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Synthesis of Two-Dimensional Nanostructures at Low Temperatures

Abstract. The paper presents the results of experiments on the synthesis of two-dimensional carbon nanostructures by thermal chemical vapor deposition using iron slugs as catalysts and substrates. The synthesis was conducted at a temperature of 250 ° C, a working pressure of 500 mbar, and a duration of 1 hour. From the SEM results it is evident that a two-dimensional structure is synthesized on the surface layer of the Fe slug with a vertical alignment. According to the detailed morphological characteristics of the results obtained by the scanning electron microscope, the nanostructures are two-dimensional carbon nanostructures, i.e. graphene-like. For a detailed determination of the structure of the obtained samples, a study was carried out by the method of Raman scattering and scanning electron microscopy. According to the Raman spectroscopy results, all spectra show the main carbon peaks D and G. In the high-frequency region of the spectra, second-order peaks D′, 2D and D + G are also observed, indicating the presence of graphene.
Keywords: two-dimensional carbon nanostructures, iron catalyst, thermal chemical vapor deposition method, scanning electron microscope, Raman spectroscopy.

Introduction

Carbon nanomaterials have been extensively studied over the past three decades due to their unique properties [1-4]. Sp² carbon nanomaterials mainly consist of zero-dimensional (0D) fullerenes, one-dimensional (1D) carbon nanotubes (CNTs), and two-dimensional (2D) graphene, which have attracted significant interest both in scientific research and in industry [5-6]. The structure based on a hexagonal lattice formed by carbon atoms provides them with exceptional properties such as high electrical and thermal conductivity, remarkable mechanical strength, superabsorbency, unique flexibility, and high carrier mobility [7-8]. Due to these unique properties, sp² carbon nanomaterials show broad applications in field-effect transistors (FETs) [9], capacitors [10], sensors [11], and composites [12]. A key requirement for achieving practical applications of carbon nanomaterials is to reduce the synthesis temperature, decrease production costs, and increase the safety of industrial manufacturing, in order to minimize energy consumption.

Various methods have been developed for the preparation of carbon nanostructures, such as arc discharge [13], laser ablation [14], pyrolysis [15], mechanical and chemical exfoliation of graphite [16], thermal decomposition of SiC [17], chemical vapor deposition (CVD) from the gas phase [18], [19], and others.

Transition metals such as Ni, Cu, Fe, and others with particle sizes of several tens of nanometers are typically used as catalysts. Today, various methods for producing metallic nanoclusters for carbon nanostructures synthesis are employed, including plasma-chemical and mechanochemical synthesis, thermal decomposition and condensation, and electrical explosion of conductors. Since the dissociation, diffusion, and precipitation of carbon/hydrocarbon basic unit are supposed to take place on the surface of the metal catalyst, any features of the iron catalyst are of great importance.

Currently, almost all methods for synthesizing carbon nanowalls (CNWs) involve high synthesis temperatures. It is known that using methods that reduce the synthesis temperature can decrease economic costs. In [20], CNWs were synthesized at temperatures of 600°C and 700°C on magnetron-sputtered Fe thin films using a combination of $C_2H_2/NH_3/H_2$ and $CH_4/NH_3/H_2$ gases with a flow ratio of 20:80:100 cubic centimeters per minute. Authors [21] grew CNWs directly at 1130°C on various substrates such as quartz, silicon, SiO2/Si, and ZrO2/Si, using methane or ethanol as the carbon source. One of the main disadvantages of the T-CVD method is the difficulty in controlling the density and height of the produced carbon nanowalls.

Considering the above, this work presents the result of synthesizing two-dimensional nanostructures at lower temperatures using a thermal chemical vapor deposition (CVD) method.

Materials and Methods

Catalyst preparation

Since the dissociation, diffusion, and precipitation of carbon/hydrocarbon basic unit are supposed to take place on the surface of the metal catalyst, any features of the iron catalyst are of great importance. The relationship between the size of metal catalyst particles and their activity of catalyzing can only be deduced when initial catalysts with different features are available. This strategy also allows determining the critical size above or below which iron particles are not active for nanostructure growth any more. With this concern metal catalysts were prepared in following route.

