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Short communication

Facile preparation of graphene nanosheets by pyrolysis of coal-tar pitch with the presence of aluminum

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ABSTRACT

An efficient method to fabricate graphene nanosheets (GNs) from pitch was developed. Results show that crystalline GNs can be prepared by pyrolysis of coal-tar pitch with the presence of aluminum. The resultant Al_4C_3 provides a growth environment for graphene sheets. After HCl pickling treatment the GNs have an average thickness of 3.95 nm with a high C/O molar ratio of 60:1.

1. Introduction

Graphene nanosheets (GNs), which possess unique physical, chemical and mechanical properties [1], are promising candidates as components in applications such as energy-storage materials, catalyst carriers, polymer composites and mechanical resonators [2–4]. In recent years, the widely used methods for preparing GNs, including micro-mechanical cleavage, epitaxial growth, arc discharge, chemical reduction of graphene oxide, thermal exfoliation of graphite intercalation compounds, solvent-thermal method, liquid-phase exfoliation and chemical vapor deposition [5], however, confront problems like small-scale preparation, complex process or high cost, which restrict the extensive application of GNs. Therefore, it is necessary to develop a simple and efficient method to fabricate GNs for industrial use.

As a solution, we introduce coal-tar pitch, a very cheap organic material made from coal, to fabricate GNs. It has since been established that, when pitch is pyrolyzed, the morphology of the pitch is the primary factor in determining the microstructure of the resulting carbon material [6], which may be attributed to both the stacking of mesogens and their long-range alignment [7]. With progressively increasing pyrolysis temperature, the mesogens become less defective in terms of the structure of the graphene layer, which is brought about by single atom movement within the graphene layer. The pyrolyzed product still contains a considerable amount of folded or bent graphene layers in the temperature range of 1400–2000 °C [8]. Therefore, pitch would be a suitable precursor for GNs production. Here we report an approach to produce GNs by pyrolysis of coal-tar pitch.

2. Experimental

The preparation process was described as follows: coal-tar pitch (softening point, 165 °C; coking value, 60%; quinoline insoluble content, <0.3%; mean particle size, 75 μm) and aluminum powder (purity, >99.9%; mean particle size, 30 μm) were adopted as raw materials. 100 g of coal-tar pitch was mixed with a certain amount of aluminum powder (0 or 50 g) using a mechanical mixing method. The mixture was put into a graphite crucible with a lid, placed in a furnace, degassed to remove entrapped air under high vacuum (<0.01 Pa), and then heated up to 1700 °C at a heating rate of 5 °C/min and kept for 1 h at vacuum pressures of around 100 Pa. The pyrolyzed product prepared with aluminum powder was dispersed in 1000 mL of HCl solution (0.5 mol/L) at 50 °C and stirred for 4 h. Floating objects in the solution were collected and washed with deionized water until pH value reached approximately 7, and then dried overnight in a vacuum oven at 100 °C. After that 10 g of black powder was obtained and used for further investigations.

Morphological measurements of samples were performed using a field emission electron microscope (FESEM, Carl Zeiss ULTRA 55 FESEM) and transmission electron microscope (TEM, JEM-2010, Jeol). X-ray diffraction (XRD) patterns of samples were obtained by an Ultima III X-ray model diffractometer (Rigaku, Japan) with Cu Kα radiation at a scanning rate of $10^{\circ}\ min^{-1}$ in a reflection mode

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over a 2θ range from 10 to 70°. Raman spectroscopy was performed with a Raman spectrometer (Renishaw Invia Reflex, Britain) with a 514 nm Ar-ion laser. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 high performance electron spectrometer using monochromatic Al Kα as the excitation source.

3. Results and discussion

Fig. 1(a) is the FESEM images of the fracture surface of the pyrolyzed product prepared without the presence of aluminum powder, which reveal that the pyrolyzed product has a dense structure. Fig. 1(b) and (c) shows the FESEM images of the pyrolyzed products prepared with the presence of aluminum powder before and after HCl pickling, respectively. Fig. 1(b-1) reveals that the pyrolyzed product before pickling is a porous material, which possesses the morphology of evident agglomeration and wrinkled appearance. Moreover, an overlapped morphology consisting of thin paper-like structure can be observed in Fig. 1(b-2). After HCl pickling, the pyrolyzed product exhibits an expanded and loose structure as shown in Fig. 1(c-1). In addition, papery and curly films intrinsically owned by graphene sheets can be seen in Fig. 1(c-2). The above-mentioned facts suggest that GNs can be prepared by pyrolysis of coal-tar pitch in the presence of aluminum followed by HCl pickling treatment.

