A simple method to synthesize graphene at 633 K by dechlorination of hexachlorobenzene on Cu foils

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ABSTRACT

A modified chemical vapor deposition method to synthesize graphene at 360 °C is described. Hexachlorobenzene (HCB) was used as carbon source, and copper foils were used as not only the substrates for graphene deposition but also the catalyst to HCB dechlorination. The possible growth mechanism was investigated using X-ray photoelectron spectroscopy. Enhancement of HCB dechlorination by copper played a key role in synthesis of graphene at such a low temperature.

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1. Introduction

Graphene, a flat single layer of sp^2-bonded carbon atoms packed into a two-dimensional honeycomb lattice, has been predicted to possess a wealth of fascinating physical, chemical, and mechanical properties and potential applications [1,2]. Novoselov et al. succeeded in isolating, identifying, and characterizing graphene in 2004 to win a Nobel Prize in 2010 [3]. From the day that graphene was proposed, synthesis of high quality graphene, as the key point that determine the exploration of its properties and the development of its application, have been attracted a lot of efforts. Initially, graphene was obtained by a mechanical exfoliation method [3], in which the graphene's electric properties were characterized. However, low-productivity and time-consuming made the mechanical exfoliation method not afford the need of laboratory experiment. To meet the requirement of laboratory experiment, considerable efforts had been made to explore methods to synthesizing graphene in large scale. Hummer's

method used to graphite oxidation was traced back and modified for preparation of graphene, named chemical exfoliation methods [4–10]. Using modified Hummer's method, large scale graphene oxide could be obtained with random shapes and layers. According to the micro-manipulation technology up to date, it is also a huge challenge to choose the certain graphene from the products by Hummer's method and manipulate it to the exact positions. An in situ growth technique is highly desirable. For this purpose, diverse methods were developed. Among them, two kinds of synthesis methods show great promising. One is high temperature annealing (above 800 °C) solid carbon source film on Cu foils [11]. The other is chemical vapor deposition (CVD) from gas carbon source on metal substrates [12–15] or Si/SiC single crystal surfaces [16–19] at high temperature, typically 1000 °C. Thus, before real application to in situ synthesis of graphene, these two kinds of methods should address the problem of high synthesis temperature. Growth of graphene at low temperature, which is more convenient, economical, and feasible for

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industrial application, is expected. Recently, it has been reported that monolayer graphene flakes were synthesized by a revised CVD route using benzene as carbon source at the temperature of 300 °C under a vacuum circumstance between 8 and 15 torr [20].

In this article, a simple and low-temperature method to grow graphene is developed based on the CVD route on Cu foils using hexachlorobenzene (HCB) as the carbon source. In this method, Cu foil acted as not only catalytic substrates but also reductant, which reacted with HCB and form the media product C_6 as the building block for self-assembling to graphene. And high quality graphene flakes were obtained at a temperature as low as 360 °C. The possible mechanism of the low-temperature growth was discussed on the basis of XPS analyses.

2. Experimental

2.1. Chemicals

The 25 μm-thick Cu foils were purchased from Alfa Aesar (item no. 13382). Hexachlorobenzene was purchased from Sinopharm chemical reagent company. All the chemicals were used in our experiments without further treatment.

2.2. Preparation of the graphene flakes

The schematic of low-temperature graphene growth is depicted in Fig. 1. The growth of graphene was carried out in a horizontal tube furnace, which is different from previous CVD method that solid carbon source HCB loaded in a glass tank in a oil bath heating tray were carried into the reaction zone by carrier gas through the head space of the tank. Cu foil was heated to 360 °C in argon atmosphere with the flow rate of 500 sccm for 30 min, and then the mix gases Ar/H2 with the flow rate of 400 and 100 sccm were introduced as the carrier gases. The HCB powder was heat to 115 °C by the heating tray. And the carrier gases flow through the headspace of the HCB powder and carried HCB saturated vapor as the carbon source. The saturated vapor pressure of HCB at 115 °C is about 0.13 kpa. The typical growth time was 5 min under normal atmospheric pressure. After growth, the Cu foil was co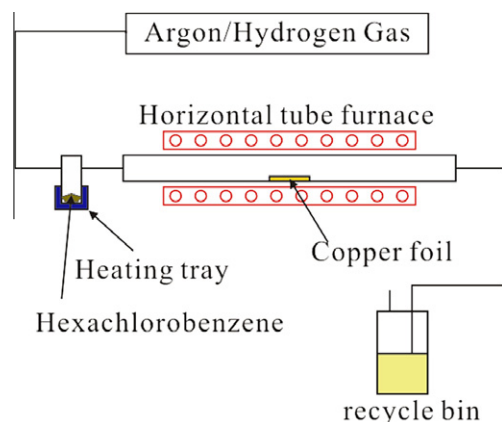oled down to room temperature in argon atmosphere. The graphene flakes were obtained. And then the graphene flakes were transferred to the target substrate in accordance with previous literature [21,22].

