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Low-temperature synthesis of few-layer graphene

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ABSTRACT

Few-layer graphene was synthesized at 95 °C by the Ullmann reaction using acetylene as the raw material. Hexabromobenzene (HBB) and cuprous bromide were used as the catalyst in this reaction. A contrast experiment performed without HBB also confirmed this point. The resulting material was characterized by Raman spectroscopy and exhibited characteristic peaks of graphene. Moreover, the structure of the as-prepared material was confirmed as few-layer graphene by transmission electron microscopy, X-ray photoelectron spectroscopy and solid-state ^{13}C nuclear magnetic resonance spectra. The synthesized graphene used as the anode of lithium-ion battery exhibited the initial and reversible capacities of 650 and 570 mAh g^{-1}, respectively, which in accordance with the theoretical capacity of graphene.

1. Introduction

Graphene, as a promising material of two-dimensional (2D) sheet of sp^2-hybridized carbon, has attracted considerable attention owing to its unique physical, chemical, and mechanical properties and excellent performance in the nanoscale electronic devices [1–3]. Graphene has been prepared via a large number of methods [4], and the organic synthetic protocols fabricating graphene [4,5] has received more attention owing to their controllable character and better quality of the resulting graphene compared to that obtained by some other approaches. For example, Yang et al. synthesized linear 2D graphene nanoribbons by the bottom up method using 1,4-diiodo-2,3,5,6-tetraphenylbenzene as the raw material [6]. Kim et al. produced graphene nanoribbons of various widths using 4,5-dibromo-1,2-benzenediol by the cyclodehydrogenation reaction [3]. Basagni et al. also performed a stepwise on-surface polymerization reaction to product graphene nanoribbons using 4,4″-dibromo-p-terphenyl as the precursor via Ullmann coupling [7]. All these methods producing graphene significantly contributed to the development of the carbon material, inspiring many researchers to explore further efforts to study the production methods of the graphene.

In this study, a simple method to synthesize few-layer graphene at low temperature (95 °C) via the Ullmann reaction is demonstrated. The as-prepared graphene possessed a multilayer structure and exhibited better electrochemical performance.

2. Experimental

HBB (0.0417 mmol), cuprous bromide (2.0 mmol), and potassium carbonate (2.5 mmol) were dissolved in the diethylene glycol dimethyl ether (100 mL) distilled beforehand. Moreover, the air in the reaction system was evacuated under a flow of argon. Afterwards, acetylene prepared by the reaction of excess deionized water with calcium carbide, purified by passing through copper sulfate solution and dehydrated in a drying tower was introduced in the reaction system. Then, the reaction system was sealed and the reaction was performed in an argon atmosphere at 95 °C by refluxing under stirring. The whole reaction system was kept in an anhydrous and anaerobic environment. After the completion of the reaction, the system was cooled down to room temperature. The cuprous acetylide possibly generated in the reaction system was quenched by hydrochloric acid solution. The as-prepared products were collected by centrifugation and rinsed using organic solvent followed by drying at 50 °C. Subsequently, the dried sample was heated at 400 °C in an argon atmosphere for 2 h. Finally, the sintered products were washed with adequate amount of deionized water and dried again at 50 °C.

The as-prepared material was investigated by Raman spectroscopy (RS, In Via Rflex), Fourier transform infrared spectroscopy (FTIR, ALPHA), thermogravimetric analysis (TGA, STA 409PC Luxx®), transmission electron microscopy (TEM, Tecnai G2 F20), X-ray photoelectron spectroscopy (XPS, PERKIN ELMZR, PHI16000)

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and solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR, Infinityplus 300). The as-prepared material was used as the anode in the electrochemical cells. The as-prepared material, Lithium tablets, and 1 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate in a volume ratio of 1:1 were used as the working electrode, counter electrode, and electrolyte, respectively, and assembled in an argon-filled glove box.

