

HYDROGEN AND METHANE ADSORPTIVITIES OF DENSELY PACKED SINGLE-WALL CARBON NANOTUBE BUCKYPAPER

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Abstract

Densely packed single-wall carbon nanotube (SWCNT) called buckypaper were fabricated by filtration process from acid-treated SWCNTs. The morphology and chemical structure of the SWCNT-buckypaper were characterized by field emission scanning electron microscopy and X-ray photoelectron spectroscopy. The SWCNT-buckypaper shows closely packed assembly structure. Pore structures of the SWCNT-buckypaper were also determined from adsorption isotherms of N₂ (77 K), CO₂ (273 K) and H₂O (303 K). The SWCNT-buckypaper gives dramatically developed microporosity and decreased mesoporosity, which is attributed to the formation of packed assembly structure and opening of SWCNT. Adsorption behaviors of the SWCNT-buckypaper were investigated by supercritical H₂ and CH₄ adsorption. The SWCNT-buckypaper donates enhanced storage capacities of supercritical gases, compared to pristine SWCNTs. This result revealed that developed microporosity of SWCNT-buckypaper is a key factor to improve the supercritical gas storage capacity.

Introduction

Storage of supercritical gas on nanostructured carbon have been gathered much interest owing to their infinite and potential application in clean energy fields. In particular, single-wall carbon nanotubes (SWCNTs) have abundant adsorption sites of hollowness inner space and interstitial space caused by bundle structure as well as high chemical and mechanical stability, which has been considered as probable candidate for reversible storage of supercritical gases such as hydrogen and methane. In spite of the theoretical great potential of SWCNTs for hydrogen and methane storages, the application of as-synthesized SWCNTs are often limited, because of their closed cap of SWCNT and low packing density due to large interbundle distance. In this study, we reported a simple and easily scalable method for the fabrication of densely packed SWCNT-buckypaper by HNO₃/H₂SO₄ treatment and subsequent sonication and filtration process. The pore structures were analyzed by N₂ (77 K), CO₂ (273 K), and H₂O (303 K) adsorption measurements. In addition, adsorption behaviors of the SWCNT-buckypaper were investigated by supercritical H₂ and CH₄ adsorption.

Experimental

SWCNTs synthesized by a high pressure CO disproportionation (HiPco) process were purchased from Carbon Nanotechnologies, Inc., USA (pristine SWCNTs). In order to fabricate SWCNT-buckypaper, the pristine SWCNTs were immersed and stirred at room temperature in a mixture of HNO₃ and H₂SO₄ for 24 h. The sample was filtrated through the membrane filter. The precipitate was washed with distilled water several times. The washed sample was again filtrated after sonication in distilled water for 30 min. The sample was dried and annealed in Ar ambient at 1173 K for 1h (SWCNT-buckypaper). Pore structures of the SWCNT samples were determined by adsorption of N₂ (77 K) using volumetric equipment after preevacuation for 2 h at 423 K, while maintaining the base pressure at 10⁻⁴ Pa. We also performed adsorption measurements of H₂ and CH₄ in order to confirm storage abilities of supercritical H₂ and CH₄ for the SWCNT-buckypaper. The H₂ adsorption at 77 K up to 0.1 MPa and the CH₄ adsorption at 303 K up to 5 MPa were measured by a volumetric equipment and a gravimetric equipment with an electric microbalance (Cahn 1100 with a resolution of 0.1 μg), respectively. Before measurement, all samples were preevacuated at 423 K under 10⁻⁴ Pa for 2 h.

