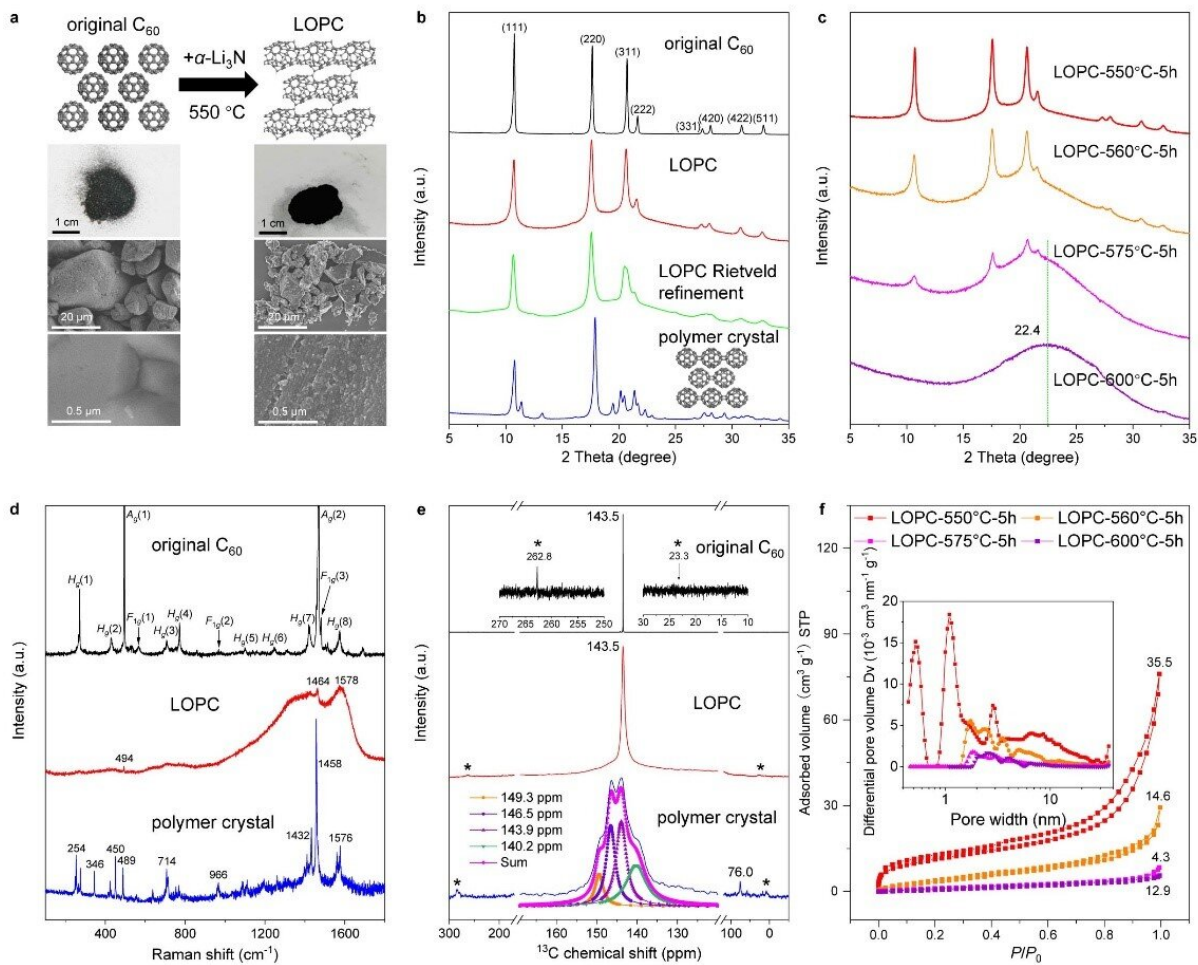


# Discovery of a new form of carbon called long-range ordered porous carbon

January 11 2023



a) Atomic structure models, optical and SEM images. b) Cu K $\alpha$  ( $\lambda = 0.15418$  nm) X-ray diffraction patterns with simulation for LOPC, based on the proposed atomic structure model. AU, arbitrary units. c) X-ray diffraction patterns of LOPCs, with the temperature indicated by LOPC-550 etc. for samples prepared at different temperatures. d) Raman spectra for the original C<sub>60</sub>, LOPC and the

