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# The structure change of graphene with few layers via microwave irradiation for different time

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**Abstract** : A series of graphene products have been prepared through mechanical milling, oxidation treatment and microwave irradiation processes. Various measurement results demonstrate that the products are the graphene nanosheets with few layers and little oxygen content due to not any  $\text{KMnO}_4$  treatment. Under the same experimental condition and procedures, the corresponding products with additional  $\text{KMnO}_4$  oxidation have also been obtained, and the compared measurements show that the products not only exhibit better dispersion, but also have much

more oxygen content. Raman spectra reveal that the G-peak of the products appears splitting into  $G^-$  and  $G^+$  peaks owing to a phonon symmetry breaking at  $\Gamma$  point, and the intensity ratio of the D to  $G^+$  peak for the products without  $\text{KMnO}_4$  oxidation treatment gradually lowers with prolonging microwave irradiation time within 48 min, indicating the decrease of the structural defects. © Global Scientific Inc.

**Keywords** : Graphene; Defects; Raman; G-peak splitting.

## INTRODUCTION

Graphene has recently attracted enormous attention due to its potential applications in energy storage fields, nanocomposites, sensors, nanodevices and catalyst support<sup>[1-3]</sup>. In general, the applications need scalable graphene nano-sheets with perfect structure. It is well known that a large quantity of graphene can be obtained from graphite oxide through a reduction reaction<sup>[4,5]</sup>, but there are concentrated structure defects in the sheet lattice. To simply and largely prepare graphene with few defects, mechanical milling method has been used. For example, based on this technique, there are

some papers to report the preparation process and characteristic of the grapheme<sup>[6-10]</sup>, and whereas the prepared product still shows relatively much more layers as compared to the graphene obtained by Hummers method. We have known that the exfoliation of graphene should overcome and break the Van der Waals forces between graphite layers mainly through a high energy transformation from surroundings (e.g. sonication or ball-milling) or an oxidation of carbon atoms (e.g. chemical functionalization). However, only mechanical activation difficultly exhibits efficient preparation process in the exfoliation of graphene with few layers and defects, and thereby another preparation pro-

cess including mechanical activation should be designed. Herein, mechanical milling combined with oxidation reaction and microwave irradiation treatment is considered to obtain high-quality graphene with few layers.

Based on the preparation of the graphene only with few layers, a Raman spectroscopy technique has been used to investigate the structure change of the prepared graphene. It has been confirmed that Raman spectroscopy technique is a kind of powerful tool providing a nondestructive and reliable method to obtain a complete set of information about graphene, including identifying thickness<sup>[11]</sup>, measuring strain<sup>[12]</sup> or thermal conductivity<sup>[13]</sup>, and investigating the electronic and structural properties and so on. The structure change of graphene can be analyzed mainly by its feature D and G peaks, such as intrinsic or extrinsic defects, generally studied by the intensity (integrated area of peak) ratio of D and G peaks ( $I_D/I_G$ )<sup>[14]</sup>.

In the paper, powder graphite was first mechanically milled for a short time, and then oxidized in a solution with a little bit concentrated  $H_2SO_4$ ,  $HClO_4$  and acetic acid. For a comparison, a certain amount of  $KMnO_4$  is also used and added into the solution under the same condition to prepare additional products. Subsequently, all of the products were performed under microwave irradiation for different time to investigate the corresponding structure discrepancy. Raman spectra confirm that the intensity ratio of D to  $G^+$  peak gradually decreases with prolonging microwave irradiation time within 48 minutes for the products without  $KMnO_4$  treatment, and whereas such ratio for the later products barely changes due to the strong oxidation of  $KMnO_4$ .

## MATERIALS AND METHODS

### Preparation procedure

A mixture of flake-like graphite, NaCl and  $NH_4Cl$  was first ground through a mechanical milling process. Then, the milled sample was added into a solution with concentrated  $H_2SO_4$ ,  $HClO_4$  and acetic acid at room temperature to react for many hours. As comparison, another sample was also prepared through an oxidation reaction of the milled sample with a mixture including concentrated  $H_2SO_4$  and  $KMnO_4$  under the same condition. After washed with water and dried for a long time, the two products were treated separately under microwave irradiation for 0, 6, 24, 48 and 60 min, respectively, to obtain two series of samples (denoted as GO-1, GO-2, GO-3, GO-4 and GO-5 without  $KMnO_4$ ; denoted as GO-k1, GO-k2, GO-k3, GO-k4 and GO-k5 with  $KMnO_4$ , respectively). The schematic preparation process has been shown in Figure 1.

