Novel Fullerene Microhorns with Microscopic Recognition Properties

–Manipulation of Structural Transformation of Fullerene Microtubes to Fullerene Microhorns Capable of Micron-Sized Particles Recognition–

A NIMS research team has demonstrated the structural transformation of fullerene microtubes into fullerene microhorns that exhibit preferential recognition of silica particles over fullerene C_{70}, polystyrene latex, hydroxylate, or carboxylate particles of similar dimensions due to strong electrostatic interactions. ("Manipulating the Structural Transformation of Fullerene Microtubes to Fullerene Microhorns having Microscopic Recognition Properties", Qin Tang, Subrata Maji, Bohong Jiang, Jiao Sun, Wenli Zhao, Jonathan P. Hill, Katsuhiko Ariga, Harald Fuchs, Qingmin Ji, and Lok Kumar Shrestha, ACS Nano, 2019).

-A NIMS research team consisting of graduate student Qin Tang, Postdoctoral Researcher Subrata Maji, MANA Scientist, Qingmin Ji, Chief Researcher Jonathan P. Hill, Group Leader Katsuhiko Ariga and Principal Researcher Lok Kumar Shrestha (Supermolecular Group, International Center for Materials Nanoarchitectonics), succeeded to manipulate microtubes composed of fullerenes C_{60} and C_{70} and directly observed the formation of novel nanocarbon assemblies called fullerene microhorns. The fullerene microhorns exhibit preferential recognition of silica particles over fullerene C_{70}, polystyrene latex, hydroxylate, or carboxylate particles of similar dimensions. This unique fullerene microhorn crystals may be applicable in different fields due to the improved availability of both internal and external surfaces, and stronger binding of molecules at their interiors including as a targeted delivery mechanism for micro-sized cells and drugs in the human body. In addition, these fullerene microhorns would be capable of selectively removing toxic particles such as PM 2.5.

-Controlled organization and direct manipulation of micron-size hollow fullerene nanostructures have substantial potential in material chemistry, biosciences, or biomedical research. Although the concept of atomic and molecular level manipulation has been established and extensively studied using well-defined systems, and various functional materials and nanosystems have been designed, the manipulation of micron-sized hollow objects remains a challenging task due to the lack of any effective strategies. Manipulation of micro-sized objects requires a large number of atoms and molecules to be controlled.

-The research team has succeeded to assemble fullerene C_{60} and C_{70} molecules into 1D tubular microcrystals with a vacant tube compartment being bisected at the center by a solid core somewhat reminiscent of bamboo tubes. These fullerene microtubes (FMTs) are of homogeneous morphology with average length ca. 20 μm, outer diameter ca. 1.49 μm, and inner diameter ca. 0.85 μm. Interestingly, post-solvent treatments of these FMTs induced secondary structural transformations leading to the formation of fullerene microhorns (FMHs).

-First, fullerene microtubes (FMTs) were produced using dynamic liquid-liquid interfacial precipitation (LLIP) method with mesitylene and *tert*-butyl alcohol (TBA) as respectively good and poor solvents for fullerenes

(C_{60} and C_{70}). In a typical crystallization, C_{60}/mesitylene (8 mL) and C_{70}/mesitylene solutions (2 mL) were mixed. TBA (3 mL) was then quickly added into the mixed fullerene solution and the mixture was incubated at 25 ºC for 12 h (Fig. 1). The structural transformation from FMTs to FMHs proceeds spontaneously when a few drops of a mesitylene-TBA mixture (volume ratio 1:3) are placed on FMTs already positioned on the surface of a silicon wafer, followed by slow evaporation of solvents.

-The team has successfully demonstrated the microscopic recognition properties of the FMHs for silica particles over fullerene C_{70}, polystyrene latex, hydroxylate, or carboxylate particles of similar dimensions due to strong electrostatic interactions (Fig. 2). The assembly of functional fullerene C_{60} and C_{70} molecules into a unique morphology reminiscent of bamboo tubes possessing manipulable microscale hollow structures and the related recognition of micron-sized objects has not previously been explored. This is the first direct observation of the microscopic level transformation of fullerene nanocrystals. It is believed that this novel material; fullerene microhorns, could be useful in smart selective drug/or biomaterials delivery applications and on the transport and release of micron-sized objects.

-This study has been published in the ACS Nano (https://doi.org/10.1021/acsnano.9b05938), a journal issued by an American Chemical Society.