polymer crystal. e)  $^{13}\text{C}$  MAS-SSNMR spectra. The pink line shows the Lorentz fit of peaks for the polymer crystal; \*indicates the spin side bands. f) Low-pressure Ar (87.3 K) adsorption/desorption isotherms and (inset) pore-size distribution (calculated by using a slit pore with a DFT equilibrium model) for LOPCs, with specific surface area values ( $\text{m}^2 \text{g}^{-1}$ ) labeled above each of the isotherm curves. Credit: Institute for Basic Science

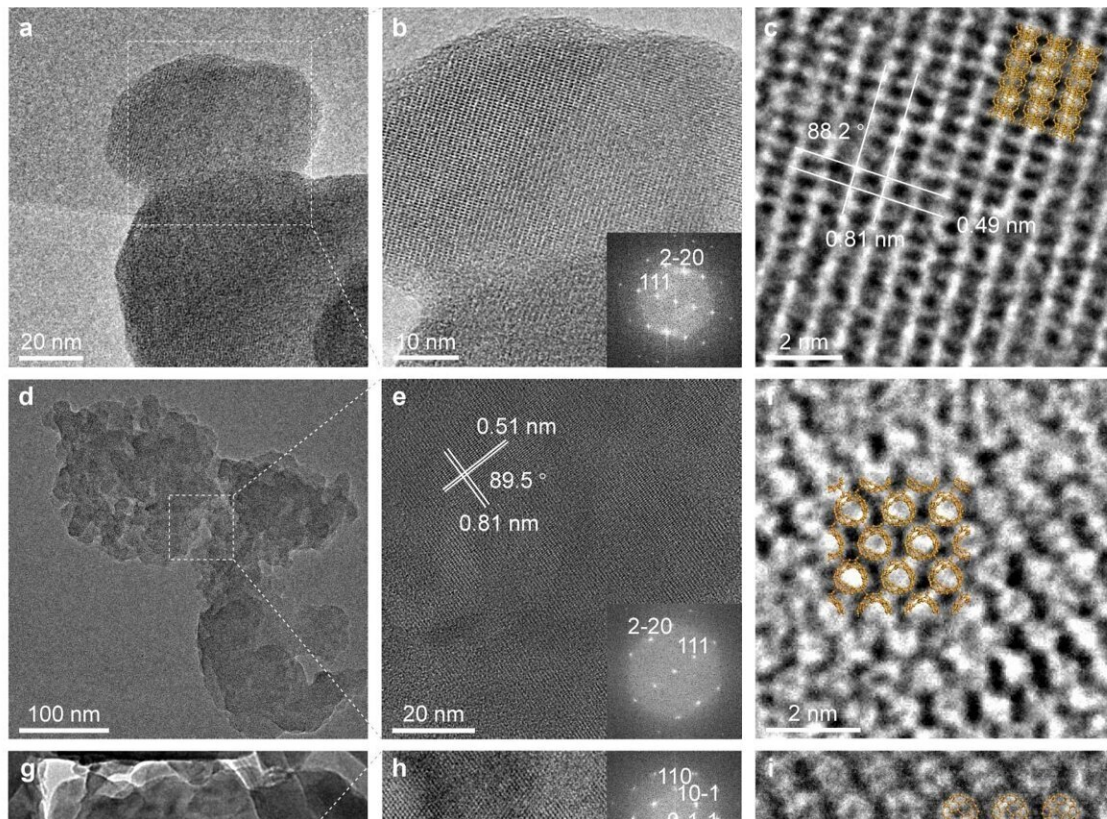
The most well-known forms of carbon include graphite and diamond, but there are other more exotic nanoscale allotropes of carbon as well. These include graphene and fullerenes, which are  $\text{sp}^2$  hybridized carbon with zero (flat-shaped) or positive (sphere-shaped) curvatures.

