

## Building up multiwall carbon nanotubes nanostructures inside millimetric channels of ceramic monoliths

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**Abstract.** Multiwall carbon nanotubes were grown inside the millimetric channels of commercial ceramic materials, cordierite monoliths, using a modified catalytic chemical vapor deposition method. Fe(CO)<sub>5</sub> liquid catalyst precursor was introduced in gas phase at the same time as the acetylene carbon source to allow a more uniform distribution of carbon nanotubes on the substrate surface. Different techniques were used for the characterization of the obtained multiwall carbon nanotubes such as scanning and transmission electron microscopies, N<sub>2</sub> adsorption isotherms, Raman spectroscopy and thermogravimetric analysis. The results show that the surface of the ceramic monolith is progressively covered with multiwall carbon nanotubes reaching total coverage for longer times under reaction. The carbon nanotubes were built up with a tree-like morphology. So, firstly larger carbon nanotubes are formed as the tree trunks on the cordierite surface, followed by the growing on them of narrower and longer nanotubes suggesting the tree branches.

### 1. Introduction

Catalysis is currently recognized as a potential field for application of carbon nanotubes (CNTs), and in the last ten years the number of publications and patents on this subject has been increasing exponentially [1-6]. In most of the cases, the use of these nanomaterials as support leads to achieve better performances than conventional carbon supported catalysts [7]. These improvements are suddenly attributed to the presence of nanopores where the active phases are placed [8]. Also the CNTs can be directly used as catalysts, for instance, in the air oxidation of organic pollutants in waste water [9]. However, the carbon nanotubes tend to agglomerate forming bundles, which limits the possibility of their application as real catalysts.

On the other hand, ceramic monolithic supports have been employed for many catalytic applications, because of their low-pressure drop, large geometric surface area, short diffusion distances, improved fluid dynamic properties, lack of attrition by vibrations and thermal shock resistance [10-12]. In the present work we aim to combine the technical advantages of monolithic macrostructures with the CNTs nanoproperties [13], to obtain heterogeneous catalysts consisting of efficient nanocarbon materials placed on real applied reactor elements. The first compulsory step in this nanofabrication process is to grow CNTs inside the millimetric channels of commercial ceramic materials. If possible, these CNTs should be produced aligned and perpendicular to the monolith walls. At this point, we present some results of the application of a catalytic chemical vapor deposition method to generate multiwall carbon nanotubes over a ceramic monolithic support. Among the different methods of carbon nanotubes synthesis [14-16], catalytic chemical vapor deposition (CCVD) is the only one which allows the growth of carbon nanotubes on solid surfaces with different chemical compositions. Many factors in this procedure have to be controlled, depending on the substrate surface where CNTs are deposited, such as source of carbon atoms, reaction temperature and contact time [17]. In this study we mainly evaluated the time of reaction, at a given temperature and using vaporized iron pentacarbonyl as catalyst, to understand the

distribution of carbon nanotubes on the walls of ceramic monoliths. The use of a liquid catalyst is a convenient and easy procedure [17,18], the catalyst is introduced in gas phase at the same time as the carbon source in contrast with the typical pre-incorporation of metallic nanoparticles on the surfaces [19].

## 2. Experimental

### 2.1. Carbon nanotubes synthesis

The cordierite monolith supports consist of small cylindrical blocks (3.7 cm diameter, 1.5 cm length) provided by Ceramiques Techniques & Industrielles S.A. The experimental set-up used to deposit multiwall carbon nanotubes (MWCNTs) by catalytic decomposition of acetylene comprises of a horizontal quartz tube reactor, of 47 mm inner diameter, within a furnace (see Figure 1).

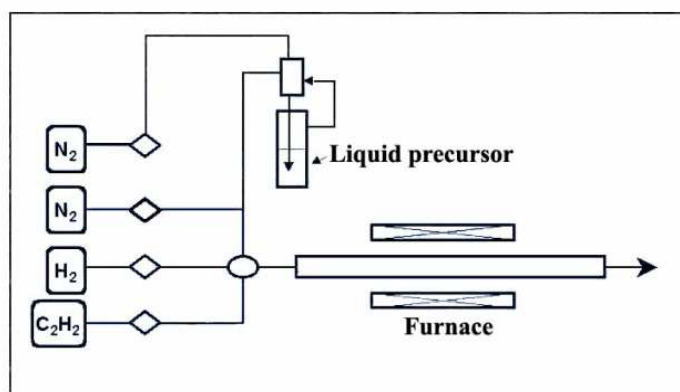


Figure 1. Schematic representation of the experimental set-up used for the preparation of carbon nanotubes from liquid catalytic precursor by CCVD.

