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Synthesis and methane storage of binder-free porous graphene monoliths

Guoqing Ning*, Hao Wang, Xiaoxin Zhang, Chenggen Xu, Guangjin Chen, Jinsen Gao

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

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ABSTRACT

Nanomesh graphene (NMG) obtained by template chemical vapor deposition was used to synthesize the binder-free graphene monoliths by simple tablet pressing. The stacking manner of the NMG sheets was crucial to the cohesion interaction between the graphene sheets, only the NMG materials with a loosely stacking manner could be pressed into binder-free monoliths. At the tableting pressure of 2–8 MPa, both the bulk densities and the specific surface areas of the monoliths keep nearly constant as the tableting pressure increases, indicating that the NMG monoliths have obvious elasticity and a porous structure due to the large corrugations and the mesh structures of the graphene sheets. As a result, an extraordinary methane storage capacity of 236 (v/v) at 9 MPa was obtained in the graphene monolith prepared by tableting at 4 MPa.

1. Introduction

Depletion of fossil oil deposits and the escalating threat of global warming have put clean energy research, including search for clean energy carriers such as hydrogen and methane as well as reduction of carbon dioxide emissions, on the urgent agenda. Physical adsorption in porous carbon materials appeared to be an attractive and promising method for methane and hydrogen storage and carbon dioxide capture due to its high performance, low cost and good safety (Cao, Zhang, Chen, Wang, & Yun, 2003; Lozano-Castelló, Cazorla-Amorós, Linares-Solano, & Quinn, 2002a, 2002b; Rodríguez-Reinoso, Nakagawa, Silvestre-Albero, Juárez-Galán, & Molina-Sabio, 2008). It has been proved that materials with high surface area, appropriate pore size and high stacking density are propitious to promote the gas storage capacities (Alcañiz-Monge, De La Casa-Lillo, Cazorla-Amorós, & Linares-Solano, 1997; Celzard, Albiniak, Jasienko-Halat, Marêché, & Furdin, 2005; Liu, Zhou, Sun, Su, & Zhou, 2011; Ramírez Vélez, 2011; Rodríguez-Reinoso et al., 2008). By producing carbon as a monolith, it is possible to reduce the interparticle void and maximize the bulk density (Chen et al., 1997; Lozano-Castelló, Cazorla-Amorós, Linares-Solano, & Quinn, 2002a). These monoliths consist of uniformly packed cylindrically-shaped pieces lessening wasted space in the storage vessel. Another advantage of producing carbons in an efficient space-filling form is that they are strong and can resist attrition. The monoliths can be produced using a binder, which helps to keep particles in a compressed state. However, most binders used for this purpose reduce the adsorption performance of the activated carbon because they block the microporosity.

In previous work (Ning et al., 2012), we reported methane storage by nanomesh graphene (NMG) with loosely or tightly stacking manners. Binder-free graphene monoliths were prepared by a simple tablet pressing using NMG as raw material (Ning et al., 2011, 2012). Although the preparation of graphene monoliths by tableting had been reported, the key factors for the graphene monolith synthesis and the properties of the graphene monoliths have not been systematically investigated. In this work, we focus on the synthesis and characterization of graphene monoliths. Drying process is found to be a key factor for successful synthesis of graphene monoliths. Bulk densities, specific surface areas (SSAs) and methane capacities of the monoliths pressed at different pressures are presented, which reveals that the as-prepared graphene monoliths exhibit obvious elasticity and a good porous structure at the tableting pressure of 2–8 MPa. The structure features of the graphene monoliths resulted in an extraordinary methane storage capacity of 236 (v/v) at 9 MPa. This work provides a feasible method to the mass production of graphene monoliths for gas storage.

2. Experimental

2.1. Material synthesis

Porous MgO layers, which served as templates for the chemical vapor deposition (CVD) synthesis of NMG, were prepared by a boiling treatment of MgO particles. First, the as-purchased MgO powder (Sinopharm Chemical Reagent Co. Ltd.) was mixed with

* Corresponding author. Tel.: +86 10 89733085; fax: +86 10 69724721.
E-mail addresses: ngq@cup.edu.cn, ninggq@qq.com (G. Ning).

