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Short Communication

Preparation of Graphene/Silver Nanohybrid Composite with Good Surface-Enhanced Raman Scattering Characteristics

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Graphene and graphene/siver nanocomposites were synthesized by the reduction process in a facile one pot method. Raman spectroscope, TEM, UV-vis and XRD were used to characterize the composites. The results indicate that the silver nanoparticles were successfully composited on the graphene sheets and the size of silver particles range from 10 to 20 nanometers. In Raman characterization, the intensity of the composite speaks would increased with the ratio increasing of silver nitrate to graphene oxide, and the SERS reached the most obviously when the ratio was 3:1. However, the Raman intensity will decrease when the silver nitrate was too much.

Keywords: Graphene; Ag nanoparticles; Nanocomposites; Raman characteristics

1. INTRODUCTION

Graphene(GN), which is a two-dimensional carbon plane with one-atomic thickness, has attracts great attention recently due to its excellent optical, electrical, mechanical and thermal properties. Etc[1-5]. However, the graphene is easily agglomerate due to Van der Waals force between the sheets. In this way, introduction of various nanoparticles into a graphene-based matrix is an important study for the investigation of their properties and applications. Among these various nanoparticles, silver (Ag) nanoparticles have attracted much more research attention due to their wide applications and unique properties in biosensing, catalysis, chemical sensing, electronics, and photonics [6-8]. In recent years, the nanocomposites based on Ag nanoparticles decorated on GN surface are reported by various research groups by different synthetic procedure with their different applications. Shanmugharaj et al. synthesized graphene-silver nanoparticles hybrids using eco-friendly microwave radiation and characterized the electrochemical performances [9]. Wang et al. reported GN-Ag nanocomposite prepared by one-pot reduction of both Ag+ and graphene oxide, and studied their electrochemical oxidation of methanol in alkaline solution [10]. Gao et al. prepared the paper like Gr-Ag nanocomposite films synthesized by in-situ reduction of graphene oxide films with Ag+ using ascorbic acid and investigated their mechanical and electrical properties [11].

The characterization and analysis for low content sample are difficult due to the weak intensity for Raman scattering. Thus the Raman enchancement technology gets more and more attention. The Raman enchancement includes resonance Raman scattering(SERS) and surface Raman enchancement. Recently, many studies have been done to obtain graphene–metallic nanomaterials for SERS. These hybrids show great promisefor applications in SERS. Ren et al. reported a sensitive SERSsubstrate for folic acid detection using graphene oxide/Ag nanopar-ticle hybrids [12]. Ag nanoparticles has strong UV-vis adsorbtion and local surface plasmon resonance effect and has brilliant future in both of SERS and nonlinear optics. Nie[13] and his coworkers found Ag nanoparticles have a obvious Raman enhancement when the excitation light lies in 514 and 633nm. Qian[14] and his coworkers prepared the graphene/Ag nanocomposites in covalent assembly process and the enchancement factor can be as high as 5.04×10^7. Xie put the SERE in detection for food disable additive and had gotten good effect. However, the graphene/silver nanocomposites prepared in different methods have some problems such as many defects of graphene and Ag nanoparticles distributing non-uniformly[15-17]. In our previous study[18], we discussed the synthesis of graphene/metal nanocomposite film with good dispersibility via solvothermal method. In this paper, we combine the sodium borohydride and sodium citrate to prepare the composites and solve the agglomeration for both of graphene and Ag nanoparticle and its non-uniform. Many methods have been used to characterize the graphene and its silver nanocomposites such as, UV-vis, FT-IR, SEM, TEM, XRD, Raman and so on.

