

# Chemical synthesis of graphene nanoribbons

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## ABSTRACT

The importance of graphene as a new material is due to its electrical and mechanical properties, good conductivity, excellent heat dissipation, flexibility and transparency. Therefore it offers a good suitable material to the actual demands on new technologies. Graphene nanoribbons (GNRs) are obtained by cutting a graphene sheet into quasi-one dimensional infinite ribbons. GNRs are materials showing different properties compared with others carbon nanostructures because they can act from semiconductors to semimetals as a function of their width. In this work, we describe an oxidative method, using only potassium permanganate ( $\text{KMnO}_4$ ) as the oxidant agent, for the synthesis of GNRs coming from the unzipping of multi-walled carbon nanotubes, which are synthesized using a mixture of xylene with an alcohol as the carbon source and ferrocene as the catalyst.

**Keywords:** MWCNTs, Graphene nanoribbons.

## 1 INTRODUCTION

In the last decade the need of new materials offering better specific properties has been increased, because of the demand of new devices, which require enhanced materials to fulfill this new era of technology. Carbon nanotubes (CNTs) have been extensively studied for their interesting physical properties that they possess. Actually one of the most interesting materials is graphene, which was discovered by Geim and Novoselov [1]. The importance of this material is due to its electrical, mechanical, electronic and optical properties, which can be used for electronic devices and other applications. On the other hand, graphene nanoribbons (GNRs) are defined as strips of graphene of a finite width [2]. It has been shown that the energy gap of GNRs decrease as their width increases. Consequently, its conductivity changes from semiconductors to semimetals as function of their width [2,3]. Semiconductive properties of GNRs structures can be used in electronics for their applications in specific devices such as sensors, batteries and nanomechanical devices.

Numerous methods have been developed to accomplish the synthesis of GNRs, such as lithographic method [3],

plasma etching [4], chemical vapor deposition (CVD) [5], and chemical methods [6, 7]. The chemical methods are a more practical and economic method than the others to obtain GNRs and also these methods can be used in the future for the GNRs production in bigger scale. Between them, one of the most interesting is the chemical oxidative method developed by Kosynkin et al. [6], which consists in the longitudinal unzipping of multi-walled carbon nanotubes (MWCNTs) by oxidation using a mixture of potassium permanganate ( $\text{KMnO}_4$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The first step consisted in suspending MWCNTs in a concentrated solution of  $\text{H}_2\text{SO}_4$  for 1-12 hours. Then  $\text{KMnO}_4$  was added to the mixture, which was stirred for 1 hour at room temperature and then gradually heated until  $70^\circ\text{C}$ . The mechanism used to explain the MWCNTs longitudinal unzipping is based on previous works on the alkenes oxidation. The oxidation of alkenes with  $\text{KMnO}_4$  basically consists on the addition of functional groups to the carbon-carbon double bond characteristic in alkenes. Note that  $\text{KMnO}_4$  is an oxidizing agent when is reduced to manganese dioxide ( $\text{MnO}_2$ ). This reaction is carried out by stirring at room temperature a mixture of the alkenes with the permanganate solution. The addition of an acid medium and heat promote further oxidation [8]. The Baeyer test is used to check the oxidation of potassium permanganate to manganese dioxide changing the solution color from purple to brown.  $\text{KMnO}_4$  attacks the carbon double bonds present in the structure to oxidize them and consequently will lead the formation of hydroxyl groups [9], where a strong oxidization will promote the formation of ketones and carboxylic acids presents in the carbon structure.

Recently, it has been shown that it is possible to incorporate functional groups on multiwalled carbon nanotubes (MWCNTs) during the synthesis process [10], increasing in this way their chemical reactivity. The introduction of small quantities of alcohol in xylene during the synthesis process was responsible of the quinone ( $1630\text{ cm}^{-1}$ ) and hydroxyl ( $3428\text{ cm}^{-1}$ ) functional groups attached on the walls of MWCNTs, such as is shown in Figure 1. An interesting feature is that the use of these alcohols as carbon source can be considered as a mild oxidation of the MWCNTs surfaces, where the anchoring of quinones group has been considered as an intermediate step of the SWNTs oxidation process [9]. Here we describe a chemical oxidative method for synthesis of graphene nanoribbons

without the use of sulfuric acid, due to the use of functionalized MWCNTs (F-MWCNTs).

