

## Modified Synthesis of Edge Scrolled Reduced Graphene Oxide with High Surface Area

R. Rajesh<sup>1\*</sup>, K. Balkis Ameen<sup>2</sup>, K. Rajasekar<sup>1</sup>

<sup>1</sup>Department of Nanotechnology, Anna University Regional Centre Coimbatore,  
Tamilnadu, India – 641046

<sup>2</sup>JCT College of Engineering and Technology, Coimbatore, Tamilnadu, India – 641105.

\*e-mel: rajesh16686@gmail.com

### Abstract

Synthesis of graphene with the high surface area has been very attractive for various energy storage applications. In this work, we describe a scalable method for producing edge scrolled reduced graphene oxide (r-GO) with the high surface area by modified Hummer's method. Strong acid treated graphite flakes were used to synthesis reduced graphene oxide. Few layered, edge scrolled reduced graphene oxide was obtained by low temperature (200°C) thermal treatment in a hydrogen atmosphere. The formation of few layered graphitic structure of reduced graphene oxide was confirmed by TEM analysis. The specific surface area of the reduced graphene oxide was measured by nitrogen adsorption technique. The reduced graphene oxide derived from acid treated graphite flakes exhibits high surface area (~ 500 m<sup>2</sup>/g) than non acid treated graphite flakes (214.4 m<sup>2</sup>/g).

**Keywords** acid treated graphite, reduced graphene oxide, high surface area

### INTRODUCTION

In the field of porous nanomaterials, synthesis and designing of chemical structures with high surface area are quite difficult and an outstanding challenge. The invention of new porous material with high surface area is important and which widely used in various fields, such as, catalysis, separation and storage of gas, energy storage and so on [12]. Nowadays researchers concentrate on the development of porous materials with high surface area in energy devices, especially, nanocarbon based porous materials are great interest due to its unique properties [1].

In order to fabricate efficient energy storage devices we need a surface area with good electrical conductivity electrode materials. Generally, carbon nanotubes (CNTs) and graphene based sp<sup>2</sup> nanocarbon materials showing good electrical conductivity than non sp<sup>2</sup> amorphous and mesoporous carbon materials. The synthesis of graphene and its composite materials has great interest than carbon nanotubes, because of one dimensional honeycomb structure, good electrical conductivity and high surface area [3]. Researchers have been developed few novel techniques for the synthesis of graphene/reduced graphene oxide materials with high surface area [12]. Korkut Sibel et al. demonstrated the production of high surface area functionalized graphene tapes by tape casting technique, they achieved ultra long (1meter) functionalized graphene/ polymer tapes with high surface area (>400 m<sup>2</sup>/g) [5]. Chemical vapor deposition technique (CVD) produces the graphene material with, very high surface area, good electrical conductivity and good crystalline structures. But, this CVD technique results in less quantity of graphene material and it is best suited for laboratory scale. For the commercialization of graphene based nanodevices we need a large quantity of graphene with desired properties. Hydrothermal and chemical activation techniques give a lot of graphene materials with high surface area. Therefore, hydrothermal and chemical activation of nanocarbon techniques are the suitable process for the production of large quantity graphene/reduced graphene oxide material with high surface area [8]. Recently, Raziheh et al. [6] believed that the intercalation component between graphene layers enhances the surface area and nano pore size of the graphene material. They have prepared the hydrazine hydrate intercalated graphene layers in various reaction time, finally achieved six layered graphenes with the surface area of 560 m<sup>2</sup>/g [6]. Similarly, Chen et al. [2] prepared the sulfuric acid intercalated graphite sheets by ultrasonic powdering techniques. Anyhow, many modification processes need to incorporate in the hydrothermal technique and chemical activation technique to increase the surface area, electrical conductivity as well as good crystallinity [2].

In this work, we used modified Hummer's technique for the production of high surface area reduced graphene oxide material. In this process, acid treated/pre oxidized graphite flakes were used to achieve high surface area. Nitrogen adsorption studies confirmed the pre oxidation process increases the surface area of reduced graphene oxide material.

## EXPERIMENTAL

Reduced graphene oxide materials were synthesized by following two steps [4, 7]. For the synthesis of high surface area reduced graphene oxide analytical grade (purity > 99.99%) chemicals were purchased and used without any purification.

### *Pre oxidation/Oxidation of graphite flakes*

In this process, 2g of pure graphite flakes were immersed in 100 ml strong acid mixture (60 ml of concentrated  $\text{H}_2\text{SO}_4$  + 40 ml of concentrated  $\text{HNO}_3$ ) for 3 hours. Then the above mixture was refluxed at  $100^\circ\text{C}$  for 8 hours to attain strong oxidation. Finally, acid treated/pre oxidized graphite flakes were washed with 5 liters of distilled water by vacuum filtration and dried at  $80^\circ\text{C}$  for 12 hours.

### *Modified Hummer's method*

In modified Hummer's method, 1g of pre oxidized graphite flakes were immersed in 50 ml of concentrated  $\text{H}_2\text{SO}_4$  and stirred for 1 hour. Then the above mixture cooled down to  $0^\circ\text{C}$  and continuously stirred for 30 minutes. 6g of  $\text{KMnO}_4$  flakes were slowly added to the above mixture, during the process the reaction temperature was maintained below  $5^\circ\text{C}$ . Again the mixture moderately stirred for further 2 hours for the complete oxidation process. Then 90 ml of distilled water drop wise added to the above dense mixture, while adding the distilled water, the reaction temperature was maintained at below  $35^\circ\text{C}$ . The above mixture further stirred for 2 hours at room temperature and 250 ml of distilled water was added under vigorous stirring. Finally, 6 ml of 30%  $\text{H}_2\text{O}_2$  were slowly added to the above gel like mixture, during this process, the solution turned to bright yellow color. The formation of bright yellow color indicates the addition of hydrogen peroxide breaks/stops the oxidation of graphite flakes and also the formation of graphite oxide.