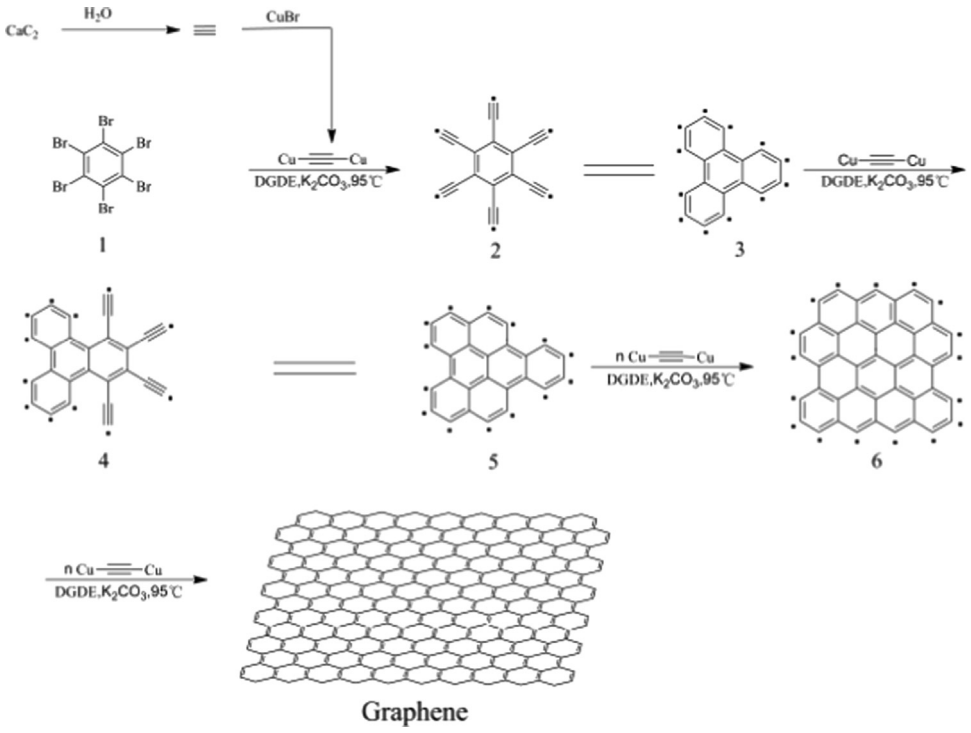
3. Results and discussion

Graphene is a sp^2-hybridized carbon material, resembling the benzene rings without hydrogen. Acetylene is easily polymerized to generate benzene structure. Benzene was first fabricated by the cyclization of acetylene on supported Ni catalysts, and subsequently prepared by the acetylene cyclization and hydrogenation on Pd/W (211) [8]. Moreover, Jiang et al. synthesized graphene films via the radical-coupling reaction. The generated HBB radicals by the breaking of the C–Br bonds of HBB during the reaction coupled effectively to form graphene sheets [4]. When HBB was heated in this reaction, it changed from dark-red to black, namely, the Ullmann coupling-reaction.

In this study, few-layer graphene was prepared using acetylene as the raw material, and HBB and cuprous bromide as the catalysts at 95 °C by the Ullmann reaction. The reacted HBB free radicals coupled to the alkynyls as the result of the debromination to form the graphene rings. Potassium carbonate acted as the base and evocating agent for the reaction. A reasonable synthesis mechanism of few-layer graphene is shown in Scheme 1. First, acetylene was produced by calcium carbide, followed by the reaction with cuprous bromide to form the cuprous acetylide by the use of potassium carbonate as the base. In the following reaction, potassium carbonate also acted as the evocator to promote the formation of graphene. Upon the breaking of the C–Br bonds of the reaction between HBB and cuprous acetylide, the Br atoms reacted with the cuprous atoms from the cuprous acetylides owing to their instability, and the HBB radicals coupled to the alkynyls to afford intermediate product **2**. Because of the activity of the acetylenic bond, product **2** easily isomerized to afford **3**. In a similar manner, intermediate **3** can react with cuprous acetylide to afford products **4**–**6**. Finally, the few-layer graphene were prepared. A comparative test was also performed under identical conditions without adding HBB. The result was that no products were fabricated, indicating that the reaction mechanism is reasonable

The Raman spectrum of the as-prepared material, as shown in Fig. 1a, shows the peaks at ~1575, 1350, 2750, and 2900 cm^{-1} corresponding to the G band of graphene attributing to the breathing vibration of the sp^2 carbon domains in the aromatic rings, the D band corresponding to the sp^3 carbon owing to the structural defects or amorphous carbon, the 2D band, and the D+G band, reapectively, which are the characteristic peaks of graphene [9]. The as-prepared graphene is a comparatively thin sheet, because the G peak position with a standard value of 1580 cm^{-1} moves towards a lower value with increasing number of graphene layers [10]. Moreover, the intensity ratio of the D to G band is 0.731, indicating the highly ordered and low defects in the graphene films. Fig. 1b shows the typical FTIR spectra of the as-prepared graphene. The peak at ~1565 cm^{-1} reflects the skeletal vibration of graphene [11]. Furthermore, the peak at 3367 and 1335 cm^{-1} are attributed to slight impurity in the material. The thermal properties of the as-prepared products were characterized by TGA in air. The TGA curve of the as-prepared graphene is shown in Fig. 1c. An abrupt weight was observed in the temperature range from 300 to 600 °C, indicating the oxidization of graphene [12,13]. After 600 °C, no further mass loss was observed, and the stability of the track indicates the nearly complete removal of the graphene. Moreover, the slight residual weight is probably because of little metal impurity.

Fig. 2 shows the TEM images of the resulting material, revealing the lamellar structure of the as-prepared few-layer graphene and the lamella is comparative filmy, corresponding to the Raman spectrum of the prepared graphene. It is clearly observed that the graphene morphology present layered structure from Fig. 2a. And the graphene is shaped by several single-deck slices with the edges as shown in Fig. 2b.



Scheme 1. Synthesis route of few-layer graphene.