2.3. Characterization of samples

Optical photographs were taken using a microscope (Nikon LV150) to observe the morphology of the as-obtained graphene flakes. Raman spectroscopy (DXR Raman microscope) with a laser excitation wavelength of 523 nm was used to characterize the quality, thickness of the grown graphene sample. The transmission electron microscopy (TEM) investigations were carried out in a JEOL JEM-2010. The atomic force microscopy (AFM) images were taken by using a scanning probe microscope (Veeco Multimode V). X-ray photoelectron spectroscopy (PHI-5702) was employed to characterize the copper foils after the growth of graphene to determine the elemental composition and valence station.

3. Results and discussion

Fig. 2a and b shows the optical image of Cu foils before growth and after growth, respectively, which clearly demonstrate that a transparent film was grown on the Cu foil through the CVD process. In its Raman spectrum (shown in Fig. 2c), the 2D band centered at 2700 cm^{-1} is symmetric and can be well fitted by a single Lorentzian peak, which shows the typical characteristic of monolayer graphene [23]. AFM image (Fig. 2d) with the height profile (Fig. 2e) shows that the as-prepared graphene sheet was about 0.8 nm in thickness, which confirms that the as-prepared graphene was monolayer in agreement with Raman result. Fig. 2f shows the high resolution C XPS spectrum of the as-synthesized graphene. It has two peaks centered at 284.50 and 288.40 eV, which can be index to C 1S of carbon element and C 1S of C=O group, respectively. The C=O group is attributed to CO_2 and H_2O adsorbed on the surface of the as-prepared graphene. TEM image and corresponding EDX (Fig. 2g and h) results demonstrate that the as-prepared sample only comprised of carbon element without chlorine, which indicate that all the chlorine atoms have been removed. It also indicates that dechlorination was predominant during the CVD process although chlorination of graphene might occur simultaneously.

We further investigated the effect of the reaction temperature on the quality of the as-obtained graphene. Fig. 3a shows the Raman spectra of graphene grown at 460 and 560 °C, respectively. From the spectra, it can be found that the intensity of D band decreased with the growth temperature increasing, and almost disappeared at 560 °C, which fully demonstrate the high quality of the as-obtained graphene flakes. Through Lorentzian peak fitting, the 2D band peak (shown in Fig. 3b) of the graphene flakes obtained at 460 °C can be well split into four peaks, which indicates the as-obtained graphene flakes are double layers, consistent with the literature [23]. To the graphene obtained at 560 °C, the 2D band peak (shown in Fig. 3c) can be split into two peaks, which is a sign of the graphene films with 3–6 layers [23]. From them, it can be seen that the layers of the as-obtained graphene flakes increased with the reaction temperature increased.

