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Synthesis of three-dimensional graphene from petroleum asphalt by chemical vapor deposition

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ABSTRACT

The synthesis of three-dimensional (3D) graphene with petroleum asphalt as a carbon source by chemical vapor deposition on a Ni foam substrate has been studied. The morphology and properties of three-dimensional graphene synthesized from asphalt were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and X-ray diffraction. The results demonstrate that most of as-prepared 3D graphene foams have 2–5 layers, and small amounts of them have sheets more than 5 layers. The hydrocarbon fragments in asphalt consist of planar aromatic ring structures are considered to play a key role during the formation of 3D graphene. The results demonstrate that asphalt is one of the suitable starting carbon sources for making 3D graphene networks.

1. Introduction

Graphene, a novel two-dimensional monolayer material consisting of a honeycomb lattice structure of sp^2-bonded carbon atoms has been attracting much attention owing to its fascinating physical properties such as quantum electronic transport, extremely high mobility, and electromechanical modulation [1–3]. Literature survey shows that numerous methods including the micromechanical cleavage of highly oriented pyrolytic graphite [1], reduction of graphite oxide [4], and chemical vapor deposition (CVD) [5] have been developed to produce graphene with different properties. Of these developed methods, the CVD method has received significant attention for growing high-quality graphene films with large area. However, two-dimensional (2D) graphene is vulnerable to cracks, wrinkling, defective sites and some other mechanical problems, which restricts their functions and applications. It is urgent to integrate 2D graphene components into three-dimensional (3D) functional architectures. Although chemically derived graphene sheets were used to fabricate 3D macroscopic structures graphene with considerable strength and stiffness [6,7], these integrated structures possess severe structural defects in graphene sheets caused during exfoliation and reduction process. By comparison, template-directed CVD is an alternative method to produce graphene with superior mechanical property and macrostructure [8,9].

However, CVD method is limited to the use of gaseous raw materials. Most of the carbon sources were purified chemicals such as CH_4 and C_2H_2 that could be expensive for mass production. Therefore, the fabrication of graphene of both using cheap carbon source and with high quality has become an important challenge. Nowadays, as the byproduct after the distillation of petroleum [10], the oil-derived asphalt has not been widely applied in the downstream petrochemical processes in the refinery due to its complex structure and unworkability. However, the asphalt is a cheap and readily available carbon source in nature which has great potential applied value as feedstock in producing high value-added materials such as graphene because it contains a large amount of carbon-rich molecules confirmed by Cheng et al. [11,12]. Herein, we report the preparation of 3D graphene from petroleum asphalt by a CVD method with nickel foam as catalyst. To the best of our knowledge, up to now, there are no reports about the preparation of 3D graphene with asphalt as the carbon source in literatures. Our results demonstrate that asphalt can be a good precursor for making high quality 3D graphene.

2. Experimental

The petroleum asphalt was supplied from Liaohe refinery, China, and some composition and property data of oil residual are as follows: asphaltene, 55.38 wt%; aromatics, 9.07 wt%; carbon

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residue, 48.08 wt%; H/C, 1.18 mol mol^{-1}. The growth of 3D graphene from asphalt was performed by the CVD method in a 4-in. chamber quartz reactor using the Ni foam as catalyst. In a typical run for graphene synthesis, 0.5 g asphalt was firstly dissolved in 37.5 mL toluene with the assistance of sonication for 1 h. At the same time a pretreatment on the nickel foam by acetic acid and ethanol was performed. Then the nickel foam was immersed in the asphalt–toluene solution, and soaked for another 1 h. After the natural drying process for 30 min, the asphalt coated nickel foam without toluene was placed in the center of the tube furnace. With Ar and H_2 flowing rate at 300 and 30 sccm/min, respectively, the pressure was maintained at about 1.5×10^3 Pa, and the quartz tube was heated to 940 °C. After 10 min reaction, the sample was cooling down to room temperature at a rate of 10 °C/min. The synthesized 3D graphene foam from asphalt was characterized by scanning electron microscopy (SEM, Quanta 200F), transmission electron microscopy (TEM, FEI F20), Raman spectroscopy (532 nm, He–Ne laser) and X-ray diffraction (XRD, Bruker D8 Advance Germany).

3. Results and discussion

It is found that the 3D graphene synthesized from asphalt exhibits good mechanical strength, as seen in Fig. 1(a). The SEM image shown in Fig. 1(b) demonstrates the as-prepared graphene adhering to the surface of the nickel foam, in which a number of winkles and ripples formed on the nickel foam are found, which is possibly due to the difference between the thermal expansion coefficients of graphene and nickel [13]. After etching the nickel skeleton by $FeCl_3$ solution, the 3D graphene maintains the interconnected 3D scaffold structure of the nickel foam template, demonstrating structural integrity and stability, as confirmed by a low-magnification SEM image of Fig. 1(c). The pore size of these materials mainly distributes in the 200–300 μm range, as seen in Fig. 1(d), which is in consistance with the pore size of nickel foam.