Meanwhile,  $\text{sp}^2$  hybridized carbon with a negative curvature, called "schwarzite," has been proposed theoretically, and its discovery has been a dream of some scientists in the field of carbon materials. It has been learned that carbon can be templated into some of the periodic pores of certain zeolites via vapor deposition but the templating is incomplete due to some pores simply being too narrow. This has thwarted the creation of carbon schwarzites by templating routes.

Recently, a team of researchers from the Center for Multidimensional Carbon Materials within the Institute for Basic Science (IBS), South Korea led by Director Rodney Ruoff and his colleagues at the University of Science and Technology of China led by Professor Yanwu Zhu, reported a discovery of a new form of carbon. The research is published in the journal *Nature*.

Zhu who led the USCT team said, "Professor Ruoff explained his interest in the triply periodic minimal surfaces that were described by the mathematician Schwartz, and how trivalently bonded carbon can in principle yield identical structures at the mathematical constructs. These

are now referred to as 'carbon schwarzite' structures, and that also can be called 'negative curvature carbon.' I told him years ago that this was an exciting research topic and that it might be possible to find ways to collaborate on his suggestion."



a) TEM image of the original  $C_{60}$  particles. b) Enlarged view with a FFT in the inset. c) High-resolution image showing the spacings of the (111) (0.81 nm) and (220) planes (0.49 nm) of fcc  $C_{60}$ . d) Typical TEM image of LOPC particles. e) Enlarged view and FFT. f) High-resolution image showing deformed and connected cages in the LOPC crystal. g) Typical TEM image of polymer crystal particles. h) Enlarged view and FFT. i) High-resolution image showing individual  $C_{60}$  cages with center-to-center distances labeled in the polymer crystal; the suggested structure is shown by the orange-colored overlays in c, f and i for each carbon. j) Neutron PDF for the original  $C_{60}$ , LOPC and the polymer crystal. Distances are labeled for the major peaks below 0.7 nm, which is the diameter

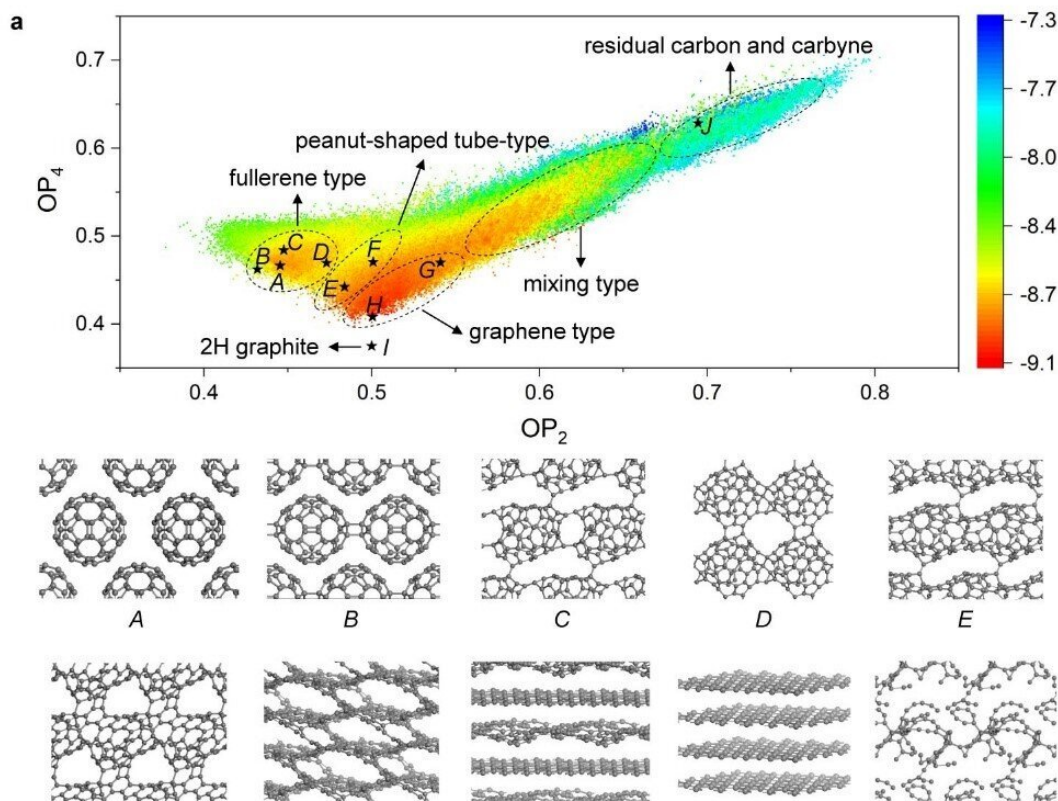
of a  $C_{60}$  cage. Green arrows indicate the changes of peak positions and intensities in LOPC and polymer crystal, compared to the original  $C_{60}$ . Credit: Institute for Basic Science

