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Short communication

Few-layer graphene-like flakes derived by plasma treatment: A potential material for hydrogen adsorption and storage

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ABSTRACT

A novel, one-step, wet-free, environmental friendly and high-yield method for producing few-layer graphene powders with large surface areas (up to 800 m^2/g) and narrow nanopore sizes (0.7–0.8 nm) using plasma-induced exfoliation of natural graphite is presented. Advanced characterization techniques were employed, including scanning and transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction and N_2 gas adsorption/desorption measurements at 77 K, to investigate the morphological, elemental, structural and textural/porosity properties of these nanomaterials. Fully reversible H_2 gas adsorption/desorption isotherms with maximum gravimetric capacities of up to ~2 wt.% at 77 K and ~60 bar are reported here. The H_2 storage performance at 77 K is well correlated with certain textural features such as specific surface area and microporosity. The results of this work provide a valuable feedback for further research on plasma-processed graphene-based materials towards efficient H_2 storage via cryo-adsorption.

1. Introduction

Exfoliated graphene has been a subject of considerable research during the last decade attributed to its unique electronic, thermal, optical and mechanical properties. Recently, porous graphene has also attracted significant attention as a potential solid-state medium for storing gases and especially a highly-dense energy carrier such as hydrogen (H_2) [1–11]. Few-layer graphene (FLG), an extremely "thin" graphitic analogue composed of a limited number of stacked carbon atomic layers, could become an efficient adsorbent material in applications related to H_2 cryo-adsorption and storage mainly due to the large surface areas achieved in combination with the tunable pore sizes. Density Functional Theory simulations by Yadav et al. [9] showed that defect-engineering of graphene could lead to effective H_2 gravimetric capacities of up to ~7 wt.%. Combined theoretical and experimental studies by Baburin et al. [10] indicated that graphene sheets with defect-induced porosities exhibit surface areas greater than that of single-layer graphene (i.e. 2630 m^2/g), thus leading to enhanced H_2 adsorption at cryogenic liquid nitrogen (N_2) temperature (i.e. 77 K). Indeed, Grand Canonical Monte-Carlo simulations in perforated graphene revealed capacities of up to 6.5 wt.% H_2, while volumetric measurements on a thermally-exfoliated and chemically-activated high-surface area (~2900 m^2/g) graphene recorded 5.5 wt.% H_2 at 30 bar. Recently, Klechikov et al. [11] reported an impressive H_2 uptake of up to 7.5 wt.% at 77 K and ~120 bar for highly-porous graphene scaffolds with extremely high surface areas of up to ~3400 m^2/g prepared by KOH activation and H_2 annealing.

Micro-mechanical cleavage of graphite [12], catalytic chemical vapor deposition of carbonaceous sources [13] and reduction of graphite oxide are few of the principal methods currently used to produce graphene [14]. Despite the large variety of graphene-like

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materials presented in the literature [1–8,10,11], there are no references available describing the H_2 adsorption properties of FLG powders derived by direct plasma-assisted exfoliation of natural graphite. Plasma-processing technology is considered a novel, wet-free, cost-effective and environmental-friendly "top-down" method for producing graphene of high quality and purity in an industrial-commercial scale, while allowing its modification with a variety of surface functionalities (e.g. carboxyls, amines, etc). The plasma interacts with and subsequently modifies a graphitic surface both physically (i.e. ablation) and chemically (i.e. functionalization) depending on the gas stream (e.g. argon, oxygen, etc) and the operating power [15,16]. Herein, nanoporous and high-surface area FLG-like powder materials were produced based on a plasma-induced graphite-exfoliation process [17]. The presented method offers a series of advantages, including production of bulk quantities (i.e. 30 kg per batch), relatively low power consumption (i.e. maximum ~6 kW) during plasma formation, absence of metal catalysts usually employed in graphene industry as well as lack of wet chemical procedures for purification. The morphology, elemental composition, structure and porosity/texture was studied by scanning and transmission electron microscopy (SEM and TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and N_2 gas adsorption/desorption measurements at 77 K, respectively. The characterization studies revealed that the controlled "destruction" of the graphitic surface using plasma could lead to three-layered graphene-like flakes with enhanced surface areas (up to 800 m^2/g) and defect-induced microporosities (pore sizes below 1 nm). Finally, the H_2 storage performance of these powders was systematically evaluated by high-pressure (i.e. 0–100 bar) H_2 gas adsorption/desorption measurements at 77 K. Even though the H_2 uptake values presented in this study are not superior to those reported for other graphene-like materials usually derived by wet chemical treatment of graphene oxide (e.g. KOH activation) [2,5,7,10,11], it is the first time that the H_2 storage potential of plasma-processed carbon-based materials is explored in such detail.