Furthermore, for the purpose of comparison, a TEM image for the raw material is also shown in Fig. 2(a) which indicates that asphalt is amorphous carbon consists of alkyl chains linked to aromatic cores [14]. As shown in Fig. 2(b), a typical TEM image of 3D graphene with 2 layers and 3 layers (indicated by arrows) can be identified clearly though the folded edge, along with the SAED pattern shown in the inset of Fig. 2(b), revealing the typical hexagonal crystalline, which provides strong evidence that it is possible to convert the disordered asphalt into ordered graphene by the CVD method. Besides, it is found that 3D graphene foam is composed of graphite layers and most of them have 2–5 layers and small amounts of graphene have sheets more than 5 layers. It is worth noting that as the concentration of carbon source increases, the multi-layered graphene sheet with layer numbers over 5 tends to be formed.

Fig. 3(a) shows the Raman spectrum of the synthesized 3D graphene on Si. The two most prominent features are the G band at 1569 cm^{-1} and the 2D band at 2699 cm^{-1}. The I_{2D}/I_G intensity ratio of our synthesized graphene foam is 0.37, known to strongly correlate with the number of graphene layers [5], which is predicted to be a hallmark of multilayered graphene, being consistent with TEM observations. Besides, a low intensity peak at 1341 cm^{-1} corresponding to the defect-related D band is observed, which indicates only few sp^3 carbon atoms or defects existed in the sample. In addition, there is a very sharp peak around $2\theta = 26.59°$ in the XRD pattern of the synthesized graphene in Fig. 3(b). According to the Bragg equation $2d \sin\theta = n\lambda$, the layer spacing is estimated to be 0.335 nm, which is the reflection (002) of graphene. The fairly sharp reflection (002) suggests that the samples are regularly ordered along the stacking direction.

In order to get a more comprehensive understanding of the growth mechanism of 3D graphene foam from petroleum asphalt, we have carried out a series of experiments under different conditions. We have compared the results of 3D nickel substrates immersed in both asphalt–toluene solution and pure toluene under the same experimental conditions. In contrast, after the CVD process

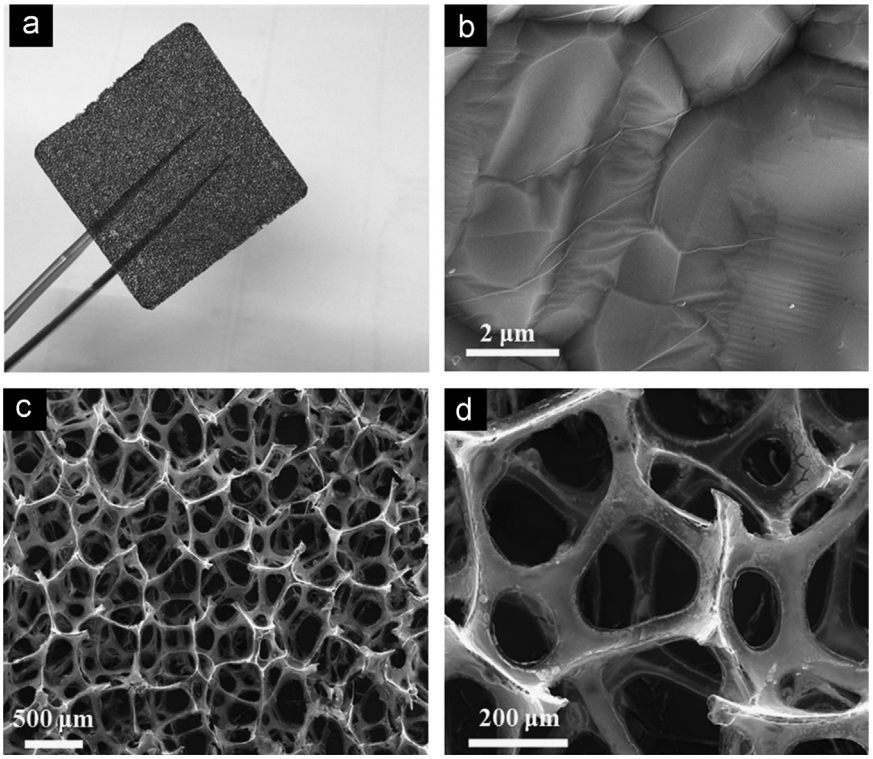

Fig. 1. (a) A microphotograph of 3.5×3.5 cm^2 free-standing graphene foam. (b) A SEM image of graphene on surface of the nickel foam. (c) A low-magnification and (d) a high-magnification SEM image of 3D graphene foam.