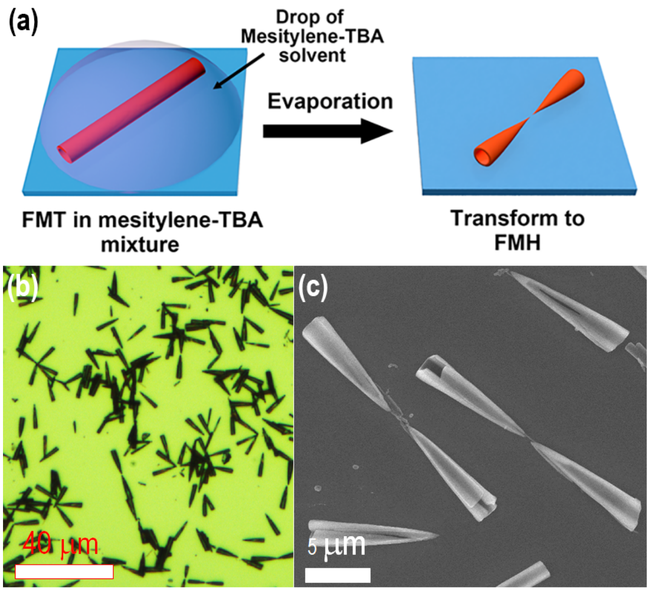

Figure 1. Scheme for the structural transformation of fullerene microtubes (FMTs) to fullerene microhorns (FMHs). (a) Transformation of FMTs to FMHs by solvent engineering. Mesitylene-TBA solvent is dropped onto FMTs inducing the formation of FMHs. (b) Polarized optical microscopy image of FMHs, (c) SEM image of FMHs.

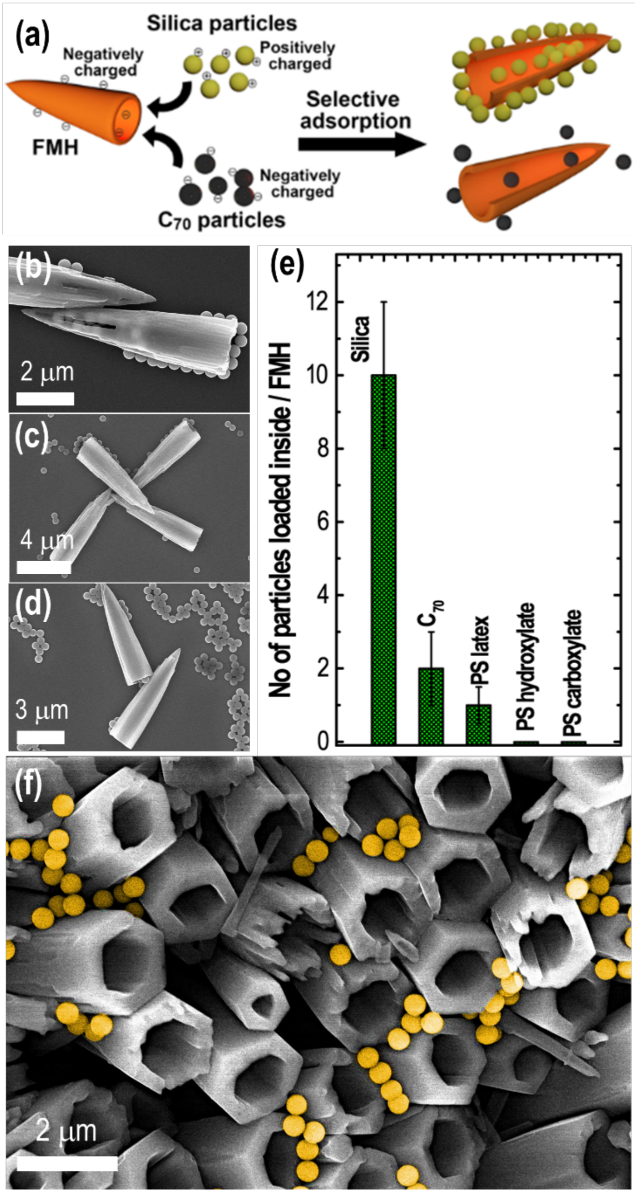

Figure 2. (a) Scheme for selective adsorption of particles in FMHs based on electrostatic interactions. SEM observations showing the different loading capacities of FMHs towards (b) Silica particles, (c) PS latex particles, and (d) PS carboxylate particles. (e) Comparison of the different particles loaded inside the hollow space per FMH and (f) False-colored SEM image of Fullerene Microhorn Array repelling polymer microparticles.