2. Experimental

2.1. Plasma processing

Two FLG powder materials with large surface areas (denoted hereafter as FLG-400 and FLG-800) were prepared by plasma-processing of natural graphite using a custom-made multi-electrode dielectric barrier discharge (DBD) plasma reactor, as described elsewhere [17]. Flake graphite powders (30 kg; Asbury Carbons) were initially exposed in an argon (Ar) plasma (0.01 mbar pressure and 600 sccm flow) for 60 min using lower (~3 kW) and higher (~6 kW) power inputs, respectively. The process causes the exfoliation of graphite by generating Stone-Wales, single- and double-vacancy surface defects and consequently negating the van der Waals forces between the stacked graphene layers [10]. The as-produced FLG powders were subsequently treated in an oxygen plasma for 30 min, under similar conditions to the previous process, to introduce surface oxygen-based functionalities with the view to reduce agglomeration.

2.2. Characterization methods

Surface images were obtained by a JEOL JSM-7401F field emission SEM and a Philips CM-20 high-resolution TEM equipped with a LaB_6 filament. XPS studies were carried out by a Kratos Axis Ultra-DLD system equipped with a monochromatic AlKα radiation, a dual Al–Mg anode and a delay-line detector. XRD patterns were collected in the 2θ region of 10–60° by a Shimadzu XRD-6000 equipped with Ni-filtered CuKα radiation (λ ~1.54 Å). The interlayer distances (d) and crystallite thicknesses (L_c) were estimated using Bragg's law and Scherrer's equation, respectively. Low-pressure (0–1 bar) N_2 adsorption/desorption isotherms were

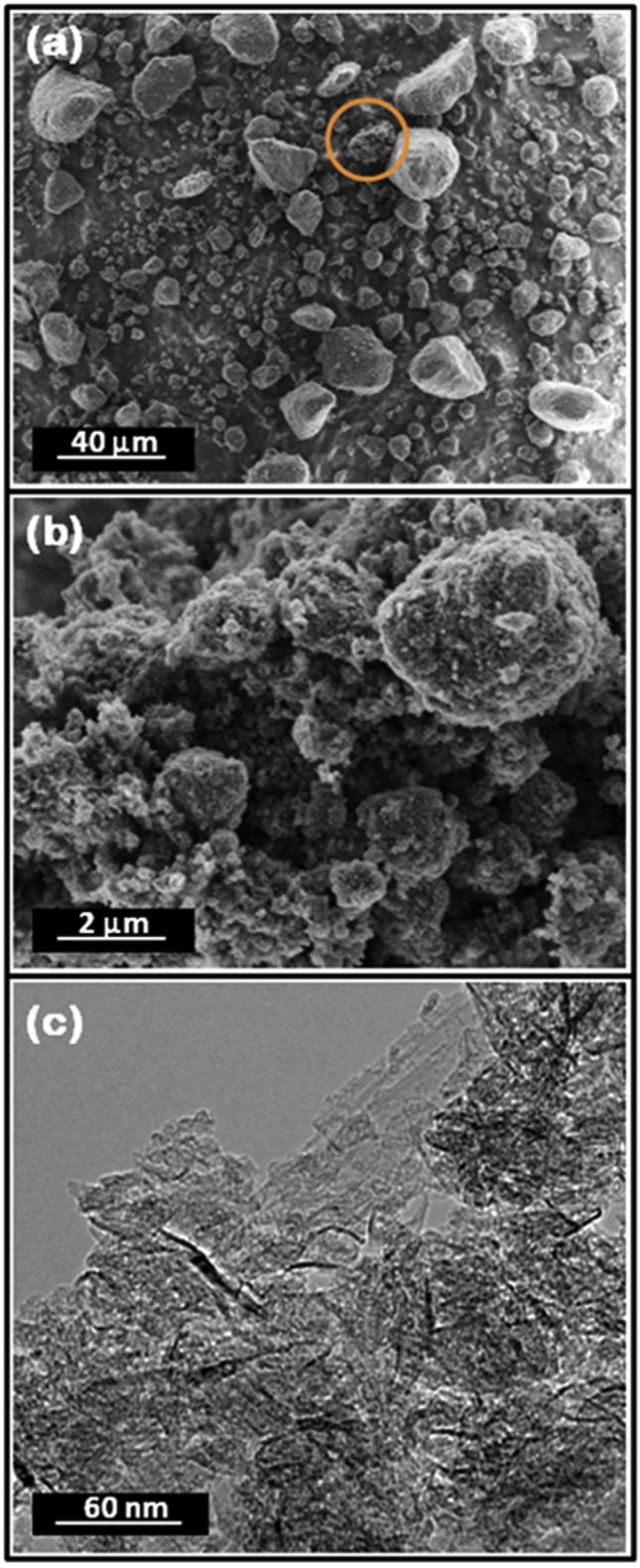

Fig. 1. Field emission SEM images at (a) low- and (b) high-magnification and (c) high-resolution TEM image of the FLG-800 powder.