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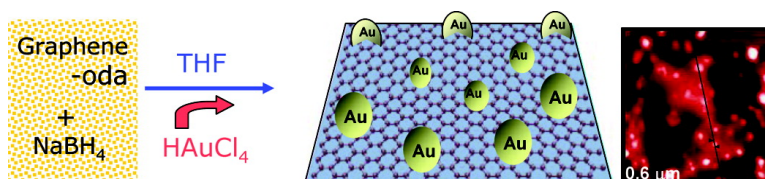**536** PUBLICATIONS   **44,073** CITATIONS

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Decorating Graphene Sheets with Gold Nanoparticles

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Renewed interest in graphene architectures has opened up new avenues to utilize them in electronic and optoelectronic applications. The desire to design graphene–metal nanohybrid assemblies has led us to explore a solution-based approach of chemical reduction of $AuCl_4^-$ ions in graphene suspensions. The gold particles anchored on octadecylamine functionalized graphene are readily suspendable in THF medium. The dependence of particle stability on the graphene concentration and SEM analysis indicate that the gold nanoparticles are well dispersed on graphene sheets. Transient absorption spectroscopy measurements suggest that the ultrafast disappearance of plasmon absorption and its recovery are unaffected by the presence of graphene.

Carbon nanotubes and nanostructures have drawn attention because of their unusual electronic properties and ability to improve catalytic properties.[1–4] Of particular interest is the dispersion of precious metal nanoparticles on carbon nanostructures that show enhanced electrocatalytic activity in fuel cells.[5–7] Graphene is a counterpart of graphite with well separated 2-D aromatic sheets composed of sp^2-bonded carbon atoms. The π-stacked graphene sheets can be exfoliated (exfoliation energy 61 meV/C atom) by forming graphene oxide[8–10] or via manipulation of chemical functionalization.[11–13] The century old graphene oxide synthesis[8–10] has taken a new turn in recent years as both top-down and bottom-up approaches are being considered to isolate single graphene sheets and probe their electronic properties with and without modification.[11–15]

Graphene-based composite materials prepared via molecular-level dispersion in polymers have shown to improve electronic and thermal conductivity.[14,16] The dispersion of metal nanoparticles on graphene sheets potentially provides a new way to develop catalytic, magnetic, and optoelectronic materials. Encapsulation of metal clusters inside multishell graphitic cages is usually achieved during carbon arc-discharge at high temperatures.[17–19] Similarly, interesting hybrid structures of carbon nanotubes[7,20–24] and graphite oxide nanoplatelets[25,26] have been developed by depositing metal nanoparticles. Efforts have also been made to synthesize silver particles protected by graphite oxide sheets and assemble them as ultrathin films using layer-by-layer self-assembly technique.[27] The ability to react the graphene oxide sheets with $SOCl_2$[11] and amines[28] has made it convenient to develop chemical synthetic strategies and tailor their properties via chemical functionalization. In a recent study, Haddon and co-workers[11] synthesized suspendable graphene sheets by chemical functionalization with octadecylamine (ODA). Such suspendable graphene offers the possibility to develop carbon–metal nanocomposites as new catalyst materi-

als. We have now succeeded in using chemically modified graphene sheets to support gold nanoparticles of dimensions 3–30 nm diameter. The synthesis and optical properties of graphene-stabilized gold nanoparticles are presented here.

The graphene oxide was first prepared by refluxing commercially obtained graphite powder (Aldrich) in a mixture of H_2SO_4, HNO_3, and $KClO_3$ adapting the method described in the literature.[9] After repeated washing, the powder was dried. The dried powder was then reacted with thionyl chloride followed by the reaction with ODA.[11] The final product (graphene-oda) was washed and centrifuged three times and was dried by evaporating the solvent. Graphene–ODA can be readily suspended in both polar and nonpolar solvents. The detailed experimental procedure and the techniques employed in the present study are given in the Supporting Information.

