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Surface modified graphene oxide nanosheets by gold ion implantation as a substrate for surface enhanced Raman scattering

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ABSTRACT

Graphene oxide (GO) nanosheets are the nanoscale building blocks for stabilization of metal nanoparticles with new hybrid nanocomposite properties. Here, we report on GO nanosheets implanted with low energy gold (Au) ion induced reactive sites for nucleation and intercalation of Au particles in a few layers of GO nanosheets. The nucleation and intercalation mechanisms were dependent on the doses of implanted Au ions in GO nanosheets. Atomic force microscopy (AFM) and Raman analysis of Au ion implanted GO nanostructure showed surface roughening and altered surface chemical states in GO nanostructure. We also observed that Au ion implantation induced reduction of GO surface as confirmed by X-ray diffraction (XRD) analysis and enhanced current-voltage (*I-V*) characteristics. Our study also indicated that the Au implanted-GO nanocomposites exhibited excellent surface enhanced Raman scattering (SERS) effects which can be used as an excellent SERS substrate.

1. Introduction

Graphene is a monolayer of sp^2-hybridized carbon atoms packed in a two-dimensional hexagonal lattice. Graphene possesses excellent thermal, mechanical, chemical, electronic and optical properties and has great potential applications in many fields such as biosensors, energy storage devices and catalysts [1,2]. Graphene-based hybrid nanocomposites have attracted large attention as potential nanoscale building blocks for new and novel materials with interesting properties for new applications [3]. Recently, hybrid graphene-based composites were synthesized using different materials, such as metal nanoparticles [3], boron nitride [4], metal oxides-based nanostructures [3,5] and multilayer graphene [3,6]. Among these nanocomposites, the impact in the association of graphene with Au metallic nanoparticles producing nanocomposites has been much of interest because of their potential applications in biosensing, energy devices, catalytic and environmental fields [7,8]. Recently, large numbers of studies reported on the synthesis of graphene/metal nanocomposites using various methods such as electrochemical deposition, metal evaporation and hydrogen reduction in metallic salts-graphite composites [9,10]. The strong interfacial interactions play an important role in order to chemically functionalize carbon-based materials in a controlled manner. This interaction allows the formation of a strong bond between the material and functionalized or deposited molecules. The adhesion of metal nanoparticles on the surface of graphene requires pre-functionalization of some organic spacer molecules as adhesives [10,11]. The organic spacers play a crucial role in immobilizing metal nanoparticles with graphene surfaces and further the graphene itself can be used as a template to control the nucleation of nanoparticles [10,12]. However, the chemical functionalization process requires organic molecules to react in multistep processing that give rise to unreacted residual molecules on the graphene surface, which makes it difficult to control physio-chemical properties of graphene-metal nanocomposites. Therefore, it is imperative to find possible alternative new physical methods, such as ion implantation to prepare graphene-metal nanocomposites without leaving any organic chemical residues on graphene surfaces.

Recently, there are many reports on simple metal nanostructures/thin-films that are good substrates for surface enhanced Raman scattering (SERS) including noble-metal-carbon nanostructure based composites [13–17]. Mostly of these reports utilize complex chemical method for the preparation of SERS substrate. Ion implantation technique is another unique and effective way to modify surface properties of carbon based materials that utilizes implantation of ions in a controlled manner [18]. Implanting Ni-ions into diamond-like carbon (DLC) films is shown to

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modify their sp^2 contents [19], while fluorine ion implantation lead to amorphization of few surface layers of carbon [20]. C^+ ions irradiation has been shown to introduce defects in graphene nanosheets [21]. However, Ti ion implantation results in enhanced adhesion between DLC films [22]. More recently, a few studies showed improved physico-chemical properties in graphene layers by Ti, N, B and C ions implantation [23–25]. Ion irradiation can also dope and cut the graphene controllably [26] that could open the band gap by introducing foreign atoms into the bilayer graphene [27]. Furthermore, molecular dynamics (MD) simulations and first-principles calculations demonstrated that the intercalation of different elements such as B, N, C, Au or other transition elements resulted in an opening of band gap due to changes of impurity states and or knocked C forms a C-C dumbbell defect in graphene layers [28–30].

In this study, we reported the use of Au ion implantation to modify the surface properties of graphene oxide substrate for surface enhanced Raman scattering (SERS). Our results revealed that the low energy gold ion implantation induced reduction of GO and favors nucleation and intercalation of gold ions in a few layers of GO nanosheets. The Au ion implanted GO nanocomposite exhibited altered physico-chemical properties that were characterized by a combination of tools, such as AFM, XRD, Raman and *I-V* characteristics. The Au ion implanted GO nanostructures exhibited reduction of GO, altered the nanostructure properties and enhanced *I-V* characteristics as compared to un-implanted GO nanostructure. The Au ion implanted GO nanocomposite also exhibits efficient SERS characteristics and potentially serves as an excellent SERS substrate. Our results showed that ion implantation is an effective route to modify the surface properties of GO controllably for a variety of future optical, biological and electronic applications.

