R&d of CVD technique for graphene production

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Currently production of large-sized graphene samples is of great importance due to the broad potential applications of this material with high physical performance. In this paper we consider one of the widely used methods of graphene production - chemical vapor deposition (CVD), which was worked out by our team. We used as a catalyst of Ni foil and carbon source were benzene vapor. Also, we show results of computer simulation by DFT methods that demonstrate possibility and effectiveness of graphene production by CVD method. The characteristics of graphene have been studied by optical microscopy and Raman spectroscopy. The results show high quality and homogeneity of the obtained graphene.

Key words: graphene, CVD, optical microscopy, Raman spectroscopy.
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1 Introduction

Graphene is a crystal system consisting of a single layer of graphite, which elementary structural unit is a hexagonal cell, with its geometry resembling a honeycomb. Graphene causes a great interest because of its unique electronic, optical properties as well as chemical, thermal and mechanical characteristics [1]. The maximum electron mobility in graphene, as compared with all other known materials, making it promising for use in various applications, such as a future basis for nanoelectronics and possible replacement of silicon integrated circuits. The electronic properties of graphene depend to a large extent on the number of layers of graphene.

The famous "Scotch tape method" is a pioneer laboratory graphene production technique for basic research. But recently there was developed a variety of methods of controllable large-sized-graphene production. The two of these methods are the method of chemical vapor deposition (CVD) [2] and diffusion-based method. These techniques allow to control the number of graphene layers precisely.

Typical CVD graphene growth uses gaseous hydrocarbons at elevated temperatures as the carbon source, such as methane, ethylene, and acetylene [3,4]. While carbon nanotube growth has been demonstrated using liquid precursors, there have been only a few, recent attempts at graphene growth with liquid precursors. Single-layer graphene were synthesized from ethanol on Ni foils in an Ar atmosphere under atmosheric pressure by flash cooling after chemical vapor deposition, but a wide variation in graphene layer number was observed over the metal surface [5-7].

In this study single and few-layer graphene were successfully grown on nickel substrate using benzene as a precursor.

2 CVD graphene

2.1 Mechanism of graphene growth from benzene molecules on Ni

To produce graphene samples by CVD method we use benzene as precursor due to the similarity of benzene molecule with elementary hexagonal cell of graphene. The idea is not to decompose the whole molecule of precursor, as it commonly occurs in CVD processes, but just to dehydrogenate the benzene molecule, as it require less energy. Thereforecomputer simulation of graphene fragment formation from benzene molecules was performed using DFT method.

Figure 1a demonstrates the model of benzene molecule on nickel surface optimized by energy. Due to the probability of catalytic dehydrogenation on Ni substrate hydrogen atoms can be torn off the benzene molecule and adsorbed on the nickel surface (Fig.1 b). Fig.1c demonstrates two of the benzene molecules after the separation and adsorption of hydrogen atoms on nickel in the starting position at the distance between the nearest atoms of the carbon is 1.9 Å after energy optimization.

