

# Synthesis of graphene through direct decomposition of CO<sub>2</sub> with the aid of Ni–Ce–Fe trimetallic catalyst

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**Abstract.** In this study, few-layered graphene (FLG) has been synthesized using the chemical vapour deposition (CVD) method with the aid of a novel Ni–Ce–Fe trimetallic catalyst. Carbon dioxide was used as the carbon source in the present work. The obtained graphene was characterized by Raman spectroscopy, and the results proved that high-quality graphene sheets were obtained. Scanning electron microscopy, atomic force microscopy and transmission electron microscopy pictures were used to investigate the morphology of the prepared FLG. The energy-dispersive X-ray spectroscopy results confirmed a high yield (~48%) of the obtained graphene through this method. Ni–Ce–Fe has been shown to be an active catalyst in the production of high-quality graphene via carbon dioxide decomposition. The X-ray photoelectron spectroscopy spectrum was also obtained to confirm the formation of graphene.

**Keywords.** Chemical vapour deposition; carbon dioxide; Ni–Ce–Fe trimetallic catalyst; graphene.

## 1. Introduction

The allotropes of carbon differ in the way the atoms bond with each other and arrange themselves into a structure. Some of the common structures are carbon nanotubes, graphene, fullerenes, carbon nanofibres and diamonds. In the most commonly used form, graphite, atoms of carbon form planar layers of graphene [1]. Each layer is composed of rings containing six carbon atoms. The rings are linked to each other in a hexagonal structure. Each atom has three sigma bonds with an angle of 120° which connect to three neighbouring rings. The fourth electron of each atom becomes part of an extensive  $\pi$ -bond structure. Graphite conducts electricity owing to the electrons in the  $\pi$ -bond structure, which can move around throughout the graphite structure. Bonds between atoms within a graphene layer are strong, but the Van der Waals force between the layers is weak [2]. One property of graphene is that the layers can slip past each other. Naturally existing graphite occurs in two forms: alpha, which is hexagonal, and beta, which is rhombohedral. These two forms have identical physical properties but different crystal structures. These two forms can be converted to each other: the alpha form can be converted to the beta by mechanical treatment, and the beta form can be converted to the alpha form if heated above 1000°C.

In most of the applications of graphene, such as microelectronics, optoelectronics, graphene-based batteries, graphene-based sensors [3], supercapacitors and thermal control [4] and

methanol storage materials [5], graphene with a large, high-quality surface area, and few structural defects is needed. Graphene, which has a hexagonal arrangement of carbon atoms forming a one-atom thick planar sheet, is a promising material for future electronic applications due to their high electrical conductivity as well as chemical and physical stabilities [6]. Planar graphene films have been synthesized using various methods including mechanical exfoliation from highly oriented pyrolytic graphite, chemical exfoliation from bulk graphite, thermal decomposition of carbon-terminated silicon carbide and chemical vapour deposition (CVD) [7,8]. The CVD method is a method which typically produces high-quality graphene with few defects [9]. The catalytic CVD is currently the most viable process for the synthesis of graphene. The first study on the synthesis of few-layered graphene (FLG) using the CVD method was reported by Somani *et al* [10]. Since then, the CVD process has become a common and reliable method for the production of high-quality graphene [11]. The CVD process has numerous advantages such as obtaining large graphene domains. Most importantly, since some transition metals can be dissolved in acidic solutions, the graphene deposited over the surface of metallic catalysts can be easily purified.

The growth of high-quality graphene over the surface of metallic catalysts using CVD technology has been the subject of both fundamental and technological attention in recent years. The growth of graphene mono-layers on single-crystalline transition metals such as Co, Pt, Ir, Ru, Ni, Fe and Mo is well known. For example, Fe-based catalysts can operate at higher temperatures when compared with Co- or

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Ni-based catalysts without suffering from deactivation. Additionally, in order to improve the graphitization degree of Fe-based catalysts, several transition metals such as Co, Ni, Mo and Cu have been employed as catalyst additives [12]. However, the formation of a uniform monolayer of graphene has still remained a challenge [13].

