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研究課題名(和文) Production of mesoporous fullerene (C60) with highly crystalline framework to deal with environment and energy problems

研究課題名(英文) Production of mesoporous fullerene (C60) with highly crystalline framework to deal with environment and energy problems

研究代表者

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研究成果の概要(和文)：このプロジェクトにおいて、フラーレンC60結晶をゼロ次元から高い次元に構築し、結晶格子をもつメソポーラスフラーレンからなる新しいナノカーボン材料の一群を開発することに成功した。溶媒和したフラーレン結晶からの穏やかな熱条件による溶媒の脱離が孔の形成に重要であったと考えられる。極端な高温処理では、フラーレン結晶は共役を持つsp²-炭素の堅牢な骨格をもつ新しい類のナノポーラス炭素に変換された。これらの新しいナノポーラス炭素は、市販の活性炭と比して優れた電気化学容量と芳香族化合物のセンシング特性を有する。

研究成果の概要(英文)：Under this project, I was successful to produce fullerene C60 microcrystals from zero to higher dimensions including newer class of nanocarbon material called mesoporous fullerene crystals with crystalline frameworks. Solvent drying out (upon mild heat-treatment) from the solvated fullerene crystals is expected to play a key role in pore formation. Upon extremely high temperature heat-treatment, the fullerene crystals were converted into a new family of nanoporous carbons having π -electron conjugation within the sp²-carbon robust frameworks. These new nanoporous carbons show excellent electrochemical capacitance and superior sensing properties for aromatic compounds compared to commercial activated carbons.

研究分野：Nanomaterial chemistry

キーワード：Mesoporous fullerene

1. 研究開始当初の背景

Nanomaterials comprising nanopores or mesopores have become one of the effective materials to address the social needs particularly in the field of environment and energy. Such materials display multifunctional properties owing to the high surface areas and large pore volumes offered by the nano-spaces and their three-dimensional arrangements. It is the size of nano-space that enables to differentiate and adsorb and interacts with molecules or clusters and controlling its architecture in three dimension in advanced nanomaterials, one can achieve unique surface, structural, and bulk properties useful in high energy storage, better sensing, ion exchange, separation, catalysis, biological molecular isolation, and purifications. These wider applications offer exciting opportunities for researchers or engineers to develop new strategies and techniques for the design of functional materials having meso- or nanopores. Based on pore size, International Union of Pure and Applied Chemistry (IUPAC) classified porous materials into three categories: microporous (diameter < 2 nm), mesoporous (2 nm ≤ diameter ≤ 50 nm), and macroporous (diameter > 50 nm). Nanoporous materials, on the other hand, are classified as new materials with nano-space size less than 100 nm. Needless to say there has been increasing interests and research efforts in the production, characterization, and functionalization of nanoporous materials. Nevertheless, despite the tremendous efforts given to molecular modeling and design of nanoporous materials, the fundamental understanding of structure-property relations and tailor-design of novel nanomaterials for specific properties and applications are still the remaining main challenges of this field. This demonstrates the necessity of new materials design essential to develop simulation and structural analysis technologies.

Fullerene (C₆₀) exhibits intriguing electron accepting property due to energetically unstable double bonds within the pentagon rings, and it has been extensively used in optical or electronic device fabrications. However, nanoporous fullerene crystals with crystallized framework have not been

explored despite its potential impact in fundamental and practical implications. Until now, efforts have been made to increase the crystallinity of the frameworks. In the case of mesoporous metal oxides, controlled-thermal and hydrothermal treatments have resulted in effective crystallization. However, large mesostructural variations such as mesopores expansion mostly occur through fusion of several mesopores during framework crystallization, which significantly reduces the surface area. Several groups reported several mesoporous organosilica with perfectly crystallized frameworks and demonstrated its great utility as a light-harvesting material. Similarly, crystallized mesoporous zeolites demonstrated high catalytic activity for various acid-catalyzed reactions involving bulky molecules. Thus, by considering highly crystalline frameworks, one can discover solid state properties and dramatic upgrade of inherent properties, which cannot be realized by amorphous or poorly-crystallized frameworks.

2. 研究の目的

The main purpose of this project was to create new class of fullerene crystals comprising of meso- or nanopores with particular emphasize given to the high level design with controllable pore size, gaps, and their spatial arrangements. Insertion of nano-sized pores within the morphology-controlled fullerene crystals can drastically increase the electrochemically accessible surface area and display enhanced electrochemical supercapacitance required in high-power devices. Nanoporous fullerene crystals with highly crystalline frameworks is anticipated to have potential implications in the development of high energy storage system and excellent sensor material for selective sensing of toxic aromatic molecules. Nanoporous fullerene crystals represent novel class of carbon-based functional materials and could open a new cutting edge research field in material science or engineering.

3. 研究の方法

Material preparation: Fullerene C₆₀ crystals were prepared following a liquid-liquid interfacial precipitation

(LLIP) method. In LLIP method, the crystal formation mechanism is driven by supersaturation related to the low solubility of fullerene in alcohols (antisolvent). Therefore, the solubility difference of C_{60} in antisolvent and solvent should be taken into account during solvent selection, i.e. morphology of the derived fullerene crystals depend on the solvent combination chosen during LLIP method.