2. Experimental section

2.1. Preparation and characterization of few layers of GO on substrate

Engineered GO (<4 layers; 1–15 nm thickness; surface area 700 m^2/g, diameter 2 μm) was purchased from Carbon Solutions Inc., USA. GO suspension was prepared in *N*, *N*-Dimethylformamide (DMF) and homogenized using probe ultrasonicator. The homogeneous stock suspension of GO was spin-coated on the silicon substrate. The GO-coated substrate was further annealed at 170 °C for 1 h. After spin coating of GO on substrate, a surface profiler (KLA-TENCOR P6 Surface Profiler) was used to measure the step height difference between the coated and bare region. The center and a portion at edge of the substrate was covered with a hydrophobic tape (1 mm diameter) to create the step-height difference on the same surface. The spin coated GO structure was characterized by attenuated total reflectance-IR (ATR-IR -Nicolet iS10, Thermo Scientific, USA).

2.2. Au ion implantation in GO nanosheet layers

Au ion implantation on GO nanosheets was carried out using low energy ion beam (LEIB) facility at Inter University Accelerator Center, New Delhi. The low energy ions were produced using electron cyclotron resonance ion source (ECR NAnogan Panteknik). Here, 100 keV Au ions were implanted in spin coated GO nanosheets at various fluences ranging from 5×10^{11} to 1×10^{14} ions/cm^2. The electronic, nuclear energy stopping power and projected range for 100 keV Au ions in the sample were calculated using SRIM (Stopping and Range of Ions in Matter-2003) [31]. The electronic stopping power $(dE/dX)_e$, nuclear stopping power $(dE/dX)_n$ and projected range were found to be 87.45 eV/Å, 315.85 eV/Å, and ~37 nm, respectively.

2.3. Material characterizations

Optical imaging (Carl Zeiss Axio Scope) and Atomic Force Microscopy (AFM, Nanoscope) were employed to investigate the surface morphology of GO before and after Au ion implantation. In order to investigate the structure and composition of the samples, Raman spectra were recorded using Renishaw Raman spectrometer (excitation wavelength of 532 nm with spectral resolution of 5 cm^{-1}). Powder X-ray diffraction (Bruker D8 DISCOVER, GmBH) was recorded using Cu Kα radiation counter ($\lambda = 1.5406$ Å) at 40 kV. Spectra of Au implanted GO was obtained using Ultraviolet–visible (UV–vis) spectrophotometer (Thermo Scientific). For *I–V* characteristics measurements, gold was deposited to form the electrodes on GO sample surface and *I–V* characteristics of the pristine and Au ion implanted GO nanosheets were measured using a Keithley 6571B electrometer. SERS measurements were carried out on pure and implanted GO surface using Rhodamine 6G (R6G) dye and related experimental procedure is given in the supplementary information (SI).

3. Results and discussion

3.1. Thickness and FTIR characterization of a few layers of GO on substrate

Thickness of spin coated GO surface was measured to ensure the homogeneity of GO coated surface. The step height surface profile of surface coated GO nanosheets showed the thickness of ~50 ± 4 nm (Fig. S1a). Fig. S1b shows FTIR spectra obtained for substrate and a few layers of GO coated on substrate. The peaks observed at 1150 and 1012 cm^{-1} are due to presence of Si-O-Si bonds [32]. The FTIR spectra of a few layers of GO showed a strong and broad absorption peak at 3400 cm^{-1} due to the O–H stretching vibration (Fig. S1b). The C=O stretching peak was observed at 1730 cm^{-1} and the peak at 1620 cm^{-1} which is attributed to C=C stretching vibration of carbon skeleton vibrations in control sample. The peak at 1400 cm^{-1} is assigned to tertiary C–OH groups. The peak at 1216 cm^{-1} represents stretching of C–O–C and the peak at 1082 cm^{-1} corresponded to C–O groups [33,34]. The FTIR results provided a clear evidence of the presence of different types of oxygen functionalities and confirm coating of GO nanosheets on substrate surface.

3.2. Optical and AFM characterization of GO nanosheets before and after Au ion implantation

The optical images GO nanosheets before and after implantation of Au ions at different fluences are shown in Fig. 1a–d. The implanted GO nanosheets initially appeared relatively flat surface with occasional protuberances and corrugations (Fig. 1b–c). Au ions implanted GO nanocomposites showed minor structural damages or defects in a few GO-layers at a fluence of 5×10^{14} ions/cm^2 (Fig. 1d).

Surface topology of pure GO nanosheets (unimplanted) and GO nanosheets implanted with Au ions at the fluences of 5×10^{11} and 5×10^{14} ions/cm^2 were acquired by using a tapping mode AFM (Fig. 2a–c). Pure GO nanosheets appeared smooth with uniform distribution of GO nanosheets in 3D and 2D AFM images (Fig. 2a, (i-iii)). The root mean square (RMS) roughness and average roughness measured from histogram profiles of pure GO nanosheets were found to be 1.18 nm and 0.95 nm, respectively (Fig. 2a(iii)). However, the surface of pure GO nanosheets transformed into relatively