Controlled electrodeposition of gold nanoparticles onto copper-supported few-layer graphene in non-aqueous conditions

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ABSTRACT

Graphene-Au hybrid materials show promise for applications ranging from biosensing to field emission devices. Electrodeposition is an inexpensive, fast and technically simple method for controlled deposition of nanoparticles but its use with graphene prepared by chemical vapor deposition (CVD) presents some problems. Cu foil is commonly used to catalyze the CVD process and the resulting graphene is most conveniently handled while retained on the Cu support. However Cu is able to spontaneously reduce Au salts in aqueous solution and hence deposition of nanoparticles via galvanic displacement occurs simultaneously with electrodeposition, and control of the growth process is lost. We show here that Au nanoparticles can be controllably electrodeposited onto Cu-supported few layer graphene (FLG) from N,N-dimethylformamide (DMF) solutions of a $[AuCl_4]^-$ salt because spontaneous deposition of Au nanoparticles does not occur in this medium. Deposition occurs by the instantaneous nucleation mechanism when driven by an applied potential enabling the Au nanoparticle density to be controlled by the deposition conditions, predominantly the deposition potential. Following nucleation, nanoparticle growth is diffusion controlled. Our results demonstrate that the growth rate is similar in the presence and absence of an applied potential and control of growth time is key to controlling nanoparticle size.

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1. Introduction

Graphene, a two-dimensional material comprised of a single sheet of sp^2-hybridized carbon atoms [1–3], has numerous exciting properties which allow for a range of potential applications, from sensors to energy storage materials [2]. An ongoing area of research is the development of graphene-metal hybrid materials which give composites with additional properties [4]. Often, graphene is decorated with noble metal nanoparticles such as Au, Ag, Pt, and Pd [5]. Metal nanoparticles with sizes less than 100 nm may display different properties to the bulk material, hence hybrid graphene-nanoparticle composites offer the opportunity of combining the advantageous properties of both the graphene and the metal nanoparticles, as well as novel properties that result from interactions between two components.

Au nanoparticles are a popular choice for the development of graphene-metal nanoparticle hybrid materials [6]. Valcárcel et al. recently demonstrated that Au-decorated reduced graphene oxide (RGO) can function as a substrate for surface enhanced Raman spectroscopy (SERS), and used this for the detection of the antibiotic metronidazole [7]. Zhang et al. thermally evaporated Au nanoparticles onto graphene and demonstrated enhanced function as a field emission device [8]. Lee and coworkers used an in-situ chemical vapor deposition method for the preparation of Au nanoparticles encapsulated within few-layer graphene and utilized the material as a non-enzymatic glucose sensor [9]. Yong et al. used a graphene-gold system in plasmonic biosensing [10]. They found that by transferring graphene to an Au thin film, they could achieve a four-fold increase in sensitivity, compared to the Au film alone. They then showed a further order of magnitude increase by incorporating Au nanoparticles on to the graphene/Au surface. As a final example, Chen and Ju deposited Au nanoparticles onto nitrogen-doped graphene, and demonstrated a high sensitivity and selectivity for the electrochemical detection of hydrogen peroxide [11].

Clearly, graphene-Au nanoparticle composites have applications in a wide range of fields. Many of these applications are

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dependent on the size and morphology of the Au deposits, which are dictated by the deposition method. The traditional routes to make graphene-, graphene oxide (GO)- and RGO-Au composites use *ex situ* (mixing) or *in situ* (growth) methods to deposit particles, or wrap particles within, the graphene, GO or RGO sheets [6]. Solution phase methods have the advantage of simplicity, however spontaneous *in situ* growth methods can be difficult to control. In contrast, electrodeposition is a particularly useful method for introducing metal nanoparticles onto conducting substrates as varying the deposition parameters can readily control the morphology of the nanoparticles [12]. The majority of work involving Au electrodeposition onto graphene materials has been carried out using RGO supported on a conducting substrate such as glassy carbon (GC) [13–15]. RGO typically has a small particle size and a significant number of residual oxygen groups whereas graphene prepared via chemical vapor deposition (CVD) has a low oxygen content [16] and can have a large surface area [17,18]. CVD graphene is usually grown on a Cu foil catalyst [19] and is most easily handled before removal from the solid support. Hence it is desirable to undertake further functionalization procedures on the Cu-supported graphene.

Electrodeposition of Au nanoparticles is commonly carried out in aqueous conditions. For graphene supported on Cu this presents a significant challenge. In water, the standard electrode potential of the Au/$[AuCl_4]^-$ couple (+1.00 V *vs*. SHE) is more positive than that of the Cu/Cu^{2+} couple (+0.34 V *vs*. SHE) [20]. Thus the Cu support is able to reduce Au(III), resulting in galvanic displacement of Cu for Au [21]. Furthermore, Jung et al. [22] showed that RGO itself can the reduce $[AuCl_4]^-$ to Au(0) in aqueous solution. It is therefore possible that graphene is also able to spontaneously reduce $[AuCl_4]^-$. The operation of the galvanic processes makes it difficult to control the size of the Au deposits formed during electrodeposition in water, as both processes will occur simultaneously. Navarro et al. [23] recently demonstrated that applying a negative potential to the graphene/Cu working electrode prior to adding the metal salt precursor could prevent the spontaneous reaction and demonstrated this with Ag and Pd nanoparticles. An alternative approach for nanoparticle growth on graphene/Cu is to use non-aqueous conditions. The standard electrode potential of the Au/$[AuCl_4]^-$ couple in organic solvents is typically more negative than in water, due to the difference in solvation energy of the $[AuCl_4]^-$ ion [24]. For example, in 1,2 dichloroethane, the potential was calculated to be −1.14 V *vs* SHE [24]. Under these conditions, the chemical reduction of $[AuCl_4]^-$ by Cu is thermodynamically non-spontaneous, which allows better control of the deposit morphology, and prevents the Cu foil from being oxidized, and the graphene delaminating, during the deposition.

