Activated graphene-derived porous carbon with exceptional gas adsorption properties

Aswathi Ganesan, Manikoth M. Shaijumon[*]

School of Physics, Indian Institute of Science Education and Research Thiruvananthapuram, CET Campus, Sreekaryam, Thiruvananthapuram, Kerala, India

ARTICLE INFO

ABSTRACT

Designing nanoporous materials with high surface area, large porosity, superior structural stability and amenability to various processing conditions, is important to meet the commercial demands of large-scale reversible gas storage systems. Here, we demonstrate a simple approach to synthesize highly porous activated graphene-derived carbon (a-GDC), with ultra-high surface area (~3240 m^2 g^{-1}) and enhanced porosity characteristics, from thermally exfoliated graphite oxide (TEGO), through an efficient and finely controlled KOH chemical activation process. a-GDCs with highly interconnected network of micro- and mesopores show excellent gas storage properties for CO_2, CH_4 and H_2, with exceptionally high adsorption capacities and fast sorption kinetics, superior to other high surface area nanoporous carbons. The results show great promise for the development of efficient carbon based sorbents for effective CO_2 capture and energy storage applications.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Porous materials including porous carbon, metal organic frameworks (MOFs), zeolites, porous organic polymer networks, porous covalent organic frameworks (COFs) etc., [1–11] offer a wide variety of chemical composition and structural architectures that are suitable for the adsorption and storage of different gas molecules including hydrogen, methane and carbon dioxide. In addition, these materials display great promise in other important and relevant applications including electrochemical energy storage (Batteries, Supercapacitors etc.), catalysis and separation [2,10–19]. Lot of remarkable efforts have been made to synthesize such materials from a variety of precursors using different synthesis techniques [10,20,21]. Among this, porous carbonaceous materials are particularly interesting due to its fascinating properties, which include high surface area, high amenability to pore structure modification and surface functionalization, relative ease of regeneration, high thermal stability etc [3,5,9,19,20,22–25]. Physical and chemical activation techniques have been used by several researchers to produce activated porous carbon from different carbon precursors [5,19,26–29]. The former process involves carbonisation through pyrolysis followed by activation of the resulting char at

elevated temperatures (normally, 600–1200 °C) in presence of suitable oxidising gases such as CO_2, steam, air or their mixtures and the latter involves impregnating carbon containing raw materials with chemical agents such as NaOH, KOH, H_3PO_4, $ZnCl_2$ etc., and simultaneously heating it to high temperatures (normally, 450–900 °C) under inert atmosphere. Chemical activation involves lower activation temperature and results in increased yield and is hence preferred over physical activation for the synthesis of activated carbon materials. Moreover, materials that result from chemical activation show higher surface area and porosities than those activated physically [23,30,31]. Recent reports on synthesis of porous carbon from MOFs and graphite oxide, following KOH activation approach, gained lot of attention [9,28,29,32–37]. However, further improvements in their porosity characteristics and gas uptake properties can be achieved with controlled activation conditions. The activation parameters such as the annealing temperature, precursor properties, inert atmosphere etc., are very critical in achieving better porosity characteristics for such materials [30,31]. Here, we report an efficient strategy, through controlled activation conditions, for the synthesis of highly porous activated carbon derived from few layered graphite oxide (GO), exhibiting ultrahigh surface area and exceptional gas uptake properties. Thermally exfoliated few layered GO sheets with BET surface area ~560 m^2 g^{-1} are chemically activated using KOH, under controlled conditions. The as-obtained highly porous carbon with BET surface area as high as 3240 m^2 g^{-1} showed excellent porosity

* Corresponding author. Tel.: +91 04712599417.
E-mail address: shaiju@iisertvm.ac.in (M.M. Shaijumon).

characteristics and exceptionally high gas adsorption capacities for H_2, CO_2 and CH_4.

2. Experimental section

2.1. Materials synthesis

Activated graphene derived porous carbon (a-GDC) was prepared from thermally exfoliated graphite oxide (TEGO) by controlled KOH chemical activation process. Graphite oxide (GO) was synthesized by oxidising graphite powder (Bay carbon) in a strong acidic medium using an improved Hummer's method [38]. TEGO was then prepared from the as-synthesized GO by thermal treatment at 300 °C for 10 min under ambient air. Activation procedure involves the mixing of TEGO (800 mg) with 7 M KOH aqueous solution (40 ml) and stirring for 6 h at room temperature at 800 rpm, followed by another 20 h of static soaking in ambient conditions. The extra KOH solution was removed by filtering the mixture through a polycarbonate membrane (Whatman, 0.2 μm); then the mixture was dried at 65 °C for 24 h. The dried TEGO-KOH mixture was then transferred to an alumina boat and heated at 800 °C for 1 h under argon flow (170 sccm) in a quartz reactor (50 mm diameter). The temperature was increased from room temperature to 800 °C at a ramp rate of 5° per min. Two samples were prepared under different activation conditions. For a-GDC-1, the activation was carried out under flowing argon gas (170 sccm) for 1 h without applying vacuum. For a-GDC-2, the reactor was initially evacuated to 10^{-3} bar for 30 min, followed by argon flow for 1 h. The annealing temperature and argon flow rate was kept unchanged under both conditions. The samples were allowed to cool down gradually under argon flow and were later washed repeatedly with de-ionized water, until pH of final washing solution reached ~7. The samples were then dried at 65 °C in ambient air for 4 h followed by vacuum drying at 120 °C for 24 h.