Out of monometallic catalysts, Ni has a relatively high carbon solubility at elevated temperatures when compared with other metals [14]. Moreover, cerium has been reportedly used in the chemical oxidation of graphene to facilitate production [15]. However, metallic nanoparticles (NPs) consisting of more than one metal have attracted a great deal of attention because of their unique electronic and catalytic properties [16,17]. The superior catalytic activity of multi-metallic NP-based catalysts in comparison with monometallic catalysts is believed to be due to the interplay between the electronic and lattice effects of the metal mixture [18,19]. A number of reports exist on the bimetallic systems, however, studies with regard to the NPs consisting of multiple metal components are scarce [20]. Therefore, in this study, the (Ni–Ce–Fe) trimetallic catalyst has been prepared and employed in the CVD process for the production of graphene.

The nucleation and growth of graphene usually occurs by exposure of the transition metal surface to a carbon containing gas [21]. Hydrocarbon-based reactants such as methane ( $\text{CH}_4$ ) are commonly used as the carbon source for the production of graphene [22]. Carbon dioxide ( $\text{CO}_2$ ) is an alternative carbon source: it is one of the most abundant carbon containing and also one of the main greenhouse gases [23]. The increase in the  $\text{CO}_2$  concentration of the atmosphere has become an alarming issue in recent decades. This has led the researchers to find a way to reduce  $\text{CO}_2$  emissions from all sources. One of the promising methods was found to be the catalytic reduction of  $\text{CO}_2$ . Furthermore,  $\text{CO}_2$  has the potential to be used as a raw material in the synthesis of organic molecules. Although a few studies have employed carbon dioxide as a carbon source for the production of graphene [24,25], the literature still lacks investigation

concerning the application of bi and trimetallic catalysts for graphene production. For this reason, the possibility of thermally splitting  $\text{CO}_2$  has become the subject of numerous studies [26]. Trimetallic catalysts have been successfully employed for the synthesis of CNTs [27], however, to the best of our knowledge, no reports are available to address the effect of trimetallic catalysts on the production of graphene. In the present work, a novel trimetallic catalyst has been prepared and used to produce graphene in a CVD process via  $\text{CO}_2$  decomposition.

## 2. Methodology

All materials were purchased from Sigma Aldrich with high purity (99.9%) and were used without further purification. The co-precipitation method was carried out by dissolving a mixture of 8 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 8 g  $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  and 5 g  $\text{Ce}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in water. The mixture was stirred while heated at  $100^\circ\text{C}$  for 5 h. The obtained solution was precipitated by sodium hydroxide at room temperature and centrifuged. The result was filtered and washed with ethanol and then dried in oven at  $120^\circ\text{C}$  for 24 h. After drying, the catalyst was calcined at  $600^\circ\text{C}$  for 6 h.

For the graphene production, the obtained catalyst was placed in a horizontal stainless-steel tubular reactor (figure 1) and heated while Ar was introduced to drive air out. Then, the reaction tube was purged with  $\text{H}_2$ , and the temperature was raised to  $800^\circ\text{C}$ . Subsequently, the carbon dioxide was introduced at an elevated temperature of  $1100^\circ\text{C}$  with a flow rate of  $900 \text{ cm}^3 \text{ min}^{-1}$  while the flow rate of  $\text{H}_2$  was raised to  $1500 \text{ cm}^3 \text{ min}^{-1}$  and kept for 1 h. The black flakes of the as-prepared carbon soot in the tube were formed within the catalyst powder in the combustion boat and was collected to be characterized. The obtained carbon soot was dipped in 37% HCl and successively into water to remove the catalyst. The schematic picture of the CVD instrument is presented in figure 1.

