Support information:

1. Synthesis of GO and Al_2O_3/Graphene nanocomposites.

GO was prepared from expanded graphite though liquid oxidation on a modified Hummers method as originally presented by Kovtyukhova and Li. All the materials used were commercially obtained and used as received. Firstly, about 200.0ml concentrated sulphuric acid was added into a three flask. After the temperature of the flask was cooled to 0℃, about 5.0g expanded graphite, 5.0g $NaNO_3$ and 30.0g potassium permanganate were carefully added into the flask. The reaction time was about 30min under the low temperature. Then, the temperature was rose to 35℃ and the reaction time was about 1h. At the end, a mount of ultrapure water and H_2O_2 were added into the flask and the reaction was sustained about 1h.

The as-synthesized graphite oxide was suspended in ethanol to give a golden dispersion, which was subjected to dialysis to completely remove residual salts and acids through a series of purge and centrifugation procedure. Then, the purified graphite oxide suspensions were dispersed in ethanol to create a 0.005wt% dispersion. Exfoliation of graphite oxide to GO can be obtained through ultrasonic treatment. The obtained golden dispersion was then subjected to centrifugation at 3,000 r.p.m for 30min to remove any unexfoliated GO using a centrifuge.

The gas response of Al_2O_3 powder had been reported for long time. However, because of the low efficiency of gas response performance and difficulty of sensor device preparation through Al_2O_3 powder, the Al_2O_3 particles were often coated on some substrate, espically the nanoscale substrate. As the novel nano-materials, graphene was very suitable for using as a substrate. It not only had higher surface area and more regular structure, but also was much easier to be prepared as a membrane. The above advantages made it more suitable for fabricating gas sensor. Here, the Al_2O_3/Graphene nanocomposite was prepared as a paper. The nanocomposite was firstly solved in water. Then the settled aqueous solution was filtrated. After peeling from filter, a Al_2O_3/Graphene nanocomposite paper was successfully fabricated. The obtained Al_2O_3/Graphene nanocomposite paper was shown in following Figure 1-1.

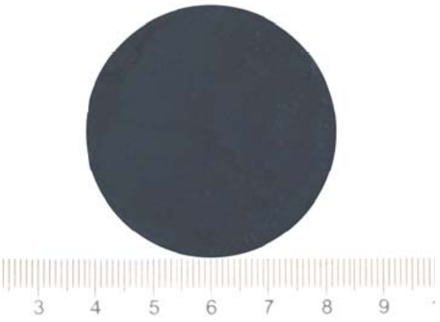

Fig.1-1 Picture of Al_2O_3/Graphene nanocomposite paper.

Graphene was known as a material with quantum-mechanical nature of tunneling effect. High conductivity made graphene widely applied in electronic products. While the graphene, prepared by chemical method, typically lost the tunneling effect. However, this was very useful for gas sensor fabricated. The resistance can generate enough heat, which was indispensable to the gas sensor work. Thus, this moderated resistance was suitable to prepare gas sensor with simple fabricated method. Furthermore, the nanocomposites, we prepared, can easily be prepared into film. So a gas sensor can be easier fabricated when a voltage was applied onto the nanocomposite paper. An example picture was shown in Figure 1-2.