A mixture of nitrogen, flow rate of 3850 sccm (standard centimeter cubic per minute) and hydrogen, flow rate of 40 sccm, was used as carrier gas. As mentioned above, the carbon source used was acetylene (40 sccm). On the other hand, the iron catalyst precursor employed was iron pentacarbonyl, Fe(CO)<sub>5</sub>. To introduce the metal catalyst precursor into the reaction zone, N<sub>2</sub> (150 sccm) was bubbled through the liquid carbonyl which was held at 0 °C [17]. The cordierite monoliths were placed in the reactor with the open channels in the direction of the gas flow. Metal catalyst precursors were thermally decomposed in the tubular reactor in order to form iron nanoparticles, on which MWCNT were nucleated and grown. Different reaction times were tested: 15, 30 and 60 min. The temperature was maintained constant during the reaction time at 1023 K. Finally, the furnace was cooled down to room temperature in inert atmosphere. The carbonaceous material deposited on/within the monolithic structures was subsequently characterized.

### 2.2. Characterization of product

Textural properties of the generated CNTs were studied by N<sub>2</sub> adsorption at 77 K, which were measured in Micromeritics ASAP 2010 equipment. Prior to adsorption isotherms, the samples were outgassed at 523 K for 8 h under vacuum. From N<sub>2</sub> adsorption isotherms, the surface areas were calculated by the Brunauer-Emmett-Teller equation, S<sub>BET</sub>. Transmission electron microscopy (TEM) was performed in a JEOL JEM 2000FX instrument. This technique enables the determination of the outer and inner diameter of the carbon nanotubes. Also, scanning electron microscopy (SEM) measurements, obtained in a Hitachi S-3000N equipment, were carried out on the coated monoliths in order to evaluate the alignment of the CNTs and their distribution on the channels of the monolithic material.

Thermogravimetric analysis was conducted using a C.I. Electronics microbalance. With this method the amount of grown carbon nanotubes can be deduced. The experiments were conducted under air atmosphere (100 ml/min), using an amount of 200 mg of sample, heating up to 1073K with a rate of 10K/min.

A Horiba iHR 320 Jobin-Yvon microspectrometer has been used to investigate the Raman spectra of the carbon nanotubes, which is equipped with 10x objective lens and a Synapse CCD detector. It works in the visible radiation range with an excitation laser source emitting at 632.81 nm. The exposition time was 30 seconds and the obtained spectra are the average of thirty runs.

### 3. Results and discussion

In order to analyze the influence of the reaction time on the generated carbon nanotubes, three equal parts of ceramic monolith were submitted to the reactants during periods varying from 15 to 60 minutes. Some representative SEM micrographs of the resulting composite MWCNT-monolith materials are presented in Figure 2. From these micrographs, it can be observed that MWCNTs are present all along the ceramic monolith internal channels. This latter was confirmed by examination of the lengthwise cut of the MWCNT-monolith composite. This situation would be of special interest from the point of view of engineering applications in a catalytic reactor. Also it can be seen that there is a higher amount of carbon nanofilaments on the sample submitted to longer reaction times (comparing the sample after 15 minutes in reaction with that at 30 minutes), which is indicating that the amount of deposited carbon nanotubes strongly depends on the reaction time.