Fullerene C_{60} nano-structures:

Saturated solutions of C_{60} were prepared in different organic solvents (mesitylene, carbon tetrachloride, toluene, etc.) by dissolving excess amount of C_{60} powder with ultrasonication for 30 min followed by filtration. In a typical crystallization, 1 mL of saturated C_{60} solution was taken in a cleaned and dry 10 mL Al-foil-covered glass bottle then 5 mL of aliphatic alcohol (antisolvent) was added slowly while the temperature was maintained at 5 °C using in a temperature-controlled water bath during the addition. The above mixture was kept for 15 to 20 min without disturbance and then a gentle sonication was applied for ~ 1 min to avoid inhomogeneous crystal growth. Finally, the mixture was stored in an incubator at 5 °C for 24 h to grow crystals of C_{60} . Fullerene C_{60} crystals were fabricated by altering the crystal synthesis temperature, mixing ratios of antisolvent and C_{60} solution to optimize the method and to get dimensionally-controlled C_{60} crystals.

Advanced characterizations:

The prepared fullerene crystals were subjected to various advanced characterizations including scanning electron microscopy (SEM: S-4800, Hitachi Co. Ltd. Japan operated at 10 kV), transmission electron microscopy (TEM: JEOL Model JEM-2100F operating at 200kV), powder X-ray diffraction (XRD); X-ray the diffraction patterns were obtained using a Rigaku Model RINT2000 diffractometer with $Cu-K_{\alpha}$ radiation (wavelength = 0.1541 nm) Japan operated at 40 kV and 40 mA), and Raman Scattering (Raman spectrometer Jobin-Yvon T64000, samples were excited using green laser; 514.5 nm and 0.025 mW power). Additionally, the crystals was characterized using X-ray photoelectron spectroscopy (XPS). The XPS was performed on a Sigma Probe spectrometer (Thermo

Scientific Co. Ltd., Yokohama Japan) using monochromated Al K_{α} radiation (photon energy 1487 eV). High resolution spectra; the core level C 1s, and O 1s, with sufficient to ensure a high signal to noise ratio, were recorded in 0.05 eV steps. An electron flood gun was used to prevent sample charging. After the linear baseline subtraction, curve fittings were performed assuming a Gaussian peak shape. The textural surface properties (surface area, average pore size, and total pore volume) of the thus prepared fullerene crystals was investigated by nitrogen adsorption/desorption measurements. Nitrogen adsorption isotherms were recorded on an automatic adsorption instrument (Quantachrome Autosorb-iQ2 USA) and specific surface area, pore volume and average pore diameter were calculated. For each measurement about 20 mg of sample was taken and degassed for 24 h at 120 °C prior to the measurement. The isotherms were recorded at liquid nitrogen temperature 77.35 K.

Optical properties:

UV/Vis absorption spectrum of the prepared fullerene crystal and pristine C_{60} were recorded on a UV/Vis spectrometer V-570 at 25 °C in the wavelength range of 200-900 nm. PL spectra were measured at room temperature in air using a spectrometer equipped with a liquid-nitrogen-cooled CCD detector. Samples were casted on a silicon substrate and excited using the 514.5 nm line of an Ar^{+} laser. All the PL spectra are corrected for the wavelength-dependent sensitivity of the photodetection system.

Photovoltaic properties:

Photovoltaic cells consisting of thin films of P3HT and synthesized fullerene nanorods were prepared as active layers which were sandwiched between transparent anode indium tin oxide (ITO) and metal cathode aluminum (Al). P3HT was used as the *p*-type donor polymer and C_{60} was used as the *n*-type acceptor in the active layer. Current density-voltage (J-V) characteristics of the devices were measured using a Keithley 2420 Source Measure Unit in the dark and under AM1.5G illumination at 100 mW/cm² supplied by a solar simulator.

Electrochemical performance:

Electrochemical performance of the prepared fullerene crystals and derived nanoporous carbons were studied

recording cyclic voltammograms (CV) with a three-electrode system in 1 M aqueous H₂SO₄ solution at 25 °C. A bare glassy carbon electrode (GCE) used as working electrode was mirror polished with Al₂O₃ slurry and cleaned with double-distilled water and sonicated in acetone for 5 min. 2 mg of sample was dispersed in 2 mL of ethanol (1 mg/mL) and the mixture was sonicated for 30 min in a sonication bath. 3 μL of this dispersion was added onto the GCE surface and dried at room temperature. After the solvent was evaporated, 5 μL Nafion solution (5%) was added as binder on the surface of the GCE and dried at 70 °C for 3 h. Platinum wire was used as a counter electrode and Ag/AgCl as the reference electrode. The cyclic voltammetry response and chronopotentiometry were performed on a CH instruments model: (CHI 850D Work station (USA)). For the calculation of specific capacitance (C_s) from CV curve, we have used the following equation. Sensing performance: Vapor sensing performance was studied by quartz-crystal microbalance (QCM) technique.