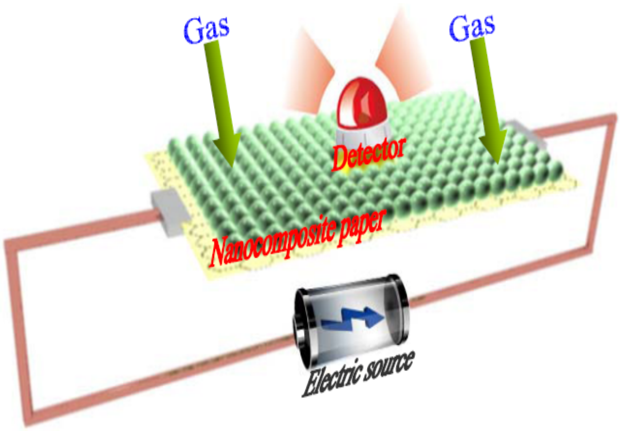

Fig. 1-2 A simple nanocomposite gas sensor

2. Effect of $Al(NO_3)_3{\cdot}9H_2O$ used on nanocomposite morphologies.

As known, the ethanol response was mainly attributed to the Al_2O_3 nanoparticles on graphene surface. And the graphene was only used as a substrate. Thus, the amount of Al_2O_3 on graphene surface was important to the performance of nanocomposite. While the amount of Al_2O_3 on graphene surface was attributed to the $Al(NO_3)_3{\cdot}9H_2O$ used. So the effect factor of $Al(NO_3)_3{\cdot}9H_2O$ used should be studied.

Here, the $Al(NO_3)_3{\cdot}9H_2O$ used were about 1.0mmol, 2.0mmol, 4.0mmol, 8.0mmol, respectively, and their responding TEM images were shown in Figure 2-1. As shown, the amount of Al_2O_3 on graphene increased with the amount of $Al(NO_3)_3{\cdot}9H_2O$ as expected. As the $Al(NO_3)_3{\cdot}9H_2O$ amount used is 1.0mmol, the graphene surface was not uiformly covered by Al_2O_3 nanoparticles (see Figure 2-1(a), red arrow). The Al_2O_3 nanoparticle clusters would be formed on/out graphene surface when the $Al(NO_3)_3{\cdot}9H_2O$ used was 4.0mmol and 8.0mmol. The graphene surface had been uniformly and densely covered by Al_2O_3 nanoparticles when $Al(NO_3)_3{\cdot}9H_2O$ used was 2.0mmol.