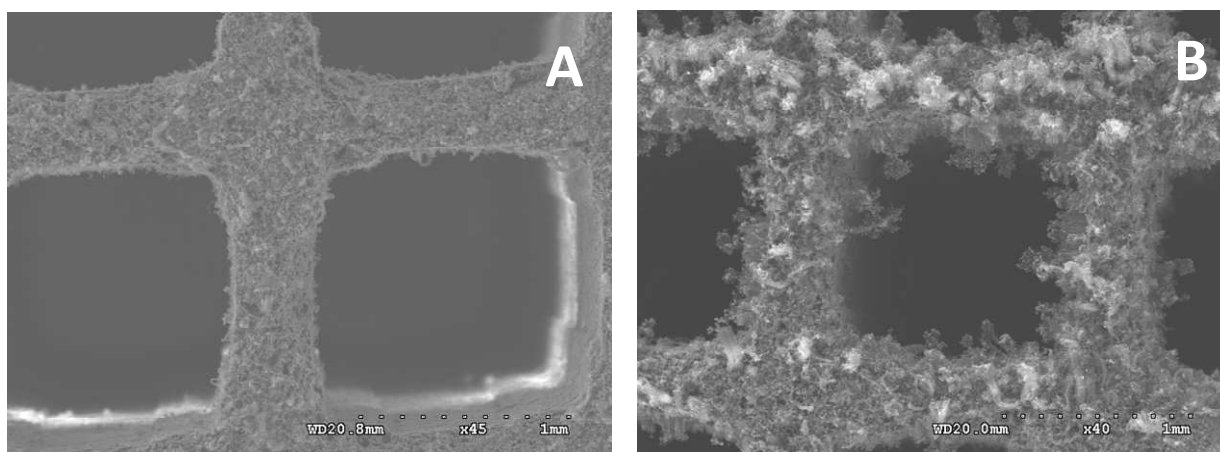


Figure 2. SEM micrographs of the sample after 15 minutes of reaction, A, and after 30 minutes of reaction, B.

Regarding the morphology of these carbon nanofilaments, different structures can be observed depending on reaction time. MWCNT bundles show different lengths and morphologies as it can be observed in an enlarged view of the micrograph 2 B (Figure 3A). In the micrograph 3B, it can be seen that the filaments have grown in a vertically aligned manner which is characteristic of carbon nanotubes grown on a planar surface, like for instance that obtained on quartz surfaces using this same preparation method [17]. Also, the presence of smaller filaments on the top of the initially generated CNTs indicating a production of MWCNTs with a smaller diameter should be emphasized.

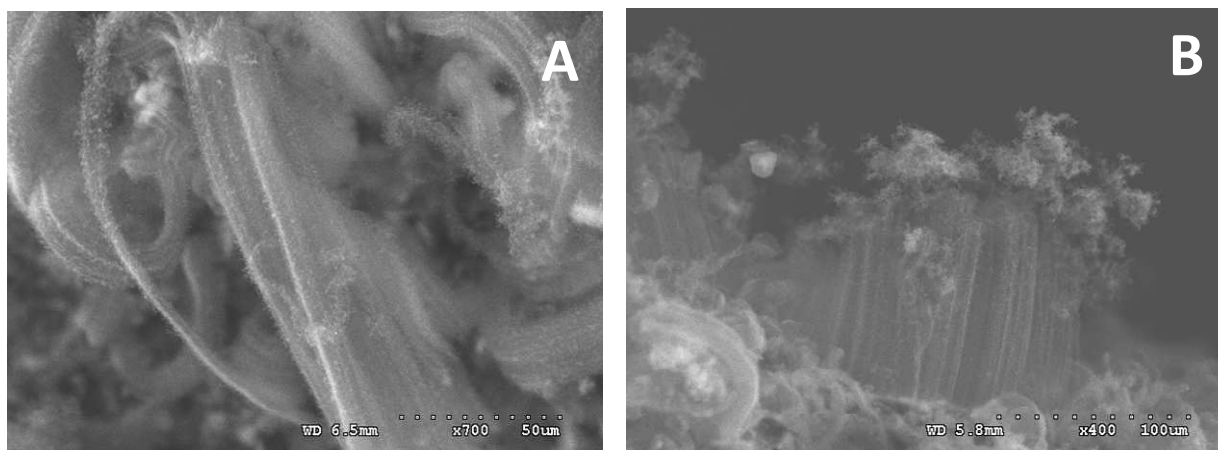


Figure 3. SEM micrographs of the sample after 30 minutes of reaction. It can appreciate nanofilaments in a bundle structure, A, and in a vertically aligned manner, B.

On the other hand, Figure 4A displays a detail of a monolithic wall covered with nanotubes after 60 minutes in reaction. MWCNT structures are raised on the two ceramic wall faces. It should be also noted that its special appearance is like a tree structure (Figure 3B), where there are big nanofilaments similar to the tree trunk and smaller nanofilaments like the branches. Formation process of such as structures could consist in the development of large nanofilament from large metal particles generated on the ceramic surface, and subsequent formation of smaller metal nanoparticles on the previous nanocarbon surfaces, on which smaller diameter nanotubes are deposited (Figure 4B).