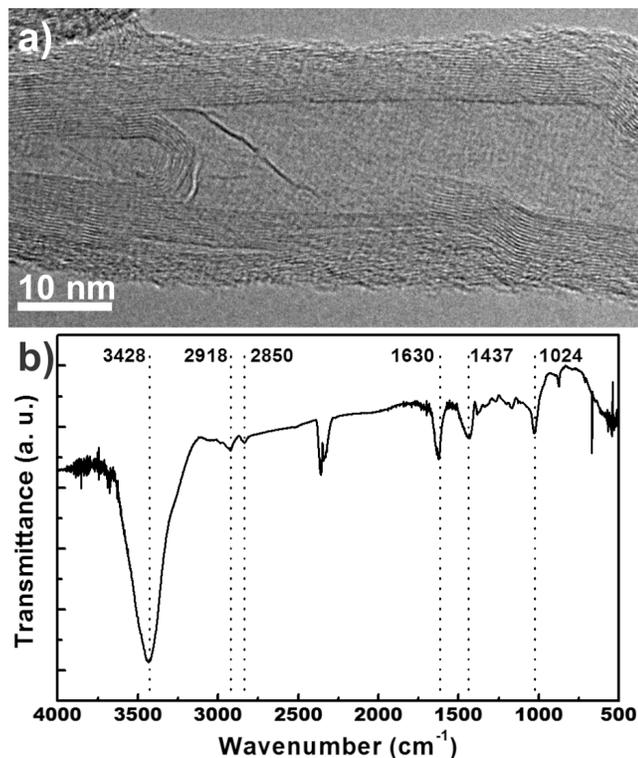


Figure 1: (a) HRTEM image of F-MWCNTs synthesized by using a mixture of xylene with ethanol and carbon source and ferrocene as catalyst. (b) FTIR spectrum of as produced F-MWCNTs.

## 2 EXPERIMENTAL

### 2.1 F-MWCNTs purification

F-MWCNTs were purified to remove amorphous carbon and iron catalytic particles used during the functionalization process, F-MWCNTs were heated in the oven to remove the amorphous carbon and then suspended in hydrochloric acid for 1-12 hours. The mixture was sonicated for a few minutes and then filtered with a PTFE membrane (5.0 μm pore size). Finally F-MWCNTs were heated again to obtain a loss weight of 70% over original material.

### 2.2 Synthesis of Oxidized Graphene Nanoribbons.

Synthesis of oxidized graphene nanoribbons was based on Kosynkin experimental procedure [6]. First, KMnO<sub>4</sub> was dissolved in water and F-MWCNTs (previously purified)

were added to the mixture and stirred for 1 h at room temperature. After that, the mixture was heated in an oil bath at 55°C for 30 minutes, The Baeyer test was used to check the reaction progress by preparing two test tubes, one containing 1 ml of water with four drops of the mixture and 2-3 drops of hydrogen peroxide. The other tube only contains 1 ml of water. They were sonicated for 3 min and the first tube must indicate a yellow-brown color and a precipitate solid broken in small pieces. The other one must present a red-violet color indicating the reduction of KMnO<sub>4</sub>. If the reaction was not completed, the temperature was increased to 65°C and the reaction progress was again checked.

When the Baeyer test indicated the reduction of KMnO<sub>4</sub>, the temperature was slowly increased until a temperature of 70°C was reached and stabilized. After the temperature stabilization, the mixture was removed from the oil bath and cooled at room temperature. When the mixture reached room temperature, it was poured into ice containing 1.8% weight of H<sub>2</sub>O<sub>2</sub>. Later it was vacuum filtered using filters with PTFE membrane (5.0 μm pore size). Finally, the mixture was washed with ethanol and then centrifugated at 3100 rpm to remove insoluble manganese dioxide and purify the final product.