4 . 研究成果

I succeeded to demonstrate ultra-rapid interfacial formation of one-dimensional (1D) single crystalline fullerene C₆₀ nanorods at room temperature in 5 seconds. The fullerene nanorods of ~11 micron in lengths and ~215 nm in diameter are developed in hexagonal close-pack crystal structure. Vibrational and electronic spectroscopy provide strong evidences that the nanorods are the van der Waals solid as evidenced from the preservation of electronic structure of the C₆₀ molecules within the rods. Steady state optical spectroscopy reveals a dominance of charge transfer excitonic transitions in the nanorods. A significant enhancement of photo-generated charge carriers is observed in the nanorods in comparison to pristine C₆₀ revealing the effect of shape on the photovoltaic properties. The ultra-rapid large scale room temperature synthesis with single crystalline structure and excellent optoelectronic properties the nanorods is expected to be promising for photo-sensitive devices applications. Upon extremely high temperature heat-treatment, the fullerene nanorods or nanotubes were converted into a new

family of nanoporous carbons having π -electron conjugation within the sp²-carbon robust frameworks. These new nanoporous carbons show excellent electrochemical capacitance and superior sensing properties for aromatic compounds compared to commercial activated carbons.

The mesoporous crystalline fullerene C₆₀ exhibited higher surface area (100 to 300 sq. m/g depending on the system) compared to pristine C₆₀ and displayed enhanced electrochemical supercapacitance. Nevertheless, due to poor conductivity of these crystals, the specific capacitance was found to be less than expected judging from the higher surface area.

5 . 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文](計 4 件)

[1] Shrestha, L.K.*; Shrestha, R.G.; Yamauchi, Y.; Hill, J.P.; Nishimura, T.; Miyazawa, K.; Kawai, T.; Okada, S.; Wakabayashi, K.; Ariga, K.

Nanoporous Carbon Tubes from Fullerene Crystals as the π -Electron Carbon Source.

Angew. Chem. Int. Ed. **2015**, *54*, 951-955. DOI: 10.1002/anie.201408856 (査読 有)

[2] Shrestha, R.G.; Shrestha, L.K.*; Khan, A.H.; Kumar, G.S.; Acharya, S.*; Ariga, K.

Demonstration of Ultra-Rapid Interfacial Formation of 1D Fullerene Nanorods with Photovoltaic Properties. *ACS Appl. Mater. Interface* **2014**, *6*, 15597-15603.

dx.doi.org/10.1021/am5046235 (査読 有)

[3] Shrestha, R.G.; Shrestha, L.K.*; Abe, M.; Ariga, K.

Production of self-assembled fullerene (C₆₀) Nanocrystals at liquid-liquid interface

J. Nanosci. Nanotechnol. **2014**, *15*, 2394-2399.

DOI: 10.1166/jnn.2015.9702 (査読 有)

[4] Shrestha, L.K.

Self-Assembled Fullerene Nanostructures at Liquid Interface

Austin J Nanomed Nanotechnol. **2014**, *2*, 1031-1032. (査読 有)

[学会発表](計 5 件)

Invited lectures:

[1] Shrestha, L.K.* Hill, J.P.; Yamauchi, Y.; Miyazawa, K.; Ariga, K. " Self-Assembled Fullerene Nanostructures: From Zero to Higher Dimensions, 1st Asian Congress on Oleo Science (ACOS-2014), September 8-10, 2014, Hotel Royton, Sapporo, Hokkaido, Japan. (Invited)

[2] Shrestha, L.K.* Hill, J.P.; Yamauchi, Y.; Miyazawa, K.; Ariga, K. " Self-Assembled Fullerene Nanostructures: From Zero to Higher Dimensions, 15th IUMRS-International Conference in Asia (IUMRS-ICA 2014), August 25-30, 2014, Fukuoka University, Fukuoka, Fukuoka, Japan. (Invited)

[3] Shrestha, L.K.* " Self-Assembled Fullerene Nanostructures: From zero to higher dimensions " CSJ Asian International Symposium, March 28, 2014, Nagoya University, Nagoya, Aichi, Japan. (Invited: Received the Distinguished Lectureship Award)

[4] Shrestha, L.K.* Hill, J.P.; Yamauchi, Y.; Miyazawa, K.; Ariga, K. " Fullerene nanoarchitectonics from zero to higher dimensions, ICYS/MANA Reunion Workshop, March 3-4, 2014, NIMS (Namiki-site), Tsukuba Ibaraki, Japan. (Invited)

[5] Shrestha, L.K.* " Fullerene nanoarchitectonics: From zero to higher dimensions " IUPAC 9th International Conference on Novel Materials and Synthesis (NMS-IX) & 23rd International Symposium on Fine Chemistry and Functional Polymers (FCFP-XXIII), October 17-22, 2013, Shanghai, China. (Invited)

〔図書〕(計 件)

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〔その他〕
ホームページ等
<http://www.nims.go.jp/super/HP/Lok/Lok.htm>

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