2. EXPERIMENT SECTION

2.1Materials

Graphite powder(99wt.%) was purchased from Qingdao Da Yu grahite Co. Potassium permanganate($KMnO_4$), sulfuric acid(H_2SO_4)(98wt.%), hydrochloric acid(HCl)(35wt.%) were purchased from Shanghai AiBi Chemistry Preparation Co.LTD. Hydrogen peroxide(H_2O_2)(30wt%), potassium peroxydisulfate($K_2S_2O_8$)(99wt.%), phosphorus pentoxide(P_2O_5)(99wt.%), sodium borohydrite(99wt.%), sodium citrate(99wt.%) and silver nitrate(99wt.%) were purchased from Tianjin Guangcheng Chemical Reagent Co. LTD. Deionized water was used as solvent throughout the experiments.

2.2 Preparation of graphene/silver nanocomposites

We used the improved Hummers method to synthesize the graphene oxide(GO)[19]. Fig.1 is the schematic illustration of the reduction process of graphene and graphene/silver nanocomposites. Then 100mg graphene oxide was put into 100ml deionized water with ultrasonic process for 1 hour.

0.55g sodium citrate with silver nitrate for different amount of 0mg, 20mg, 50mg, 100mg, 200mg, 300mg, 1000mg were added into the solution repectively with another ultrasonic process for 0.5 hour to obtain a homogenous suspension. After stirring for 30min, 0.5g sodium borohydrite was put into the solution, the temperature was raised to 100℃ and retained at this temperature for 9 hours. The solid product was obtained after filtrating, washing and drying in a vacuum at 55℃ for 24 hours. Then the solid obtained was put into 100ml 50% dilute sulfuric acid with ultrasonic for 1 hour and then the solution was put into a 500 ml three- neck flask. After violent stirring for 30min, the temperature was raised to 100℃ and retained at this temperature for 12 hours. The solids were obtained after filtrating, washing many times with deionized water and dring in a vacuum at 55℃ for 24 hours. The products were named GN/Ag(0), GN/Ag(20), GN/Ag(50), GN/Ag(100), GN/Ag(200), GN/Ag(300), GN/Ag(1000).