The goal of this work was to combine the advantages of electrodeposition with the convenience of working with graphene on its Cu support, to prepare few layer graphene (FLG) decorated with Au nanoparticles of controlled size and density. We show that in *N,N*-dimethylformamide (DMF), spontaneous deposition of Au nanoparticles on Cu-supported FLG does not occur, allowing exclusively potential-driven initiation of the deposition. After electrodeposition of Au, a PMMA-free method [16] was used to transfer the modified graphene from the Cu support to Si wafer for analysis. Electrodeposition from DMF is thus a simple and convenient strategy for controlled deposition of Au nanoparticles on FLG.

2. Experimental

2.1. Reagents and substrates

All chemicals were used as received. MilliQ water, resistivity >18 MΩ cm, was used to prepare electrolyte solutions and for cleaning samples. Tetraoctylammonium tetrachloroaurate (TOA) $[AuCl_4]$ was prepared by mixing TOACl and $HAuCl_4.3H_2O$ in ethanol, followed by recrystallization [25]. FLG was grown on a Cu foil coupon by atmospheric pressure (AP) CVD as described previously [16]. Si/SiOx wafers were cleaned in acetone and MilliQ water prior to use and then dried under N_2.

2.2. Electrochemical deposition of Au nanoparticles and transfer of FLG

Electrochemical depositions and measurements were made using an Eco Chemie Autolab PGSTAT302N potentiostat running Nova software. The working electrode was a 1 cm × 1 cm FLG/Cu coupon, with a Cu foil electrical contact. The Cu coupon has FLG on both sides, and both sides were exposed to the deposition solution. A Pt wire was used as a pseudo-reference electrode and a Pt mesh as the counter electrode. Electrodepositions were carried out in a solution of 0.36 mM (TOA)$[AuCl_4]$ and 0.1 M tetrabutylammonium perchlorate (TBAClO$_4$) in DMF. Prior to deposition experiments, a cyclic voltammogram (CV) was obtained (scan rate = 100 mV s^{-1}) in a separate solution, and with added ferrocene (Fc), using a Pt wire-working electrode to confirm the peak potential for $[AuCl_4]^-$ reduction and $E_{1/2}$ for the Fc/Fc$^+$ redox couple. $E_{1/2}$(Fc/Fc$^+$) was 0.10 V *vs* the Pt pseudo-reference electrode and it was assumed that the same $E_{1/2}$ applies at FLG/Cu allowing all potentials to be reported *vs* Fc/Fc$^+$. Note that a FLG/Cu working electrode was not used to obtain CVs of the Fc/Fc$^+$ couple to avoid possible complications from oxidation of Cu. Depositions of Au nanoparticles were carried out at fixed potentials of −0.4, −0.6 or −0.8 V for times ranging from 30 s to 10 min. After Au deposition, the FLG/Cu coupon was washed with fresh DMF and floated on 0.5 M aqueous ammonium persulfate solution for 15 min. The FLG was released from one side of the Cu coupon; this FLG was discarded. The coupon was then refloated, Cu-side down, on ammonium persulfate solution to remove the Cu. The ammonium persulfate solution was removed and replaced with MilliQ water to wash the sample [16]. For analysis, the FLG/Au sheet was collected onto a 1 × 1 cm^2 Si/SiOx substrate, then dried in air for 1 h and at 60 °C for 30 min [16]. Where the results of duplicate experiments are reported, samples were prepared separately beginning with FLG grown in different furnace runs.

2.3. Microscopy and spectroscopy

Atomic force microscopy AFM (Multimode 8 from Bruker, USA) topographical images were collected in peak force quantitative nanomechanical mapping (QNM) mode with scan assist activated with a Si cantilever (SNL-10). Square images were collected with 512 samples per line at a scan rate of 0.65 Hz. Particle height and density were measured using NanoScope Analysis software. The particle height was determined using the section tool. A line profile was drawn across a nanoparticle, and the height of the nanoparticle was taken as the vertical distance from immediately before the nanoparticle to the highest point on the particle. The heights of 15 individual nanoparticles over a 1 μm × 1 μm area were measured, and the average reported. Particle density was calculated using the particle analysis tool over a 2.5 μm × 2.5 μm area.

Scanning electron microscopy (SEM) images were collected using an FEI Quanta 650 ESEM-FEG operating in high vacuum at 20.0 kV.

Raman Spectroscopy was carried out using a Renishaw RM 264N94 (532 nm laser) spectrometer operating at power ≤ 1 mW. For each sample 3 spectra were recorded at 3 separate points on the sample, meaning the results listed are an average of 9 spectra for each sample.