Dual Catalytic Purpose of the Tungsten Filament During the Synthesis of Single-Helix Carbon Microcoils by Hot-Wire CVD

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ABSTRACT

We report on the deposition of crystalline single-helix carbon microcoils, in the as-deposited state, by the hot-wire chemical vapor deposition process without any special preparation of nano-sized transition metal catalysts and subsequent post-deposition annealing. Tungsten, originating from the heated tungsten filament, is identified as the catalyst material responsible for the growth of the microcoils. High-resolution transmission spectroscopy, combined with Raman spectroscopy, confirm that the as-deposited microcoils are crystalline, which is induced by the high deposition temperature in the vicinity of the heated filament. These results suggest a simplified, less tedious deposition process for the growth of carbon microcoils, once the process has been optimized.

KEYWORDS

Carbon microcoils, hot-wire CVD, crystallinity, high-resolution transmission electron microscopy

1. INTRODUCTION

Carbon microcoils (CMCs), with its three-dimensional helical structure and unique properties, are considered as potential candidates for absorbers of electromagnetic waves[1], micro sensors[2] and hydrogen absorption materials[3]. CMCs are traditionally synthesized via chemical vapour deposition (CVD) of carbon precursors such as propane[4] and acetylene[5] over nano-sized transition metal catalysts, such as nickel or iron, at growth temperatures ranging from 700 – 1100 °C. Recently, hot-wire CVD (HWCVD) was employed for the deposition of amorphous single-helix CMCs (SHCMCs)[6] and double-helix CMCs (DHCMCs)[7] with methane as a carbon source.

At present, there are two dominating mechanisms that describe the growth of these peculiar structures and they differ on the exact cause of the fiber coiling on a transition metal catalyst. According to Motojima's mechanism[8] the anisotropy of the catalyst particles, formed by the different concentrations of carbon, sulphur and oxygen at the respective crystal faces, is proposed to be the driving force for coiling formation of carbon fibers. Conversely, Amelinckx et al[9] suggest a growth mechanism of a graphitic coil based on a difference in the extrusion velocities of carbon from the bulk of the catalysts particle.

However, some drawbacks to the synthesis of CMCs still exist. Controlled and, sometimes, tedious nano-catalyst preparation is crucial to ensure the formation of CMCs. Furthermore, the as-deposited CMCs are amorphous and require further heat treatment at 2500 °C to be graphitised[7]. Another concern is the addition of hazardous sulphur to the reaction, which resulted in an enhancement in the coil yield and reproducibility[10].

We report on the deposition of crystalline SHCMCs using HWCVD in the absence of any special catalyst preparation and without any post-deposition annealing at high temperatures. The results suggest a significant reduction in the processing time and cost to obtain graphitized SHCMCs.

2. EXPERIMENTAL

2.1 Synthesis

Carbon microcoils were deposited using a horizontal quartz tube-based hot-wire CVD reactor. A detailed experimental set-up of the system is reported elsewhere[11]. A gas mixture consisting of 10 sccm methane and 100 sccm hydrogen was introduced to the system via the gas inlet and passed parallel over a coiled tungsten filament (length of 350 mm and diameter of 0.5 mm), resistively heated to a temperature of 1600 °C. The pressure in the reactor was maintained at 150 Torr during deposition and the total deposition time amounted to 15 minutes. It should be noted that no transition metals, such as Ni, Co or Fe, necessary for the nucleation of CMCs, were specially prepared and present in the reactor during deposition. Black soot, containing the CMCs, was collected on the inner walls of the quartz tube, about 12 mm below the filament where the temperature during deposition was ~ 1200 °C.