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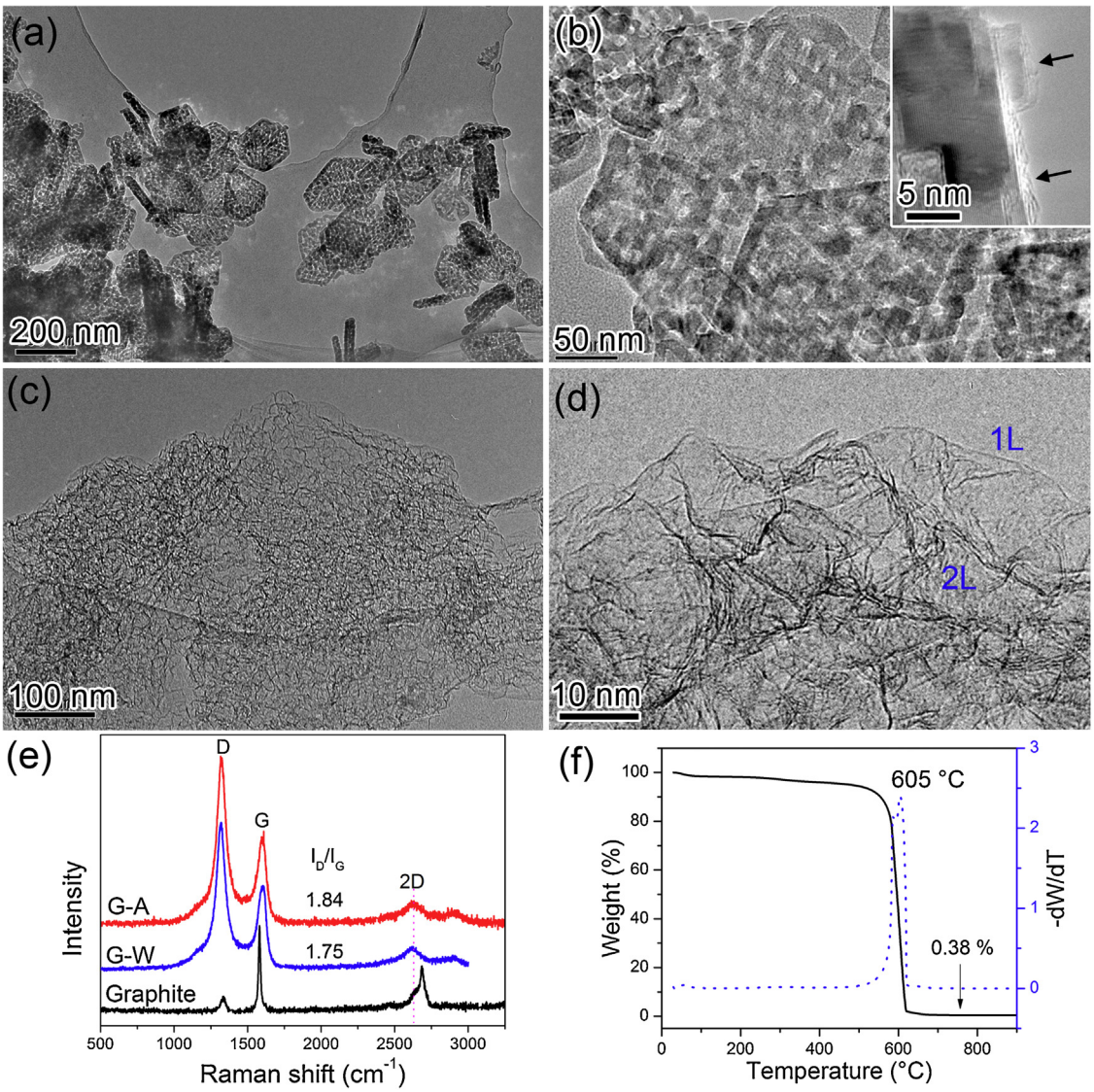

Fig. 1. TEM images of (a) the porous MgO templates, (b) graphene/MgO, and (c and d) the porous NMG after template removal. The inset of (b) is the high resolution TEM image of graphite layers (indicated by arrows) deposited on MgO surface. (e) Raman spectra of the NMG samples in comparison with graphite. (f) A typical TG curve of the NMG.

deionized water and boiled for 24 h in a reflux apparatus. After filtration and drying, the obtained material was ground into a fine powder. Finally, the powder was calcined at 500 °C for 30 min to obtain porous MgO layers.

NMG was synthesized by CH_4 cracking at 875 °C in a vertical quartz reactor, as previously described (Ning et al., 2012). In a typical run, the quartz reactor was mounted in an electrical tube furnace and was heated to 875 °C in an argon flow. Once the reaction temperature was reached, CH_4 was introduced into the reactor, and the MgO template was fed into the reactor from the top hopper. After carbon deposition for 10 min, CH_4 was turned off and the reactor was cooled to room temperature in an Ar atmosphere. The as-obtained material was purified by acid washing (excessive amount of condensed hydrochloric acid diluted by deionized water, with volume ratio of 1:3) with reflux for 1 h to remove MgO. Three batches of graphene materials were prepared using different drying processes. (1) The as-obtained suspension was vacuum filtrated and rinsed by deionized water, followed by drying at 100 °C overnight in an oven. The resulted material was labeled as G-W. (2) The as-obtained suspension was vacuum filtrated and rinsed by alcohol, followed by drying at 80 °C overnight in an oven. The material was labeled as G-A. (3) The as-obtained suspension was vacuum filtrated and rinsed by deionized water, followed by drying at −20 °C for 24 h in a freeze drying machine. The material was labeled as G-F. All the three materials were slightly ground into a fine powder for characterization and application.

The powdered NMG samples were used to make NMG tablet monoliths by a tablet press machine using a 13 mm mold at different tableting pressures. Photos of the tablets were taken to measure their volume. The tablets can be regarded as cylinders in diameter of 13 mm, and the volume of the tablets was calculated by measuring the photos. The height of the tablets was measured using the diameter as a ruler.

2.2. Characterization

The NMG samples were characterized by transmission electron microscope (TEM, JEM 2010 operated at 120 kV), scanning electron microscope (SEM, Quanta 200F), Raman spectroscopy