Fig. 1 – Schematic of the CVD growth.
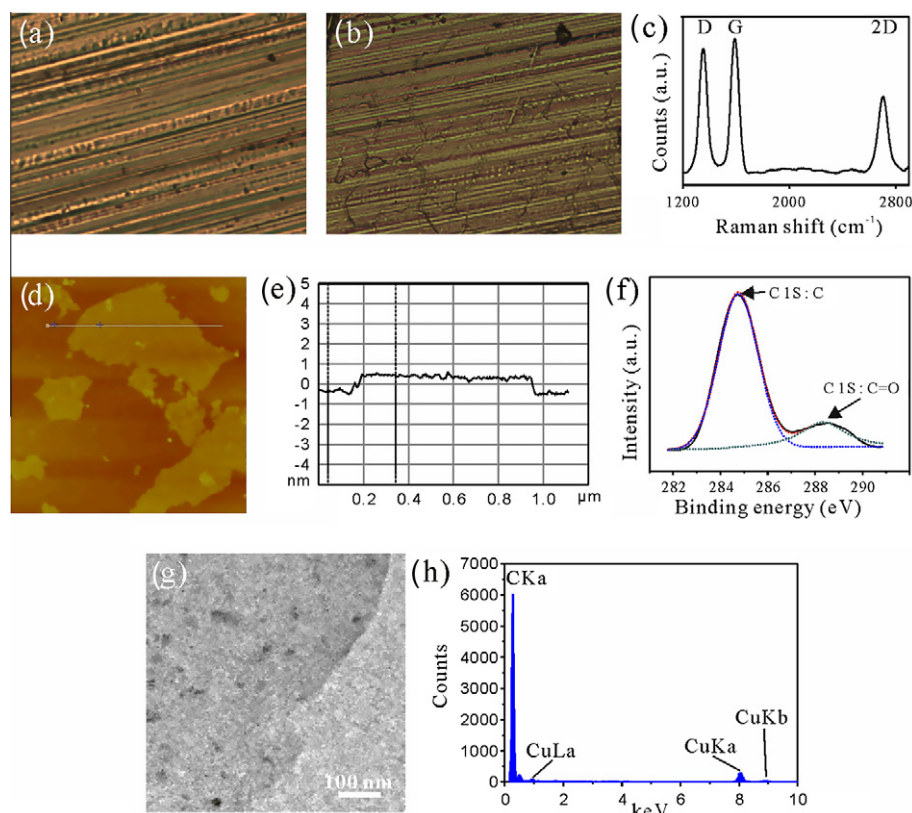
Fig. 2 – (a) and (b) Optical microscopy of Cu foils before and after the growth of graphene; (c) Raman spectrum, (d) and (e) AFM image and height profile, (f) XPS spectrum, (g) and (h) TEM image and corresponding EDX of graphene grown at 360 °C.
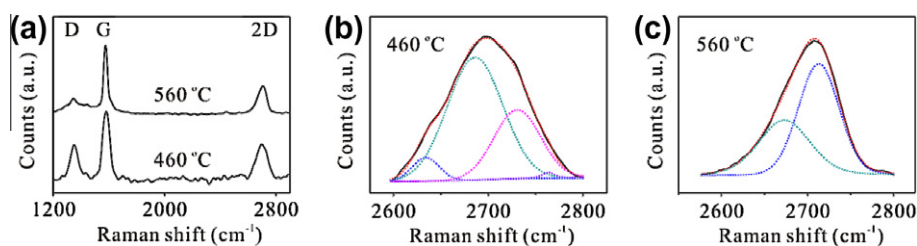

Fig. 3 – (a) Raman spectra of graphene grown at 460 and 560 °C; (b) and (c) 2D band peaks of graphene grown at 460 and 560 °C, respectively. The dash lines show the Lorentzian peaks used to fit the data, red dash lines are the fitted results. The solid lines are the raw data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To understand the growth mechanism of the graphene flakes at low temperature, XPS analysis is employed. Fig. 4a shows the XPS spectrum of Cu foils after the growth of graphene, which has a clear shoulder peak. It can be split into two peaks centered at 932.70 and 934.40 eV, which can be index to Cu $2P^{3/2}$ of copper elementary substance and Cu $2P^{3/2}$ of $CuCl_2$, respectively [24,25]. Cl 2P and Cl $2P^{3/2}$ binding energy peaks of $CuCl_2$ can also be found in the XPS spectra [26,27] (shown in Fig. 4b). The XPS analysis results prove that the redox reaction between Cu and HCB existed in the process and $CuCl_2$ had been produced. On the basis of results, we propose the possible growth mechanism of the graphene obtained under low temperature. As shown in Fig. 4c, the graphene flakes growth process is depicted as three stages: Stage (I), the metal

copper atoms on the surface of the foil reacted with HCB and prompted the dechlorination of HCB. Stage (II), under the Cu catalytic reaction, the HCB molecules entirely put off chlorine atoms to form the media product C_6 rings, as well as $CuCl_2$ was produced. Stage (III), the as-produced media C_6 rings assembled together and form the graphene flakes on the surface of the copper foil.