Figure 1 shows the absorption spectra recorded at different graphene–oda concentrations in THF. Graphene suspension showed featureless absorption in the visible and increases steeply in the UV region. The graphene–oda suspension exhibits a linear dependence of absorbance on the concentration of graphene (inset in Figure 1), confirming the compliance of Beer's law. The broad absorption in the 400 nm region can thus be utilized to determine the concentration of graphene in a given suspension. As will be discussed in the following discussion, the graphene–oda suspension was convenient to prepare gold nanoparticles as the graphene–oda sheets rendered necessary stability.

The gold nanoparticles were synthesized using chemical reduction of $AuCl_4^-$ (Aldrich) with $NaBH_4$ in a graphene–oda suspension. A concentrated aqueous solution of $NaBH_4$ was first mixed with a graphene–oda suspension in THF. Addition of an excess of $NaBH_4$ to the graphene solution facilitated reduction of any remaining oxide sites that evaded chemical functionalization. A total of 0.05 mL of 30 mM $AuCl_4^-$ was then injected into this THF suspension with stirring, and the mixture was allowed to stand for at least 15 min before

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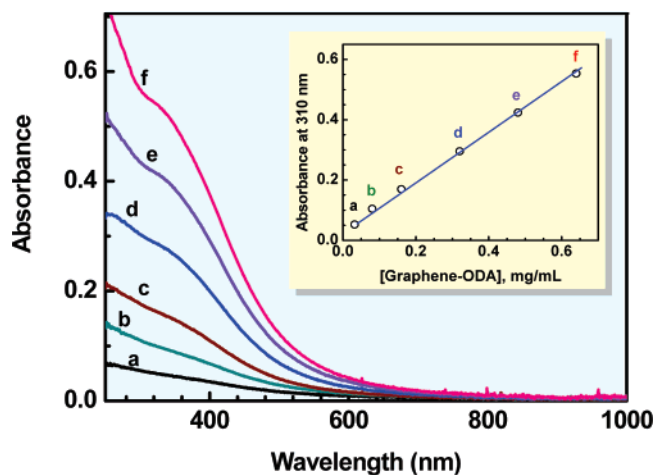
Figure 1. Absorption spectra of gaphene-oda (0.025−0.65 mg/mL) in THF. The concentration of each spectrum is identified in the inset.
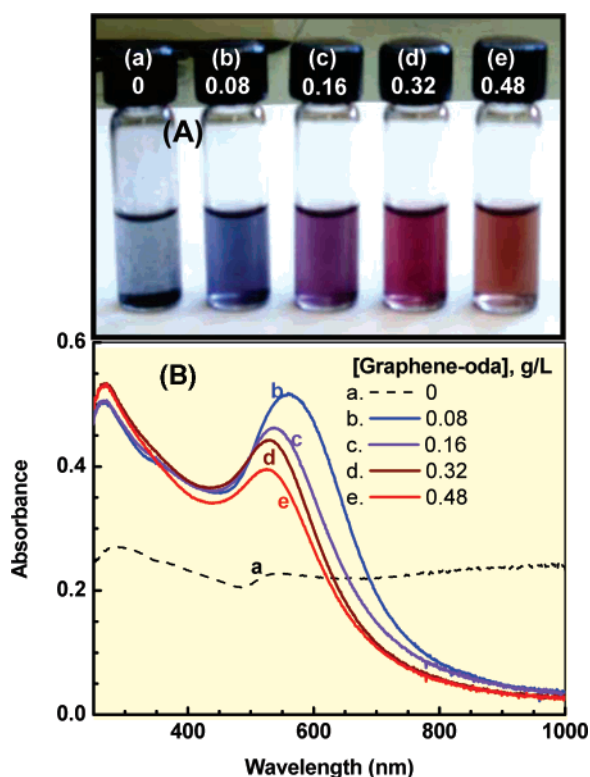

Figure 2. Photograph (top) and absorption spectra (bottom) of 1 mM gold nanoparticles in THF containing different concentrations of graphene−oda.

