Oral/Invited

Fri. Aug 1, 2025 2:45 PM - 3:45 PM JST | Fri. Aug 1, 2025 5:45 AM - 6:45 AM UTC Room B(2F The SalonThe Grand Ballroom East)

[4B11-13] Session 11

Chair:Takayoshi Hara(Chiba University)

2:45 PM - 3:05 PM JST | 5:45 AM - 6:05 AM UTC

[4B11]

Maximizing the internal tube space of single-walled carbon nanotubes by selective removal of end caps

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3:05 PM - 3:25 PM JST | 6:05 AM - 6:25 AM UTC

[4B12]

Ultramicropore analysis of carbon-based nanoporous materials with PALS method

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3:25 PM - 3:45 PM JST | 6:25 AM - 6:45 AM UTC

[4B13]

Safe and Controllable Methane Storage at Ambient Pressure Enabled by Graphene-Coated Porous Carbon

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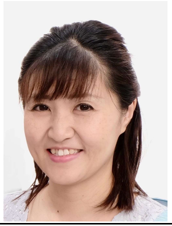

Maximizing the internal tube space of single-walled carbon nanotubes by selective removal of end caps

The internal tube space of single-wall carbon nanotube (SWCNT) provides a very strong attractive interaction potential for gaseous molecules even for supercritical gases, which induces the highly dense adsorbed layer formation inside the SWCNTs spaces[1]. However, the caps on both ends of prepared SWCNT are closed and it need to be removed without damaging the tube wall for utilizing the internal tube space. In this study, we studied the optimal conditions for cap-removal to maximize the internal tube space of SWCNT by air oxidation and a new method to determine the opening ratio using reliable specific surface area (SSA)[2] evaluated by the subtracting pore effect (SPE) method[3].

SWCNTs were thermally oxidized in air at different temperatures ranging from 623 to 823 K. The porosity of the oxidized SWCNTs was determined with nitrogen adsorption at 77 K. The SSA and microporosity were evaluated by the SPE method using a high-resolution α_s-plot[3]. The crystallinity change of SWCNTs due to oxidation was evaluated from Raman spectroscopy.

The air oxidation at 773 K of SWCNT bundles obtained a maximum surface area of 1840 m^2 g^{-1} without damaging the graphene walls of SWCNTs. The cap opening percentage of SWCNT is 98 % by comparing geometrical and observed SSA values. The selective removal of SWCNT end-caps can provide a new pathway for the highly selective modification of SWCNT bundles[4] utilizing the internal tube space.

1) (a) K. Kaneko *et al.*, *J. Chem. Phys.*, **87**, 776-777 (1987). (b) K. Urita e*t al., J. Am. Chem. Soc.*, **133**, 10344-10347 (2011). (c) T. Fujimori *et al.*, *Nat. Commun.* **4**, 2162-2169 (2013). 2) A. Furuse *et al.*, *Adsorption*, **29**, 1-7 (2023). 3) S. Wang *et al.*, *Carbon* **175**, 77–86 (2021). 4) Y. Kawamata *et al.*, *J. Phys. Chem. C*, **128**, 12632-12641, (2024).

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Ultramicropore analysis of carbon-based nanoporous material with PALS method

Positron annihilation lifetime spectroscopy (PALS) is used to analyze ultramicropore structures of various Si-based materials[1)]. The probe size of the positronium of the PALS is only 0.1 nm and thereby the PALS analysis of ultramicropores of porous carbons is strongly requested for promotion of energy storage technologies. However, the applicability of PALS to carbon materials is not necessarily well established. We must obtain the key parameter of δ associating with the effective electron cloud thickness of carbon materials for the positronium using well-characterized carbon samples such as single wall carbon nanotube (SWCNT).

The SWCNT bundle has two kinds of pores of the internal tube space and interstitial space. The sizes of the inside tube space and the interstitial subnanoscale space (ISS) can be determined by Ar adsorption at 87 K and X-ray diffraction (XRD). Consequently, PALS measurements of two kinds of SWCNT bundles having different tube diameters enable to determine the key parameter of δ for PALS analysis of carbon materials. The average widths of internal tube spaces and ISS of two kinds of SWCNT bundles were determined by XRD and Ar adsorption. Thus, we determined $\delta = 0.23$ nm for carbon materials.

We applied the PALS method to reduced graphene oxide (rGO) using $\delta = 0.23$ nm. The PALS analysis gave new pore information on rGO. We will discuss the physical meaning of the obtained pore sizes from PALS at the conference.

References

1) T. L. Dull and D. W. Gidley *et al.*, *J.Phys.Chem.B*, **105**, 4657, (2001).

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Safe and Controllable Methane Storage at Ambient Pressure Enabled by Graphene-Coated Porous Carbon

Methane (CH_4) is a high-energy, abundant fuel with strong potential for cleaner energy applications. However, its storage and transport pose significant challenges. Compressed natural gas (CNG) at around 25 MPa is energy-intensive and carries safety risks. Adsorbed natural gas (ANG) systems, which use nanoporous materials to store CH_4 at moderate pressures (~3.5 MPa), offer a safer and more energy-efficient alternative. However, this method suffers from thermal sensitivity, releasing stored gas rapidly with slight temperature increases.

In this study, we report a novel methane storage strategy that operates at ambient pressure using graphene-coated porous carbon. Graphene is deposited via chemical vapor deposition (CVD), forming a thermally responsive “valve” that controls pore accessibility. The graphene-coated porous carbon material is capable of being charged with CH_4 at high pressure and retaining it at ambient pressure, with no significant release below 318 K, which greatly enhances storage safety. This design enables a reversible volumetric CH_4 capacity of 142 v/v, higher than that of various existing ANG technologies.

This ambient-pressure, thermally controlled system offers a scalable, cost-effective, and inherently safe approach for methane storage. By enabling on-demand gas release via low-grade heat, it presents a transformative pathway for energy storage and gas-handling technologies.