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Short communication

Fluorine-rich carbon nanoscrolls for CO_2/CO (C_2H_2) adsorptive separation

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ABSTRACT

Carbon nanoscrolls have shown great potential in gas adsorption and storage. In this paper, a feasible method for synthesizing one-sided fluorine doped carbon nanoscroll (F-CNS) is proposed, and the adsorption behavior of CO_2, CO and C_2H_2 on one-sided F-CNS has been firstly investigated via Grand Canonical Monte Carlo calculations. It is demonstrated that the one-sided F-CNS possesses outstanding CO_2 uptake with good CO_2/CO and CO_2/C_2H_2 selectivity compared with pristine CNS. Specially, at 300 K and 1 bar, one-sided F-CNS shows a CO_2 uptake of 68.87 mmol/mol and CO uptake of 12.09 mmol/mol, which is much higher than those of CO_2 (16.6 mmol/mol) and CO (6.02 mmol/mol) for pristine CNS. Furthermore, our results demonstrate that the excellent selective CO_2 adsorption capacity of one-sided F-CNS is owing to its stronger interactions with CO_2 molecules than CO and C_2H_2 molecules. Our research suggests that one-sided F-CNS is a promising candidate for high selective CO_2 capture.

1. Introduction

Acetylene (C_2H_2) is a significant chemical feedstock, which has been widely used in the synthesis of chemical products and electric materials, such as polyurethane and polyester plastics. Therefore, the high-quality C_2H_2 is extremely in demand for the preparation of these industrial materials [1,2]. In addition, recycling carbon monoxide (CO) is also important to reduce the consumption of coke and environmental stress [3]. Given the fact that carbon dioxide (CO_2) usually exists in many industrial process, so there has been notable interest in the effective separation of CO_2/CO and CO_2/C_2H_2 to obtain high-quality C_2H_2 and CO. However, it is noted that the separation of C_2H_2 (kinetic diameter: 0.33 nm) and CO_2 (kinetic diameter: 0.33 nm) is quite challenging due to their similarities in molecular size and shape [1,4].

Up to now, abundant research has been carried out to investigate CO_2/CO and CO_2/C_2H_2 separation [2–9]. Zhang et al. [6] found MAF-2 with unique static and dynamic pore characteristics showed extraordinary C_2H_2/CO_2 sorption behaviors. In addition, it was found that MAF-2 permitted a usable C_2H_2 storage capacity which was 20 times higher than its volume or 40 times higher than that of a gas cylinder working between practical limits of 1.0–1.5 atm due to its large C_2H_2 uptake (70 cm^3/g) at the 298 K and 1 atm. Yang et al. [8] prepared a unique bifunctional porous metal-organic framework modified with free-standing carboxyl and pyridyl groups, which revealed unusual selective CO_2 adsorption over C_2H_2. Besides, Sapchenko et al. [3] investigated the adsorptions of CO, CO_2 and C_2H_2 on the porous MOF material with free N-donors and found this material showed pronounced affinity for CO_2 and C_2H_2. Exactly, at 298 K and 1 bar, the uptakes of this sorbent were found to be 32.5, 12.0 and 3.0 ml/g for C_2H_2, CO_2 and CO, respectively. Very recently, a new flexible porous coordination polymer (PCP) with zero-dimensional pores was found to possess an adsorbate discriminatory gate effect that this material showed gate opening type adsorption for C_2H_2 but not for CO_2 [2].

In addition to MOF, various porous carbons such as carbon nanotube (CNT) [10,11], carbon nanofiber [12,13], activated carbons [14,15] and carbon nanoscroll (CNS) [16,17] have been widely used for CO_2 storage and capture because of their well-defined pore geometry and volume, high surface area, good chemical/thermal stability, controllable pore structure. However, it should be noted that pristine carbons show limited CO_2 uptake [18,19]. Abundant studies have shown that nitrogen (N-) containing and sulfur (S-) containing functional groups are considered to boost CO_2 adsorption capacity of carbons [20–25]. Chen et al. [20] found that N-doped porous carbons exhibited an excellent CO_2 uptake of 5 mmol/g at 298 K and 1 bar owing to its high microporosity and nitrogen content. Xia et al. [25] prepared a series of structurally ordered and S-doped microporous carbon materials, which were discovered to show a high CO_2 adsorption energy of 59 KJ/mol, indicating strong physical interactions with CO_2 molecules.

Recently, one-sided fluorine doped (F-) graphene has been achieved, which was also studied experimentally and theoretically [26–30]. Robinson et al. found that graphene films that grew on Cu foils could be fluorinated with xenon difluoride gas on one and even both sides.