subjecting it to spectroscopic and microscopic analysis. All concentrations of gold nanoparticles described in this paper are expressed in terms of atomic (Au) concentration. A photograph and spectra of five different suspensions of gold nanoparticles synthesized using different amounts of graphene-oda are shown in Figure 2, panels A and B, respectively. In the absence of graphene−oda, the gold nanoparticles aggregate, and these unstable particles slowly settle to the bottom. At a low graphene concentration (<0.1 mg/L), the gold particles show rather broad absorption (spectrum b in Figure 2A) as these particles remain suspended but in the aggregated state. The observed blue color and broad absorption of the plasmon band supports the existence of aggregates in the suspension. With increasing graphene concentration, the gold nanoparticles become dispersed as individual particles, and we observe a pronounced sharp surface

plasmon absorption corresponding to 10−20 nm size gold nanoparticles. At the highest graphene concentration (0.48 g/L) employed in the present study, we observe a dampening of the plasmon absorption band. As shown earlier,[29] the surface plasmon bands of gold nanoparticles are prominent when they attain a diameter greater than 5 nm in diameter. At relatively low diameter (∼2 nm), the feature of surface plasmon absorption of gold nanoparticles disappears. On the basis of the response of surface plasmon absorption, we expect the gold nanoparticles at higest graphene concentration (spectrum e in Figure 1) to be relatively small particles (diameter ≤5 nm). These absorption changes (Figure 2A) indicate that the graphene−oda plays an important role in dictating the size of gold nanoparticles. This important feature in turn enables us to modulate the surface plasmon absorption of gold−graphene composites.

Figure 3 shows scanning electron micrographs of the graphene film before and after modification of gold nanoparticles. The sample of graphene−oda suspension was dropcast on a carbon fiber paper (Torray paper), and selective areas with good contrast were sampled to record the images. It is evident from the micrographs in Figure 3, panels A and B, that the chemical functionalization method employed in the present study was satisfactory in separating individual graphene sheets. These 2-D sheets served as a foundation to disperse the gold nanoparticles as seen from the micrographs B in Figure 3. The TEM image of the sample (dropcast on a carbon grid) shows the particle distribution of gold nanoparticles. These images confirm our ability to achieve fairly uniform dispersion of gold nanoparticles on graphene sheets (see the Supporting Information for the dependence of particle size on the graphene concentration).

Based on the TEM analysis (see the Supporting Information), we estimate an average particle diameter of 11.7 (±3.4) nm for suspension prepared using 0.08 mg/mL of graphene−oda. When the concentration of graphene-oda was increased to 0.64 mg/mL, the gold particles were stabilized with a smaller diameter of 5.9 (±1.8) nm. This observation of decreasing gold particle size with increasing concentration of graphene−oda during $AuCl_4^-$ reduction is consistent with the trend observed in absorption spectra (Figure 2).

Figure 4 shows an AFM image of a graphene sheet modified with gold nanoparticles. The dispersion of the gold nanoparticles on the 2-D sheet of carbon can be visualized by the AFM image. The section analysis of the image indicates a background height of 1−2 nm which corresponds to the graphene flake thickness. The peaks seen in this section analysis (3−5 nm height of smaller peaks) correspond to the gold nanoparticles anchored on the graphene sheet. The AFM analysis further confirms our ability to achieve uniform distribution of 5−11 nm gold nanoparticles on micron scale graphene sheets. These results differ from an earlier study in which individual silver nanoparticles were encapsulated in a shell of graphite oxide nanoplatelets.[27]

It is important to note that an optimal concentration of graphene−oda is desirable for obtaining a good distribution and small size gold nanoparticles. Since the graphene−oda does not have any reactive functional groups, we do not expect chemical interaction to stabilize gold nanoparticle suspensions. It is likely that simple physisorption of gold nanoparticles on graphene sheets assist in achieving desired stability. Similar interaction was also noted in capping silver nanoparticles with graphene nanoplatelets.[27] We have also considered the possible role of ODA in providing stability to a gold nanoparticle suspension. Although the interaction of gold nanoparticles with amine groups of ODA has been shown to provide stability,[30,31] such functional

