



Methanol wetting enthalpy on few-layer graphene decorated hierarchical carbon foam for cooling applications



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ABSTRACT

Vertical few-layer thick graphene petals are grown on macro-porous carbon foam surfaces having an intrinsic open porosity of 75%. This provides a hierarchical porous structure with a potential for surface adsorption/desorption or wetting/dewetting based thermal energy storage applications. Carbon foams have a combined advantage of large surface area and high thermal conductivity critical for thermal energy storage, but they are prone to oxidation and exhibit low adsorption enthalpies for lightweight hydrocarbons. Here we report graphene petal decoration of carbon foam surfaces and subsequent chemical modification through boron nitride incorporation in hexagonal carbon planes of both carbon foams and graphene petals. This chemically reactive hierarchical structure is characterized with FESEM, Raman, XRD, and XPS measurements. Methanol wetting enthalpy of this three-dimensional hierarchical material was measured with a solution calorimeter, and had shown a six fold increase (from 78 to 522 J/g of foam) as compared to the carbon foam prior to the surface modification. Influences of petal decoration on the surface morphology of carbon foam, BN chemical modification, structure and stoichiometry of the hierarchical material surface, and methanol wetting enthalpy improvement are discussed in detail. The applicability of this hierarchical porous material for thermal energy applications is established.

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1. Introduction

Emerging applications, such as sustainable energy generation, water purification, and energy storage, require advanced porous materials with well-defined structural, interfacial, compositional, and morphological properties [1–7], and hierarchically porous materials have been found to be important for these applications [4,8]. Besides the unique structural characteristics, these materials have emerged as promising alternatives in energy technologies due to their wide range of pore sizes from nanoscale to macroscale dimensions for effective heat transfer, but these structures must be functionalized to improve applicability for desired performance.

Macro-porous carbon foam is well known for its beneficial thermal and mechanical properties. Graphitic carbon foam is reported to have small specific surface area (~0.2–0.3 m²/g), depending on the type and density of foams [3], but offers good mechanical and thermal properties as compared to other powder-based or porous materials [9,10]. The thermal conductivity of graphitic carbon foam is a function of the solid material density [11]. Therefore graphitic carbon foam could serve as a base material for surface structuring that would increase its surface

area. Although highly dense carbon foam has thermal conductivity in the range 180–200 W/mK [11], its thermal interface behavior tends to be poor [10]. Recently there have been efforts to synthesize CNTs on carbon foam and CNT-carbon foam composites to increase surface area and thermal properties respectively [12–14].

The soaring price of fossil fuels together with environmental concerns has motivated renewed interest in adsorption-desorption or wetting-dewetting cycles to recover waste heat [2,15]. Such technologies have historically been restricted to niche applications such as those in remote or extreme environments, yet today they are being developed for more mainstream use. Measuring the wetting enthalpy of a liquid adsorbate with a solid porous material can quantify the ability of the material to act as efficient adsorbent [16,17]. Polar functional groups on a material surface are influential in regard to wetting enthalpy [17]. Boron-carbon-nitride (C-BN) with relative electro negativity variation among its elements (boron = 2.05, carbon = 3.0 and nitrogen = 3.5), can produce surface structures with strong bond polarization that alters sorption process. With BN incorporation C-BN becomes thermally and chemically more stable [18,19] having active polar domains on the surface that are crucial for adsorbent material used in thermal energy storage [20].

Our recent work [18,20] on BN domain formation on carbon foam surfaces through microwave heated chemical modification showed considerable increases in methanol wetting/dewetting enthalpy and

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thermal stability against oxidative atmosphere. To increase the low intrinsic surface area of carbon foam without significant contributing to mass increase, nanometer thin petal-like structures made of few-layer graphene have been decorated over the surface by microwave plasma chemical vapor deposition in the present work. This work considers petals decoration on the entire surface (including inside the pores) of carbon foam to realize a spatially hierarchical structure and the structural functionalization through BN incorporation for improved adsorption performance. A number of surface analytical techniques were used to characterize in detail this hierarchical material morphology, chemistry, and structure, and correlate such with a significant enhancement of methanol sorption enthalpy as measured by a wet calorimetric method. The applicability of this hierarchical material toward thermal energy storage, rapid heat exchange and fluid adsorption/desorption cooling applications is assessed.

2. Experimental

Macroporous graphitic carbon foam (CF) obtained from KFOAM (Koppers Inc., Pittsburgh) has 75% open porosity and bulk density of 0.23 g/cm^3 [18]. The petal decoration on the surface of the carbon foam is performed in a microwave plasma chemical vapor deposition (MPCVD) [21]. Carbon foam of size $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ is used to decorate petals on both sides. A hydrogen (H_2) plasma (50 sccm H_2 gas flow) of 600 W and a substrate temperature of $700 \text{ }^\circ\text{C}$ are used to activate the CF surface, after which the methane (10 sccm) is fed into the chamber for graphene petal growth of 30 min. During petal growth the foam is elevated by 1.5 cm from the base of the molybdenum puck by a ceramic stand of 4 mm diameter. This type of elevation to the growth substrate above the puck is found to be critical as the interaction of microwave plasma with the elevated substrate produces localized field enhancement facilitating graphene petal growth.