2.2 Characterization

The morphology and microstructure of the soot were investigated using a LEO 1525 field emission scanning electron microscope (SEM) operated at 10 kV and equipped

with energy dispersive X-ray spectroscopy (EDS) facilities for elemental composition. A Tecnai F20 field emission high-resolution transmission electron microscope (HR-TEM), operated at 120 kV and equipped with EDS was employed to examine the internal structure, elemental composition and crystallinity of the CMCs. Specimens for HR-TEM analysis were prepared by dispersing the soot in methanol, of which a drop was subsequently transferred to a holey-carbon copper grid and dried at ambient conditions. The structural properties were investigated using a Jobin-Yvon HR800 micro-Raman spectrometer in backscattering geometry at room temperature. The Raman spectra were collected in the region 100 – 1000 cm^{-1} with a spectral resolution of 0.4 cm^{-1}, using an excitation wavelength of 514.5 nm.

3. RESULTS AND DISCUSSION

Fig. 1 shows a representative SEM micrograph of the soot collected after the deposition. The soot is composed of amorphous carbon, straight fibers (probably carbon nanotubes) and SHCMCs with various coiling morphologies and diameters. The percentage of CMCs in the soot was roughly estimated to be 25 – 30 %. Both flat and circular SHCMCs are present with fiber-diameters of ~ 0.3 µm. The coil diameter and length of the two types of SHCMCs is approximately 1 µm and 10 µm, respectively. The pitch of the flat coil is ~ 0.5 µm while that of the circular SHCMC is roughly 0.9 µm. EDS analysis reveals that W is present in the sample, which originates from the heated W-filament (see insert in Fig. 1). Given that CMCs require a nano-sized transition metal to grow; this result illustrates that the W-filament serves a dual purpose. Firstly, it catalytically dissociates the precursor gasses and, secondly, acts as a supplier of catalysts particles for the growth of CMCs. However, at this point

it is not clear whether the growth occurs in the gas phase or if the W-catalysts particles are supported on the quartz tube.

Fig. 2 presents a TEM micrograph of an isolated SHCMC, indicating that its internal structure is comprised of areas with crystal planes that are orientated parallel to the coiling direction. This is most evident at the bends of the coils where the crystal planes appear to have dislocated, possibly due to severe strain induced at these positions. EDS analysis, shown in Fig. 3, performed on the coil at the position marked "X" in Fig. 2 confirms the presence of W in the CMC. It should be noted that the trance amounts of Cr, shown in the EDS spectrum, originate from the electrical contacts of the W-filament. An interesting observation is that the coil appears to have regions with reduced compactness, contrary to previous reports on either a completely compacted structure[7] or a tubular internal structure[9]. The HR-TEM micrograph presented in Fig. 4 illustrates that the as-deposited SHCMCs are crystalline with a spacing of ~ 0.35 nm, consistent with that of graphite.

The crystalline nature of the soot is confirmed in the Raman spectrum shown in Fig. 5. The vibrational mode at ~ 1580 cm^{-1} corresponds to the first order peak of well crystallized graphite (G-band) while the disorder (D-band) centered around 1350 cm^{-1} corresponds to the first order peak of defects in the graphite lattice and amorphous carbon impurities[12]. The high ratio of the G-band to D-band intensity (I_G/I_D ~ 6.44) and the narrowing of the G-band confirm the graphitic nature of the soot. The graphitic structure of the as-deposited SHCMCs at our deposition conditions suggests that the conventional post-deposition annealing step at high temperatures, required to induce crystallinity, is not mandatory[7].

We propose a growth mechanism for the crystalline SHCMCs based on that of Amelinckx et al[9] in terms of a combination of the vapour-liquid-solid (VLS) mechanism and a screw dislocation in the crystal lattice. Initially, the VLS mechanism occurs, i.e. the carbon generated by the CH_4 dissociation process at the filament dissolves into the W-catalysts particles until supersaturation occurs and subsequently precipitates on the W-catalyst surface. The different carbon extrusion velocities induce strain on the lattice causing it to dislocate between the regions of different carbon deposition rates. Subsequently, this process leads to an alteration in the crystal orientation, i.e. a coil, as illustrated in the TEM micrograph presented in Fig. 2. Provided that the catalyst particle retains its activity; this process promotes the successive rearrangement of the deposited carbon into the shape of a helix. The crystalline structure of the CMCs is induced by the high growth temperatures, originating from the radiative heating of the filament.