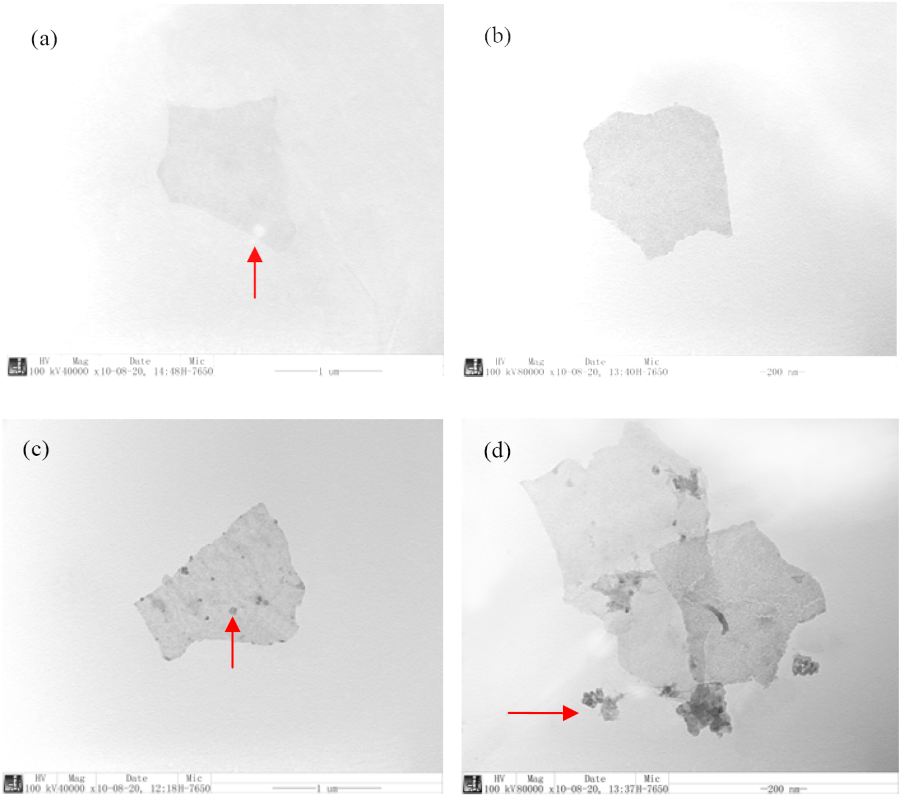

Fig.2-1 Effect of $Al(NO_3)_3{\cdot}9H_2O$ used on the TEM images of Al_2O_3/Graphene nanocomposites. (a) $Al(NO_3)_3{\cdot}9H_2O$ used was 1.0mmol; (b) $Al(NO_3)_3{\cdot}9H_2O$ used was 2.0mmol; (c) $Al(NO_3)_3{\cdot}9H_2O$ used was 4.0mmol; (d) $Al(NO_3)_3{\cdot}9H_2O$ used was 8.0mmol.

In order to see the state of the Al_2O_3 nanoparticles on grephene clearly, a diagram of Al_2O_3 nanoparticle aggregation morphologies were shown in Figure 2-2. The Al_2O_3 nanoparticles had not entirely covered the graphene surface when the $Al(NO_3)_3{\cdot}9H_2O$ used was 1.0mmol. This may significantly affect its gas responsibilities for ethanol, which had been proved by CL experiments. The graphene was fully covered by Al_2O_3 nanoparticles when the $Al(NO_3)_3{\cdot}9H_2O$ used were higher than 2.0mmol, and the ethanol responsibilities of these nanocomposites were almost the same (the response time and ethanol response amount in CL experiment were almost the same). The gas response performances of the nanocomposites may be related to the active area of Al_2O_3 nanoparticle layer (active area: the area that nanoparticle contacted with the gas). As the $Al(NO_3)_3 \cdot 9H_2O$ used was 2.0mmol, the Al_2O_3 nanoparticles uniformly covered the graphene surfaces, and the active Al_2O_3 nanoparticle layer area nearly reached its biggest active area. Though the Al_2O_3 nanoparticle layer thicknesses, the active area may not be significantly increased (as seen in Figure 2-2(d)). In addition, the increase of $Al(NO_3)_3 \cdot 9H_2O$ lead to the increase of Al_2O_3 clusters. The clusters would significantly reduce the ethanol response efficiencies of the nanocomposites, due to the small active area of Al_2O_3 nanoparticle clusters. Beyond this, there still may exist the wasted problem of $Al(NO_3)_3 \cdot 9H_2O$. Thus, it was seem that the amount of 2.0mmol $Al(NO_3)_3 \cdot 9H_2O$ used was near the optimal levels.