a – benzene molecule after optimization by energy on Ni surface;
b – benzene molecule after the separation and adsorption of H atom on Ni;
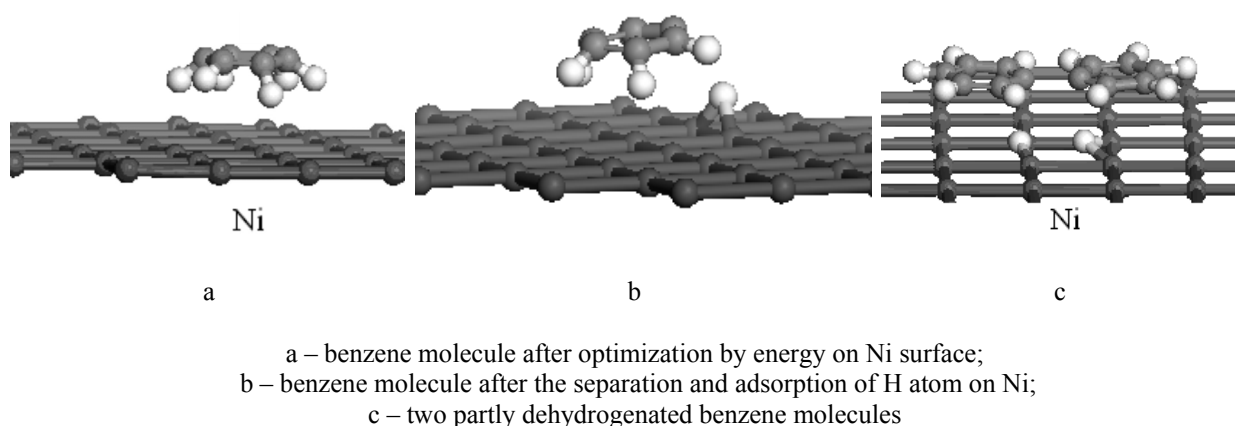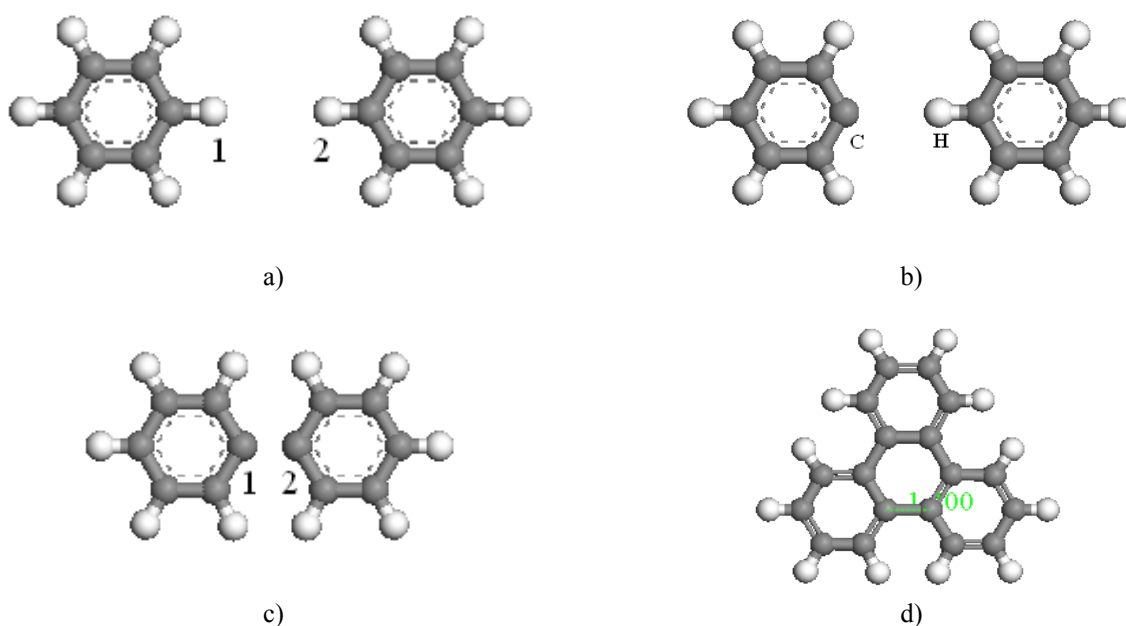c – two partly dehydrogenated benzene molecules

Figure 1 – Modeling of graphene formation from benzene molecules.