4. CONCLUSION

We have successfully employed HWCVD to deposit graphitized flat and circular SHCMCs with various coil pitches and lengths. The filament has a dual role in the deposition process by dissociating the precursor gases and supplying the catalysts for the growth of the SCMCs. The suggested growth mechanism involved a combination of the traditional VLS mechanism and a screw dislocation theory induced by the different carbon extrusion velocities. Thermal radiation from the heated filament enhanced the graphitic structure of the SHCMCs. The results presented in this study

suggest further optimization in terms of the selectivity, catalytic activity and control of the morphology and coil yield.

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LIST OF FIGURE CAPTIONS

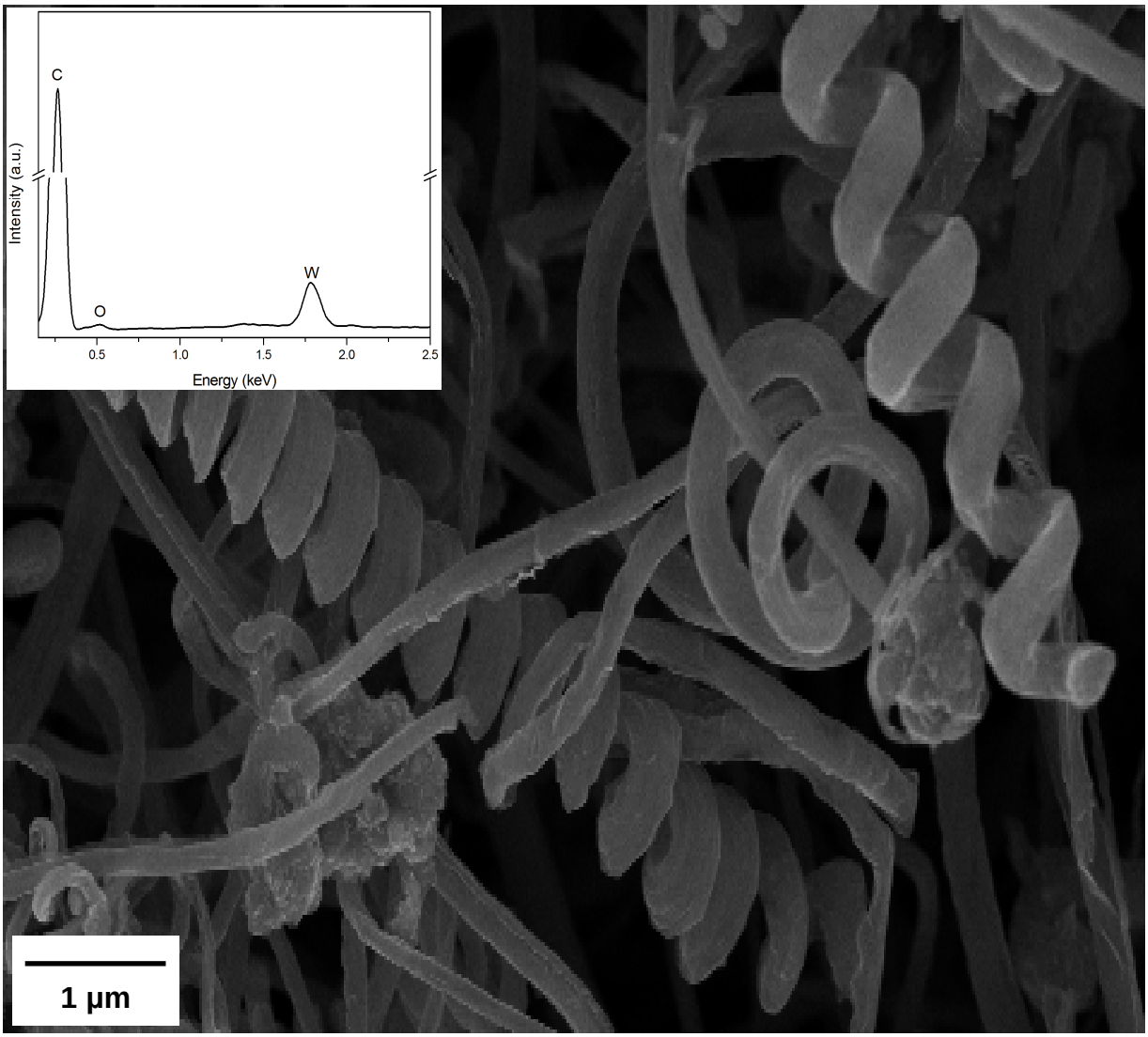
Figure 1 SEM micrograph of the soot and its corresponding EDS spectrum (insert)