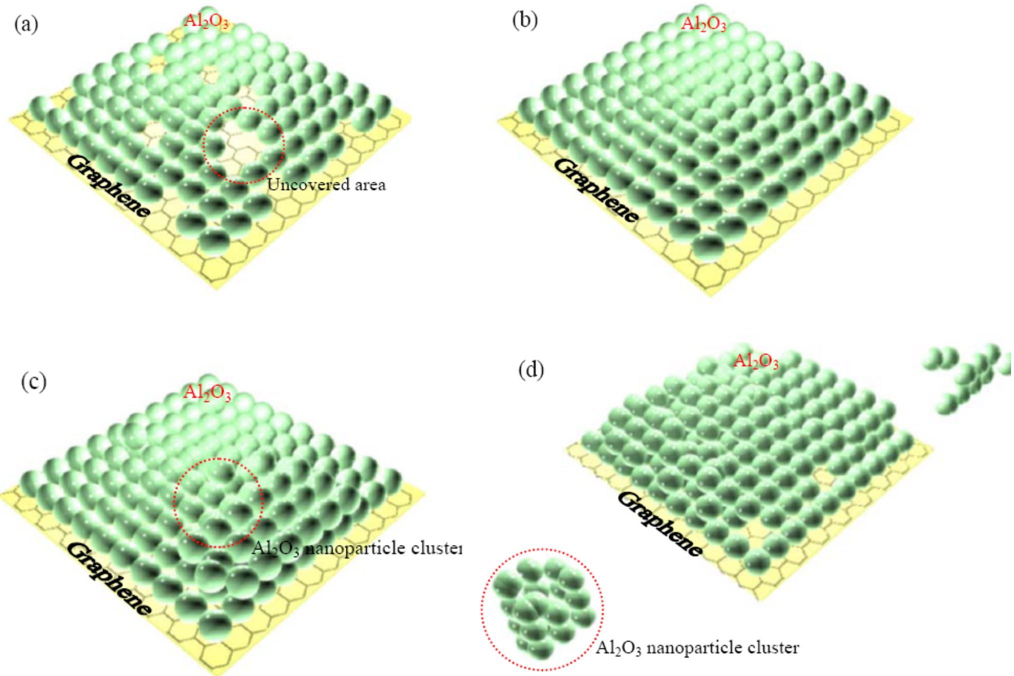

Fig.2-2 Illustration pictures of Al_2O_3 nanoparticle aggregation morphologies on graphene surfaces. (a) $Al(NO_3)_3 \cdot 9H_2O$ used was 1.0mmol; (b) $Al(NO_3)_3 \cdot 9H_2O$ used

was 2.0mmol; (c) $Al(NO_3)_3{\cdot}9H_2O$ used was 4.0mmol; (d) $Al(NO_3)_3{\cdot}9H_2O$ used was 8.0mmol.

Of significantly importance was that the thickness of graphene had no significant increase after coated with Al_2O_3 nanoparticles. This can be clearly seen from its AFM image, which was shown in Figure 2-3 ($Al(NO_3)_3{\cdot}9H_2O$ used was 2.0mmol). As seen, the graphene thickness was increase about 0.13nm after coated with Al_2O_3 nanoparticles (the graphene thickness was about 0.9nm). This confirmed the above conclusion that the Al_2O_3 particles were in nanoscale. It could ensure the gas sensitive of the nanocomposites obtained.

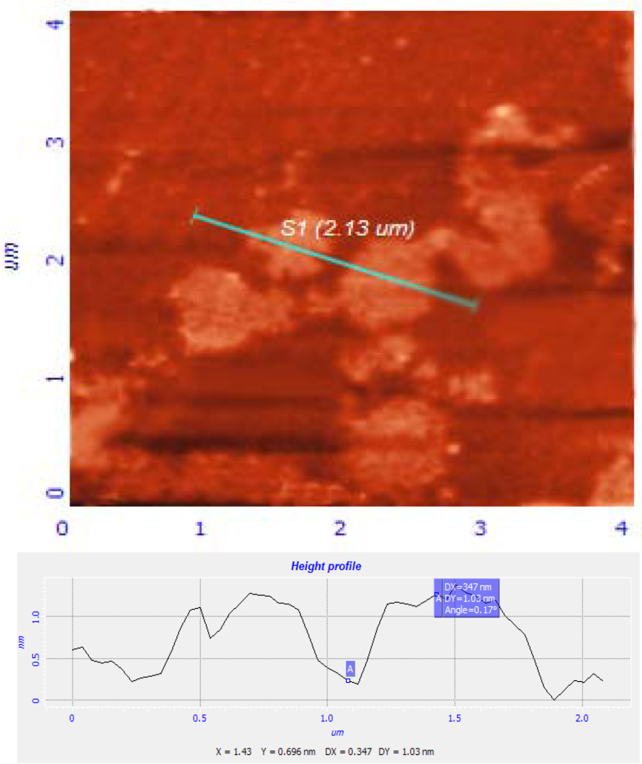

Fig.2-3 AFM image of Al_2O_3/Graphene nanocomposite ($Al(NO_3)_3{\cdot}9H_2O$ used was 2.0mmol).

3. The crystal structure of Al_2O_3 on graphene surface.

As reported, some of the metal oxide may be existed with crystal structure on nanomaterials surface. As one of the characterization method for crystallization, high-magnification TEM is considered as an effective method. So high-magnification TEM is used for the determination of the Al_2O_3 crystal structure. Figure 3-1 shows the high-magnification TEM images for the Al_2O_3/Graphene nanocomposites (the $Al(NO_3)_3 \cdot 9H_2O$ used was 2.0mmol). The characterizations have been repeated not only for different graphene layers, but also for different places of one graphene layer. Here, we present the images of different places of one graphene layer in Fig.3-1. As seen, the Al_2O_3 nanoparticles are uniformly cover the graphene surface. While we do not see the crystal structure of Al_2O_3 nanoparticles after huge finding for sample surfaces. Thus, it can be sure that the Al_2O_3 nanoparticles on graphene surface is amorphous state.