Results and Discussion

Figure 1a shows N₂ adsorption isotherms of the pristine SWCNTs and SWCNT-buckypaper at 77 K. The pristine SWCNTs show typical IUPAC type II adsorption isotherm with a gradual uptake of N₂ at the medium relative pressure (P/P₀). The predominant adsorption of N₂ at higher P/P₀ originates from the multilayer adsorption on the external surface and in larger mesopores or macropores formed at spaces between SWCNT bundles. On the other hand, the N₂ adsorption isotherm of SWCNT-buckypaper is close to type I (microporous structure) with a precipitous uptake at below P/P₀ = 0.1 and a long plateau at high P/P₀ due to completion of micropore filling. The N₂ adsorption amount at low P/P₀ dramatically increases after HNO₃/H₂SO₄ treatment for 24 h, as shown in inset of Figure 1a. This is related to the development of uniform microporosity and reduction of mesoporosity through formation of closely packed assembly structure. According to adsorption isotherms of

CO₂ (273 K) and H₂O (303 K), the SWCNT-buckypaper has a closely packed assembly structure, showing the dramatically developed microporosity. The SWCNT-buckypaper gives much more H₂ adsorption amount than the pristine SWCNTs (not shown here). In order to measure CH₄ storage ability of the SWCNT-buckypaper, we performed high-pressure CH₄ adsorption at 303 K by using gravimetric adsorption method. Figure 1b shows the high-pressure CH₄ adsorption isotherms of pristine SWCNTs and SWCNT-buckypaper. The CH₄ storage capacity of SWCNT-buckypaper considerably increases. In particular, at low pressure below 3 MPa, the SWCNT-buckypaper exhibits a remarkable CH₄ storage capacity, compared with the pristine SWCNTs. On the other hand, at high pressure above about 4 MPa, CH₄ storage capacity of SWCNT-buckypaper is nearly saturated. According to the study results by Menon et al., an adsorbent for supercritical CH₄ storage should have predominant microporosity, high surface area, and low mesoporosity. Consequently, the increment of CH₄ storage capacity should be associated with development of narrow micropores less than 0.7 nm.

Our approach has shown a simple and easily scalable method for the fabrication of highly microporous SWCNT-buckypaper. The SWCNT-buckypaper gives remarkably improved microporosity and reduced mesoporosity, which is attributed to the formation of packed assembly structure and cap opening of SWCNT. This results suggest that the developed microporosity of the packed assembly structure of the SWCNT-buckypaper is a key factor to improve the storage ability of the supercritical gases such as H₂ and CH₄.

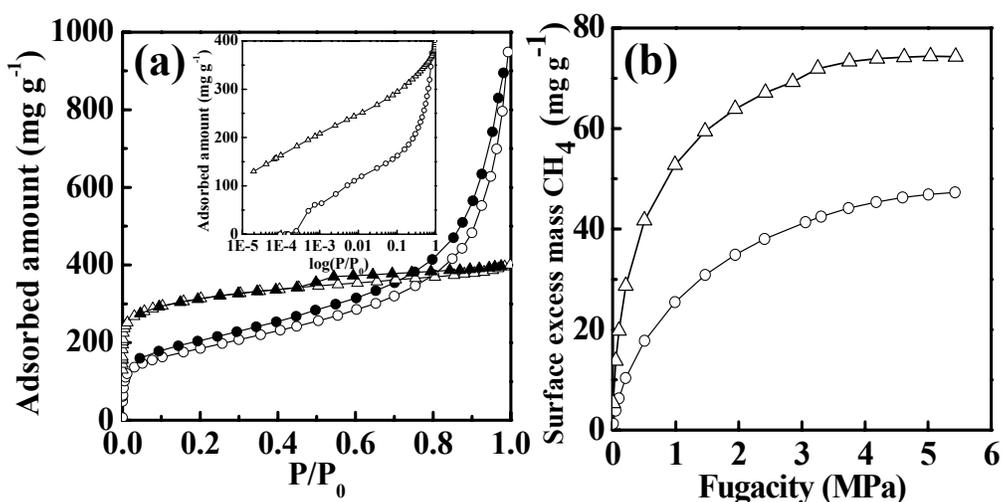


Figure 1. (a) N₂ adsorption isotherms of SWCNT samples at 77 K. The open and filled symbols indicate adsorption and desorption branches, respectively. The inset shows N₂ adsorption isotherms in logarithmic scale. (b) CH₄ adsorption isotherms at 303 K: pristine SWCNTs (○) and SWCNT-buckypaper (△)

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