen.

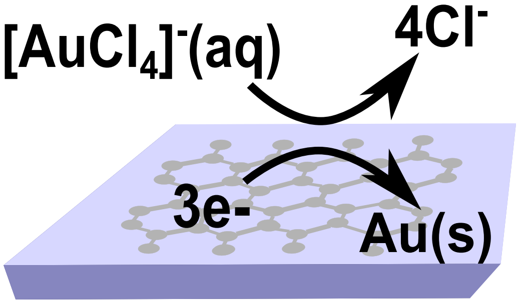

FIG. 1. Catalyst-free and electroless deposition reaction for gold ion reduction on graphene. The difference in redox potential between the gold ion and the graphene carbon is the driving force for the reaction.

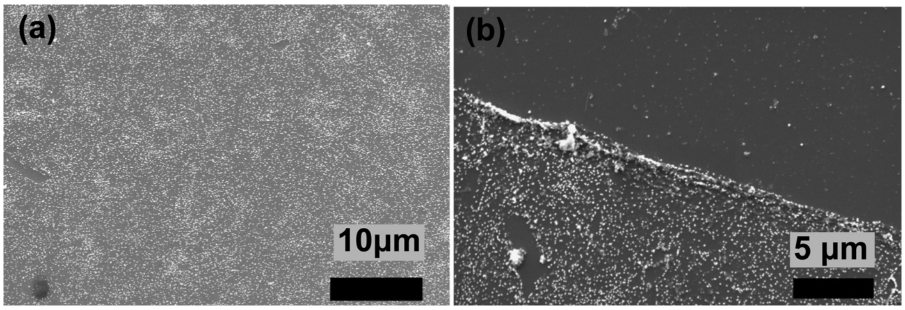

FIG. 2. SEM image of gold nanoparticles deposited on graphene on silicon in a region with (a) high graphene coverage and (b) an edge of graphene transfer. Gold nanoparticles preferentially form on continuous graphene.

The target substrates are silicon (boron doped, ⟨100⟩, <0.01 Ω cm), periodically poled lithium niobate (with 15 μm wide alternately charged domains), and single crystal diamond. Scanning electron microscope (SEM) images are obtained with an FEI XL30 microscope, and post-image analysis was completed with Image-J to determine coverage.

On silicon, gold nanoparticles deposit wherever the graphene is continuous. As shown in Fig. 2, there are regions where the gold nanoparticles do not form, due to the graphene being torn or missing in these regions. Examining the graphene-bare silicon edge shows that gold nanoparticle formation on bare silicon is limited compared to regions where the graphene is continuous. Overall, about 20% of the graphene coated silicon surface is covered in gold nanoparticles.

Gold nanoparticles form on graphene on copper with the highest density of the substrates tested. As shown in Fig. 3(a), this system results in larger gold deposits alongside the nanoparticles. In this case, about 60% of the area is covered with deposits.

In contrast, gold nanoparticle formation on insulators occurs at a more limited rate, and preferentially on folds and edges. Figs. 3(b)–3(d) show gold nanoparticle formation on graphene coated diamond and periodically poled lithium niobate. On lithium niobate, only about 3% of the area is covered with gold nanoparticles, and the nanoparticles preferentially form on the graphene folds. We observe only weak dependence on polarity for nanoparticle formation. CVD-grown, intrinsic single-crystal diamond ⟨100⟩ results in a coverage of about 3%. Interestingly, other reports have found that ⟨100⟩ diamond is an inert substrate for graphene.[14] The substrate with the least deposition is aluminum oxide, with gold nanoparticles on <1% of the graphene. Given that the percent of the area with folds is idiosyncratic to each transfer, we do not claim that the difference in percent coverage of nanoparticles for each insulating substrate to be statistically significant.

In order to determine that the particles observed in the SEM indeed correspond to gold nanoparticles, we perform energy dispersive x-ray analysis (EDAX) using an accelerating voltage of 20 kV. The result of EDAX on a single nanoparticle deposited on the copper substrate, shown in Fig. 4(a), reveals that gold lines at 9.7 keV and 11.5 keV are present, as well as copper lines, as expected. These results are consistent with other studies of gold chloride reduction on graphene on copper foil.[9] Fig. 4(b) presents an EDAX map of Au-M intensity and the corresponding SEM image of nanoparticles on the diamond sample. There is a strong correlation between the gold signal and nanoparticle presence. We find similar results for the other substrates, clearly indicating that the nanoparticles observed in the SEM images are gold nanoparticles.

