Electronic and optical properties of metal-nanoparticle filled graphene sandwiches

Anna M. Zaniewski,[1,2,3] Maria Schriver,[2,4] J. Gloria Lee,[1,3] M. F. Crommie,[1,2,3] and A. Zettl[1,2,3]
[1]*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA*
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*Center of Integrated Nanomechanical Systems, University of California, Berkeley, Berkeley, California 94270, USA*
[4]*Department of Mechanical Engineering, University of California at Berkeley, Berkeley, California 94720, USA*

(Received 12 October 2012; accepted 3 December 2012; published online 17 January 2013)

We sandwich gold nanoparticles between graphene sheets and contrast the electronic and optical properties of these hybrid structures to those of single layer graphene with and without gold nanoparticle overlayers, and laminated unfilled double layers. Undecorated graphene has the highest sheet resistance while filled sandwiches have the lowest. The optical extinction spectrum for sandwiches is redshifted and broadened compared to decorated single layer graphene. We also find that the presence of gold nanoparticles in sandwiches shifts the work function relative to unfilled double-layer graphene. The low sheet resistance and favorable optical properties of metal-filled sandwiches make them attractive candidates for optoelectronic applications. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4772542]

The unique physical properties of graphene have stimulated significant scientific and technological study,[1] and the recent synthesis of large-area graphene[2] demonstrates scalability. Graphene can be tuned for a diversity of applications by geometric confinement to tune the band gap,[3] chemical doping to modify electronic transport,[4] and the addition of nanoscale metals to the surface for optical modification.[5–8] The latter modification exploits strong coupling between light and metallic nanoparticles, due to plasmon excitation, and is an interesting system that warrants further study. Graphene-based sandwich structures have been demonstrated as a general route to produce hybrid materials,[9] and graphene sandwiches were recently used in conjunction with lithographically defined nanoscale antennas to construct wavelength-specific photodetectors.[8]

In this work, we contrast the electronic and optical properties of (a) graphene monolayers, (b) graphene monolayers decorated with gold nanoparticles, (c) gold nanoparticles sandwiched between two graphene sheets, and (d) "empty" sandwiches consisting of two laminated graphene sheets, as shown schematically in Fig. 1. We find that the dc electrical sheet resistance is quite different for the different configurations, with single sheet undecorated graphene having the highest sheet resistance and gold-filled sandwiches having the lowest. In the optical response, we find that sandwiching the metallic nanoparticles between sheets rather than decorating a single sheet results in a stronger redshift and broadening of the plasmon resonance, due to enhanced coupling between the graphene and the metal nanoparticles. Using Kelvin probe force microscopy (KPFM), we demonstrate a shift in the work function between laminated double graphene sheets and metal-filled sandwiches.

Figure 2 shows a scanning electron microscope (SEM) image of gold nanoparticles on graphene. The graphene is grown by a chemical vapor deposition (CVD) method previously described,[2] which results in high quality polycrystalline monolayers with a typical grain size of 5 μm. The graphene is transferred onto a quartz substrate using the poly(methyl methacrylate) (PMMA) method.[10] The gold nanoparticles in this study are produced with a method that is both scalable and produces a broad size distribution, resulting in desirable broadband optical response. To produce gold nanoparticles, a 5 nm film of gold is deposited onto monolayer graphene by electron-beam evaporation. The graphene/gold film is then annealed under a mixture of argon and hydrogen at 350 °C for 90 min to produce 50–200 nm gold islands, as is described elsewhere.[11] To produce metal-filled sandwiches, we transfer an additional PMMA/graphene layer to the stack, and remove the PMMA as for the first layer.

Our samples are typically 1 cm × 1 cm in size, meaning that for a given sample, we measure over numerous crystalline orientations. The crystalline grains on opposite side of the sandwich structures are rotationally randomly oriented.