This new form of carbon was produced using  $C_{60}$  fullerene (buckminsterfullerene, also called buckyball molecules) powder, as a base material. The  $C_{60}$  was mixed with  $\alpha$ - $Li_3N$  ("alpha lithium nitride") and then heated to moderate temperatures while holding at one atmosphere of pressure. It was learned that the  $\alpha$ - $Li_3N$  catalyzed the breaking of some of the [carbon-carbon bonds](#) in  $C_{60}$ , and new C-C bonds were then formed with neighboring  $C_{60}$  molecules through electron transfer to the  $C_{60}$  molecules.

Ruoff said, "In this particular effort, Prof. Zhu and team at USTC used a potent [electron transfer](#) agent ( $\alpha$ - $Li_3N$ ) to drive the formation of a new type of carbon by starting with crystalline fullerene."

Professor Zhu and team named their new carbon, "long-range ordered porous carbon" (LOPC).

LOPC consists of "broken  $C_{60}$  cages" that are connected with long-range periodicity. That is, the broken  $C_{60}$  cages are each still centered on the lattice sites of the face-centered cubic lattice, but they have been "opened" to a degree and formed bonds with each other. This is a somewhat unusual situation—there is still long-range periodic order of a certain type, but not every broken  $C_{60}$  cage is identical to its neighbors.



a) Potential energy surface of fcc C<sub>60</sub> expressed with Steinhardt-type order parameter (OP). According to the geometric characteristics of the carbons obtained, five distinct regions are circled to guide the eye, and the representative structures are listed for four of these: (A) fcc C<sub>60</sub>, (B) polymer crystal composed of 1D fullerene polymer chains, (C) polymer crystal composed of 2D fullerene polymer network, (D) polymer crystal composed of 2D fullerene polymer network with rings as connection, (E) 1D peanut-shaped tube with intertube polymerization, (F) open-caged peanut-shaped tube, (G) 3D connected graphene-like structure, (H) 2D curved graphene-like structure, (I) 2H graphite, and (J) residual carbyne. b) <sup>13</sup>C chemical shift spectra depending on temperature, obtained from in situ MAS-SSNMR data while heating 500 mg C<sub>60</sub> with 100 mg α-Li<sub>3</sub>N. c) Calculated reaction energy path of 2+2 polymerization of two isolated C<sub>60</sub> cages without Li adsorption ('0 Li'), with one Li atom adsorbed near the sp<sup>3</sup> bonding site ('1 Li near') or one Li atom adsorbed far from the sp<sup>3</sup> bonding ('1 Li far'). Credit: Institute for Basic Science