The above gel like mixture maintained at room temperature for 24 hours (without stirring). Then the supernatant was decanted and 500 ml of distilled water added to the above gel under constant stirring for 10 minutes. These last two steps were repeated for 5 times. Finally, the graphite oxide washed with 2 liters of 10% HCl and recovered by centrifuge process (2000 rpm for 10 minutes). Then the graphite oxide was dried at room temperature for 7 days. Well dried graphite oxide (1g) was dispersed in 1 liter of distilled water by ultra centrifugation process. Then the solution vacuum filtered and dried at  $80^\circ\text{C}$  for 5 hours. The above graphene oxide was further exfoliated thermal treatment at  $200^\circ\text{C}$  for 3 hours in a hydrogen atmosphere.

The black reduced graphene oxide mesh was collected from the furnace and sealed in air tight container for further process. For the comparison, we have synthesized the reduced graphene oxide material by using pure graphite flakes (without oxidation) with the same procedure.

## RESULTS AND DISCUSSION

The synthesized reduced graphene oxide was characterized by transmission electron microscope and nitrogen adsorption studies.

### *Morphological studies of r-GO*

The transmission electron microscope image revealed the details of the microstructure of reduced graphene oxide and shown in Figure 1. From the TEM image we observed that the synthesized reduced graphene materials have wrinkled layered structure, which is similar to previously reported graphene materials [9, 11].



**Figure 1** TEM images of reduced graphene oxide

Furthermore repeated acid treatments results edge scrolled folded 3D layered structure. Many researchers suggested that these kinds of three dimensional nanocarbon structures are the reason for the high surface area [12, 10]. From the TEM image we did not observe any carbon particles and other impurities of the layered structure, which indicate the purification process completely removed the residual ions. The multiple acid treatment did not collapse the graphitized structure and we obtained the graphene layers by successive exfoliation of acid treated graphite flakes.

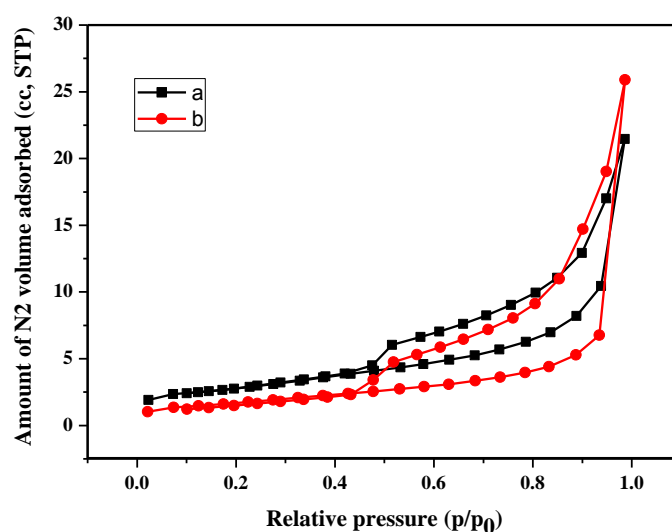
For the physical comparison, during the synthesis process we have taken some optical images of this graphitic carbon material and shown in Figure 2. This photographic image also clearly indicates the complete exfoliation of graphite flakes and the formation of mesh like reduced graphene oxide.



**Figure 2** Photographic images of graphitic carbon materials

#### *Nitrogen adsorption studies of reduced graphene oxide*

The nitrogen adsorption and desorption isotherm of reduced graphene oxides are shown in Figure 3. From the nitrogen adsorption studies, we observed that the r-GO derived from acid treated graphite flakes exhibits relatively high surface area of 494.2 m<sup>2</sup>/g. Anyhow, this is very smaller than the theoretical surface area (~2600 m<sup>2</sup>/g) of monolayer graphene. The agglomeration between the layers and edge scrolled structure of reduced graphene oxide lowers the surface area. This edge scrolled r-GO exhibits type IV isotherm, this type of isotherm do not exhibit saturation limit and indicates the formation of finite multilayer after the completion of the successive monolayer. The wide area at the mid region indicates the complete filling of capillaries and the adsorption terminates near the unity of relative pressure. Reduced graphene oxide derived from pure graphite flakes exhibits less surface area of 214.4 m<sup>2</sup>/g.



**Figure 3** Nitrogen adsorption-desorption isotherm of reduced graphene oxide derived from a) pre oxidized graphite flakes and b) pure graphite flakes

## CONCLUSION

In this work, we have synthesized reduced graphene oxide by modified Hummer's method. Strong acid treatment of graphite flakes results in the high surface area. TEM morphological studies of r-GO confirm the exfoliation of graphite flakes and the formation of few layered folded graphitic structure. The increasing specific surface area of the reduced graphene oxide derived from pre oxidized graphite flakes was confirmed by nitrogen adsorption studies. The synthesized reduced graphene oxide exhibits high surface area 494.2 m<sup>2</sup>/g.

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