Figure 2 TEM micrograph of an isolated SHCMC

Figure 3 EDS spectrum collected at position X shown in Figure 2

Figure 4 HR-TEM micrograph of the SHCMC

Figure 5 Raman spectrum of the soot



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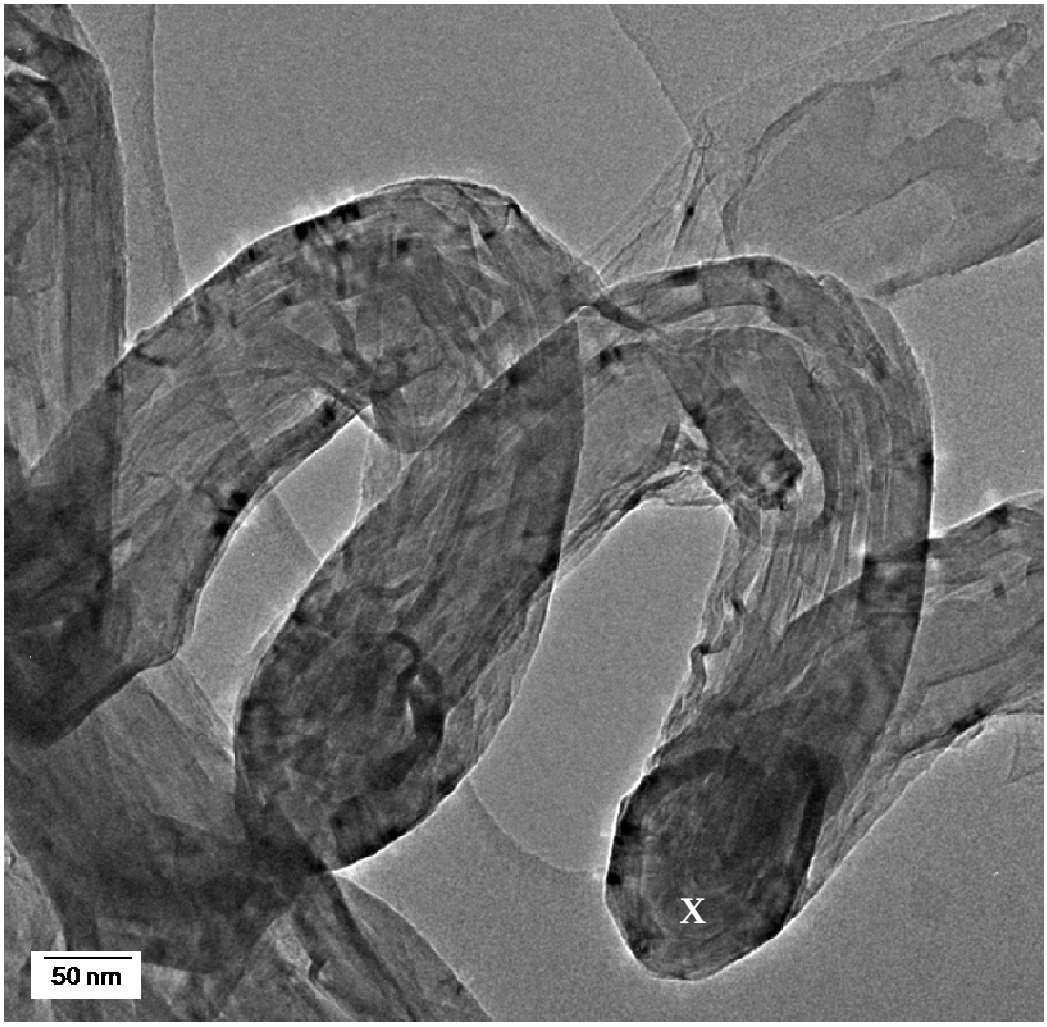