We also note that several months after the gold chloride exposure, the copper foil is visibly blackened, indicating increased oxidation of the underlying foil. Long term

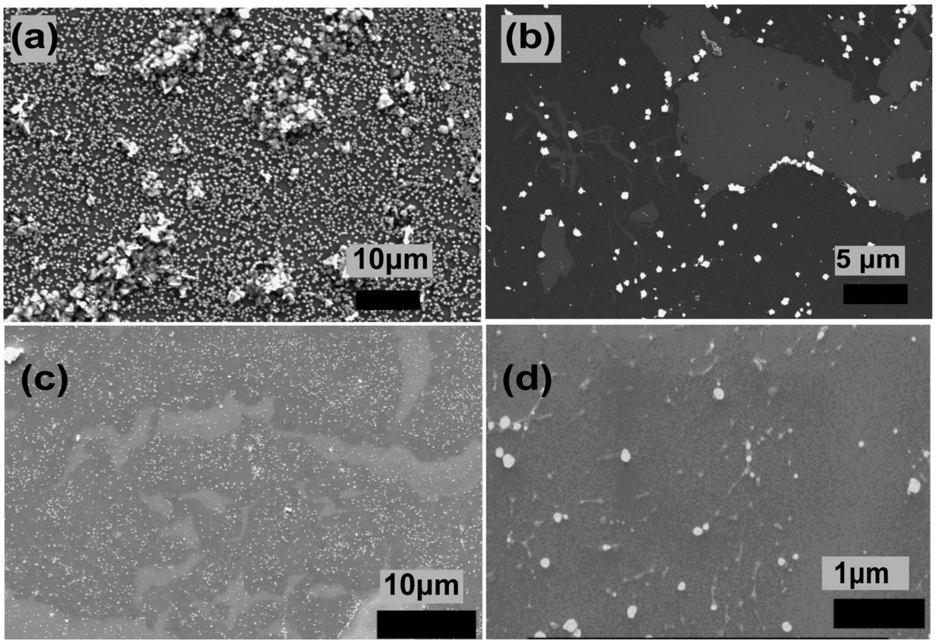

FIG. 3. SEM images of gold nanoparticle deposition on graphene on (a) copper, showing nanoparticles and larger deposits and (b) CVD-grown diamond, showing preferential deposition on edges (c) periodically poled lithium niobate, with little evidence for periodic deposition following the lithium niobate polarization and (d) lithium niobate, under high magnification, showing preferential deposition on folds.

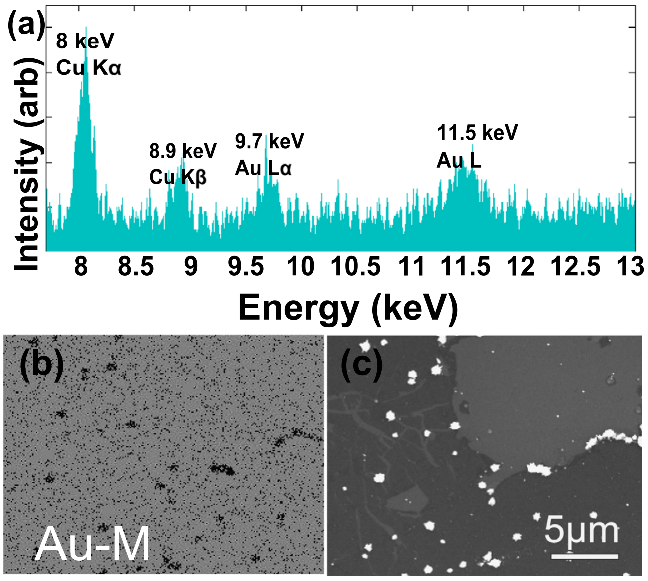

FIG. 4. X-ray emission (EDAX) intensity (a) from a nanoparticle on copper and (b) as a count map of the Au-M line on diamond and (c) SEM image of same area as (b).

oxidation of copper under CVD graphene has previously been observed, but at a slower rate.[20] This observation is another indication of the carbon oxidation during the redox reaction- and an increase in graphene defects which enable long-term oxidation.

Fig. 5 shows the reduction potential of gold chloride as well as the conduction band minimum and valence band maximum of lithium niobate and Fermi energies of the p-type silicon and copper. A range of energies is shown for copper, representing the multiple facets on the copper surface. Prior studies have found that the work function of the substrate plays a large role in determining the work function of graphene, with a resulting shift in work function of a few hundred meV.[21,22]

Energetically, copper and silicon are similar. However, copper substrates result in three times the deposition rate of silicon. Hence, we postulate that electron availability for gold chloride reduction is the rate limiting process for comparing these substrates. Deposition along folds and edges is consistent with other work on graphene reactivity.[23,24]

In conclusion, reaction rates for the spontaneous reduction of gold chloride into gold nanoparticles on the surface of graphene are highly sensitive to substrate selection. For the systems we studied, it appears that the energetics of the substrate in addition to the conductivity of the substrate play a large role in the gold deposition rate.

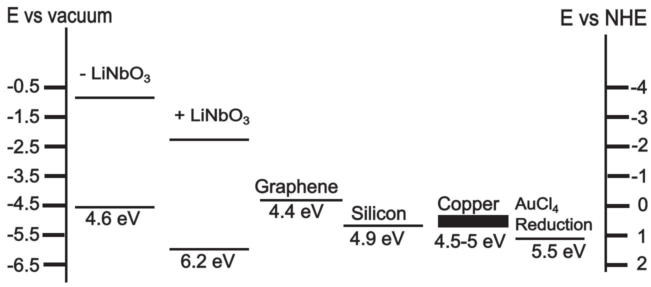

FIG. 5. Energy levels of substrates and gold chloride reduction vs. vacuum and vs. normal hydrogen electrode for select substrates which result in gold nanoparticle formation.[15–19]

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