We investigate first the dc electrical sheet resistance of the different sample configurations. Previous studies of multiple layers of CVD-grown graphene transferred to glass show that a single layer of graphene has a sheet resistance of 2100 $\Omega/\square$, and two sheets of graphene have a sheet resistance of 1000 $\Omega/\square$.[10] For all measurements, we use the four point van der Pauw method. The measured sheet resistances of the as-transferred single layer graphene, double layer graphene, graphene with gold nanoparticles, and graphene-gold nanoparticle sandwich are 2300, 1200, 1300, and 730 $\Omega/\square$, respectively. There could be several mechanisms by which the sheet resistance of the graphene is reduced by the gold nanoparticles. One such mechanism is parallel conduction through the gold nanoparticles and sheets of graphene. The gold nanoparticles cover a large area of the graphene, and are typically separated from each other by $\leq 1\mu$m, leading to frequent opportunities for parallel conduction. Since the

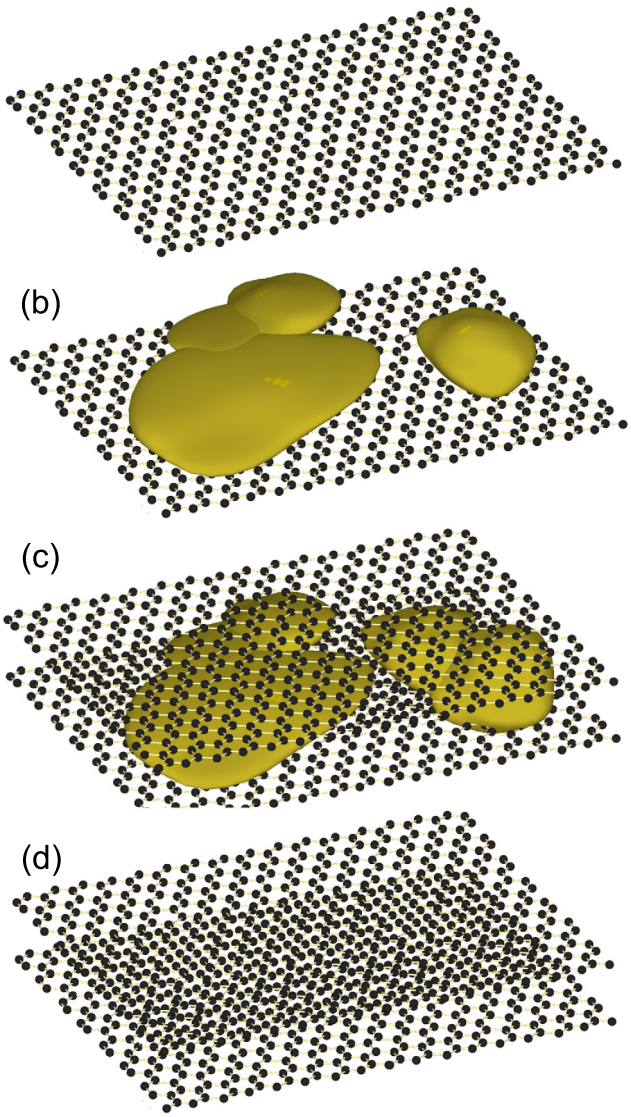

FIG. 1. Schematic representation of the materials studied in this work: (a) single layer graphene, (b) single layer graphene with gold nanoparticles, (c) graphene-metal nanoparticle-graphene sandwich structure, and (d) unfilled double layer graphene.

sandwich structure incorporates a second layer of graphene, the total sheet resistance would also be expected to drop due to parallel conduction through the top graphene sheet.

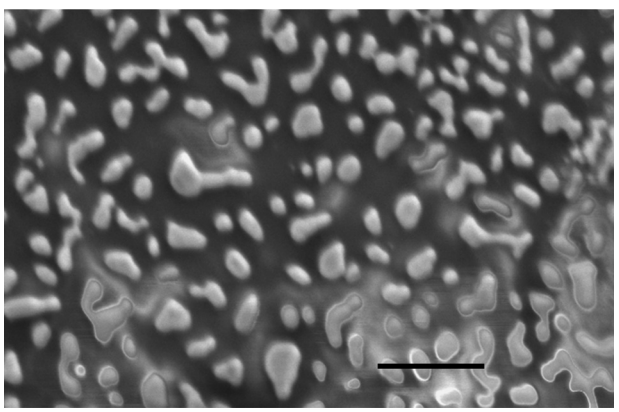

FIG. 2. Scanning electron microscope image of self-assembled gold nanoparticles grown on graphene substrates. Scale bar is 1 μm.