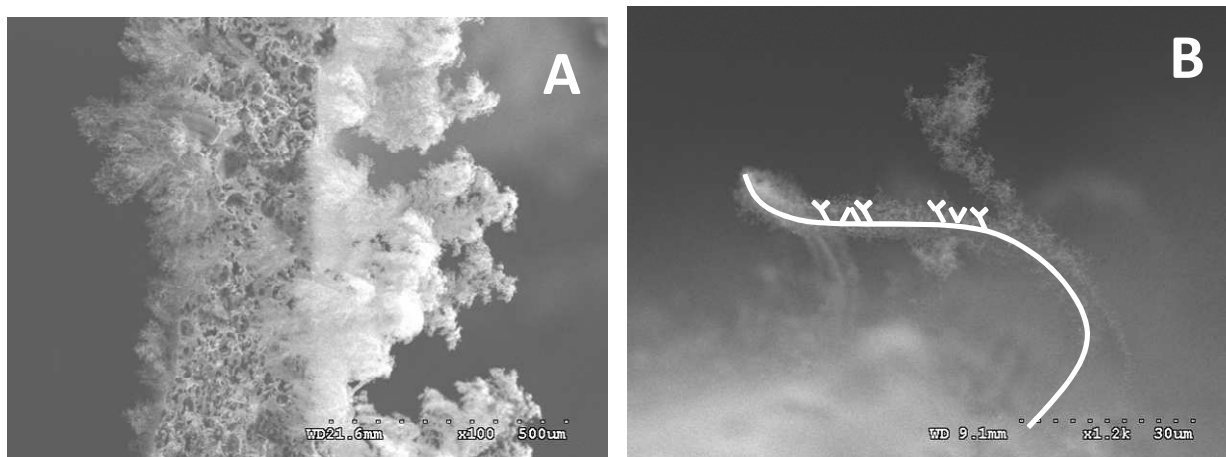


Figure 4. SEM micrographs of the sample after 60 minutes of reaction.

TEM micrographs of the carbon structures are shown in Figure 5. As it can be observed, these micrographs confirm that deposited carbons are multiwall carbon nanotubes (MWCNT). The images show some heterogeneity in all samples since carbon nanotubes with various diameter sizes can be seen. Also these MWCNTS exhibit closed and open ends, although this property seems not to be affected by the reaction time. The average inner and outer diameter is close to 10 nm and to 23.7 nm, respectively. Some metal catalyst particles are observed although these are scarce, even considering that these materials have not been purified after reaction. On the other hand, TEM images of MWCNT grown on monolithic material reveal certain similarities with to those grown on a quartz surface [17]. Amorphous carbon was not detected in the TEM micrographs.

