



Effect of graphene oxide on the adsorption properties of ordered mesoporous carbons toward H₂, C₆H₆, CH₄ and CO₂



Barbara Szcześniak^a, Jerzy Choma^a, Mietek Jaroniec^{b,*}

^a Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland

^b Department of Chemistry and Biochemistry, Kent State University, Kent 44-242, OH, USA

ARTICLE INFO

Keywords:

Ordered mesoporous carbon
Graphene oxide
Gas adsorption
Benzene vapor
Hydrogen
Carbon dioxide
Methane

ABSTRACT

Graphene oxide/ordered mesoporous carbon (GO/OMC) nanostructures with narrow mesopore size distribution were obtained via soft-templating synthesis followed by KOH activation. Microporosity and mesoporosity of these composite nanostructures were additionally controlled by adjusting the amount of added GO and by post-synthesis KOH activation. Incorporation of GO into OMC structure resulted in improving adsorption uptakes of benzene and hydrogen, which reached 9.6 mmol/g (at 20 °C and pressure close to the saturation vapor pressure) and 11.7 mmol/g (2.3 wt% H₂ at −196 °C and 760 mm Hg), respectively. At the same conditions bare activated OMC adsorbed 8.1 mmol/g and 10.8 mmol/g of benzene and hydrogen, respectively. Also, these adsorbents showed high uptakes of CH₄ (2.1 mmol/g at 20 °C and 760 mm Hg) and CO₂ (6.0 mmol/g at 0 °C and 760 mm Hg). The GO/OMC composite nanostructures were characterized by nitrogen adsorption, scanning electron microscopy, Raman spectroscopy and thermogravimetry. To the best of our knowledge, this work represents the first comparative study of adsorption properties of the GO/OMC composite nanostructures toward various gases.

1. Introduction

Ordered mesoporous carbons (OMC) attract a lot of attention because of their tunable well-defined mesoporosity, thermal stability, chemical inertness and relatively low cost [1–4]. These features make them attractive materials for a variety of applications including adsorption, catalytic and electrochemical processes. Their micro-mesoporous structure can be achieved by hard- or soft-templating methods. The latter seems to be more feasible strategy because of greater capability for controlling mesoporous structure and fewer preparation steps – it does not require fabrication of the hard template and its dissolution after carbonization step. Porosity of OMCs can be further enhanced via activation using activating agents such as KOH, CO₂ or H₂O vapor [5–7]. The post-synthesis activation by CO₂ and H₂O vapor reported by Górka et al. [7] allowed obtaining OMCs with ultrahigh surface areas up to 2800 m²/g and pore volumes up to 6 cm³/g. These OMCs were synthesized using triblock copolymer as a soft-template, and TEOS-generated silica and colloidal silica as hard templates. The as-fabricated carbons possessed cylindrical (12 nm) and spherical (20 or 50 nm) mesopores. It was shown that both physical and chemical activations of these OMCs were effective ways for improving their microporosity [6,7].

Recently, there is also a great interest in exploring various

possibilities for the development of the OMC-based composites [8–16]. Apparently, ordered mesoporous carbons can be relatively easily combined with other materials including polymers [8,9], graphene [10–14], carbon nanotubes [15] or silica [16]. OMCs can be also decorated with nanoparticles such as Fe, Fe₂O₃, Pt, Pd, or Ag [17–19]. Exfoliation of graphite to single two-dimensional sheets – graphene – results in its unusual physicochemical properties. Moreover, graphene flakes feature high specific surface area, which make them ideal for incorporation into/coupling with various materials such as OMC. Qiu et al. [13] demonstrated the synthesis of graphene-containing OMCs by one-pot synthesis using triblock copolymer as a soft template. They reported that the pore structure of the composites can be controlled by adjusting the ratio of graphene oxide and soft template in the synthesis mixture. They also suggested the formation of hydrogen bonds between polymeric micelles and functional groups of graphene oxide, which resulted in a “sandwich-like” structure, in which OMC domains are covered by graphene sheets. Also, GO/OMC composite structures were synthesized by Song et al. [11]. Both materials studied, OMC and GO/OMC composite, exhibited quite similar BET surface areas (~460 m²/g), however KOH activation of GO/OMC afforded activated composite, GO/aOMC, with much higher specific surface area (~2100 m²/g) than that obtained for activated bare OMC (1475 m²/g). The authors inferred that both GO/OMC and OMC possessed highly ordered

* Corresponding author.