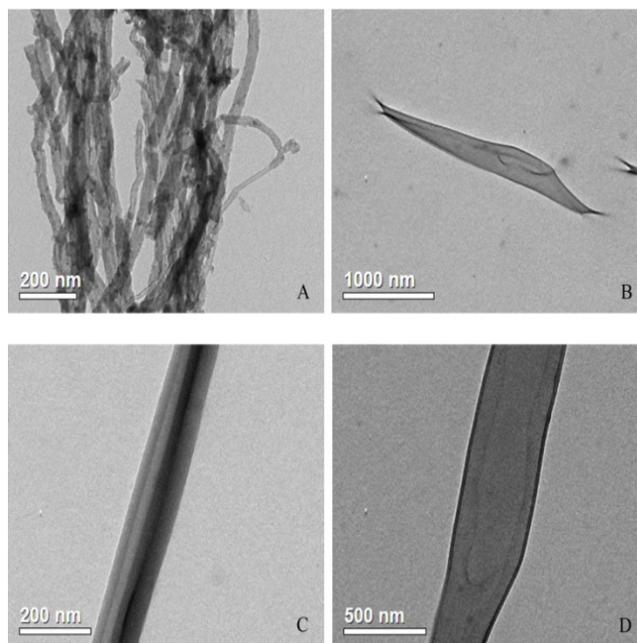


Figure 2: TEM Micrographs of graphene nanoribbons and purified F-MWCNTs. (a) Purified F-MWCNTs before KMnO<sub>4</sub> treatment. (b) Oxidized graphene nanoribbons. (c) Partially oxidized F-MWCNTs (d) Oxidized graphene nanoribbon completely unzipped.

### 3. RESULTS AND DISCUSSION

The transmission electron micrographs (TEM) were obtained using a microscope JEM-1230. Figure 2a shows the purified F-MWCNTs, which were used for the synthesis of graphene nanoribbons. F-MWCNTs were synthesized by using the spray pyrolysis method of a mixture of ethanol with xylene [10]. These F-MWCNTs were previously purified before starting the oxidation reaction. Purification is a required process in order to obtain more oxidized nanoribbons. Figure 2b shows an oxidized graphene nanoribbon, which is not completely opened. From this figure, it can be supposed that  $\text{KMnO}_4$  first attacks the double bonds on carbon nanotubes approximately in a specific zone, making that  $\text{KMnO}_4$  to continue oxidizing and unzipping the nanostructure next to the last attack, step by step until finally it reaches the edges of the carbon nanotube. However figure 2b also shows that it is not a longitudinal unzipping such as the Kosynkin procedure [6]. From here it can be proposed that these MWCNTs were unzipped in a random way, where carbon nanotubes are cut in pieces and then opened by the chemical oxidation of the  $\text{KMnO}_4$ . Figure 2c shows a partially oxidized F-MWCNT; although it has started to be opened, graphene nanoribbons are not formed. Finally Figure 2d shows a completely oxidized graphene nanoribbon with an approximate width of 350 nm. Figs. 2b, c and d were obtained from the same experiment, which indicates that a variety of unzipping levels can be found for oxidized graphene nanoribbons by this method. Another point to consider is the presence of manganese dioxide ( $\text{MnO}_2$ ), which is produced by the reduction of  $\text{KMnO}_4$ ;  $\text{MnO}_2$  is an insoluble compound, which should be separated from graphene nanoribbons to improve solubility and purity.

The main difference between Kosynkin procedure and our experimental procedure is the acid environment due to the use of sulfuric acid. Moreover, Higginbotham et al. [11] have reported an improved method to obtain GNRs with lower defects with the use weaker acids in mixture with  $\text{H}_2\text{SO}_4$ , although the presence of sufficient  $\text{H}_2\text{SO}_4$  (~90 vol %) is still fundamental for the complete oxidation and exfoliation of MWCNTs. We consider that it is important to study the specific role of  $\text{H}_2\text{SO}_4$  in this process; it could be that it only accelerates the reaction and for that reason avoiding the use of sulfuric acid will promote an incomplete oxidation. The other possibility is that  $\text{H}_2\text{SO}_4$  also contributes in the functionalization and exfoliation resulting in a longitudinal unzipping of carbon nanotubes.

### 4. SUMMARY

Graphene nanoribbons were synthesized by oxidation with  $\text{KMnO}_4$  using F-MWCNTs. Organic functional groups present in F-MWCNTs allow  $\text{KMnO}_4$  to perform the oxidation of the carbon nanotubes and a gradual and random cut of carbon nanotubes, which are unzipped to

obtain oxidized graphene nanoribbons. Sulfuric acid used in Kosynkin et al. [6] methods is not necessary due the presence of functional groups in MWCNTs. However, TEM micrographs demonstrate that not all the F-MWCNTs were completely unzipped and  $\text{KMnO}_4$  does not cut MWCNTs in a longitudinal way. Furthermore a considerable quantity of manganese dioxide produced by the reduction of  $\text{KMnO}_4$  in GNRs has to be separated to produce graphene nanoribbons with a higher purity grade, which can be applied in future devices applications.

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