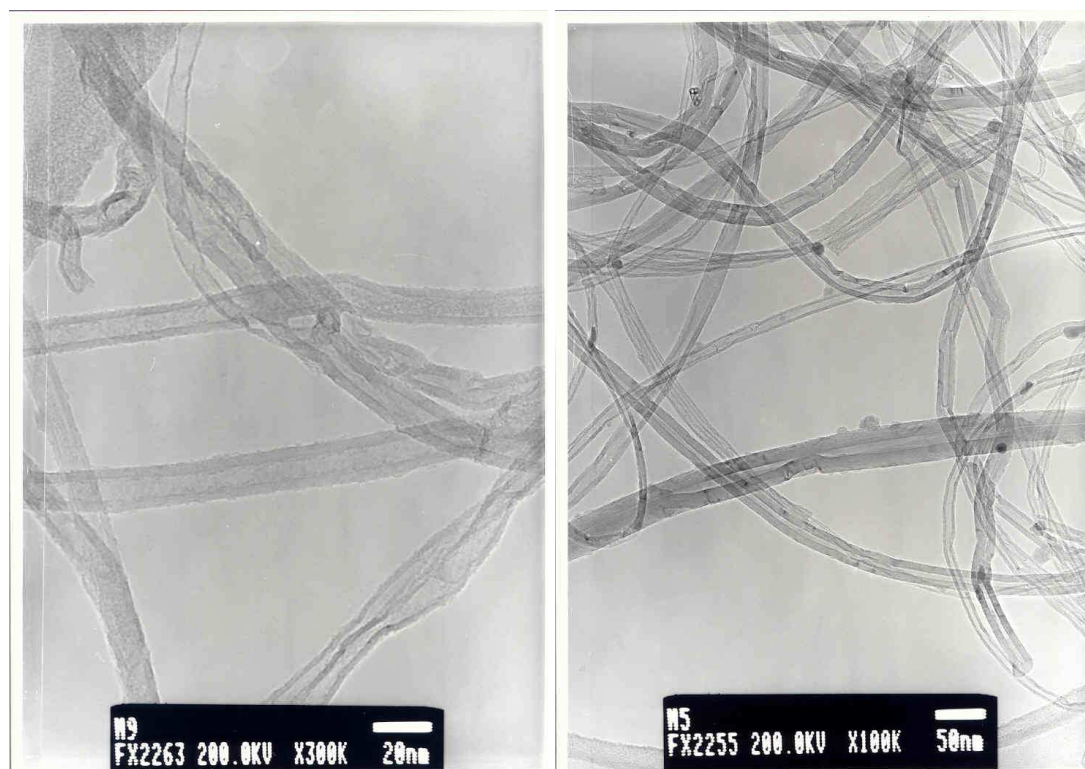


Figure 5. TEM image of MWCNTs synthesized at 1023 K using  $\text{Fe}(\text{CO})_5$  as metal catalyst precursor over cordierite monolith.

### 3.1 Thermogravimetric analysis

The thermogravimetric curves (TGA) of MWCNT-cordierite for two growth times are given in Figure 6. The loss of weight under air atmosphere of the samples after 15 and 60 minutes of reaction are 0.09% and 0.64%, respectively. This result confirms that the reaction time is a key factor in the amount of grown carbon nanotubes on the surface of the monolithic cordierite. The highest burning temperature for the sample treated during 15 minutes indicates that in this case, carbon nanotubes are more graphitized than in the sample after 60 minutes of reaction. This behavior could be due to the thinner and smaller nanotubes grown on the top of the larger nanotubes (Figures 3, 4). The smaller diameter size of these nanotubes could be the reason of the lower burning temperature. According to our hypothesis the tree grown structure consists of large nanotubes, acting as the tree trunk, and smaller nanotubes, as the branches. Lower burning temperature is present in smaller nanotubes because of their poorer graphitization.

### 3.2. Porosity

The nitrogen adsorption-desorption isotherm at 77 K for MWCNT generated on the cordierite monolith after 60 minutes of reaction is shown in Figure 7. The samples obtained after 15 and 30 minutes under reaction have not been studied because of the low yield of the carbon nanotubes produced. The isotherm corresponds to type II according to the IUPAC classification [20]. These isotherms are usually obtained for aggregates of plate-like particles and are indicative of capillary condensation. It is considered that porosity in MWNTs consists mainly of the inner hollow cores and aggregated pores formed by interaction of isolated MWNTs [21-23].

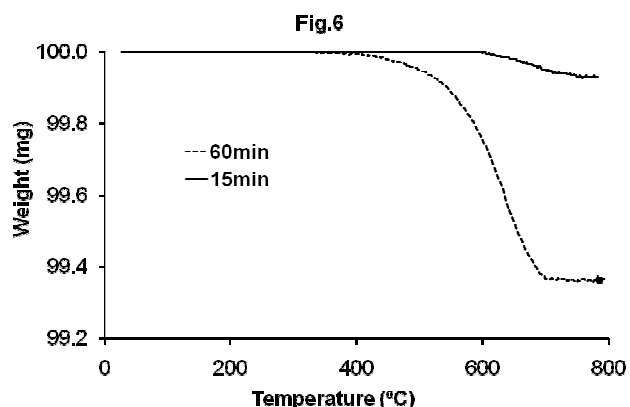


Figure 6. TGA of the samples after 15 and 60 minutes of reaction.

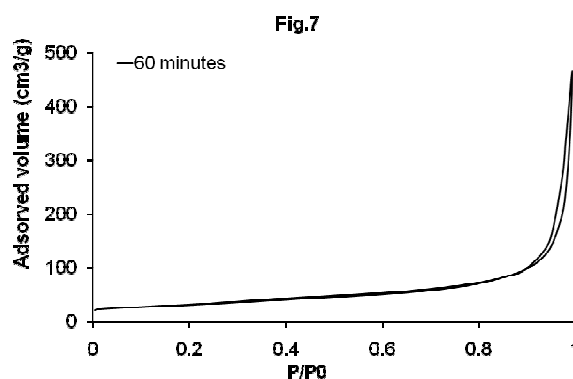


Figure 7. N<sub>2</sub> Adsorption-desorption isotherm of the MWCNT-cordierite sample after 60 minutes of reaction.