From previous study [28], it has been shown that Cu could enhance HCB dechlorination. In the presence of Cu, the dechlorination temperature decreased to 300 °C and the dechlorination efficiency increased drastically. Without Cu, HCB began to dechlorinate higher than 350 °C and the dechlorination efficiency was lower than 8%. In our case, when the reaction temperature was 360 °C, the monolayer graphene
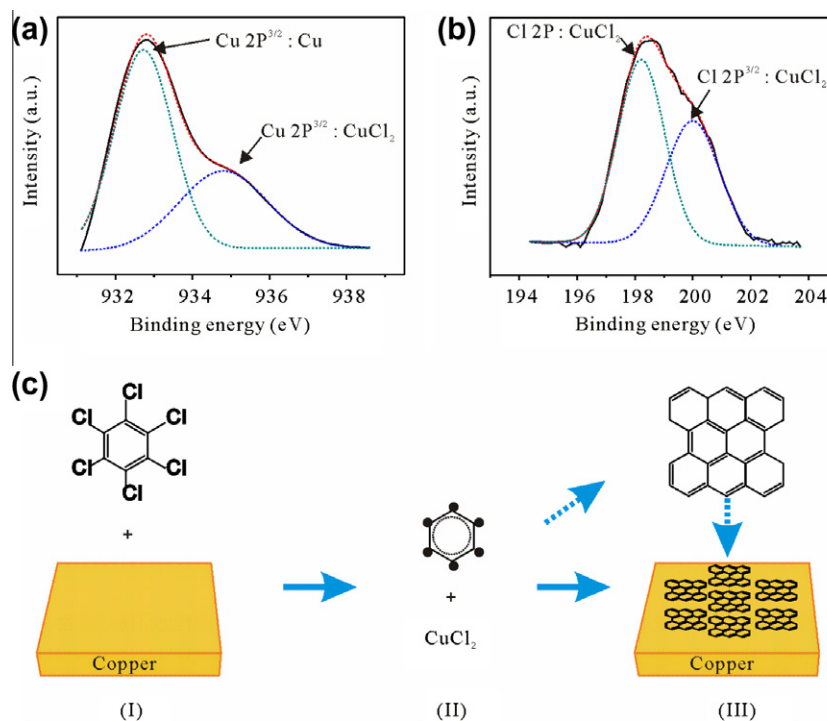
Fig. 4 – XPS spectra of the copper foil after graphene growth: (a) high resolution of Cu spectrum and (b) high resolution of Cl spectrum. The dash lines show the Lorentzian peaks used to fit the data, red dash lines are the fitted results. The solid lines are the raw data. (c) The schematic of graphene flake growth process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

flakes were obtained. When the temperature increased to 460 °C, double-layered graphene flakes were obtained. Following the temperature increasing to 560 °C, mutli-layered graphene flakes were obtained. The main reason of monolayer graphene flakes obtained at the temperature as low as 360 °C can be contributed to HCB dechlorination enhancement by copper. Although HCB can dechlorinate at 360 °C, the dechlorination efficiency is very low. Meanwhile, as to single HCB molecule, it is difficult to put off six chlorine atoms totally and form C_6 ring at such a short time heating. Only the HCB, which touched the Cu atoms on the surface of the copper foil, put off chlorine entirely and formed C_6 rings to assemble graphene. With a monolayer graphene flake film assembly and deposition on the surface of copper foil, the following HCB cannot touch Cu atoms any longer, the growth of graphene stops. Therefore, at the reaction temperature of 360 °C, only monolayer graphene can be formed on the copper foil. With the reaction temperature increasing, the dechlorination efficiencies of HCB increased, and the entire dechlorination HCB molecules became more and more in the absence of Cu. Consequently, the likelihoods of assembly C_6 rings to form graphene layers increased. As a result, the double-layered and multi-layered graphene flakes were obtained at the reaction temperature of 460 and 560 °C, respectively. In the process of graphene growth, Cu played an important role in the formation of graphene, not only as the substrate, but also as the catalyst to HCB dechlorination. And the reaction temperature was another key parameter to control the layers number of graphene.

4. Summary

We present a new and easy method to synthesize graphene at a low temperature of 360 °C. HCB was used as a solid carbon source. Copper foils were used as not only the substrates but also the catalyst to increase HCB dechlorination, which played a key role in the formation of graphene at this low temperature. By changing the reaction temperature, the number of graphene layers obtained can be controlled.

Acknowledgements

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