As a compare to those catalysts which have nanoparticle appearance, metal (Fe) slugs and plates were also used as catalyst directly. To obtain adjustable catalytic activity, the surfaces of metals were pretreated to have changing roughness. Relatively rough surfaces were prepared by polish using sandpapers from 500 to 4000 mesh, and adopting diamond slurry with the particle size of 3μ, 1μ and 40 nm respectively induced smoother one. At last, an electrolytic polish process allowed producing extremely smooth surface, see Figure 1. Not only the roughness, effect of surface chemical state on catalytic activity was also a concern in investigation, for this purpose the polish process was followed by a H_2 reduction treatment in some cases.

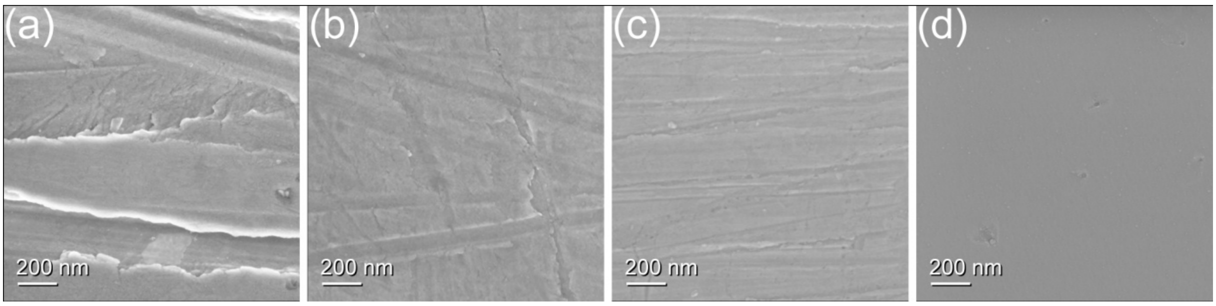


Figure 1 – SEM images of Fe slugs polished using (a) 4000 mesh sandpaper, (b) 3μ Diamond slurry, (c) 1μ Diamond slurry, (d) electrolytic polish.

The obtained Fe slugs were used as a substrate and catalyst for the synthesis of nanostructures from the gas phase using a thermal chemical vapor deposition (CVD) method. The synthesis of carbon nanostructures was carried out in the volume of a horizontal three-zone tubular furnace. The setup diagram for the synthesis of graphene nanostructures is shown in Figure 2.

This device is primarily based on a three-zone tubular furnace, equipped with a quartz tube serving as the reaction chamber. On one end, it is connected to a gas supply system, and on the other end, to a downstream vacuum pump. This setup allows synthesis processes to be conducted in pure or mixed gas environments, as well as under vacuum conditions.

In a standard synthesis process, catalyst samples are pre-placed in the reaction chamber to initiate the growth of the corresponding nanostructures. After heating the samples to the required technological temperature under a vacuum of less than 0.1 mbar, the chamber is filled with pure C_2H_2 to a specified pressure. The system is then maintained at the set temperature for various process durations to enable the growth process.

Finally, the residual gases in the process chamber are pumped out, the chamber is evacuated and cooled down to room temperature. The synthesized structures are then collected from the chamber for the next stage of the experiment characterization. The synthesis was conducted at a temperature of 250°C, a working pressure of 500 mbar, and a duration of 1 hour.

