

Green preparation of Ag nanoparticles/graphite nanosheets composite

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A simple chemical edge doping method to prepare the Ag nanoparticles/graphite nanosheets (Ag/GNS) composite is presented. The GNS were fabricated in water with the assistance of a high pressure homogenisation (HPH). Ag nanoparticles (Ag-NPs) were decorated on GNS by edge doping. HPH was proved to be an efficient way to fabricate GNS with active sites to anchor metal nanoparticles in the authors' work. The Ag/GNS composite synthesised by edge doping barely had any defects. The average diameter of the Ag-NPs in this case was 52.6 nm. It was observed that the fabricated Ag-NPs distributed mainly on the edge of GNS where the active sites were. The Ag/GNS composite exhibited a distinct surface-enhanced Raman scattering effect with a low concentration of silver. The Ag-NPs on the composite had improved stability (up to a month). It is believed that this simple and green method of nanocomposite preparation will shed some lights on the large-scale production of metal-nanoparticles-decorated carbon matrices.

1. Introduction: Metal nanoparticles decorated carbon matrices have attracted much attention for their unique structure and excellent properties [1, 2]. Usually, carbon matrices are functionalised, as the functional groups could provide anchoring sites for metal nanoparticles [3, 4]. However, the functionalisation process involves using toxic reagents and it destroys the original carbon matrices' structure. Recently, Brenner *et al.* [5] showed that naturally occurred defect sites had higher chemical doping efficiency than defect-free sites on the 2-dimensional (2D) graphene sheets. Thus, the idea of creating defects on carbon matrices to enhance the efficiency of decorating metal nanoparticles is feasible. However, the existing methods to fabricate graphene is not only time and energy consuming, but also harmful to the environment, it is thus considered not desirable for commercial application [6, 7]. Recently, a scalable and eco-friendly method to synthesise few-layer graphene and graphite nanosheets (GNS) through a high pressure homogeniser (HPH) has been proposed [8, 9]. HPH has been widely used in food production to improve product quality [10]. In our study, liquid phase exfoliation of graphite by HPH shows its potential in producing high quality GNS in big quantity. It is observed that graphite can be exfoliated and cleaved easily under high shear stress effect, cavitation effect and impact effect of HPH. The GNS fabricated through this way exhibit large specific surface area, available defects, excellent mechanical strength, high electrical and thermal conductivity which together made it an ideal kind of carbon matrices to decorated with metal nanoparticles [11, 12].

In 1974, Fleischmann discovered that the Raman signals of pyridine which absorbed at a roughened silver electrode had been enhanced [13]. Then researchers found that surface-enhanced Raman scattering (SERS) can be generated on transition metals as well as on noble metals [14]. Among these above metals, Ag nanoparticles (Ag-NPs) has higher enhancement factor (EF) however its chemical instability limited its long-term use [15, 16]. Recently Ag nanoparticles has been reported to support on graphene nanosheets for SERS and the hybrid material not only acquired a high chemical stability but also preserved or even enhanced the SERS properties of the Ag nanoparticles [17, 18].

Herein, we fabricated the GNS in a simple, efficient and green HPH way using water as the liquid exfoliating medium. We took advantage of the high chemical doping efficiency of the naturally produced defects on GNS to decorate the Ag-NPs on GNS

through an edge doping mechanism. We observed the morphology of the Ag/GNS composite and studied edge doping mechanism and the basic properties of Ag/GNS composite. To examine the SERS effects of Ag/GNS composite, we used Rhodamine B (RhB) as probe molecule.

2. Experimental

2.1. Materials: Graphite powder (>99.95%) with an average diameter of 45 μm was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Sodium borohydride (NaBH_4 , A.R. > 98.00%) was provided by Damao Chemical Reagent Co., Ltd. (Tianjing, China). Silver nitrite (AgNO_3 , A.R. > 99.8%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). RhB was supplied by Tianxin fine chemical development centre (Tianjin, China). All reagents were used as received without further purification. All aqueous solutions were prepared with deionised water.

2.2. Synthesis of Ag/GNS composite: GNS was obtained by a HPH process. First, 0.5 g graphite was dispersed in 400 ml deionised water and stirred for 20 min. Then transferred the suspension to the high-pressure homogeniser (Ningbo Scientz Biotechnology Co., Ltd., Ningbo, China) with constant stirring at 80 MPa followed by six batch runs, this HPH process takes ~ 15 min. The GNS suspension was obtained.