### Characterization

The samples were characterized by powder X-ray diffraction (XRD) with a Shimadzu XRD-6000 diffractometer equipped with monochromatic high intensity  $Cu K_\alpha$  radiation ( $\lambda = 0.1541$  nm) at 40 kV and 100 mA. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) were recorded on JEOL JSM-6490 and JEOL JEM-2010, respectively. Fourier Transform infrared spectroscopy (FTIR) was performed on Nicolet Avater-370. Raman spectroscopy was measured on HR 800 with 633 nm radiation with an output power of 8 mW.



Figure 1 : Schematic process of graphene oxide with few layers.

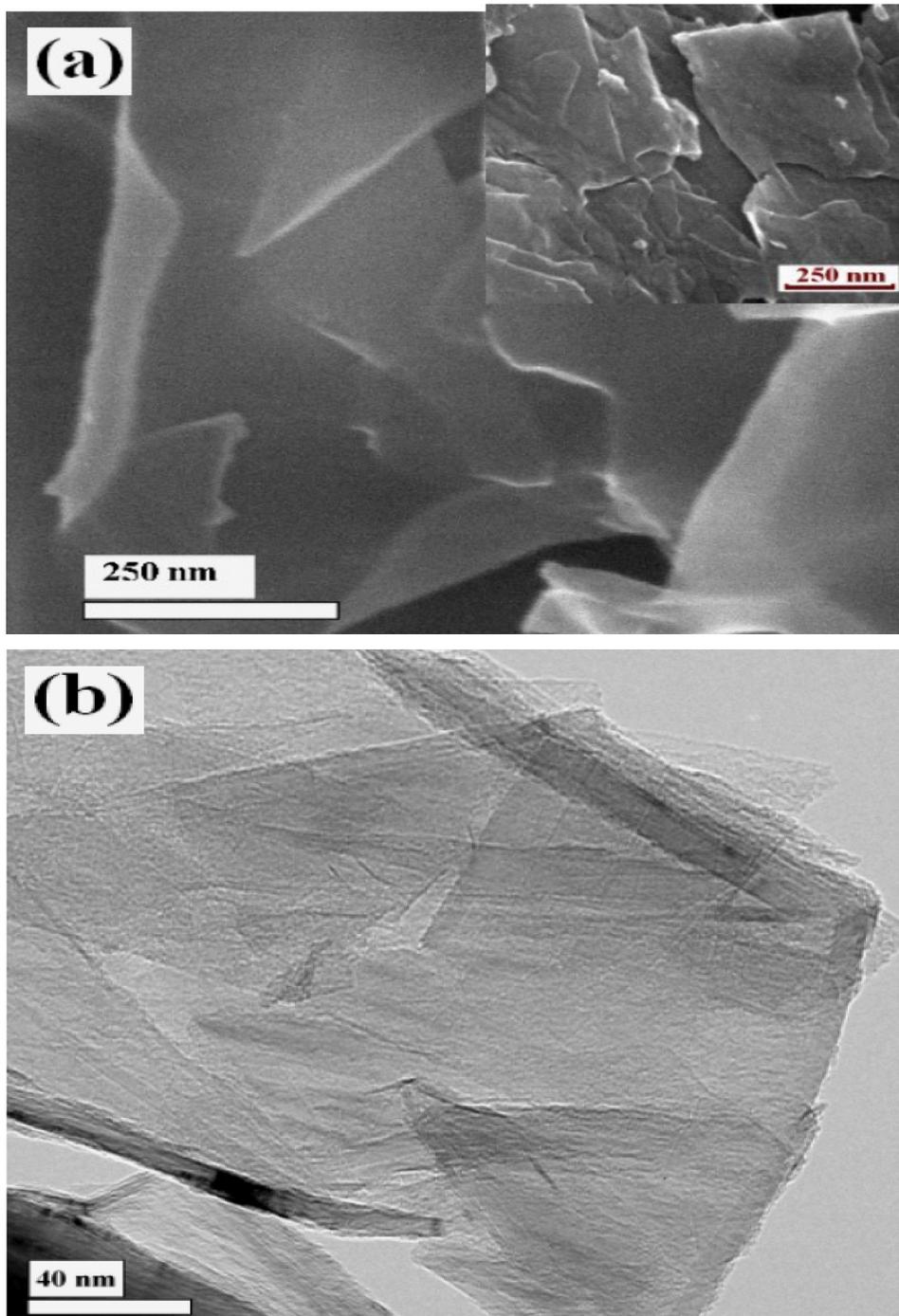
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## RESULTS AND DISCUSSION