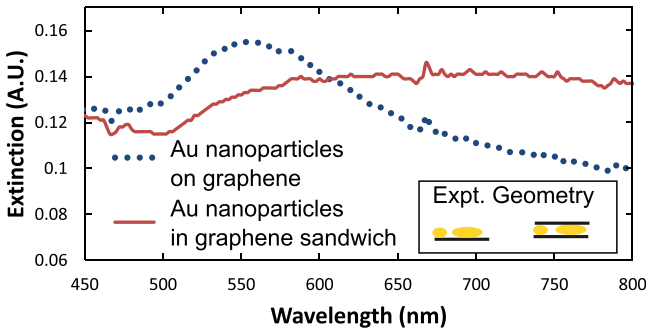

FIG. 3. Measured optical extinction spectrum of a single layer graphene with gold nanoparticles and a graphene-gold nanoparticle sandwich. Inset: a schematic of the two geometries tested in this experiment.

Furthermore, since the gold islands are relatively large, they could bridge any tears or gaps in the graphene common to the CVD growth and transfer process. Finally, gold nanoparticles would shift the Fermi energy of the graphene, potentially introducing a higher charge density to the graphene sheets. These effects would all increase the sheet conductivity.

Figure 3 shows the extinction (absorption and scattering) spectrum of a gold nanoparticle-graphene sandwich structure and a single layer of graphene with gold nanoparticles for comparison. Metal nanoparticles on a single sheet of graphene show a moderately sharp plasmon resonance peak, in agreement with prior measurements.[5] The sandwich structure, however, shows a dramatically altered optical response. The extinction spectrum is greatly red-shifted and broadened. This is likely due to enhanced coupling of the collective electron excitation within the gold nanoparticles to the graphene. Bimetallic nanoparticles have a similarly tunable plasmonic scattering spectrum[12] as a result of hybridization of the plasmon excitation in neighboring metals.

To investigate this hybridization effect in the case of graphene and gold nanoparticles, we use Mie theory[13] to compute the scattering cross section for a set of spherical gold nanoparticles with an average radius of 100 nm and a standard deviation in the radius of 50 nm, to reflect the size dispersion of our nanoparticles. We also perform the calculation including a 10 nm thick shell with graphene's optical constants ($n = 2.4$, $k = 1.1$).[14] We note that this geometry (shown in the inset of Fig. 4) differs from the geometry of

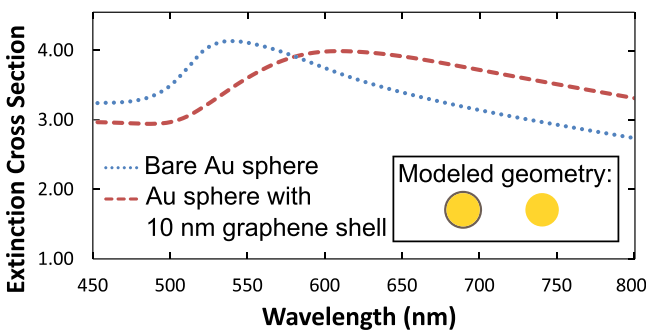

FIG. 4. Calculated extinction cross section spectrum for bare gold nanoparticles and gold nanoparticles with a graphene shell. Inset: a schematic of the modeled geometries.

the experiment. However, this approach has the advantage of simplicity, and avoids computational complications that arise when modeling structures with large variations in geometric length scales (e.g., single atom vs 100 nm particles) as occurs with finite element or finite difference time domain approaches. The results of the model, Fig. 4, show that gold nanoparticles with a graphene shell have a redshifted and broadened resonance peak compared to bare nanoparticles, and these effects increase with shell thickness (not shown). This model verifies that the hybridization trend for the gold-graphene system is to redshift and broadens the plasmon resonance, in good agreement with observations. This implies that the electron cloud of the gold nanoparticles is more strongly coupled to the graphene when embedded in the sandwich structure than when assembled on a single layer of graphene. This trend is clearly evident, and more studies would be useful to investigate this effect in more detail.

We consider the work function for the different graphene configurations shown in Fig. 1. Previous studies have shown that single layer graphene doped with gold nanoparticles formed by reduced $AuCl_3$ has a work function shift of up to 500 mV,[15] and graphene with evaporated gold particles has a work function shift of 170 mV.[16] We here employ Kelvin probe microscopy to explore the work function of metal decorated graphene and metal-filled sandwiches. To perform the measurements, a conducting tip is electronically connected to the sample, and rastered at a constant height across the sample. A feedback loop zeros the voltage between the tip and the sample that arises from a difference in work function.[17] In this way, the local variation in surface potential, or the contact potential difference (CPD) can be monitored. Measurements are performed using an Asylum MFP3D instrument with a conducting titanium nitride coated probe (Ultrasharp NSG03, work function 4.4 eV), under flowing dry nitrogen to maintain a low humidity environment.