XRD patterns of the pyrolyzed product prepared without and with the presence of aluminum powder are presented in Fig. 2(a). It can be observed that the pyrolyzed product prepared without the presence of aluminum powder has (0 0 2), (1 0 1) and (0 0 4) peaks of graphite, indicating that it is composed of graphite carbon layers. The (0 0 2) and (0 0 4) peaks represent perpendicular direction (c-axis) to the graphite hexagonal planes [9]. However, the (0 0 2), (1 0 1) and (0 0 4) peaks become weak and new peaks

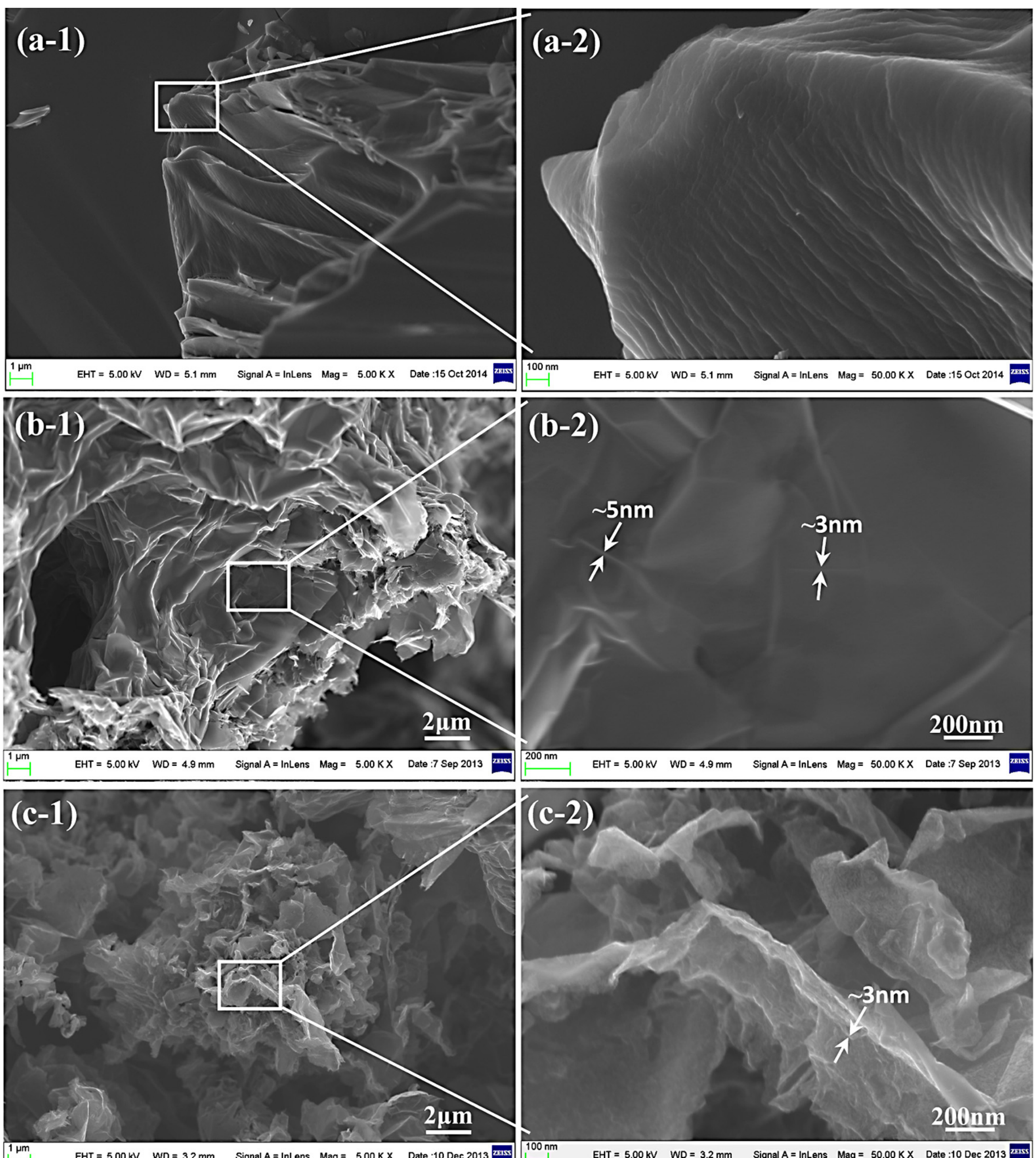

Fig. 1. FESEM images with different magnifications of the pyrolyzed products prepared from coal-tar pitch. (a) Without the presence of aluminum powder; (b) with the presence of aluminum powder before HCl pickling; (c) with the presence of aluminum powder after HCl pickling.