Ag nanoparticles were decorated on GNS to produce corresponding composite. Briefly, silver nitrite (AgNO_3) solution (4.8 $\text{mmol}\cdot\text{l}^{-1}$, 25 ml) was first mixed with freshly prepared GNS suspension (1.25 mg/ml, 200 ml) and sonicated for 1 h using a VGT-1730QT ultrasonic cleaner (China). Then sodium borohydride (NaBH_4) (6 mg/ml, 10 ml) was added slowly and agitated by a magnetic stirrer at room temperature for 1 h, heated to 50°C for 1 h, then, heated to 70°C for 1 h. The resulting nanocomposite was designated as Ag/GNS. Following this procedure, the reference sample with graphite as carbon matrices was also decorated with Ag-NPs, corresponding composite was designated as Ag/graphite

2.3. Experiment for SERS effect: The sample for SERS measurement was prepared as follows: Ag/GNS composite was soaked in ethanol solutions of RhB (1×10^{-6} , 1×10^{-5} , 1×10^{-4} $\text{mol}\cdot\text{l}^{-1}$) for 12 h, then washed with deionised water. The resultant sample was dried at 60°C and measured by the Raman microscope (Renishaw series RM2000) with an excitation wavelength of 514

nm. The exposure time of each SERS spectrum was 10 s with five accumulations.

2.4. Characterisation: The phase composition of Ag/GNS composites was characterised by XRD (X'Pert PRO X-ray diffractometer) using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 300 mA. The surface morphology was examined by FESEM (Nova NanoSEM430 ultra high resolution field emission scanning electron microscope) and the surface composition was examined by an EDS appurtenance (Oxford XMax 20 Energy Dispersive Spectrometer). The structure and element composition of graphite, GNS and Ag/GNS composites were characterised by Fourier-transform infrared spectroscopy (Bruker Vector33 FTIR), samples were mixed with KBr for analysis, the spectra were collected with the resolution of 4 cm^{-1} after 32 continuous scans with the wavenumber in the range of $400\text{--}4000 \text{ cm}^{-1}$. The structure and element composition of graphite, GNS and Ag/GNS composites were further characterised by XPS (Axis Ultra DLD X-ray Photoelectron Spectroscopy/ESCA) and Raman spectra (LabRAM Aramis Laser Confocal Raman Microscope) with a He-Ne laser (excitation wavelength of 633 nm) at room temperature.

3. Results and discussion: Figs. 1*a* and *b* showed the FESEM images of Ag/graphite and Ag/GNS composite. As shown in Fig. 1*a*, Ag-NPs fell on graphite sheets randomly and aggregated. By contrast, in Fig. 1*b*, Ag-NPs were supported on and inserted into both sides of the GNS and the edge of GNS had higher concentration of Ag-NPs than in-plane which was in accordance with the distribution of defects on GNS. The different Ag-NPs distribution on graphite and GNS indicated that the newly emerged edge C-atoms created by HPH process has higher efficiency for anchoring Ag-NPs. The ultra-thin GNS in Fig. 1*b* suggested that graphite was exfoliated by HPH and the thickness is $\sim 10 \text{ nm}$. Fig. 1*d* showed the magnification of the Ag nanoparticles on Ag/GNS composite, and the cubic particle shape could be observed. The EDS spectrum for Ag/GNS composite in Fig. 1*e* showed three elements: C, O and Ag, which suggested that the synthesised sample had less impurities. The histogram of Fig. 1*c* showed the particle-size distributions of the Ag-NPs on Ag/GNS composite based on the FESEM image (Fig. 1*b*). It demonstrated that the average Ag-NPs size was 52.6 nm and the Ag-NPs had a narrow diameter distribution.