In order to reduce variations in CPD that can arise from variables such as tip wear, we examine the border region between an area containing gold nanoparticles embedded in a graphene sandwich and a region of unfilled double layer graphene, so that the two regions are probed in a single line scan. The sample geometry is shown in Fig. 5. By comparing the average CPD in the two regions, we find that gold nanoparticles result in a local CPD on average 50 mV over the bilayer graphene-only region. Our results are consistent with hole-doping of the graphene, in agreement with previous graphene-gold measurements.[15,16] The red line shown in Fig. 5(b) is a section graph of the CPD averaged over the y-direction. The contact potential difference is related to the sample and tip work functions by

$$CPD = \phi_{sample} - \phi_{tip}, \tag{1}$$

where ϕ_{sample} and ϕ_{tip} are the work functions for the sample and tip, respectively. The tip work function is measured to be 4.4 eV, based on CPD measurements on a highly ordered pyrolytic graphite sample. Therefore, the work function of the unfilled bilayer graphene region is 4.55 eV, and the work function of the gold sandwich region is 4.60 eV. However, since KPFM is extremely sensitive to tip contamination or wear, which impacts the effective tip work function, the relative work function shift between the unfilled and filled sandwich, 50 meV, is more reliable than these absolute values.

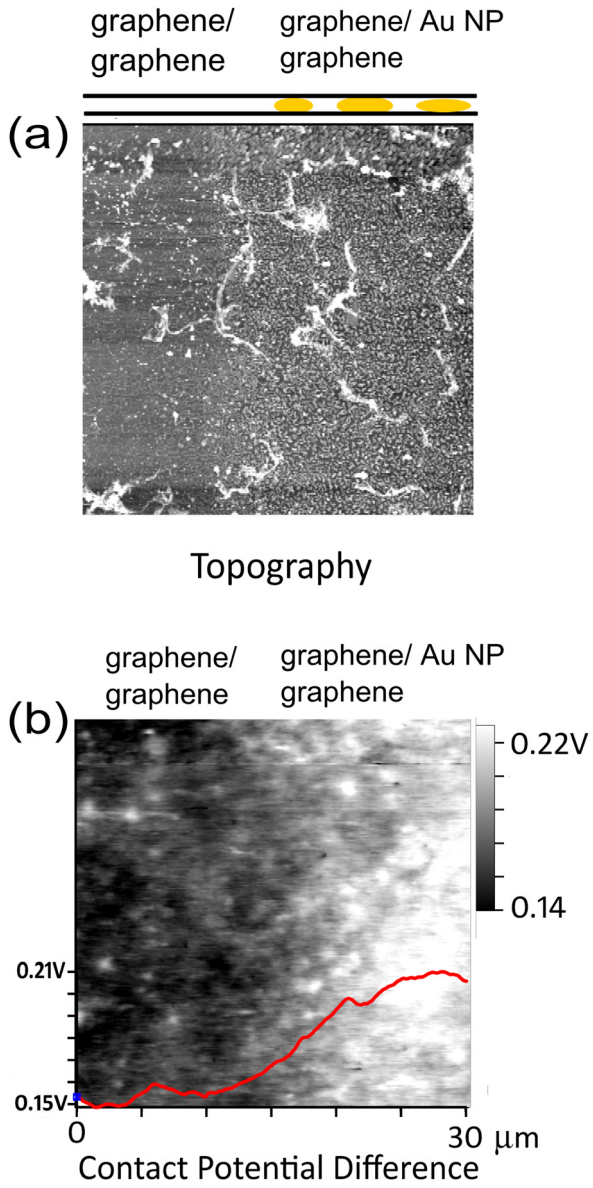

FIG. 5. (a) Topography and (b) contact potential difference of two layers of graphene on a silicon substrate across the border between the areas with gold nanoparticles between the sheets (right) and without (left). The fast scan direction is *x*, and the slow scan direction is *y*. The curve in (b) shows the contact potential difference averaged over the *y* direction.