The SEM and TEM images of the pristine graphite, GO-1 and GO-5 were first acquired as shown in Figure 2. From the edges of the graphite flakes in the inset of Figure 2(a), the average thickness shows about many tens of nanometer or much thicker owing to the connection of the flakes with each other. Through a series of simple treatment, the thickness of the GO-1 and GO-

5 becomes notably thinner, evincing the nanosheets only with few layers. It is also demonstrated that one hour of microwave irradiation barely changes the size and thickness of the nanosheets.

The XRD patterns and XPS profiles of the pristine graphite, GO-5 and GO-k5 are displayed in Figure 3. The graphite shows a very strong (002) peak at ca.  $26.4^\circ$ , much far higher than that of the GO-5, in which a weak shoulder peak at ca.  $26.1^\circ$  attributed to (004)



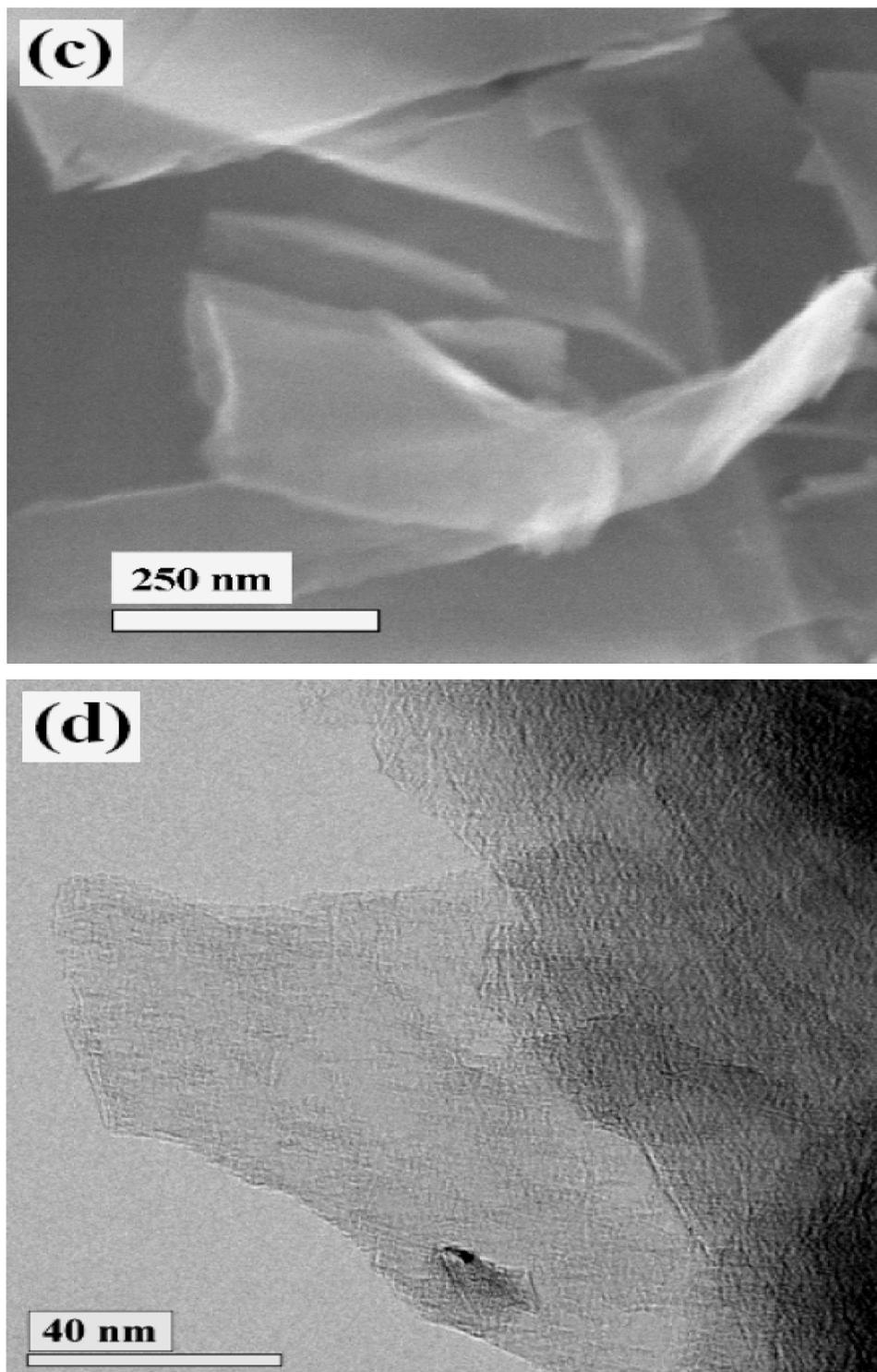


Figure 2 : SEM and TEM images of the pristine graphite (inset), GO-1 (a, b) and GO-5 (c, d).

plane also appears on the left of the (002) peak, deducing that the nanosheets in GO-5 have become much thinner and the distance between the nearest neighboring layers has partly exhibited longer<sup>[15]</sup>, in good agreement with the SEM and TEM measurements. How-

ever, the (002) peak for the GO-k5 (the inset in Figure 3(A)) not only obviously broadens and weakens, but also shows an asymmetric shape due to the mixture of amorphous and nanocrystalline phases, inferring that the addition of  $\text{KMnO}_4$  remarkably enhances the oxida-