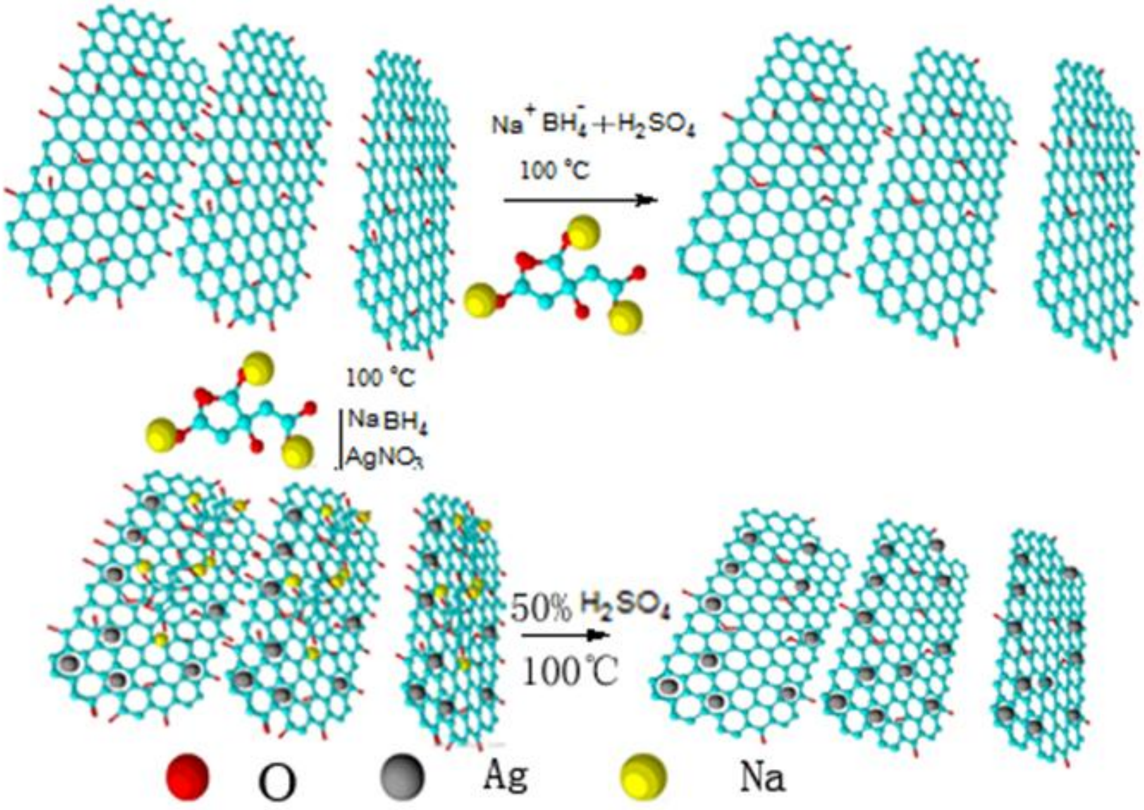

Figure 1. Schematic illustration of the reduction process of graphene and graphene/silver nanocomposites

2.3 Characterization

Transmission electron microscope(TEM) measurements were performed on a JEOL2011 TEM(JAP) with an accelerating voltage of 80kV and Scanning electron microscopy(were performed on a JSM-6390LV) SEM(JAP) with an accelerating voltage of 20Kv. XRD data were measured on a

D8 Advance X-ray Diffractometer(Bruker, Germany) with a Cu Kα X-ray radiation source. SERS spectra were collected with a Renishaw inVia model confocal microscopy Raman spectromenter(Renishaw, UK). A 532nm laser was used for SERS excitation.

3. RESULTS AND DISCUSSION

The morphologies of graphene and graphene/Ag nanocomposites were investigated by SEM at the same magnification. Fig.2A shows the surface morphologies of graphene. It can be observed that the sheets of graphene are much plainful, and there are obvious drapes between the sheets, Which attribute to the cross linking effect of π-π bonds which are easily to make the graphene stack in layered structure. Fig.2 B shows the graphene/Ag hybrid composites. Compared with the pury grphene, the graphene sheets of composites are much disorganised and curl randomly. There are many holes between the sheets and the sheets separate obviously. This is as a result of the effect between the silver nanoparticles and graphene sheets[20]. On one hand, the graphene sheets can act as the carrier for the attactment of silver particles and the barrier to keep them from agglomerating. And on the other hand, when the particles attach to the sheets, they can also prevent the agglomeration of graphene sheets.

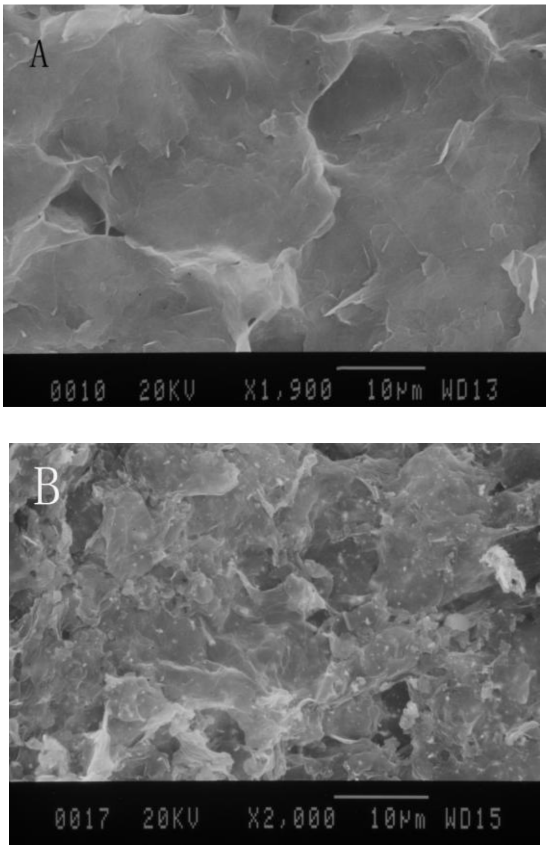

Figure 2. SEM images of graphene(A) and graphene/Ag nanocomposites(B)

