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Electrospun graphene oxide/carbon composite nanofibers with well-developed mesoporous structure and their adsorption performance for benzene and butanone

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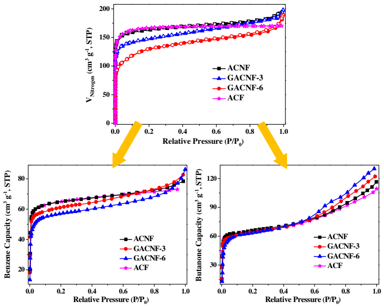
HIGHLIGHTS

- Graphene oxide/carbon composite nanofibers with abundant mesopores were prepared.
- Mesoporosity and surface oxygen content increased with GO addition increasing.
- The composite nanofibers exhibited high benzene and butanone adsorption capacities.
- GO embedment improved the adsorption tendency for butanone over benzene.

GRAPHICAL ABSTRACT



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ABSTRACT

Freestanding porous carbon nanofibers have been interesting candidate for the adsorption and removal of volatile organic compounds (VOCs). In this study, novel graphene oxide (GO)/carbon composite nanofibers with well-developed mesoporous structure are prepared easily from polyacrylonitrile and different content of GO by electrospinning and subsequent steam activation, and their adsorption performance for VOC vapors is evaluated for the first time. The resultant nanofibers were characterized by scanning electron microscopy, Raman spectroscopy, nitrogen adsorption and X-ray photoelectron spectroscopy. Dramatically, embedment of GO achieves the increased mesopores and high surface oxygen content of series of continuous composite nanofibers, and further mesopore volume, ratio and oxygen content show positive dependence on the amount of GO addition. Owing to such outstanding features, the novel composite nanofibers exhibit improved benzene and butanone adsorption capacities at high relative pressures and enhanced adsorption tendency for butanone over benzene, compared to pristine activated carbon nanofiber and conventional activated carbon fiber. The highest benzene and butanone adsorption capacities of the prepared composite nanofibers at 20 °C and relative pressure of 0.98 reach 83.2 and 130.5 cm^3 g^{-1}, respectively. The introduction of GO simultaneously improves the adsorption capacities and adsorptive tendency of the nanofibers for polar VOCs. These results prove the great potential of composite nanofibers in practical adsorption for VOCs, especially polar ones.

1. Introduction

Emission of volatile organic compounds (VOCs) leads to environmental pollution, which is harmful for human health [1,2]. Development of reasonable method to abate the pollution of

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VOCs has attracted much attention. Adsorption technique is considered as an easy and effective operation to remove organic gases [3,4]. Porous carbons such as activated carbons and activated carbon fibers have been widely studied as adsorbents for VOCs [5,6]. Currently, electrospinning is an effective method to achieve mass production of continuous nanofibers [7–9]. Porous carbon nanofibers prepared by electrospinning and following thermal treatment show great potential for VOC adsorption due to freestanding monolithic characteristic and porous structure [10,11]. The electrospun nanofibers could be used directly as practical adsorbents for pollutant gases without shaping process, which is convenient for replacing and recycling the materials.

Porous structure is a crucial factor to determine VOC adsorption performance of porous carbons at ambient temperature and pressure. Up to now, reported works have focused on the effects of activation (H_2O, CO_2, KOH and salt, *etc.*) conditions on the microporous structure and VOC adsorption performance of electrospun carbon nanofibers [12,13]. Excessive activation would induce the broadening of micropores and reduce the utilization degree of porous structure [14], which is detrimental to the improvement of adsorption performance for VOCs. Reported VOC adsorption capacities of common activated electrospun carbon nanofibers could not meet the practical needs. Hence, designing novel fabrication strategy is urgently needed to achieve excellent VOC adsorption performance of electrospun carbon nanofibers.

Construction of hierarchical nanocomposites is a hot topic in the field of new materials. Outstanding properties for various applications can be formed through the combination of different component materials [15]. Literature reveals that electrospinning is a good method to synthesize carbon-based composite nanofibers [16–18]. Graphene oxide (GO), the functionalized graphene with oxygen-containing chemical groups, possesses high theoretical specific surface area, tunable chemical properties and good mechanical features [19]. Especially, its abundant oxygen functional groups promote the strong interaction between GO and polymer (electrospinning precursor), which is favorable for the formation of uniform and stable electrospun composite nanofibers. Therefore, adding GO into polymer substrate combined with electrospinning is expected to obtain novel composite nanofibers with modified porous structure and surface chemical properties, which is of great significance for practical VOC adsorption. However, graphene and graphene oxide/carbon composite nanofibers in reported works were mainly used for electrochemical electrodes and chemocatalysis [20–22], and little attention is paid to the design and modification of hierarchical porous structure of the composite nanofibers. To our best knowledge, VOC adsorption performance of novel GO/carbon composite nanofibers has never been reported previously.