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tion reaction of graphite during preparation process, also supported by the following XPS measurements.

In Figure 3(B), the change of C1s binding energy for the three samples can be observed. The C1s band of the GO-5 located at  $\sim 284.8$  eV for carbon atoms in C=C for unoxidized structures, similar to that of the graphite, mainly exhibits one component. Also, some carbon atoms for the two samples have been partly oxidized due to the asymmetric shape of the peak. Therefore, we can elicit that it is not efficient to oxidize carbon atoms without an addition of  $\text{KMnO}_4$ . If a little bit  $\text{KMnO}_4$  is added, much more carbon atoms can be obviously oxidized, proved by the C1s bands at  $\sim 286.7$  and  $288.6$  eV, assigned to the carbon atoms singly

bonded to oxygen in hydroxyl/epoxy groups and carbon atoms in C=O, respectively<sup>[4,16]</sup>.

To further investigate the change of the functional groups of the five products, the FTIR spectra as shown in Figure 4 have been performed. The peaks shown in the range of  $1000\text{--}1750\text{ cm}^{-1}$  mainly correspond to C-O stretching vibration, C-OH stretching vibration, C-O-H deformation vibration and C=O stretching of COOH groups situated on GO sheets, in which the peak at  $1640\text{ cm}^{-1}$  is attributed to C=C skeletal stretching vibrations of unoxidized  $\text{sp}^2$  carbon atoms<sup>[17]</sup>. However, all these peaks tend to decrease after the treatment of microwave irradiation, revealing the oxygen-containing functional groups were gradually removed,