E-mail addresses: barbara.szczeniak@wat.edu.pl (B. Szcześniak), jerzy.choma@wat.edu.pl (J. Choma), jaroniec@kent.edu (M. Jaroniec).

mesoporous structures. Furthermore, in the case of GO/OMC composite, OMC was stacked above graphene layers in the form of “stripe-like” arrays, partially inhibiting aggregation of graphene sheets. Unfortunately, an increase of graphene content in the GO/OMC composite caused agglomeration of graphene sheets, which resulted in the decrease of the specific surface area [11,13]. The GO/OMC composites can be also obtained via mechanical mixing of the pre-synthesized OMC with graphene-like material [10].

Adsorption properties of OMCs towards various gases have been increasingly studied in the last few years [6,17,20–22]. Nowadays, searching for efficient adsorbents for CO₂, H₂, CH₄ or volatile organic compounds (VOCs) is of great importance [23,24]. VOCs are major air pollutants characterized by high vapor pressure and low boiling point. They enter the atmosphere easily causing photochemical reactions inducing photochemical smog and ozone destruction. Besides that, VOCs are highly toxic, mutagenic and carcinogenic. New, effective technologies for removal of VOCs are of great interest because their concentration in air is gradually increasing. In addition to catalytic oxidation, photocatalytic and absorption processes, adsorption technologies seem to be the well-suited systems due to their high efficiency and the possibility of recovery of valuable VOCs [21,25]. The capture of these relatively large-sized adsorbates requires adsorbents with specific features such as high specific surface area, large pore volume and micro-mesoporous structure.

Here we demonstrate a simple synthesis of reduced graphene oxide/ordered mesoporous carbon composites via soft-templating method using resorcinol, formaldehyde and graphene oxide as carbon precursors and triblock copolymer Pluronic F127 as a soft-template. The main objective of the study was to investigate the effect of GO addition during synthesis of OMC on the surface and structural properties of the GO/OMC composites and their potential applications for benzene, hydrogen, carbon dioxide and methane adsorption/storage. Benzene was selected as a typical VOC because it is highly hazardous, widely disseminated chemical compound in the industry. It is shown that the incorporation of GO into OMC enhances the adsorption properties of the resulting composites toward H₂ and C₆H₆, while no significant change is observed in the case of CO₂ and CH₄.

2. Experimental

2.1. Chemicals

All chemicals, namely graphite powder (99.99%), potassium permanganate (99.5%), hydrogen peroxide (30%), sulfuric acid (95%), orthophosphoric acid (85%), resorcinol (99%) formaldehyde (40%), poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) triblock copolymer (Pluronic F127), and hydrochloric acid (35%) were purchased and used without further purification.

2.2. Preparation of graphene oxide (GO)

First graphite oxide was synthesized from graphite powder using the modified Hummer's method reported elsewhere [24,26]. Next, a certain amount of as-made graphite oxide was dispersed in an ultrasonic bath for 1 h to obtain graphene oxide (GO).