For more detailed study of this process computer simulation was conducted to predict possible stable states of benzene molecules (relative to each other) using optimization by energy. Figure 2a shows the two initial molecules of benzene, and then one molecule of benzene was once dehydrogenated. Figure2c shows both ionized (partial dehydrogenated) molecules of benzene, calculated distance between the nearest carbon atoms (1 and 2) is 1.43 Å, which is close to the bond length in graphene. Figure 2d demonstrates possible fragment of graphene formed due to the dehydrogenation of benzene molecules.

a – initial benzene molecules (equilibrium distance 1-2 is 2.91 Å);
b – one of benzene molecules is once dehydrogenated;
c – two partly dehydrogenated benzene molecules (equilibrium distance 1-2 is 1.43 Å);
d – fragment of graphene formed out of 3 partly dehydrogenated benzene molecules

Figure 2 – Possible stable states of partly dehydrogenated benzene molecules.
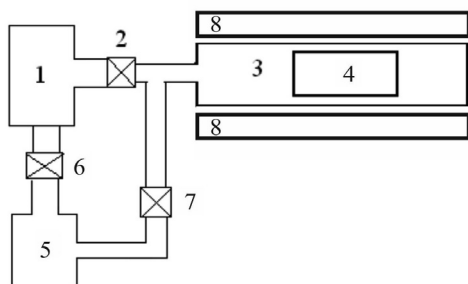
2.2 Experimental setup

Figure 3 – Scheme of experimental setup of CVD system

Source of benzene vapor - vessel 1, valve 2 separated from the reaction chamber 3. First of all argon from the vessel 5 is used for disposing the reaction chamber of an air, and then nickel substrate 4 is heated by resistive method. After that argon through the valve 6 is pulled into chamber 1 in order to press out of benzene vapor into reaction chamber. During this process nickel substrate is being covered by products of benzene dehydrogenation which results in graphene layers. All this process is accompanied by ultraviolet ($\lambda \approx 365$ nm) activation 8 of reactive medium.

Figure 4 demonstrates developed experimental setup of CVD system. It is built of the quartz tube (indicated by arrow 1), which is also mentioned as reaction chamber on the schematics; ultraviolet lamps (2); clamp terminals (3) and substrate holder situated within the tube.


1 – Quartz tube (reaction chamber); 2 – source of ultraviolet irradiation; 3 – clamp terminals, 4– sample (substrate holder)

Figure 4 – Experimental setup of CVD system

3 Results and discussion

Series of experiments were conducted varying such parameters as intensity of benzene inlet into reaction chamber and the temperature of the heated substrate.

Figure 5a is an optical image of single and few-layer graphene samples, obtained at t = 810ºC, during the inflow of benzene for 40 seconds. It was observed rather wide variation in graphene layer number on the Ni surface. In Fig. 5b it is shown the Raman spectrum of graphene, detected on the several areas of Ni substrate. The largest graphene sample is 8x6 μm^2.
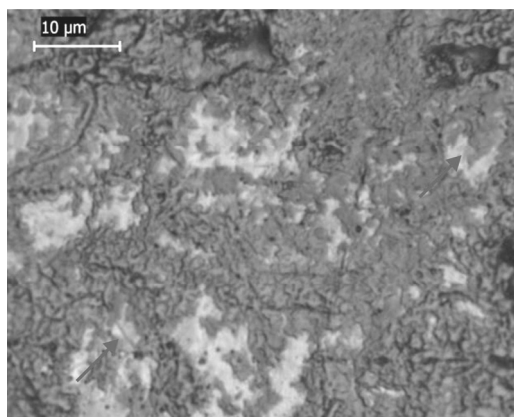
a)
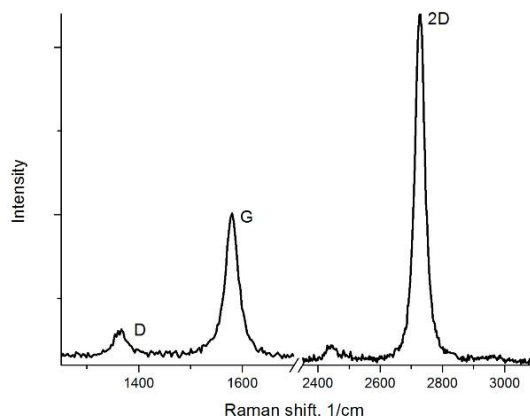
b)

Figure 5 – Optical image (a) and Raman spectrum of graphene (b),
formed during the benzene inflow for 40 seconds