2.2. Materials characterization

Structural and morphological characterizations of GO, TEGO and a-GDC samples were performed using various analytic and spectroscopic techniques. Fourier transform infrared spectra (FT-IR) were recorded on a Shimadzu IR Prestige-21 FT-IR spectrometer with KBr pellets. Powder X-ray diffraction patterns (XRD) were recorded using Empyrean, PANalytical XRD instrument with Cu-Kα radiation. Transmission electron microscopy (TEM) images were recorded using Tecnai G2 TF20 - ST electron microscope operating at 200 kV. Thermogravimetric analysis (TGA) was performed using a SDT Q600 Thermogravimetric analyzer (TA Instruments) under N_2 atmosphere.

2.3. Porosity and gas adsorption measurements

Porosity characteristics of the samples were studied using N_2 adsorption–desorption isotherms measured at 77 K up to a maximum relative pressure of 1 bar, with the Micromeritics 3-Flex surface characterization analyser. Prior to the N_2 adsorption measurements, the a-GDC samples were degassed at 350 °C under vacuum for ~12 h in a separate vacuum degassing unit followed by in-situ degassing at 300 °C for 3 h under turbo-level vacuum (~10^{-12} bar) at the sample ports. GO and TEGO samples were degassed at 60 °C and 110 °C respectively, in the vacuum preparation unit in addition to in-situ degassing at 60 °C at the sample ports.

High pressure gas adsorption measurements for H_2, CO_2 and CH_4, were carried out at different temperature and pressure and the isotherms were collected on a pressure composition isotherm (PCI)

measurement system (Advanced Materials Corporation, Pittsburgh, USA). A third order virial expansion equation of the Ideal gas law was employed in calculating the amount of gas adsorbed by the material, from its pressure, temperature and the occupied volume. Accurate volume calibration of the instrument was made before the gas adsorption experiments. Various precautions were taken to maintain steady sample temperature during the entire process of adsorption and desorption cycles. Prior to the gas adsorption measurements, approximately 100 mg of the a-GDC samples were thoroughly ground in a mortar, and were degassed at 110 °C under high vacuum (10^{-6} bar) for ~12 h. H_2 adsorption measurements were carried out at liquid nitrogen temperature (77 K) up to a maximum pressure of 10 bar. Both CO_2 and CH_4 adsorption experiments were performed at four different temperatures (25 °C, 50 °C, 75 °C and 100 °C) up to a final pressure of 20 bar and 35 bar respectively.

3. Results and discussion

3.1. Material synthesis and characterization

Thermal exfoliation followed by controlled KOH chemical activation of GO (Fig. 1) results in the formation of a-GDCs with enhanced surface area and porosity characteristics. Pore opening and pore widening occur simultaneously during the activation process resulting in the formation of highly porous carbon with micro and mesoporous characteristics. Pore development occurs through a series of chemical reactions resulting in a number of reaction intermediates such as K_2O, H_2O, K_2CO_3, CO_2, CO, H_2 *etc* [30,31]. Effective etching of the carbon matrix occurs during this process, resulting in enhanced pore development in the nanometer range.

Various functional groups present in GO, TEGO and a-GDC samples were analysed by using FT-IR spectra (Fig. 2). In the FT-IR spectrum of GO, a broad band centred around 3390 cm^{-1} is seen, which is due to the O–H stretching vibrations in the carboxyl functional groups and intercalated water content. Two sharp bands observed at wavelength of 1734 cm^{-1} and 1617 cm^{-1} are attributed to the C=O stretching vibrations of the carboxyl group and the aromatic C=C stretching respectively. Several weak bands are observed in the wavelength range between 1500 cm^{-1} to 500 cm^{-1}. The band at 1421 cm^{-1} corresponds to O–H bending from hydroxyl/phenol groups, while the bands at 1222 cm^{-1} and 1048 cm^{-1} are due to C–O stretching vibrations from both phenol and carboxyl functional groups. In contrast, the FTIR spectra of the TEGO reveal a considerable reduction in the oxygen containing functional groups indicating the de-oxygenation. C=O and C–O stretching vibrational bands observed at 1726 cm^{-1} and 1228 cm^{-1} respectively, in the FTIR spectra of TEGO is an indication of the existence of carboxyl functional groups. The vibrational band at 1581 cm^{-1} due to C=C stretching mode is also seen in the FT-IR spectra of TEGO. However, most of these functional groups are found to be absent in the FT-IR spectra of a-GDC samples, and this could have resulted from the high temperature heat treatment during the chemical activation process.

Further structural information was obtained from the powder XRD analysis (Fig. S1, *Supplementary data*). XRD pattern of GO (Fig. S1a, *Supplementary data*) shows a sharp diffraction peak centred on $2\theta = 11.3°$ due to the (002) reflection of the stacked GO sheets, which corresponds to an interlayer spacing of 0.79 nm. However, only a weak and broad (002) graphitic peak is observed for TEGO, (Fig. S1b, *Supplementary data*), corresponding to a largely decreased d_{002} spacing of ~0.36 nm, upon reduction. In the case of a-GDC samples, a very weak and broad peak is observed at 2θ ~44°, from graphitic (100) planes (Fig. S1c, d, *Supplementary data*).