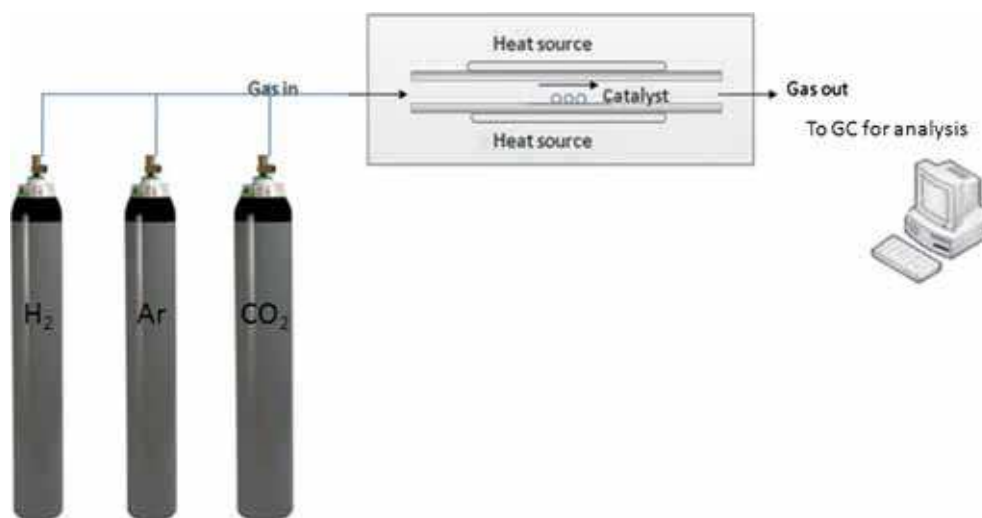
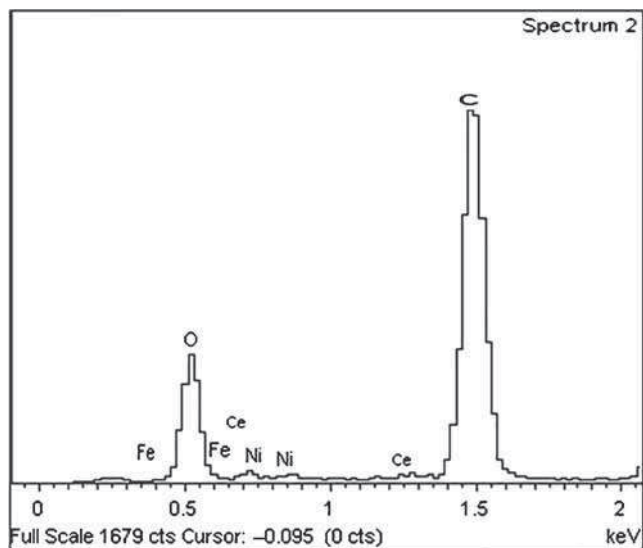


Figure 1. Schematic picture of the CVD instrument.

Scanning electron microscopy (SEM) pictures were used to visualize the graphene and determine its surface morphology using a Zeiss SUPRA55 scanning electron microscope at an operating voltage of 3 kV. Transmission electron