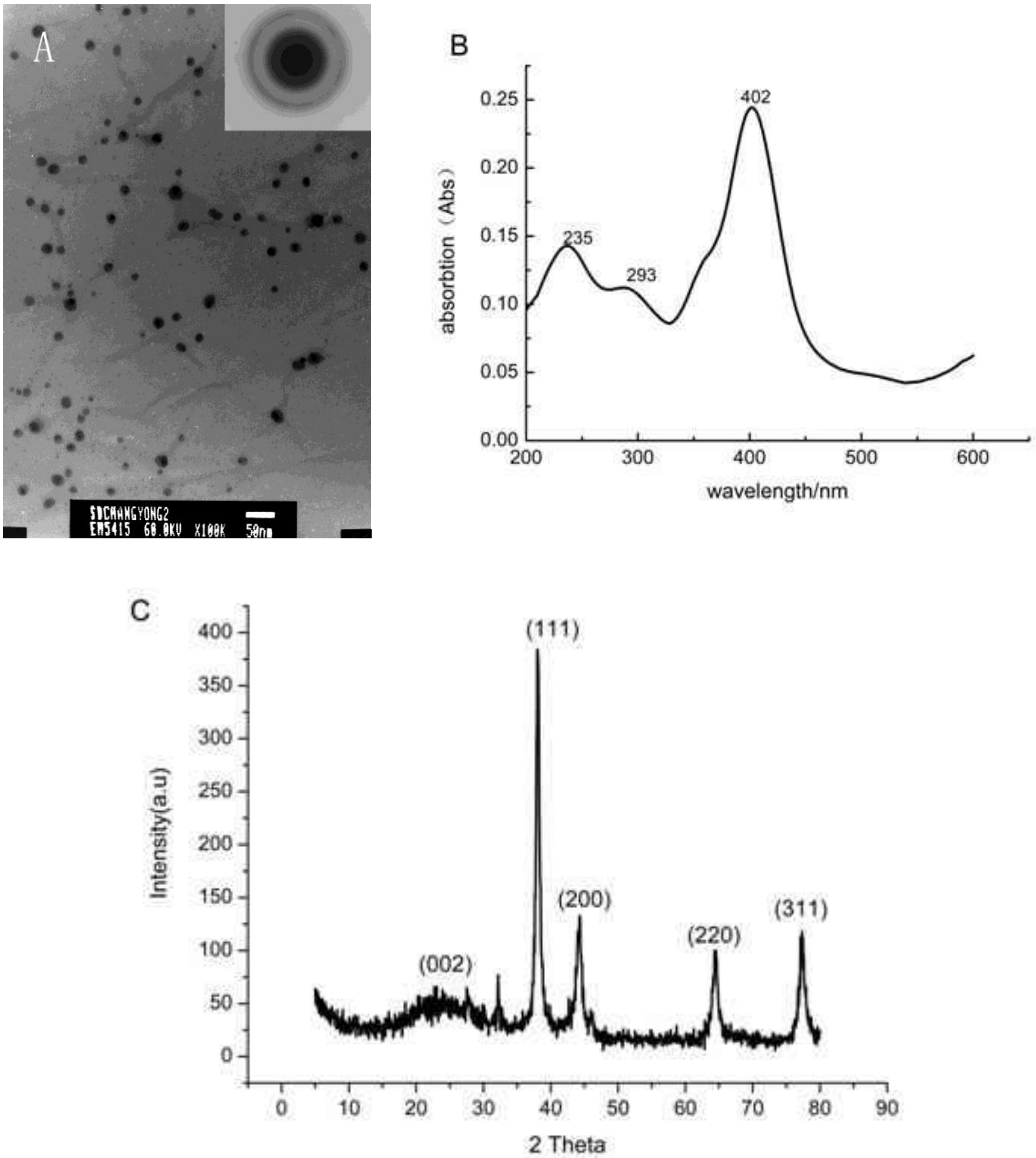

Figure 3. TEM (A), UV-vis(B) and XRD(C) image of graphene/Ag nancomposites.