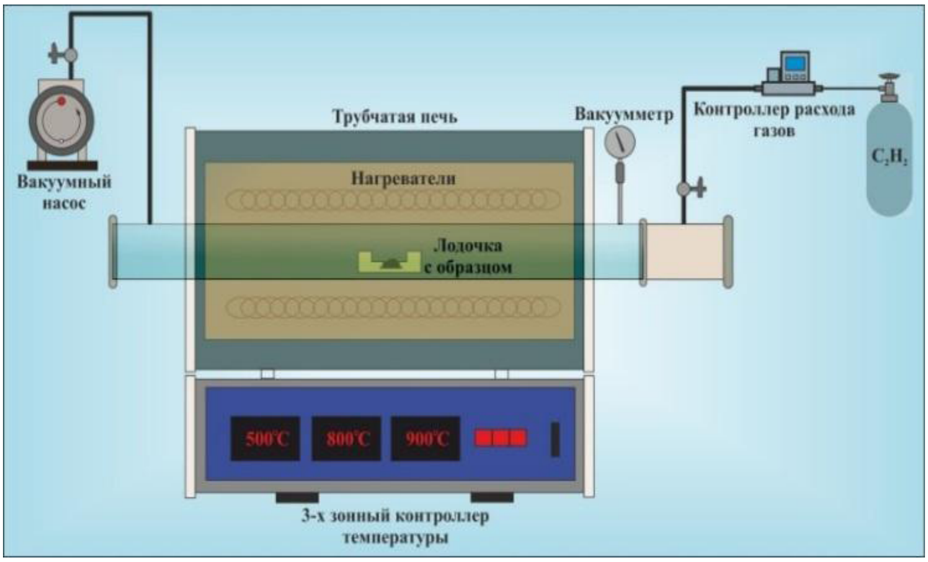
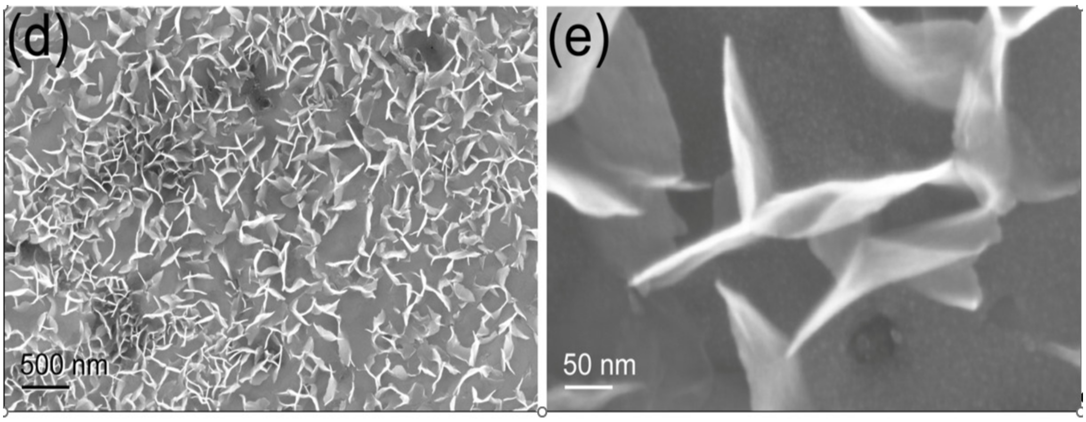


Figure 2 – Configuration of the Thermal CVD system

Results and Discussion

The morphology of the samples was studied using the Zeiss Gemini Ultra 55 ultra-high resolution autoemission scanning electron microscope (SEM). The following image shows the SEM image of a two-dimensional nanostructure synthesized at low temperature.



a *b*

Graphene-like nanostructure; (b) Enlarged view of image (a)

Figure 3 – SEM image of a two-dimensional nanostructure synthesized at low temperature

As seen in Figure 3, a two-dimensional structure is synthesized on the surface layer of the Fe slug with a vertical alignment. According to the detailed morphology feature (Figure 3(b)), this nanostructure is suspected to be graphene.

Raman spectroscopy measurement is applied to analyze the composition and the degree of graphitization of the as-grown products. The following figure shows the Raman spectrum obtained at the National Open Nanotechnology Laboratory using the NT-MDT NTegra Spectra spectrometer (laser wavelength $\lambda = 473$ nm).