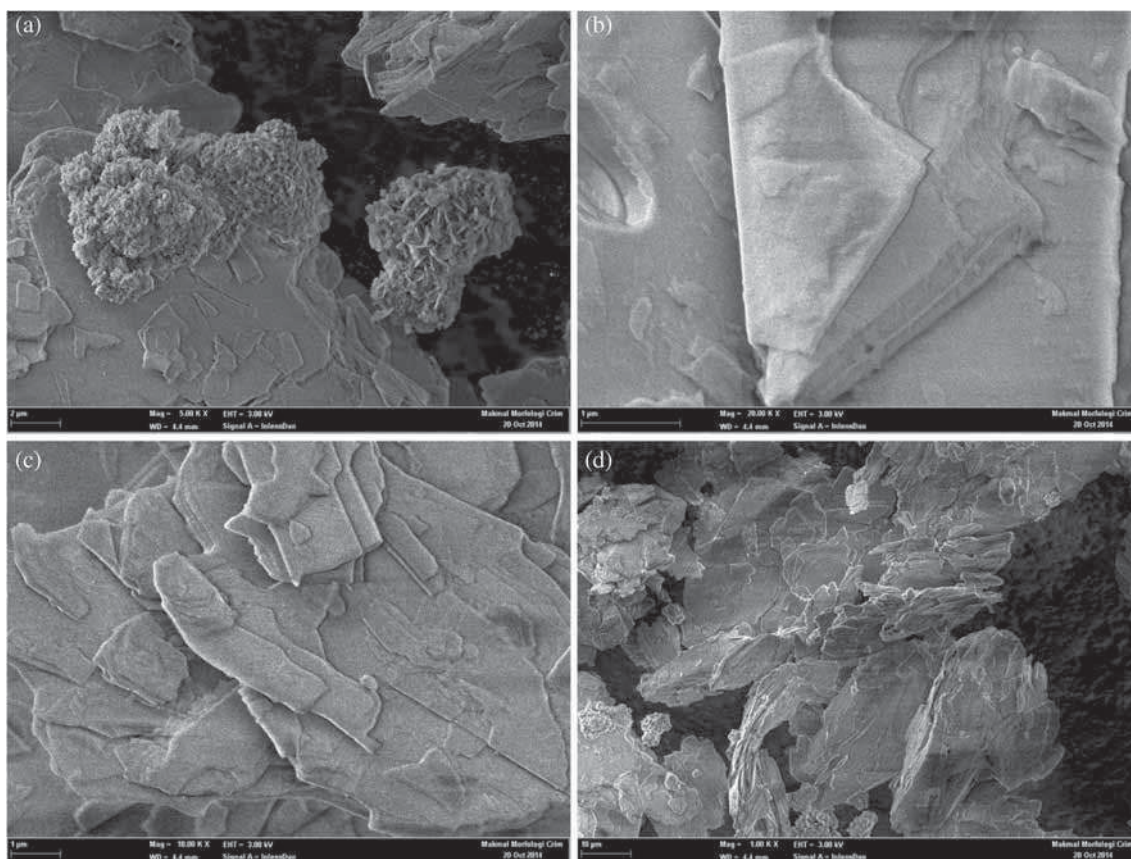
microscopy (TEM) (PHILIPS CM-12) and atomic force microscopy (AFM) (NTegra Prima, NT-MDT, Russia) were also performed to visualize the graphene sheets. Energy-dispersive X-ray spectroscopy (EDX) (Zeiss SUPRA55) was used to investigate the weight percentage of the present elements in the synthesized powder. Raman spectrophotometer with a laser of 514 nm wavelength (Horiba Jobin Yvon, LabRam HR800) was used to confirm the formation of the obtained graphene. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Analytical Digital 500, High Voltage Inc.



**Figure 2.** Energy-dispersive X-ray spectroscopy of the obtained graphene after the CVD process.

**Table 1.** Weight percentages of the present elements in the obtained powder, after the CVD process.

Element	Weight%
C	55.08
O	17.64
Fe	22.83
Ni	3.27
Ce	1.18
Total	100



**Figure 3.** SEM images of (a) the graphene grown over the trimetallic (Ni–Ce–Fe) catalysts and (b–d) the graphene sheets obtained after purification.