Figure 2 (Oliphant et al)

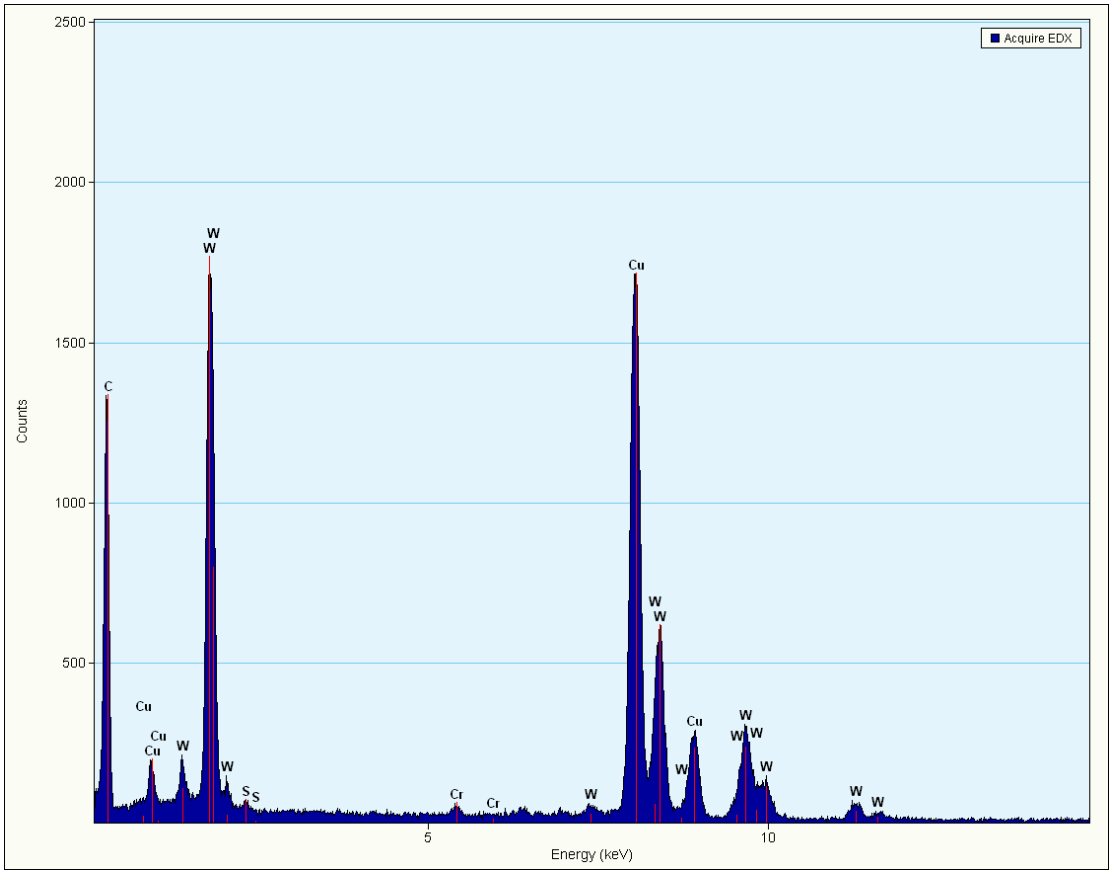

Figure 3 (Oliphant et al)