Fig. 3 A shows TEM image of graphene/Ag nanocomposites. It is observed that Ag NPs homogeneously and densely attach to the surface of graphene nanosheets with a typical diameter of 10-20nm, and the folds can be observed. It exhibits its mono- or multi-layer planar sheet- like morphology[21]. And from the inset of FFT analysis, single crystal can been seen. The measured interplanar spacing for the lattice fringes is 0.23nm, which corresponds to the (111) lattice plane of Ag. Fig 3 B shows the UV-vis absorption spectra of aqueous dispersion of graphene/Ag nancomposites. A quite strong peak of 402 nm is observed which is a characteristic peak of silver nanoparticles and due to the surface plasmon absorption[22]. And its location and shape are related with particle size and distribution. Fig 3 C shows the XRD patterns of GO sheets and graphene/Ag nanocomposites. four diffraction peaks corresponding to the (111), (200), (220), and (311) crystalline planes of sliver present at 2θ = 38.1°, 44.3°, 64.4°, and 77.5°, respectively. These results indicate that silver NPs were attached on the graphene surfaces. And a weak peak at 23.5° can be observed which corresponds to the (002) crystalline plane of graphene. It is due to the damage of the crystal structure.

Raman spectroscopy is a useful non-destructive tool to distinguish ordered and disordered carbon structures. There are four characteristic peaks for carbon materials and they are D, G, 2D, G^* respectively. The signal of D band is caused by the defects of hexgon carbon atom ring, which can be ascribed to the first-order zone boundary phonons that is absent from defect-free graphene. G band is correspond to the in-plane vibration of sp2 carbon atoms related to the first order scattering of E2g mode[23, 24]. As shown in Fig 4, ID/IG for GO, GN and GN/Ag increases gradually. It is different with the previous understanding that after reduction the defect can be removed and the crystal and conjugate structure can be repaired[25]. It is due to that the oxidation process has already damage the crystal structure for carbon materials. Although the reduction and dehydration process can remove some oxygen functional groups and the hydroxy groups become to olefin. However, the stacking during the reaction makes the graphene sheets much more disorder.