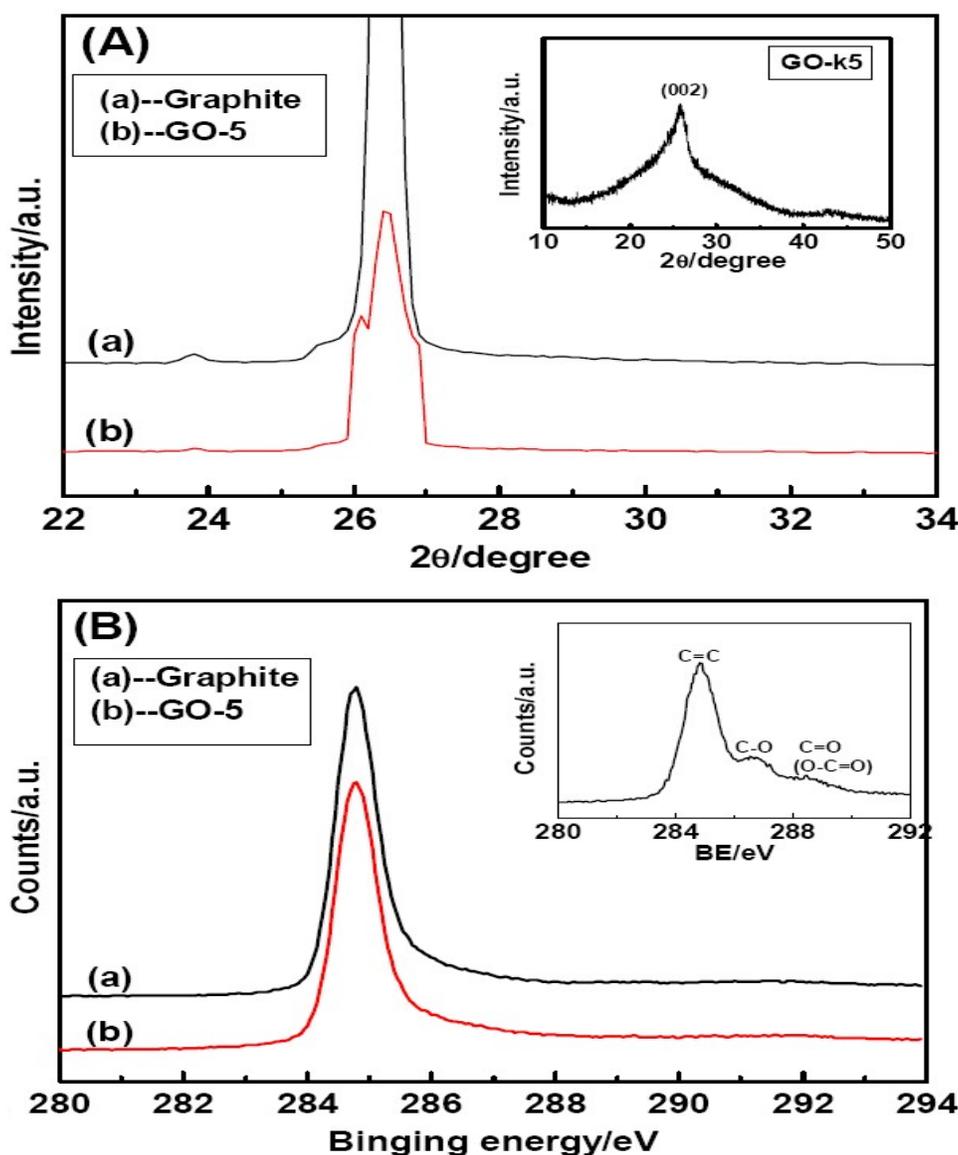


Figure 3 : XRD patterns (A) and C1s XPS profiles (B) of the pristine graphite, GO-5 and GO-k5.