We have incorporated B and N in CF and petal decorated CF (petals-CF) samples through microwave assisted thermo-chemical treatment using aqueous solution of boric acid and urea according to our previous report [18]. The samples are vacuum dried for 12 hours and then annealed at $900 \text{ }^\circ\text{C}$ for 12 hours.

The carbon foam (CF), BN modified carbon foam (BN-CF) and BN modified petal decorated carbon foam (BN-petals-CF) are characterized to evaluate chemical constituents and structural details. A field emission scanning electron microscope (FESEM; Hitachi S4800) is used to investigate the surface morphology. Specific surface area measurements were done in Micromeritics Tristar instrument. The X-ray diffraction patterns are evaluated using a Bruker D8 Focus X-Ray Diffractometer equipped with $\text{Cu K}\alpha$ X-ray source, 3 circle goniometer and lynseye 1D detector. Raman spectra are collected using a Renishaw InVia confocal Raman system (Renishaw Inc., IL, USA) with a 50x air objective at 633 nm laser excitation. Corresponding laser power and accumulation time are 20 mW and 10 s, respectively. Chemical composition of modified CF surfaces is investigated by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra DLD spectrometer with monochromatic $\text{Al K}\alpha$ radiation ($h\nu = 1486.58 \text{ eV}$). XPS data are analyzed with the commercially available CasaXPS software (www.casaxps.com), and individual peaks are fitted to a Gaussian-Lorentzian (GL) function. The resulting spectra are corrected using the position of the main C 1s component at 284.5 eV as a reference for graphitic carbon [22].

Wetting enthalpies for methanol on the CF samples are investigated with a modified Parr 1455 solution calorimeter (Parr Instrument) taking 75 ml methanol in a thermoflux. The calorimeter is modified with an aluminum bell in place of a glass bell to achieve better thermal equilibrium before wetting. The experiments are performed with strict ambient temperature stability. During experiments, the temperature inside calorimeter is continuously recorded by a thermistor every 10 s while a completely sealed rotating bell containing the foam material (adsorbent) is immersed into the methanol bath before wetting. After

maintaining the set-up for about 8 hours to reach thermal equilibrium between adsorbent and methanol, wetting experiments are performed.

3. Results and discussion

As received, the CF has an open morphology with average pore sizes within with diameter $200\text{--}300 \text{ }\mu\text{m}$ as can be clearly visible in a lower magnification image in Fig. 1(a). Such porous morphology provides an easy access of the MPCVD processing gases and surface coupled plasma into foam interior. This open macroscopic morphology remains present after the petal growth, without any blocking of these relatively large size pores (Fig. 1b). On the top of this micro-scale CF morphology, the MPCVD process produces few monolayer thick graphene petals. From a previous study of the graphene petal growth mechanism on carbon fibers, these are nucleating and growing from structural defects on graphitic surfaces and have a strong covalent bonds, extending graphitic substrate hexagonal base planes [23]. The density of CF before and after petal growth and BN modification are measured and found to be similar due to very light weight of graphene petals.

During petal growth by MPCVD, we have done two depositions: first on one side of carbon foam of dimensions $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ and second on other side of the same carbon foam to get uniform petal growth inside the pores of carbon foam. Fig. 2(a) shows digital image of a broken petal decorated carbon foam sample and we analyzed it by the cross sectional FESEM imaging. Fig. 2(b) shows FESEM image on cross section of petals decorated CF indicating points (i, ii, iii and iv) where high magnified SEM images were taken. Those high magnified images are presented in Fig. 2(i), (ii), (iii) and (iv) at different points indicated on Fig. 2(b). These images indicate clearly that petals are present throughout the interior pores.

During BN modification, CF and petals-CF soak the chemical solution containing boric acid and urea under high pressure and high temperature microwave heating. Treatment at $900 \text{ }^\circ\text{C}$ for 12 hours anneals the B and N incorporation within CF and petals-CF and helps in removing

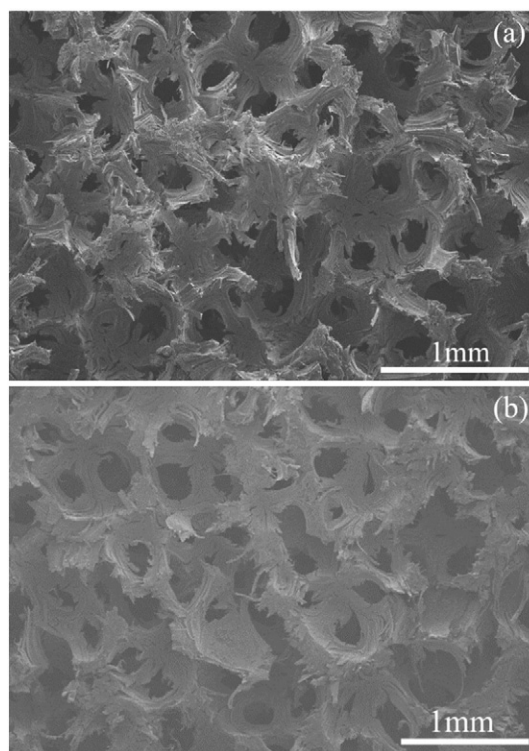


Fig. 1. Lower magnification FESEM image of (a) carbon foam (CF) and (b) petals decorated CF surface.

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