N<sub>2</sub> adsorption isotherms were analyzed by the Brunauer-Emmett-Teller (BET) equation, obtaining the surface area,  $S_{BET}$ . In addition, the Dubinin-Radushkevich (DR) equation was applied to obtain the total micropore volume. On the other hand, the volume of mesopores of  $2\text{nm} < \phi < 20\text{nm}$  was calculated by the difference between the volume of N<sub>2</sub> adsorbed at  $P/P_0=0.9$  and  $P/P_0=0.2$  (expressed as liquid). The calculated specific BET surface area, micropore and mesopore volume are presented in Table 1. BET surface area is  $119\text{ m}^2/\text{g}$  and mesopore volume is  $0.22\text{ cm}^3/\text{g}$ , both correspond to the expected values for this kind of carbon materials [24, 25].

### 3.3 Raman spectroscopy

Raman spectra of samples after 15 and 60 minutes of reaction are presented in Figure 8. The bands G, D and D' (as a shoulder of band G) are depicted. Band G, at about  $1580\text{ cm}^{-1}$ , arises from ideal lattice vibration mode with  $E_{2g}$  symmetry. Bands D and D', usually around  $1350$  and  $1620\text{ cm}^{-1}$ , respectively, are related with defects [26]. D is due to graphene layer edges, D' was assigned to a lattice vibration analogous to that of the G band, but involving graphene layers at the surface of a graphitic crystal, i.e. graphene layers which are not directly sandwiched between two other graphene layers.

Comparing the spectra of the different samples, significant modifications are found in the defects band D ( $1350\text{ cm}^{-1}$ ), being considerably less intense in the sample submitted to reaction during 15 minutes. The ratio  $I_D/I_G$  that serves as a measure of the amount of defects [27], has been calculated for the two samples. The  $I_D/I_G$  ratio calculated is increased in the 60 minutes sample, which means that the structural disorder increases with the reaction time and with the growth of smaller and disorganized carbon nanotubes, in agreement with the above discussion of the TG results.

### 4. Conclusions

This work describes the preparation of MWCNTs by CCVD, inside the channels of cordierite ceramic monoliths, using different times of reaction to follow the growing mechanisms (morphology and characteristics of the generated nanocarbon materials). The synthesis method, catalytic chemical vapor deposition, where the liquid catalyst is introduced at the same time as the carbon source seems to be especially well adapted to this nanofabrication process inside the channels. This improved method allows a uniform distribution of carbon nanotubes on the substrate surface.

Different microscopy techniques, such as TEM or SEM, have shown that these nanostructures are multiwall carbon nanotubes. These nanotubes grow in a special tree-like morphology where, firstly larger filaments are formed as the tree trunk followed by smaller filaments simulating the tree branches. In this sense, this method permits the preparation of a composite material with potential application in the field of heterogeneous catalytic processes.

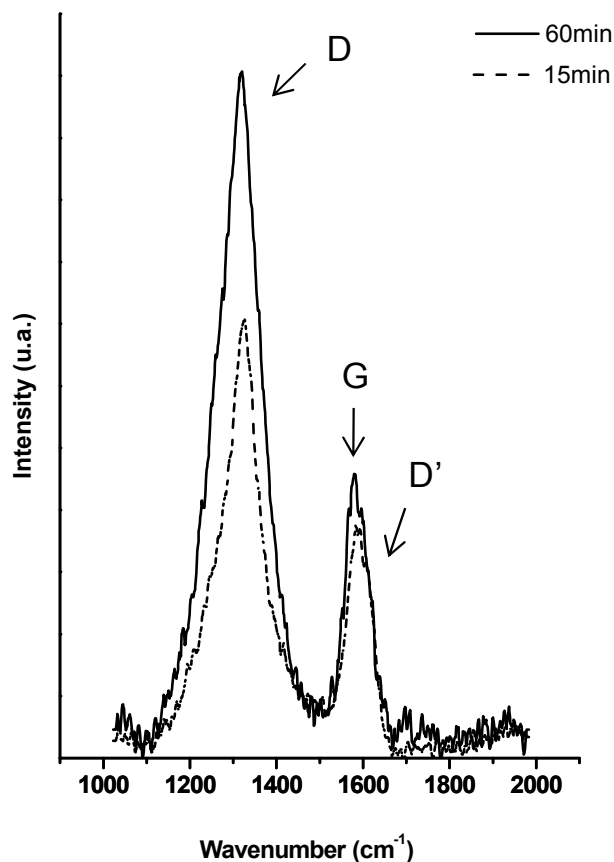


Figure 8. Raman spectroscopy spectra of samples after 15 and 60 minutes of reaction.

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