Fig. 1*f* showed the XRD pattern of Ag/GNS composite. The XRD reflection peak at $2\theta = 26.52^\circ$ and $2\theta = 54.84^\circ$ represented

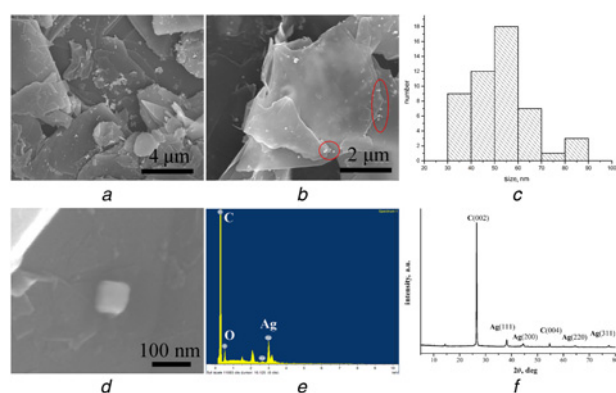


Fig. 1 FESEM images of
a Ag/graphite
b, d Ag/GNS composite
c Corresponding particle size distribution on Ag/GNS composite
e EDS spectrum of Ag/GNS composite
f XRD patterns of Ag/GNS composite

the hexagonal structure of graphite. The diffraction peaks at $2\theta = 38.15^\circ, 44.35^\circ, 64.45^\circ, 77.40^\circ$, corresponded to the (111), (200), (220) and (311) crystalline planes of Ag crystal, respectively. It matched very well with the face-centred cubic (fcc) structured Ag (JCPDS Card No. 04-0783) [19]. The absence of Ag $_2$ O reflections indicates that Ag crystal was not oxidised [20].

Fig. 2 showed the FTIR spectra of Graphite, GNS and Ag/GNS composite. They all showed strong absorption at 1579 cm^{-1} , which represent the carbon skeletal vibration. Besides, GNS and Ag/GNS composite had a weak absorption at 1713 cm^{-1} which was possible ascribed to carbonyl group indicated that GNS was slightly oxidised. The Ag/GNS composite showed a weaker oxidation peak than GNS indicated that the Ag/GNS composite was reduced. In addition of the slightly oxidised of GNS, the weak adsorption of FTIR spectra of GNS and Ag/GNS composite at 1713 cm^{-1} may also be caused by the error of the FTIR spectroscopy.

Fig. 3 showed the Raman spectra of bulk graphite, GNS and Ag/GNS composite. The Raman spectra was obtained using a He-Ne laser (633 nm) as the irradiation light source. In Fig. 3, a D band (1328 cm^{-1}), a G band (1573 cm^{-1}), a 2D band (2672 cm^{-1}) and a tiny D' band (1608 cm^{-1}) could be observed. The D band was caused by the vibration of sp^3 -bonded carbon atoms and other defects. The D' band was usually reported as disordered graphitic lattice. The G band was related to the vibration of sp^2 -bonded carbon atoms. The intensity ratio of D band to G band was marked as $I_{D/G}$, which indicates defects content. GNS showed higher $I_{D/G}$ (0.13) than graphite (0.088), but lower than reduced graphene oxide (rGO) ($\sim 1.1\text{--}1.5$) [21]. This confirmed that HPH process created defects on GNS and the defects content was relatively low. For Ag/GNS composite, the D and D' band disappeared, indicating that Ag/GNS composite nearly had no defects. The decrease of defects may result from the passivation of defects when Ag-NPs was doped. The intensity ratio of G band to 2D band was marked as $I_{G/2D}$ and the $I_{G/2D}$ of GNS (2.75) was lower than graphite (4.04). The G band of GNS and Ag/GNS were blue shifted. The decreased $I_{G/2D}$ intensity ratio and blue shifted G band of GNS both implied successful exfoliation of graphite [22, 23].

Fig. 4*a* showed the XPS survey spectra of graphite, GNS and Ag/GNS composite which was placed for a month. The C1 s, O1 s, and Ag3d peaks could be seen at 284.6, 532 and 372 eV, respectively. The difference in C/O atomic ratio between graphite (62.69) and GNS (11.85) demonstrated that GNS contained more oxygen-containing groups after HPH than pristine graphite, but far less than rGO (~ 7.54) [3, 24]. The Ag3d XPS spectrum of the Ag/GNS composite (Fig. 4*b*) exhibited two characteristic peaks at 368.6 and 374.6 eV, corresponding to the binding energies of Ag3d $_{5/2}$ and Ag3d $_{3/2}$ of silver, respectively. The splitting of the 3d doublet of Ag was 6.0 eV, indicating the formation of silver [25]. The un-oxidised silver of Ag/GNS composite (one month old sample) indicates that the stability of Ag-NPs on Ag/GNS