As expected, the measured shift of the contact potential difference for filled vs unfilled sandwiches represent a smaller work function shift than has been reported for gold on single layer graphene vs undecorated graphene.[15,16] The top layer of graphene screens underlying materials,[18] which would reduce the contribution of the nanoparticles to the work function. The local variability of the work function can be understood by considering the morphology: the sandwiches tend to form three-dimensional tent structures,[9] producing a non-uniform graphene-nanoparticle separation, and this variability of graphene-metal separation can have a large impact on the work function modification of graphene.[19] Furthermore, due to the nature of the gold nanoparticles, a variation in crystallographic orientation would cause local variations in the surface potential. Despite these

complications, a clear trend is evident at the border between regions with and without gold nanoparticles, evidencing a shift in the work function.

This work demonstrates that plasmonic graphene sandwiches have a number of interesting properties distinct from simple graphene laminations or graphene with metallic overlayers. The electronic properties include modified work function, and the sheet resistance is reduced compared to single layer graphene with or without gold nanoparticles. Furthermore, the sandwiches couple strongly to broadband light, in contrast with metal nanoparticles deposited on a single layer or without graphene. This could have important implications for optoelectronic applications requiring broadband performance.

This work was supported in part by the Director, Office of Energy Research, Materials Sciences and Engineering Division, of the US Department of Energy under Contract No. DE-AC02-05CH11231, which provided for synthesis of the graphene membranes and SEM characterization, the National Science Foundation under Grant Nos. DMR-1206512 and EEC-0832812 which provided for optical and AFM characterization, respectively, and the Office of Naval Research under Grant No. N00014-09-1066 which provided for nanoparticle deposition and lamination. A.M.Z. acknowledges support from an NSF Graduate Fellowship and M.S. acknowledges support from a National Defense Science and Engineering Graduate Fellowship.

[1]A. K. Geim and K. Novoselov, Nature Mater. **6**, 183 (2007).
[2]X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, Science **324**, 1312 (2009).
[3]K. Nakada, M. Fujita, G. Dresselhaus, and M. Dresselhaus, Phys. Rev. B **54**, 17954–17961 (1996).
[4]H. Liu, Y. Liu, and D. Zhu, J. Mater. Chem. **21**, 3335 (2011).
[5]G. Xu, J. Liu, Q. Wang, R. Hui, Z. Chen, V. A. Maroni, and J. Wu, Adv. Mater. **24**, OP70 (2012).
[6]N. K. Emani, T.-F. Chung, X. Ni, A. V. Kildishev, Y. P. Chen, and A. Boltasseva, Nano Lett. **12**, 5202 (2012).
[7]J. C. Reed, H. Zhu, A. Y. Zhu, C. Li, and E. Cubukcu, Nano Lett. **12**, 4090 (2012).
[8]Z. Fang, Z. Liu, Y. Wang, P. M. Ajayan, P. Nordlander, and N. J. Halas, Nano Lett. **12**, 3808 (2012).
[9]J. M. Yuk, K. Kim, B. Alemán, W. Rega, J. H. Ryu, J. Park, P. Ercius, H. M. Lee, A. P. Alivisatos, M. F. Crommie, J. Y. Lee, and A. Zettl, Nano Lett. **11**, 3290–3294 (2011).
[10]X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo, and R. Ruoff, Nano Lett. **9**, 4359 (2009).
[11]R. Doremus, Thin Solid Films **326**, 205 (1998).
[12]K. J. Major, C. De, and S. O. Obare, Plasmonics **4**, 61 (2009).
[13]O. Peña-Rodríguez, P. P. G. Pérez, and U. Pal, Int. J. Spectrosc. **2011**, 1.
[14]Z. H. Ni, H. M. Wang, J. Kasim, H. M. Fan, T. Yu, Y. H. Wu, Y. P. Feng, and Z. X. Shen, Nano Lett. **7**, 2758 (2007).
[15]Y. Shi, K. K. Kim, A. Reina, M. Hofmann, L.-J. Li, and J. Kong, ACS Nano **4**, 2689 (2010).
[16]Y. Ren, S. Chen, W. Cai, Y. Zhu, C. Zhu, and R. S. Ruoff, Appl. Phys. Lett. **97**, 053107 (2010).
[17]S. Sadewasser and T. Glatzel, *Kelvin Probe Force Microscopy* (Springer, New York, USA, 2011).
[18]M. Koshino, Phys. Rev. B **81**, 125304 (2010).
[19]G. Giovannetti, P. A. Khomyakov, G. Brocks, V. M. Karpan, J. van den Brink, and P. J. Kelly, Phys. Rev. Lett. **101**, 026803 (2008).