As seen in Figure 4, the main carbon peaks, D and G, are located at 1362 cm^{-1} and 1575 cm^{-1}, respectively. These peaks are characteristic of sp^2-hybridized carbon structures. The D-band corresponds to the breathing modes of aromatic rings and is activated by defects, while the G-band represents the in-plane vibration of sp^2-bonded carbon atoms. An additional peak at 1430 cm^{-1} can be observed, which is commonly attributed to the presence of CH_3 groups or structural disorder associated with sp^3 hybridization and amorphous carbon phases [22]. Furthermore, spectral features typical of graphene are observed in the high-frequency region. The peak at 2440 cm^{-1} corresponds to the D′ band, which is a second-order Raman mode associated with disorder. The 2D band, a critical fingerprint for graphene, appears at 2723 cm^{-1}. This band arises from a two-phonon, second-order process and is highly sensitive to the number of graphene layers. A peak at 2935 cm^{-1}, corresponding to the D + G combination mode, is also present. Additionally, a weak peak at 3231 cm^{-1} is observed, which is attributed to C–H stretching vibrations [23].

The presence of these peaks confirms the formation of a graphene-based structure with some degree of disorder and possible hydrogenation. According to the study [24], the number of graphene layers can be estimated by analyzing the I_{2D}/I_G intensity ratio. A ratio of $I_{2D}/I_G \approx 2–3$ is indicative of monolayer graphene, while $1 < I_{2D}/I_G < 2$ suggests bilayer graphene, and $I_{2D}/I_G < 1$ corresponds to few-layer graphene [25, 26]. The structural quality of the graphene film can be evaluated using the I_D/I_G ratio, where a lower I_D/I_G value indicates fewer defects and higher structural perfection [27].

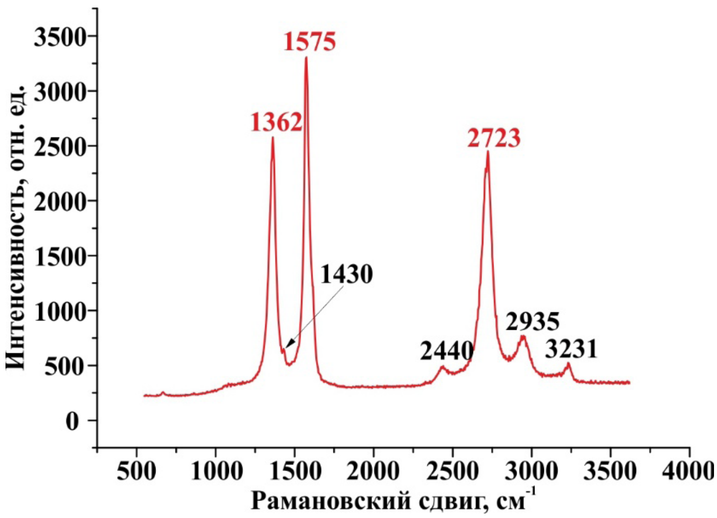


Figure 4 – Raman spectrum of the two-dimensional nanostructure synthesized at low temperature

Further investigation of the obtained nanostructure is planned to use a transmission electron microscope and X-ray structural analysis methods. Additionally, studies will be conducted to explore the physical properties of the CNW films synthesized at low temperature.

Conclusion

In this study, we successfully synthesized two-dimensional carbon nanostructures at a relatively low temperature of 250°C using a thermal chemical vapor deposition (CVD) method. Morphological analysis using scanning electron microscopy (SEM) showed the presence of thin, plate-like formations characteristic of graphene-like structures. The synthesized structures, grown on Fe slugs as substrates, demonstrated a vertical alignment characteristic of graphene-like nanostructures. For a detailed determination of the structure of the obtained samples, a study was carried out by the method of Raman scattering. Raman spectroscopy confirmed the presence of the main carbon peaks D and G, as well as additional high-frequency peaks D′, 2D, and D + G, indicating the formation of graphene or graphene-like structures. The intensity ratios of the peaks suggest the presence of defects and, likely, a multilayer graphene structure. The obtained results confirm the effectiveness of the chosen synthesis method and highlight the potential of using iron as a cheap catalyst for the production of two-dimensional carbon materials. SEM images confirmed the formation of these structures, while Raman spectroscopy provided evidence of sp^2-hybridized carbon atoms, supporting the formation of a graphene-based structure with some degree of disorder.

Further investigation of the obtained nanostructure is planned to use a transmission electron microscope and X-ray structural analysis methods. Additionally, studies will be conducted to explore the physical properties of the CNW films synthesized at low temperature.

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