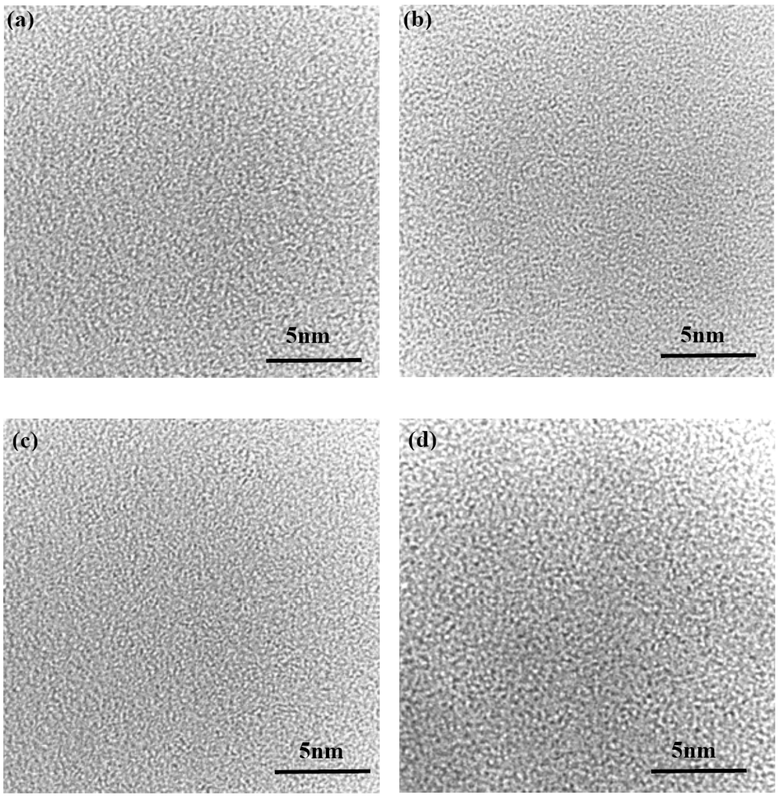

Fig.3-1 Typical high-magnification TEM image of Al_2O_3/Graphene nanocomposites. (a)-(d) are the high-magnification TEM images of different places of one graphene layer.

In addition, the local EDS of the TEM is also used. Figure 3-2 is the EDS of the nanocomposites. As seen, the element Al is obviously be seen in the spectrum. And the energy is about 1.48kV.