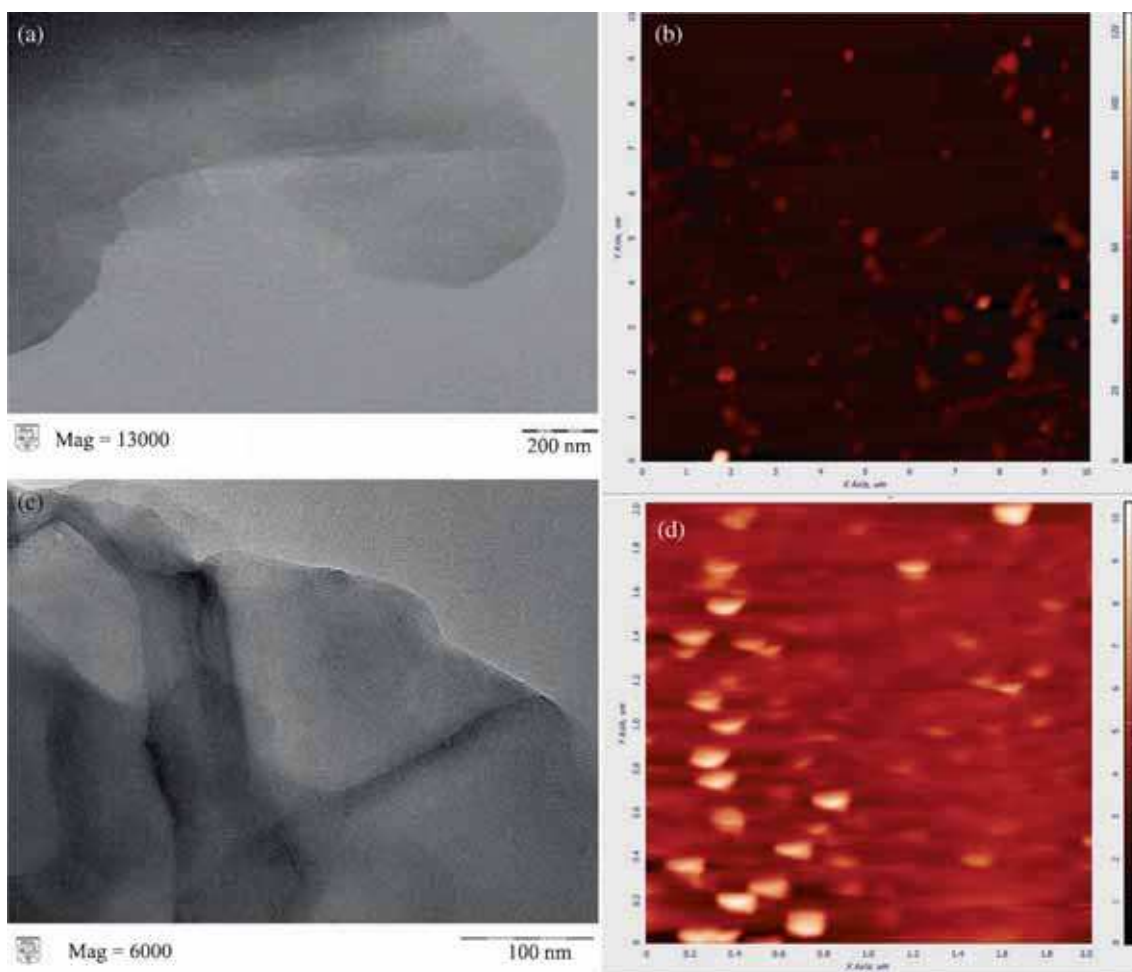
### 3. Results and discussion

The EDX result of the prepared powder is presented in figure 2. The EDX result confirms that carbon is the dominant atomic composition which is present along with oxygen as well as Ni, Ce and Fe, which are the elements of the trimetallic catalyst. The weight percentage of the present elements after the CVD process is presented in table 1. It can be noted that carbon has the highest weight percent of 55.08%. This can be concluded that the prepared novel trimetallic catalyst has played an active role in producing carbon through the CVD process. The yield of graphene achieved using this method was calculated to be 47.83%.