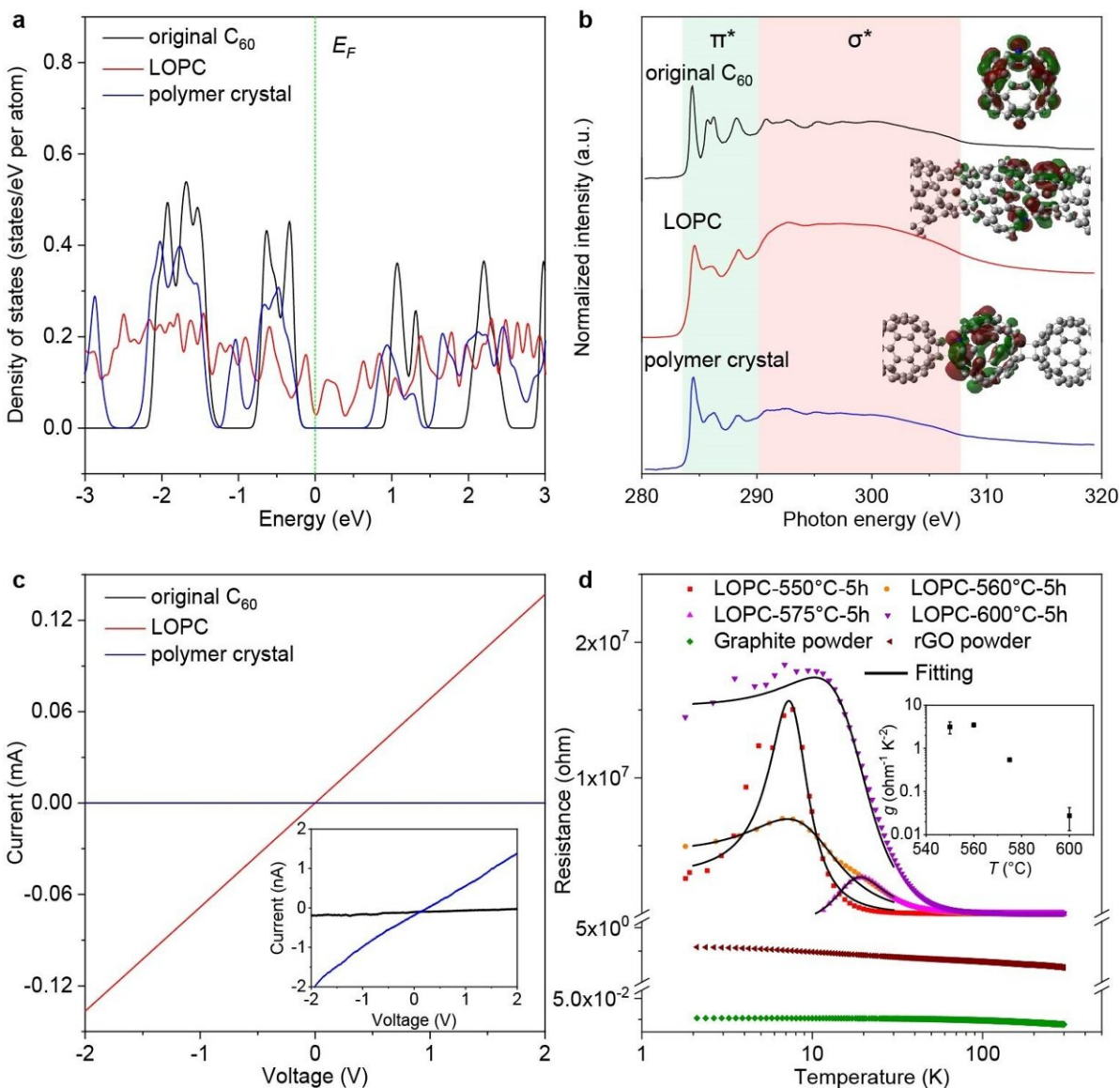
It was found that the formation of the LOPC occurred under narrow temperatures and carbon/Li<sub>3</sub>N ratio conditions. Heating up to 550 degrees Celsius with a 5:1 ratio between carbon and Li<sub>3</sub>N causes partial destruction (breaking of some C-C bonds) of the buckyballs, which resulted in discovery of the broken C<sub>60</sub> cage structure that is found in the LOPC.

A milder temperature of 480 degrees Celsius or lower level of Li<sub>3</sub>N does not damage the buckyballs, which instead join together to form a C<sub>60</sub> polymer crystal. This crystal decomposes back to individual buckyballs upon reheating. Meanwhile, adding too much Li<sub>3</sub>N or a harsher temperature above 600 degrees Celsius resulted in the complete disintegration of the buckyballs.

This new carbon was characterized by a variety of methods, and (indeed) its characterization was not easy because of the variety of slightly different "broken C<sub>60</sub> cages" that nonetheless maintain their positions in a standard face-centered cubic crystal lattice. X-ray diffraction, Raman spectroscopy, magic-angle spinning solid-state [nuclear magnetic resonance spectroscopy](#), aberration-corrected transmission electron microscopy, and neutron scattering were used to derive an understanding of the structure of this new form of carbon. Numerical simulations based on a neural network type of modeling, combined with the experimental methods mentioned above, show that LOPC is a metastable structure produced during the transformation from "fullerene-type" to "graphene-type" carbons.