Letters

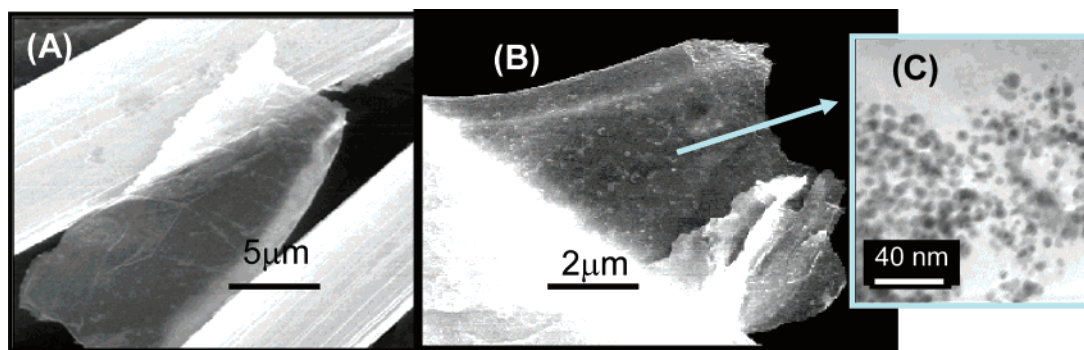*J. Phys. Chem. C, Vol. 112, No. 14, 2008* **5265**

Figure 3. Scanning electron micrographs of a graphene sheet anchored on carbon fiber paper. (A) Before and (B) after modification with gold nanoparticles (1 mM Au in 0.48 g/L graphene−oda). (C) High-resolution TEM of the sample in B (recorded separately by depositing on a carbon grid).
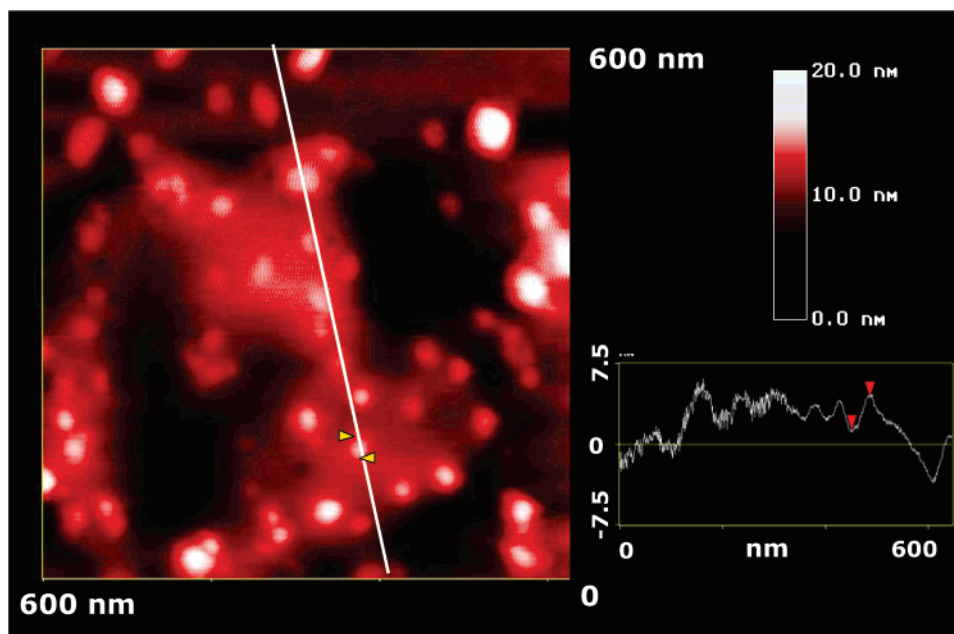

Figure 4. AFM image of gold nanoparticles anchored on graphene−oda. The cross section analysis shows the height of graphene and peaks arising from gold nanoparticles.

groups in the present case are terminated at the graphene site. Any stabilization occurred through the long hydrocarbon chain is expected to be minimum.