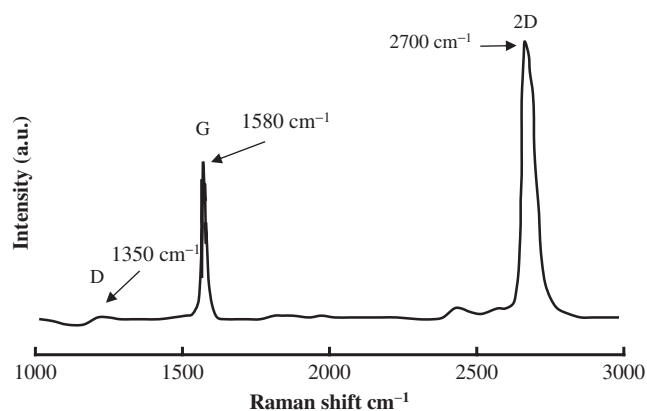
SEM was used to visualize the obtained graphene (figure 3). Figure 1a shows the graphene grown in the medium gaps surrounded by the catalysts before the purification. The SEM images of the graphene exhibit sheet-like structures (FLG) that are randomly scrolled and crumpled and are closely interacting with each other. Figure 3b–d shows the graphene sheets obtained after the purification. The interaction among the graphene sheets arise from their wrinkles, which provide graphene with good mechanical properties and prevent further aggregation [28]. Kawai *et al* [29]

described the growth mechanism of carbon graphene as such that in a high energy and low diffusion rate condition, carbon species form graphene sheets and collide to form FLG structures. This growth mechanism was predicted by tight-binding molecular-dynamics simulations.

In general, there are two types of graphene growth mechanisms: (1) surface segregation of carbon atoms and (2) surface decomposition of hydrocarbons. The mechanism of graphene layer growth is defined based on the catalyst and substrate. In the surface segregation mechanism, graphene layers grow from carbon atoms diffusing in the free surface sites of transition metals [30]. In the surface decomposition mechanism, graphene layer growth is governed by the carbon atoms that are produced by the decomposition of a hydrocarbon directly on the surface of the metal [31]. At high temperatures, the carbon source decomposes into various radicals, some of which travel to the catalyst surface. Once the radicals reach the surface of the metal, the nucleation process begins to result in the formation of graphene grains. These grains unite to form a continuous layer of graphene film [32]. However, in a typical thermal catalytic CVD method, the film grown over the metal substrate reduces the catalytic activity because of catalyst hindrance, known as ‘catalyst poisoning.’



**Figure 4.** TEM micrograph of the grown graphene sheets.



**Figure 5.** Raman spectrum of the obtained graphene.

ending the reaction and the formation of graphene film [13]. Figure 4 shows TEM and AFM micrographs of the graphene sheets formed after the synthesis reaction. The FLG sheets with average thickness equal to  $\sim 8$  nm are obvious in the TEM images. The surface morphology as well as the layers of the graphene sheets can also be observed in the AFM images.

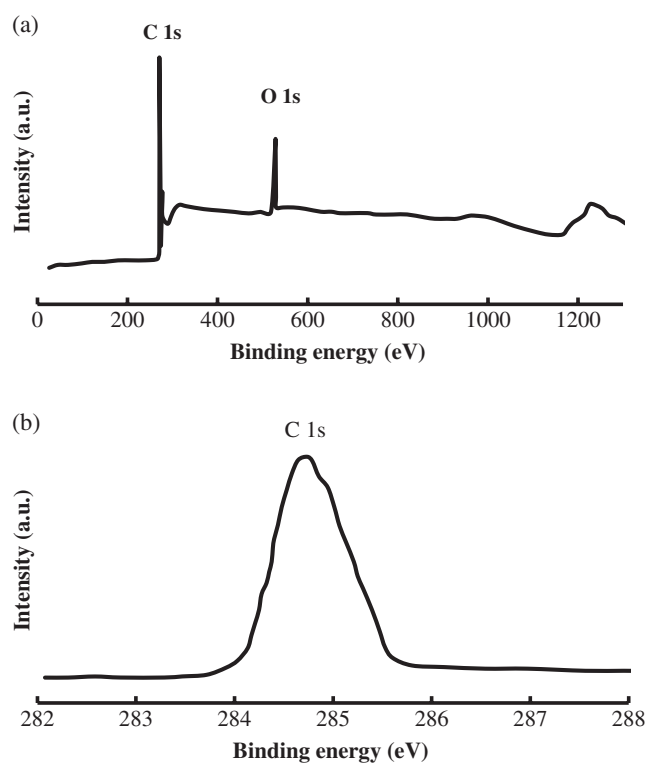
The Raman spectrum of the obtained graphene is shown in figure 5. Graphitic materials usually exhibit a Raman band at around  $1580\text{ cm}^{-1}$  which is assigned to the G-band and a peak at  $1350\text{ cm}^{-1}$  assigned to the D-band [33]. The G-band indicates original graphite features, whereas the D band is known to depend on the disorder features of graphitic structures as well as the presence of small crystalline grains. The positions of the G-band peak were observed at  $1588\text{ cm}^{-1}$  corresponding to threefold-coordinated bonds, and the D-band peak was observed at  $1353\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$  which correspond to graphene sheets [34].