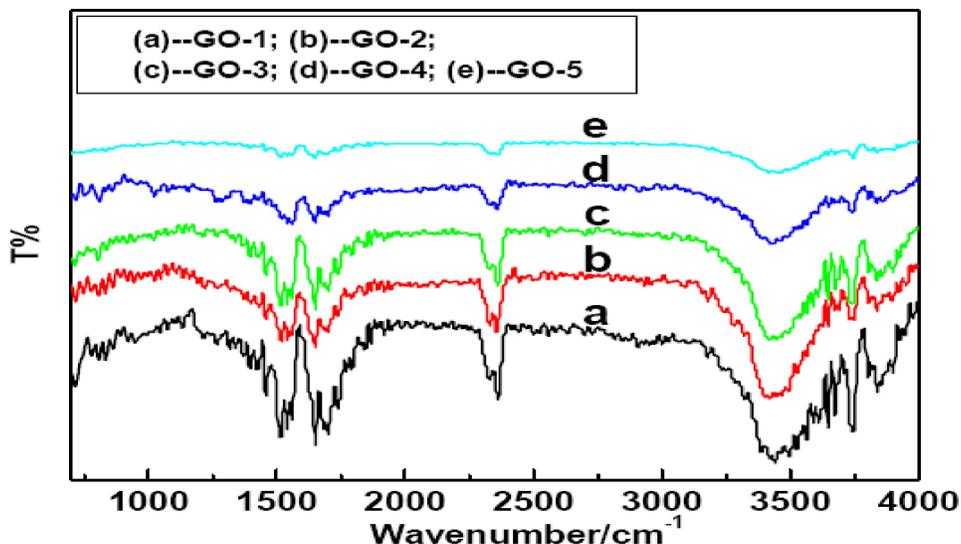


Figure 4 : FTIR spectra of the GO-1 (a), GO-2 (b), GO-3 (c), GO-4 (d) and GO-5 (e).

and thus further demonstrating the partial reduction of GO in this treatment process.

Evolution of the Raman spectra for the two series of products obtained under microwave irradiation is illustrated in Figure 5. The main features in the spectra are the D band at ca.  $1312\text{ cm}^{-1}$ , activated by finite size effect, grain-boundaries or defects, and G band at ca.  $1579\text{ cm}^{-1}$ , corresponding to in-plane carbon atom stretching vibrations, respectively<sup>[18-20]</sup>. It can be found that the D band intensity in Figure 5(A) is much weaker than the corresponding G band in the same spectrum, while the D band intensities in Figure 5(B) are relatively much stronger, showing that there exist many defects in the samples. The positions of the D and G bands of these products have barely shifted, implying that the tensile strain or compression in lattice structures is very similar.

In addition, a shoulder peak at ca.  $1554\text{ cm}^{-1}$  exists on the left of the G band in every Raman spectrum, and such peak becomes obviously stronger due to  $\text{KMnO}_4$  oxidation effect. This is a splitting behavior of the G band, termed as  $G^+$  (high wavenumber) and  $G^-$  (low wavenumber), corresponding to a mixing of the symmetric and antisymmetric combination of G modes due to a phonon symmetry breaking at  $\Gamma$  point<sup>[21,22]</sup>. Li and co-workers have also reported the splitting phenomenon after many aromatic molecules were adsorbed on graphene<sup>[23]</sup>. The splitting behavior of G-peak demonstrates the existence of a band gap, which gradually increases with the growth of  $G^-/G^+$  intensity ratio<sup>[24]</sup>. In addition, a defect-activated  $D'$  peak on the right of the

$G^+$  peak, partly covered in the  $G^+$  peak, can also be dimly observed.

It should be stressed that the D-peak intensity gradually drops with the microwave irradiation time from 0 up to 48 min for the products from the GO-1 to GO-4, and then slightly rises, and correspondingly, the intensity ratio of the D to  $G^+$  peak ( $I_D/I_{G^+}$ ) shows the same change tendency; whereas the  $I_D/I_{G^+}$  value barely changes after 6 min of microwave irradiation due to the  $\text{KMnO}_4$  oxidation. It has been reported that microwave irradiation can reduce graphene oxide owing to the deoxidation effect<sup>[25]</sup>. Density functional theory (DFT) calculation revealed that epoxy groups are much more instable than hydroxyl groups in GO<sup>[26]</sup>, and also Gao et al. demonstrated that hydroxyl groups attached to the inner aromatic domain are much more instable than those attached to the edge<sup>[27]</sup>. Hence, the epoxy or hydroxyl groups within the graphene sheets may be easily extirpated under microwave irradiation, and whereas the structure appears partly disorder due to the weakening of the  $G^+$  peak.