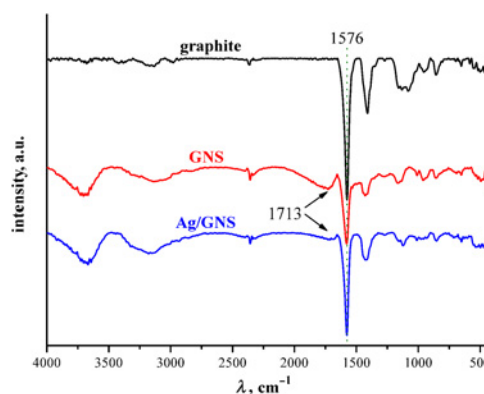


Fig. 2 FTIR spectra of graphite, GNS and Ag/GNS composite

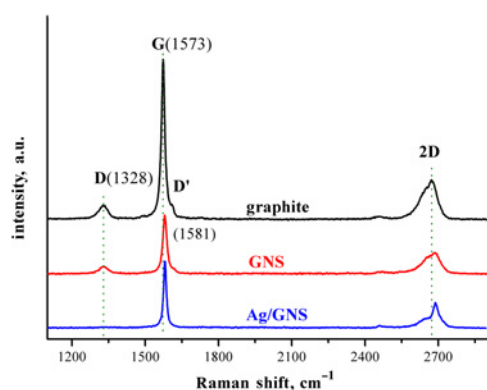


Fig. 3 Raman spectra of graphite, GNS and Ag/GNS composite

composite was improved compared with the instable Ag-NPs. This may be explained by that the interaction between Ag-NPs and GNS affected the electric field distribution of Ag-NPs. The silver content of Ag/GNS composite was 0.03%, lower than other Ag doped rGO nanocomposite [3, 26]. The C1 s XPS spectra of GNS shown in Fig. 4c exhibited five fitting curves centred at 284.6 eV (C=C/C-C), 285.4 eV (C-OH), 286.3 eV (C-O-C), 287.2 eV (C=O), respectively [3]. These evidences, together with the results of FTIR in Fig. 2, indicated that during the HPH process in water, a few amount of oxygen-containing functional groups anchored on the defect sites of GNS. Compared with the C1 s spectrum of GNS, the C1 s spectrum of Ag/GNS composite (Fig. 4d) exhibited a decreased intensity at high bonding energy and the increased content of C=C/C-C, indicated that the combined oxygen groups on GNS has been reduced and the conjugated structure of GNS was restored. This was consistent with the FTIR and Raman spectra results.

From the above characterisation, the possible reaction mechanism was demonstrated in Fig. 5. First, graphite was exfoliated and tailored by HPH and produced defects (new edges) on GNS. The defect (new edge) carbon atoms had higher reactivity than in-plane and easily combined with oxygen-containing groups in water which provided active sites for Ag^+ ions to anchor. After the Ag^+ ions were added in the suspension, the Ag^+ ions soon

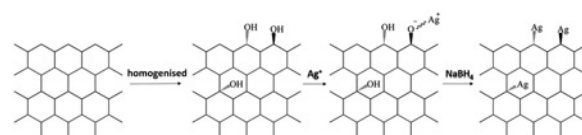


Fig. 5 Schematic procedure of the formation of Ag/GNS composite

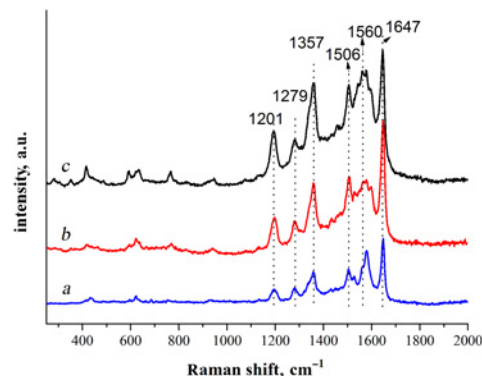


Fig. 6 SERS spectra of different concentrations of RhB absorbed on Ag/GNS

a $10^{-6} \text{ mol}\cdot\text{l}^{-1}$
b $10^{-5} \text{ mol}\cdot\text{l}^{-1}$
c $10^{-4} \text{ mol}\cdot\text{l}^{-1}$

combined with the defects. The Ag^+ ions and the oxygen-containing groups on GNS was reduced simultaneously after reducing reagents added and formed the Ag/GNS composite. The concentration of Ag-NPs decorated on GNS was related to the defects.