The carbon K-edge near-edge X-ray absorption fine-structure data shows a higher degree of delocalization of electrons in LOPC than in C<sub>60</sub>. The [electrical conductivity](#) is found to be  $1.17 \times 10^{-2} \text{ S cm}^{-1}$  at room temperature, and conduction at a temperature of less than 30 Kelvin seems to be a combination of metallic-like transport over short distances punctuated by carrier hopping. Knowing these [electrical properties](#) is

important for elucidating what [possible applications](#) there might be for such a new type of carbon.



a) Density of states. b) Carbon K-edge NEXAFS spectra. Insets show the simulated final-state molecular orbitals of the excited atoms for the first prominent peak (284.4 eV for the original  $C_{60}$ , 285.0 eV for LOPC or 284.2 eV for the polymer crystal). Atoms marked blue are excited atoms (isovalue = 0.02). c) Direct current voltage–current curves of three membranes made by mixing each carbon with 5 wt% polytetrafluoroethylene. Inset shows an enlarged view of

the ordinate. Electrical conductivities calculated from the curves are  $2.44 \times 10^{-9} \text{ S cm}^{-1}$ ,  $7.39 \times 10^{-8} \text{ S cm}^{-1}$  and  $1.17 \times 10^{-2} \text{ S cm}^{-1}$ , for the original  $\text{C}_{60}$ , polymer crystal and LOPC, respectively. d) Resistivity testing for the LOPCs, graphite powder and rGO powder. The inset shows the change of  $g$  value with the annealing temperature of the LOPC. Credit: Institute for Basic Science

Ruoff notes, "While this beautiful new type of carbon has many fascinating features, it is not a carbon schwarzite, so that experimental challenge still remains on the horizon. Indeed, this carbon is something different and unique—it opens up entirely new possibilities in new directions for carbon materials."

The preparation of LOPC paves the way for the discovery of other crystalline carbons starting from  $\text{C}_{60}(\text{s})$ —and perhaps from other fullerenes like  $\text{C}_{70}$ ,  $\text{C}_{76}$ ,  $\text{C}_{84}$ , and so on. Other exciting options would be including another element. This can be done by starting with the "endohedral" fullerenes such as  $\text{M}@\text{C}_{60}$ , where  $\text{M}$  can be an element like lanthanum or many others, which is encapsulated inside the all-carbon fullerene cage.

The team sees possible applications in harvesting, transformation, and storage of energy; in catalysis to generate chemical products; and for the separation of molecular ions or gases. An important aspect also emphasized in their *Nature* paper is the scalability of the synthesis. Zhu notes that it is readily scalable to a kilogram scale, and with continuous production processes, it may be possible to achieve ton-scale production.

"Yanwu invited me to join the effort after some initial success in synthesis and promising initial steps in their project, and fortunately, I was able to make some helpful suggestions about the science underway and through to completion of this study now published in *Nature*. Credit



for the synthesis and the hands-on experimental studies is entirely due to Yanwu and his team. It was my pleasure to provide some advice on certain topics, including some analyses to undertake and what might be learned therefrom," Ruoff says.

"Collaboration with colleagues is one of the pleasures of doing science. The topic here was a new form of [carbon](#), perfectly aligned with the interests of our CCM center that I direct and that is located at UNIST. So, I jumped into the collaboration with excitement, and a great eagerness to try to contribute in useful ways."

**More information:** Yanwu Zhu, Long-range ordered porous carbons produced from C60, *Nature* (2023). [DOI: 10.1038/s41586-022-05532-0](https://doi.org/10.1038/s41586-022-05532-0). [www.nature.com/articles/s41586-022-05532-0](https://www.nature.com/articles/s41586-022-05532-0)

Provided by Institute for Basic Science

Citation: Discovery of a new form of carbon called long-range ordered porous carbon (2023, January 11) retrieved 27 April 2024 from <https://phys.org/news/2023-01-discovery-carbon-long-range-porous.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.