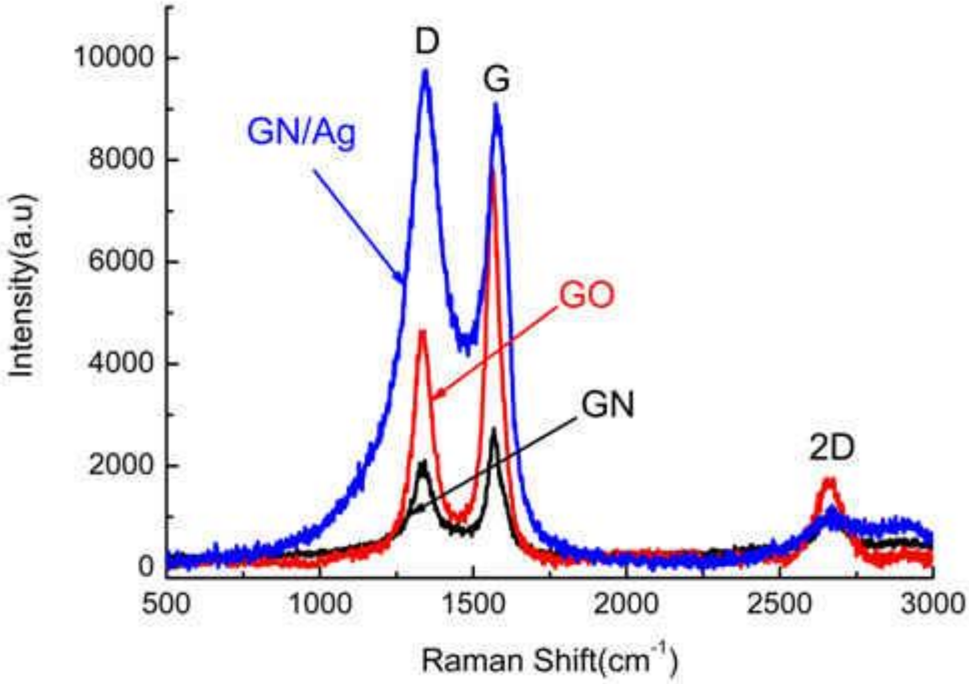

Figure 4. Raman spectra of graphene oxide(GO), graphene(GN), graphene/Ag nanocomposites(GN/Ag)

The Raman spectra of graphene and its silver composites with different silver nitrate addition are shown in Fig.5. The dark line is corresponding to the graphene and the other six lines are for composites. Compared with pure graphene, when the silver nitrate is 20mg, the intensity of D band increase from 1994 to 12167 and the ratio is 6.1:1. With the increasing of the silver nitrate addition, the intensity of both D band and G band increase and when it is 300mg, that is the weight ratio for silver nitrate and graphene oxide is 3:1, the intensity increases the most. And at this time, the D band is 22.1 times to that of graphene and G band is 15.3 times. These result from two reasons. Firstly, the interaction between surface of silver particle and excitation light make the field effect of graphene increase. The resonance of silver surface make the electron on graphene surface transfer much more easily and at the same time the big oscillation form in partial electric field. Secondly, the wave function between graphene and silver overlap in each other. But the increasing is not linear with the increasing of silver nitrate addition. When the weight of silver nitrate is 50mg, the intensity of G band and D band is weaker than when it is 20mg. The same situation is also suitable when it is 1000mg. The reason may result from the different agglomeration for the silver nanoparticles. The agglomeration of silver nanoparticles have great affect for the raman enchanced activity. The intensity of raman enchanced signal depends on the raman excitation plot and the more nanoparticles, the more excitation plot and thus the stronger of the raman intensity [26]. However, when the silver nanoparticles are excess, the two points which are list before will decrease which is also caused by the agglomerated silver nanoparticles.

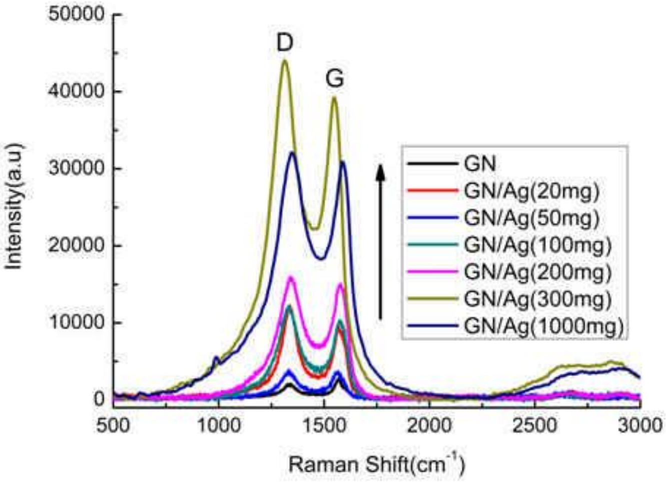

Figure 5. Raman spectra of graphene/Ag nanocomposites with different silver nitrate addition.

4. CONCLUSIONS

In conclusion, Ag nanoparticles were successfully composited onto the graphene sheets. To find out the optimize weight ratio of silver nitrate and graphene oxide for the SERS, different silver nitrate additon was tried and the result shows, when the silver nitrate addition increases, the G band and D band of graphene in raman test both increase and when the weight ratio is 3:1, the effect is the most obvious. And at this time, the intensity for D band for composites is 22.1 times as that for pury graphene and the G band is 15.3 times. When the silver nitrate increases once again, the intensity will decrease.

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