As we known, roughened silver and silver nanoparticles could enhance Raman signals [13]. Ag-NPs had higher EF compared with other metal but its chemical instability limited the long term use [16]. Recently, researchers found that Ag-NPs hybrid material not only acquired a high chemical stability but also preserved or even enhanced the SERS properties of the Ag-NPs [17]. In this Letter, the SERS effect of Ag/GNS composite was investigated with RhB as the probe molecules. The strong fluorescence of RhB made it invisible in Raman spectra.

Fig. 6 showed the Raman spectra of RhB absorbed on Ag/GNS composite, the main peaks of RhB including 1201, 1279, 1357, 1506, 1560 and 1647 cm^{-1} can be identified. 1201 cm^{-1} is assigned to C-H in-plane bending of the aromatic ring. 1279 cm^{-1} is caused by C-O-C stretching. 1357, 1506, 1560 and 1647 cm^{-1} are caused by C-C stretching of the aromatic ring. The Ag/GNS composite as the SERS substrate could eliminate the strong fluorescence and enhance the Raman signal of RhB. The Raman spectral intensities also declined with the decrease concentration of RhB (Figs. 6a-c).

The SERS is related to the content of Ag-NPs and the oxidation of Ag-NPs [3, 17]. On one hand, The Ag/GNS composite showed a good stability up to a month according to the XPS analysis (Fig. 4b), whereas, the Ag-NPs without GNS are easily oxidised. On the other hand, the composite could enhance the Raman signal efficiently at a low Ag-NPs content. Clearly, the Ag/GNS composite can be used as an efficient SERS substrate for the detection of organic pollutants and trace detection.

4. Conclusion: The GNS fabricated by HPH in water showed the ability to decorate with Ag-NPs which utilised the naturally occurred defects on GNS. Compared with the functionalisation procedure to fabricate the carbon matrices that decorated metal nanoparticles, HPH process presents many merits such as efficient, eco-friendly, scalable and low defects. The Ag-NPs decorated mainly on the edge of the GNS and the Ag/GNS

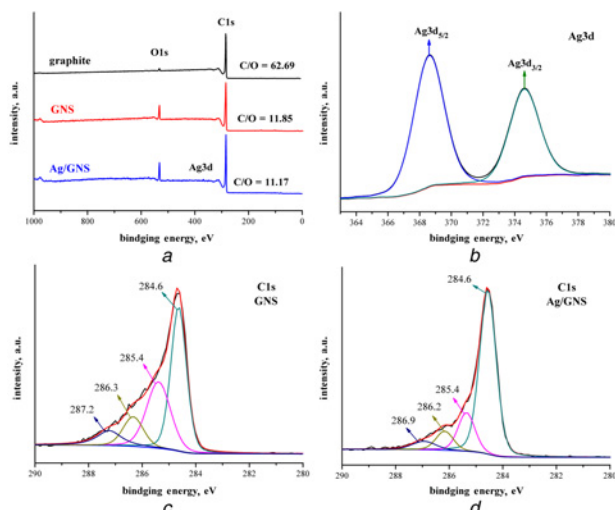


Fig. 4 XPS spectra of graphite, GNS and Ag/GNS composite which was stored for a month

a XPS survey spectra of graphite, GNS and Ag/GNS composite which was stored for a month
b Ag3d XPS spectra of Ag/GNS composite which was placed for a month
c C1 s XPS spectra of GNS
d C1 s XPS spectra of Ag/GNS composite

composite showed nearly no defects which was different from the other metal-nanoparticles-decorated carbon matrices. With this method, the stability of Ag-NPs on Ag/GNS composite were improved and low Ag-NPs content of Ag/GNS composite was able to enhance the Raman signals distinctively.

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6 References

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