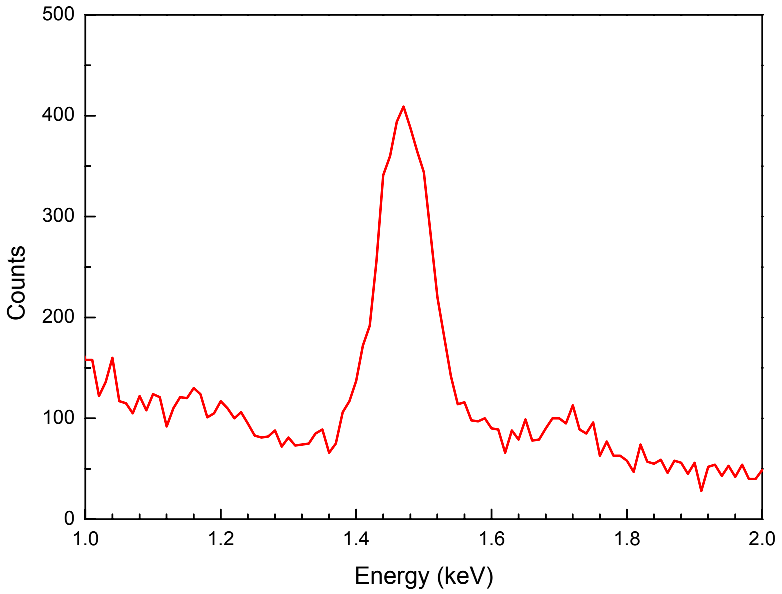

Fig.3-2 EDS spectrum of the Al_2O_3/Graphene nanocomposites

4. The possible mechanism of GO reduction reaction.

The GO was directly reduced by $SCCO_2$ method in this paper, which had not been reported yet. Of particular significance was that the formation of Al_2O_3/Graphene nanocomposites from GO and $Al(NO_3)_3{\cdot}9H_2O$ mixed solution at the same time. The prepared process of Al_2O_3/Graphene nanocomposites may contain a series reaction. Some of reaction mechanism may be clearly in present, such as the decomposition reaction about $Al(NO_3)_3{\cdot}9H_2O$ under 350℃, 20MPa in $SCCO_2$ bath.

However, the GO reduction reaction was relatively complicated. The GO reduction reaction under high temperature, high pressure and inert gas protection was not studied in present. Honestly specking, we also can not give an exact mechanism for the formation of the composites fabricated in this work. While on the basis of experimental phenomena and related results reported, we proposed a possible mechanism which was shown in Figure 4-1.

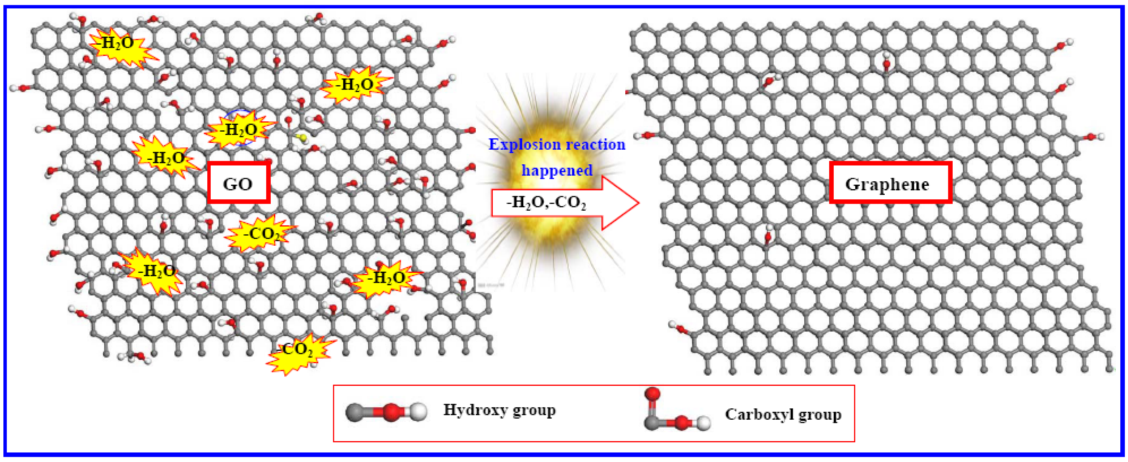

Fig.4-1 A possible mechanism for the reduction of GO by $SCCO_2$.

In the process of GO reduction, considerable amounts of heat and gas were generated by dissociation, which may lead to explosions of great violence (we called it as explosion reaction). In the explosion reaction, the heat treatment may play an important role. And the gas generated may be H_2O and CO_2. The explosion of GO can be proved by DSC and TG measurement. The thermodynamics analysis for GO was shown in Figure 4-2. It is found through the DSC curve that a great deal of heat was produced after 60.2℃, and then the same heat was absorbed. While the TG curve expressed that there are great mass loss after 60.2℃. These curves can be used as the proof of explosion reaction, whose special trend can be explained by the experimental phenomenon (as shown in Figure 4-3). Before thermodynamic analysis, small amounts of golden GO powder were put into sample cell with dimension of Φ7.0mm×3.0mm. After analysis, the dark graphene was dispersed everywhere on the sample chamber wall, the chamber dimension was about Φ120.0mm×220.0mm. And the sample cell was broken. Its process may like the preparation of popcorn. Thus, there must be an explosion happened. And the GO reduction was an explosion reaction.