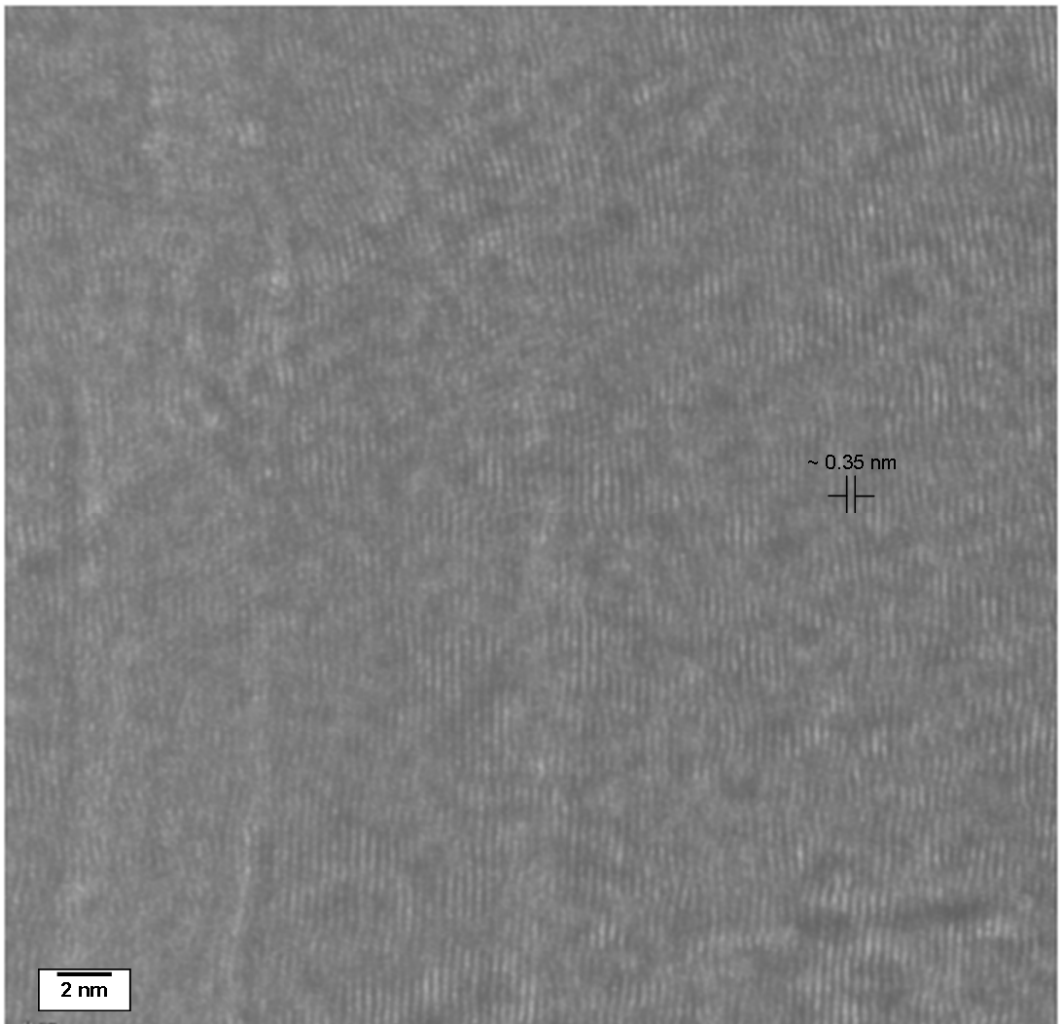

Figure 4 (Oliphant et al)