Further experiments were directed towards the varying of time of benzene inflow. Figure 6 is an optical image of the few-layer graphene sample, obtained at the same temperature - t = 810°C, but during the benzene inflow for 30 seconds. Raman spectroscopy analysis of this sample showed that the variation in graphene layer number is still rather wide. The largest graphene sample is 5x5 μm^2.
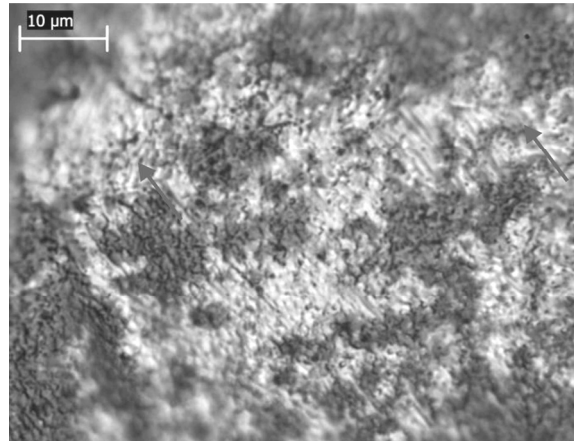

Figure 6 – Optical microphoto of single and few-layer graphene structure
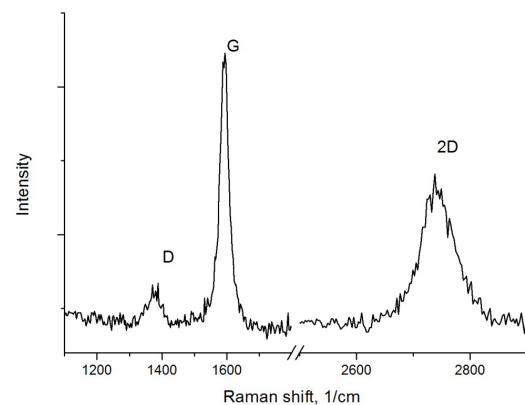obtained during the benzene inflow for 30 seconds

After different variations of temperature and time of benzene inflow it were found out the optimal parameters of the process for production of homogeneous (by the number of layers) few-layer graphene samples on Ni substrate.

The Fig.7a is a typical microphotograph of few-layer graphene sample, obtained at t = 710°C and during the lapping of benzene for 40 seconds. The Fig. 7b gives the Raman spectrum that corresponds to the most part of sample's surface. Intensity ratio of 2D and G peaks allows to attribute this sample to four-layer graphene. The largest grain of FLG is 50x65 μm^2.
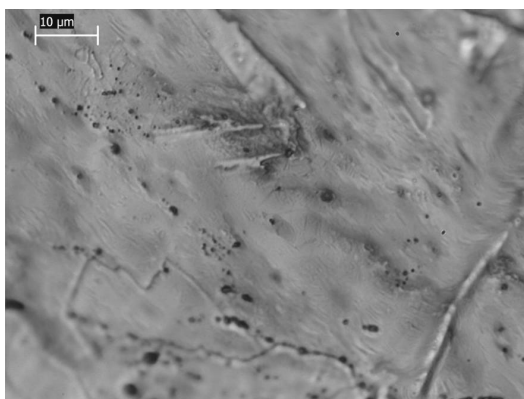
a)

b)

Figure 7 – Optical microphoto (a) and Raman spectrum (b)
of FLG structure obtained during the benzene inflow for 40 seconds

4 Conclusion

In the paper, relatively new developed method of high quality graphene mass production is presented. Possibility and effectiveness of graphene production by CVD method based on benzene was considered theoretically (computer simulation) and proved experimentally. Samples were investigated by optical microscopy and Raman spectroscopy. Performed analysis revealed a high quality of obtained FLG structures. Thus, we can say that presented in this study method of graphene production are notable for possibility of controllable production of rather large single and few-layer graphene samples of high quality.

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