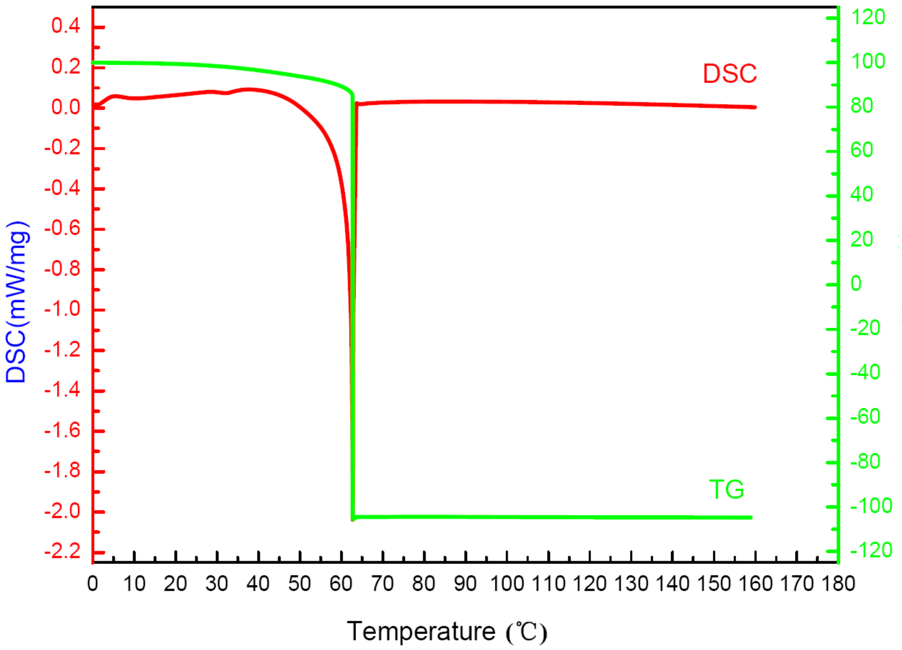

Fig.4-2 Thermodynamics analysis for GO.

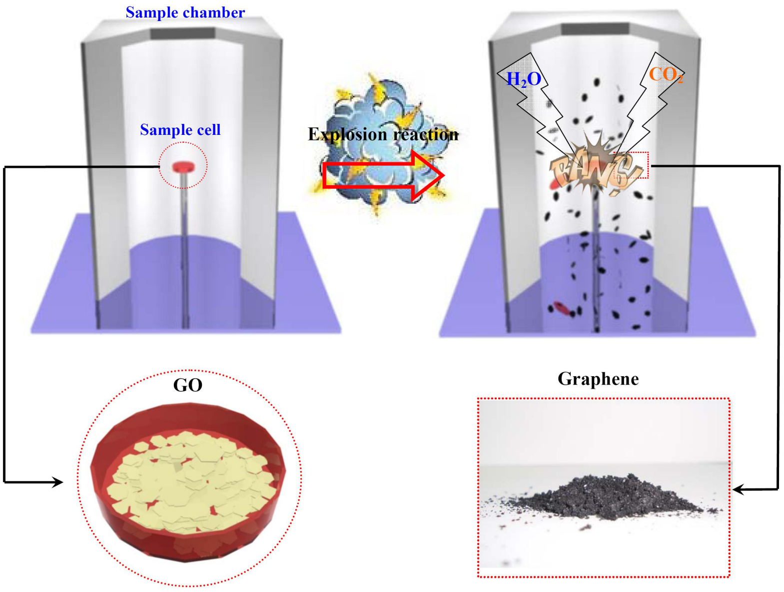

Fig.4-3 Illustration pictures for GO explosion reaction.