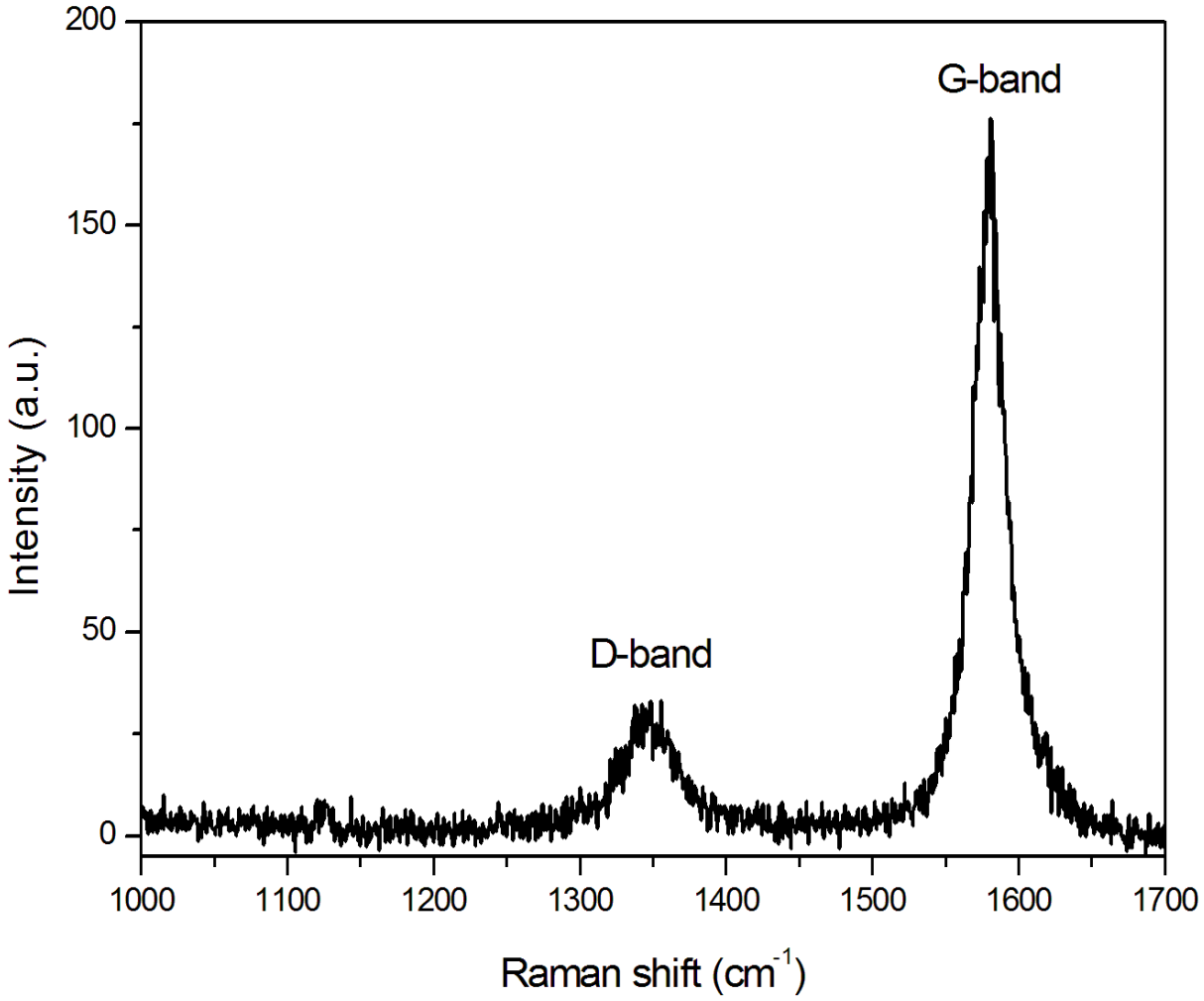

Figure 5 (Oliphant et al)