In order to further investigate the cases, especially the effect of  $\text{KMnO}_4$  oxidation on the sheet structure, the GO-k5 was again treated in hydrazine solution at  $200\text{ }^\circ\text{C}$ , and then heated under microwave condition for different time to produce four samples, measured by Raman technique shown in the Figure 6. It has been verified that to some extent, microwave treatment can lower the intensity of the D-peak within 6 min, indicating the

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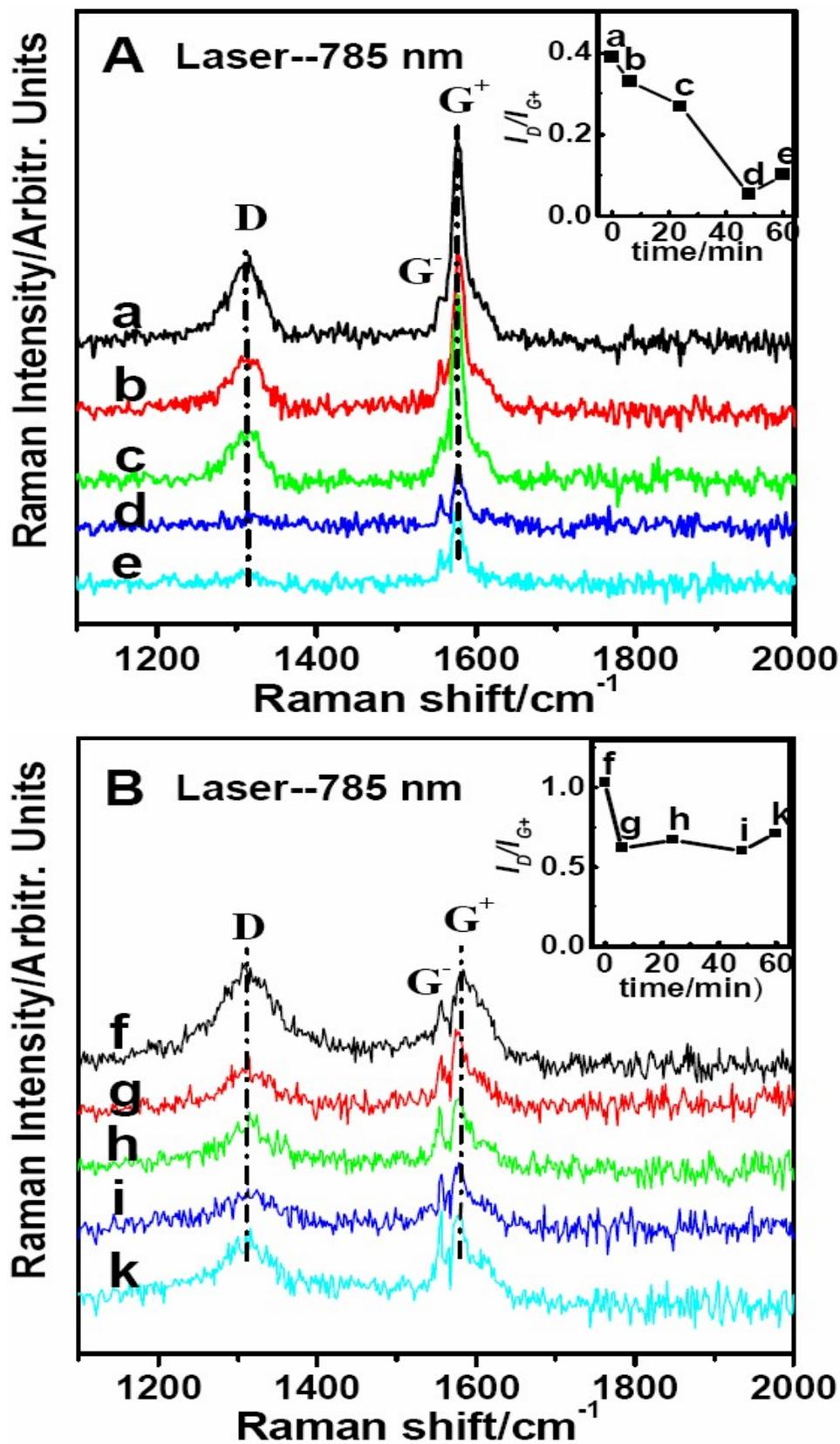
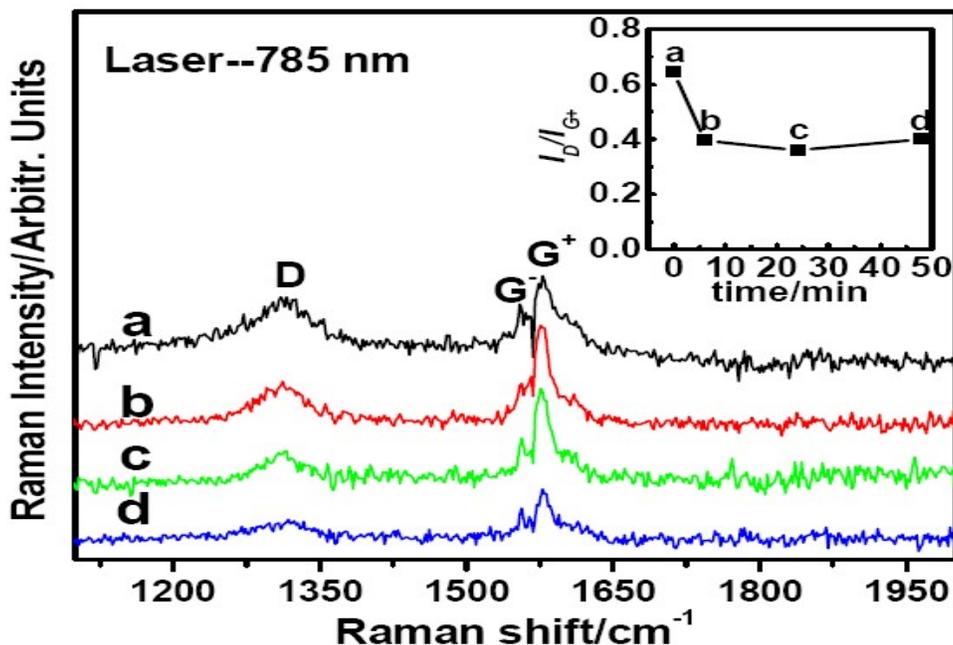