2.3. Preparation of graphene oxide/ordered mesoporous carbon composite

Ordered mesoporous carbon (OMC) was prepared according to the procedure reported by Choma et al. [4]. The GO/OMC composites were synthesized by incorporating GO into mixture containing the OMC precursors and template (Fig. 1). Briefly, 2.5 g of resorcinol and 2.5 g of Pluronic F127 were dissolved in the solution consisting of 6.6 mL of deionized water and 11.9 mL of ethanol. Next 2.2 mL of concentrated HCl were added and the mixture was stirred at room temperature for 30 min. After that, 2.5 mL of formaldehyde were gradually added to the

above mixture. After stirring for 1 h, 10 mL of aqueous GO dispersion were added and further stirred for 5 min. Next, two clearly visible phases were separated, and the polymer-containing bottom layer was spread in a quartz boat and aged at 100 °C for 24 h. Subsequently, the boat was placed in a tubular furnace and heated to 400 °C with the heating rate of 1 °C/min, next with 5 °C/min up to 850 °C and kept in this temperature for 0.5 h under nitrogen protection. After cooling down, the carbonizate was washed with acetone and deionized water and dried at 100 °C. Two different amounts of graphite oxides (5 and 7 wt% of initial carbon precursors: resorcinol and formaldehyde, denoted as x), were used to prepare GOx/OMC. We found that it is not possible to prepare GO/OMC composite with higher concentration of GO than 7 wt%.

2.4. Activation of graphene oxide/ordered mesoporous carbon composite

The as-made samples were subsequently mixed with solid KOH (1:4 carbonizate:KOH weight ratio) and activated in a tubular furnace at 700 °C during 2 h in flowing nitrogen. After cooling to room temperature, the obtained composites were washed with 8% HCl and deionized water and next, dried under vacuum at 70 °C.

3. Measurements and calculations

Scanning electron microscopy (SEM) and Raman spectroscopy (SR) were used to characterize morphology and structure of the selected samples. The SEM images were obtained using scanning electron microscope LEO 1530 manufactured by Zeiss (Germany) operated at 2 kV acceleration voltage. Raman spectroscopy was conducted on a Renishaw inVia Reflex instrument using 514 nm laser. Thermogravimetric analysis (TGA) was performed on Setaram Labsys TG from room temperature to 1000 °C in Ar atmosphere with a heating rate of 10 °C/min. Nitrogen adsorption isotherms were measured at –196 °C on ASAP 2020 volumetric analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA, USA). Benzene adsorption at 20 °C was measured using McBain – Bakr gravimetric method on a home-made apparatus equipped with a quartz-spring balance. The study of CO₂, CH₄, H₂ adsorption on the selected samples was performed by using adsorption isotherms measured at 0 °C, 20 °C and –196 °C, respectively. All samples were outgassed at 150 °C for 12 h prior to adsorption measurements. The pore size distribution functions (PSDs) were calculated on the basis of low-temperature nitrogen adsorption by using the non-local density functional theory method (2D-NLDFT) for carbon slit-shaped pores under assumption of energetic heterogeneity and geometrical corrugation of the pore walls [27,28]. The total pore volume was estimated from the amount adsorbed at $p/p_0 \approx 0.99$. The BET specific surface area (S_{BET}) was calculated on the basis of nitrogen adsorption isotherms in the relative pressure range of 0.05–0.2 [29].

4. Results and discussion

4.1. Structural characterization

Fig. 2 shows the SEM images of OMC, its composite with 5% GO (GO5/OMC) and these materials after KOH activation (aOMC and GO5/aOMC). In the image of GO5/OMC the incorporated graphene oxide can be seen in the form of layered or irregular domains on/between the OMC domains. These layers are not visible in the image of GO5/aOMC, instead a network-like structure can be observed that differs from that of aOMC. The KOH activation process caused noticeable changes in the morphology of both OMC and its composite with GO. The ordered structure of these materials is not visible on these SEM images.

Amorphous carbons can be considered as highly disordered structures composed of very small graphitic domains. Most often, OMCs are also amorphous carbons with ordered mesopores. High degree of

Download English Version:

<https://daneshyari.com/en/article/6532288>

Download Persian Version:

<https://daneshyari.com/article/6532288>

[Daneshyari.com](https://daneshyari.com)