In this work, we prepared novel series of freestanding GO/carbon composite nanofibers from polyacrylonitrile (PAN) mixed with different content of GO by electrospinning and following steam activation and evaluated their adsorption performance for VOC gases at room temperature. Effects of GO incorporation on the physicochemical properties of the resultant nanofibers are studied systematically. Benzene and butanone are chosen as target VOCs, considering that benzene is a non-polar organic compound and butanone is polar. Adsorption performance for benzene and butanone was investigated through static adsorption isotherms. Dramatically, superiority of the composite nanofibers over the pristine activated carbon nanofiber and conventional carbon fiber in VOC adsorption was demonstrated.

2. Experimental

2.1. Synthesis of GO/activated carbon composite nanofibers

GO sheets were prepared from microcrystal graphite powder according to an improved Hummer's method [23]. PAN ($M_w = 150{,}000$, Aldrich Chemical Company, USA) was used as electrospinning precursor, and N,N-dimethylformamide (DMF, A.R., Beijing Modern Eastern Finechemical Co., Ltd., China) was chosen as solvent. All chemicals were used as received without further purification. GO sheets (3 and 6 wt.% relative to PAN, respectively) were added into DMF and ultrasonically treated for 2 h. Then, PAN (10 wt.%) was immersed in the GO–DMF solution and stirred continuously at 65 °C to form a homogeneous solution. The obtained solution was subsequently electrospun into GO/PAN composite nanofibers through our previous equipment and process [24]. The supplied voltage was 25 kV, the spinning distance between the tip and the aluminium foil collector was 19 cm, and the feeding rate of solution was 1 ml h^{-1}. The as-spun nanofibers were heated at 1 °C min^{-1} and stabilized at 280 °C for 2 h. Finally, the stabilized nanofibers were heated to 850 °C (5 °C min^{-1}) under nitrogen atmosphere and activated in flowing 30 vol.% steam for 30 min. The resultant GO/activated carbon composite nanofibers associated with 3 and 6 wt.% GO addition were labeled as GACNF-3 and GACNF-6, respectively. Pristine activated carbon nanofibers without GO introduction were also prepared and denoted as ACNF. Additionally, conventional PAN-based activated carbon fiber (ACF, Jilin Carbon Plant, China) was measured as adsorbent for comparison.

2.2. Characterization

Surface morphology of the obtained samples was examined using scanning electron microscopy (SEM, LEO-1530, Germany). Raman spectroscopy (Renishaw Invia RM200, England) was employed to characterize the graphitic structure of nanofibers. Specific surface area and pore structural properties were investigated from N_2 adsorption/desorption isotherms at 77 K (Quantachrome Autosorb-1, USA). Before the adsorption/desorption test, samples were degassed at 195 °C for 18 h under vacuum. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo-Fisher) was used to measure the surface chemical concentration of nanofibers.

2.3. VOC adsorption measurement

Benzene and butanone adsorption equilibrium isotherms of various samples at 20 °C were measured by a static adsorption system (Belsorp-max, BEL, Japan). Benzene and butanone liquids (A.R., Beijing Modern Eastern Finechemical Co., Ltd., China) used to generate the vapors were fully degassed by repeated evacuation. Samples were degassed at 180 °C under nitrogen flow for 16 h and then cooled down to room temperature before the adsorption measurement. After pretreatment, the accurate weight of sample was obtained to obtain isotherms. System temperature was maintained by constant temperature water-bathing. Saturation pressures of benzene and butanone at 20 °C calculated by the Antoine equation [25] are 10.03 and 9.46 kPa, respectively. The apparatus would measure adsorption capacities at different pressures to obtain the isotherms after the above parameters were inputted into testing system software. Benzene and butanone adsorbed volume under standard temperature and pressure (STP) were obtained after the experiment.