The surface plasmon band of metal particles as explained on the basis of Mie theory involves dipolar oscillations of the free electrons in the conduction band that occupies energy states immediately above the Fermi level.[32,33] Upon laser pulse excitation, these electrons do not oscillate at the same frequency and thus cause depletion in the plasmon absorption band. The recovery of the surface plasmon bleach of excited gold nanoparticles imbedded in different media is useful to probe the effect of the immediate surroundings. We employed femtosecond transient absorption spectroscopy (see the Supporting Information) to monitor the spectral changes associated with the laser excitation of gold nanoparticles. The transient spectra recorded 0.5 ps after 387 nm laser pulse excitation (pulse width 130 fs) for four different gold−graphene samples are shown in Figure 5A. All four samples show prominent plasmon bleach mirroring the absorption seen in Figure 2B.

The bleaching corresponding to the plasmon absorption shifts to blue with decreasing particle size. The plasmon bleach recovers with fast−slow kinetic processes. The initial plasmon bleach in the first few picoseconds is the result of the relaxation of hot electrons. As these electrons are relaxed, the phonon−phonon interaction facilitates long-term recovery of the bleaching.[34,35] This slower recovery step usually occurs over several nanoseconds and is dependent on the surrounding medium. In the present study we compared the fast recovery of the plasmon bleach for the four samples by monitoring the absorption at the wavelength corresponding to maximum bleach. The fast recovery for all samples was similar and completed in about 5 ps. The variation in the recovery of long time component was also not significantly different. The similarity in the kinetic recovery confirms that the optical properties of gold nanoparticles are not significantly influenced by the surrounding medium of graphene−oda. The ability of these composites to respond to laser excitation similar to other chemically stabilized gold particles is an important feature for their utilization in plasmonics and optoelectronic devices. Further efforts are also underway to utilize graphene sheets as support to disperse semiconductor and Pt particles and use them in solar cells and fuel cells, respectively.
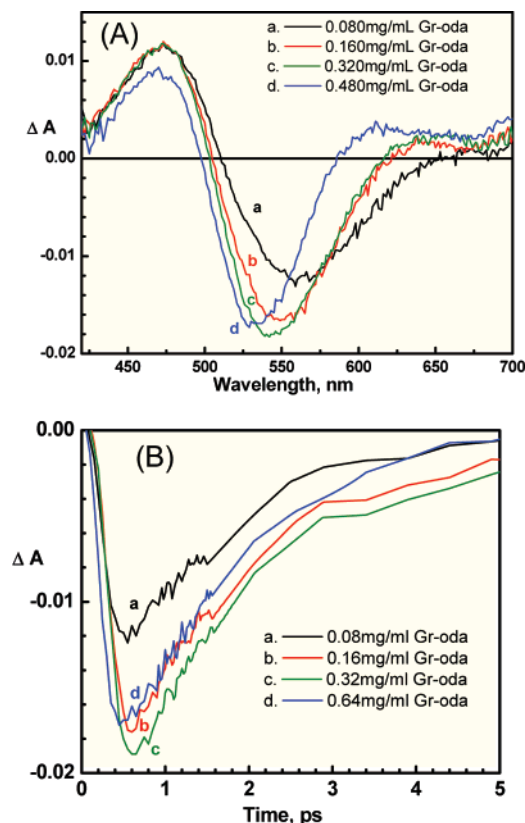
Figure 5. (A) Transient absorption spectra recorded 0.5 ps after 387 nm laser puse excitation of gold nanoparticles (1 mM) anchored on graphene-oda in THF suspensions. (B) Plasmon bleach recovery of the four samples as monitored at bleaching maximum.

discussions. This is contribution NDRL-4760 from the Notre Dame Radiation Laboratory.

Supporting Information Available: The experimental details of graphene oxide and graphene−oda synthesis and transient spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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