The intensity of the D-band is inversely proportional to the effective crystallite size ( $L_a$ ) in the direction of the graphite plane

$$\frac{I_D}{I_G} = C \frac{\lambda_L}{L_a},$$

where  $I_D$  and  $I_G$  are the integrated intensities of the D and G bands, respectively, and  $C(\lambda_L)$  is the wavelength-dependent pre-factor with the value of 4.36, according to Matthews' work [35]. The  $I_D/I_G$  ratio is an indication of the level of defects in the graphene structure. The average value of  $I_D/I_G$  is determined to be 0.19, which is indicative of an excellent graphitization degree with low defect in the graphene structure [36]. Moreover, the number of graphene layers can be identified by calculating the relative intensity ratio of  $I_{2D}/I_G$ . An integrity intensity ratio  $I_{2D}/I_G$  greater than 2 corresponds to single-layered, 1–2 corresponds to double-layered, and less than 1 corresponds to many-layered graphene. The  $I_{2D}/I_G$  ratio of the obtained graphene was calculated to be 1.6, which confirms the formation of bi-layered/FLG sheets.

The XPS spectrum of the obtained graphene (figure 6) after purification shows that the carbon product consists of carbon and oxygen with no impurities [37]. The C 1s peak



**Figure 6.** X-ray photoelectron spectroscopy (XPS) spectrum of as-synthesized (a) purified graphene and (b) C 1s XPS spectrum of the obtained graphene.

located at  $\sim 284.6\text{ eV}$  corresponds to the graphite-like  $sp^2$  hybridized carbon which suggests that most of the carbon atoms are embedded within the honeycomb lattice of graphene [38]. Additionally, the deconvolution of the C 1s spectra (not shown) further reveals three peaks attributed to oxygen functional groups comprised of carboxylate ( $289.1\text{ eV}$ ), hydroxyl ( $286.6\text{ eV}$ ) and carbonyl ( $287.9\text{ eV}$ ) [37].

#### 4. Conclusion

This study confirms that  $\text{CO}_2$  can be used as a carbonous carrier gas in order to obtain graphene. Graphene was successfully synthesized in the present work by using a novel trimetallic catalyst containing Ni, Fe and Ce. The SEM images and EDX results proved the existence of graphene with a high carbon weight percentage. The TEM and AFM micrographs exposed the graphene sheets prepared using the CVD process. Raman spectra showed a small  $I_D/I_G$  ratio and confirmed the presence of high-quality graphene with few defects in its structure. XPS spectrum was also obtained to confirm the formation of graphene. It can be concluded that the CVD method can be successfully used to produce high-quality graphene, and there is an opportunity for further studies with regard to the parameters affecting the graphene production using  $\text{CO}_2$  and the as-prepared novel trimetallic (Ni–Ce–Fe) catalyst.

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