Figure 5 : (A) Raman spectra of the products GO-1 (a), GO-2 (b), GO-3(c), GO-4 (d) and GO-5 (e); (B) Raman spectra of the products GO-k1 (f), GO-k2 (g), GO-k3 (h), GO-k4 (i) and GO-k5 (k). Insets are the dependence of  $I_D/I_{G^+}$  value for different irradiation time.



**Figure 6 :** Raman spectra of the product (a) treated with hydrazine solution using the precursor GO-k5 in Figure 5 and the graphene products microwave-irradiated for 6 min (b), 24 min (c) and 48 min (d). Inset is the dependence of  $I_D/I_{G^+}$  value for different irradiation time.

decrease of the defects caused by  $sp^3$ -hybridized carbon. However with prolonging irradiation time from 6 min to 60 min in Figure 5(B), the  $I_D/I_{G^+}$  value for the product GO-k5 unobviously happens slightly change. After the GO-k5 is reduced again at 200 °C in hydrazine solution and followed by microwave irradiation for 6 min, the  $I_D/I_{G^+}$  value can be remarkably further lowered, but it shows less change with increasing irradiation time to 48 min.

Such results reveal that the hydrazine reduction and subsequent microwave treatment within many minutes can further lower defect content and modify graphene. However in contrast to the corresponding products in Figure 5(A), the  $I_D/I_{G^+}$  values of these samples are still higher, inferring the existence of much more unrepaired hole or porous defects due to the strong oxidation reaction of  $KMnO_4$  with carbon atoms. It has been proved that  $KMnO_4$  can strongly oxidize C atoms and result in the elimination of small part of C atoms in the nanosheet lattice<sup>[28]</sup>.

## CONCLUSIONS

We have simply prepared graphene sheets with few layers and little oxygen content using mechanical milling, oxidation and microwave treatments. Various

measurement results reveal that the products obtained without any addition of  $KMnO_4$  exhibited much less defects by compared to the products prepared with the oxidation effect of  $KMnO_4$ . Raman spectra demonstrate that the G peaks of all the products appear splitting into  $G^+$  and  $G^-$  peaks, and also with prolonging microwave irradiation time within 48 min, the intensity ratio of the D to  $G^+$  peak for the products without  $KMnO_4$  treatment gradually decreases, indicating that the  $sp^3$ -type carbon atom number becomes less.

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