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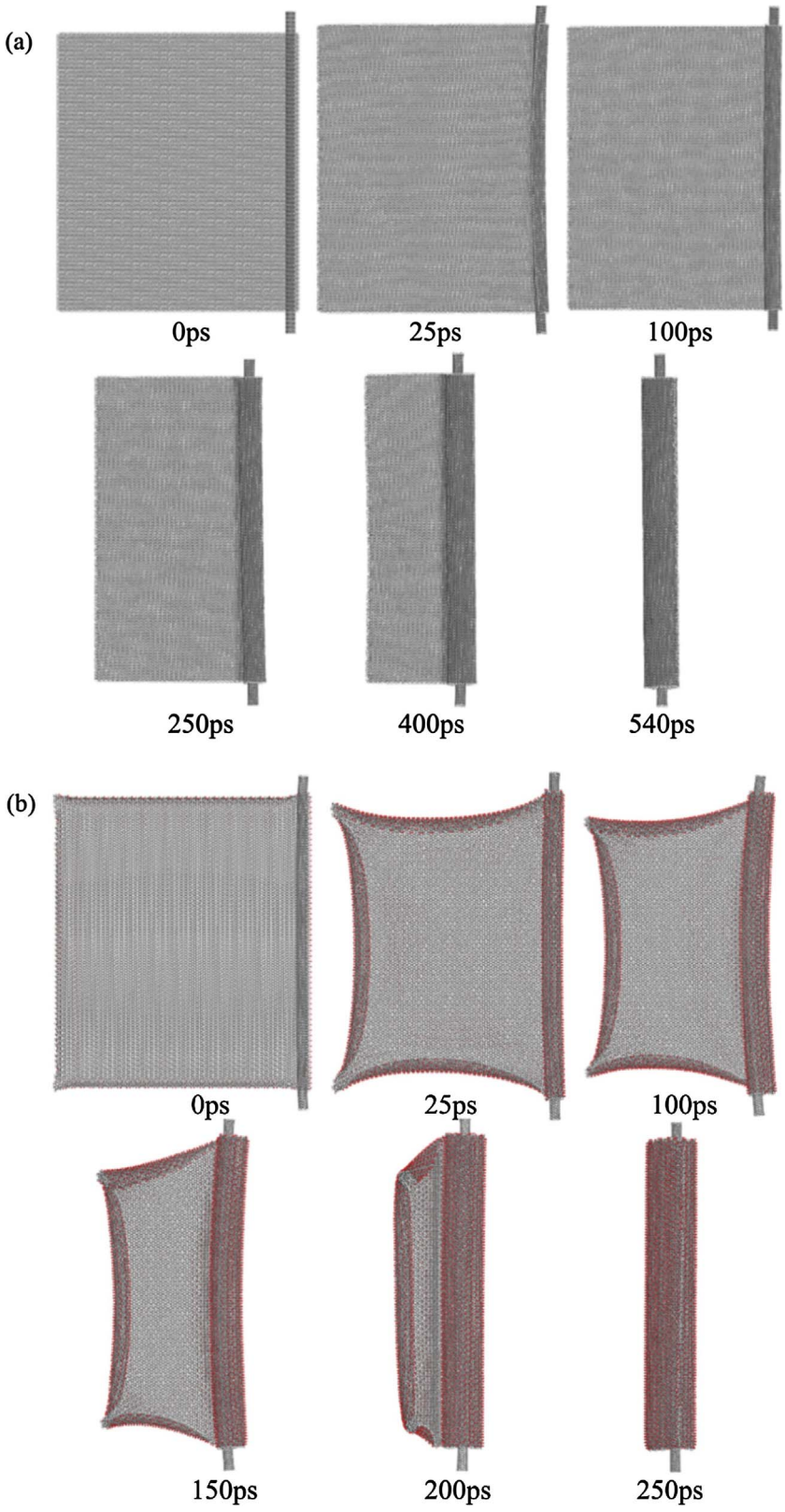

Fig. 1. Snapshots of pristine graphene (a) and one-sided F doped graphene sheets (b) rolling into carbon nanscrolls at room temperature. (Gray and red balls represent carbon and fluorine atoms, respectively.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Besides, the band gaps of fluorinated graphene (C_4F) on one side and fluorinated graphene (CF) on both sides were 2.93 eV and 3.07 eV, separately, demonstrating that fluorine doping could regulate the electrical properties of graphene [27]. Besides, it has been identified that fluorinated graphene with adjustable C/F ratio was realized through the reaction between dispersed graphene oxide and hydrofluoric acid, which had potential applications in optoelectronic and photonic devices due to its tunable band gap [29]. Moreover, carbon nanotube and metal nanowires were good candidates to activate and guide one-sided F-graphene to self-scroll into one-sided F doped CNS (F-CNS) [31,32].

Although CNS has been found to show promising applications in