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Comment

Long-range ordered porous carbon: A new carbon constructed by connecting C_{60} cages

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Carbon is a versatile element in the Periodic Table and can bind itself to many polymorphs through various bonding forms (e.g., sp, sp^2, and sp^3 hybridizations) [1]. Based on structural periodicity, carbon materials can be classified into crystalline or amorphous [2]. For example, graphene, diamond and graphite are well-known crystalline carbon materials with different periodic binding motifs in the carbon atom networks [3–5]. By contrast, the active carbons featured with high porosity are the typical amorphous carbons in which the carbon atoms are arranged in a disordered fashion [6]. The various carbon bonding forms result in various physical/chemical properties of carbon materials in terms of conductivity, transparency, thermal stability, mechanical strength [7]. These fantastic properties bring out extensive applications of carbon materials in structure materials, energy storage and conversion, catalysis, water purification, electronics, etc.

Due to the diverse bonding forms and various attractive applications, synthesizing new carbon materials and exploring their distinct properties are always the frontier topic. Thus far, most works develop new carbon materials by altering the bonding motifs of carbon atoms. Constructing new carbon materials with more complex structural units (e.g., atomic clusters) is expected to have distinctive properties with superior topologies. The buckminsterfullerene (C_{60}), initially discovered by Smalley et al. in 1985, is a typical atomic cluster consisting of sixty carbon atoms and can serve as a versatile building block for constructing new carbon materials [3]. Various C_{60} polymers, including one dimensional chains, two-dimensional planes, and three-dimensional networks, have been reported by connecting C_{60} molecules with covalent bonds from different directions [8–11]. Moreover, new carbon materials derived from collapsed C_{60} cages have been also reported. For example, Liu et al. obtained a super-hard amorphous carbon material with nearly 100% sp^3 hybridizing bonds by crushing C_{60} under harsh conditions (~27 GPa and 900–1000 °C) [12]. Treating C_{60} with KOH at high temperatures can also break the C_{60} cages and result in carbon quantum dots or amorphous porous carbons because of the violent reactivity of KOH [13, 14]. Moreover, a new crystalline carbon material can also be successfully obtained by using the collapsed C_{60}. In 2012, Wang et al., reported an ordered amorphous carbon clusters with collapsed C_{60} cages by applying an extremely high pressure (~35 GPa) on xylene-solvated C_{60} [15]. The C_{60} cages are crushed under high pressure and transformed into amorphous clusters which are separated by the xylene solvent to maintain their pristine long periodicity. This remarkable progress presents a long-range periodic carbon material that can be constructed with amorphous carbon clusters derived from collapsed C_{60}. However, the harsh fabrication condition resulted in a low yield of such carbon material and difficulty in assessing its property. Thus, a facile chemical routine to crush C_{60} cages yet remain the pristine periodicity of C_{60} solids is highly desirable. The challenge is that the collapsed C_{60} clusters are generally highly reactive because of the rich dangling bonds at the edges. They are prone to reconstruct into graphitic or diamond-like amorphous carbons initially after the C_{60} cages break.

In recent reporting on Nature (https://www.nature.com/articles/s41586-022-05532-0), Yanwu Zhu, Rodney S. Ruoff, and their colleagues have synthesized a crystalline porous carbon constructed with covalent connected broken C_{60} cages through a facile electron injecting approach that can be easily scaled up [16]. The C_{60} molecule is an electron-acceptor, and injecting electrons into C_{60} molecules can promote their reactivity. As a result, the C_{60} molecules collapse and interconnect with adjacent broken C_{60} cages after the electron injection from α-Li_3N under a relatively mild condition (e.g., 550 °C, ambient pressure), finally forming a long-range ordered porous carbon constructed with periodic arranged broken C_{60} cages, as shown in Fig. 1(a). Such new carbon material inherits the face center cubic stacking from the C_{60} crystals verified by the X-ray diffraction (Fig. 1(b)). The absence of characteristic peaks of C_{60} molecules from the Raman spectra indicate the feature of the broken C_{60} cages (Fig. 1(c)).

This work presents a facile approach to synthesize a new long-range ordered porous carbon material with broken C_{60} cages, contributing to the understanding of structure evolution starting from C_{60} and refreshing our knowledge on carbon materials [17]. Moreover, this work opens the door for synthesis new carbon materials with complex atomic clusters. For example, other

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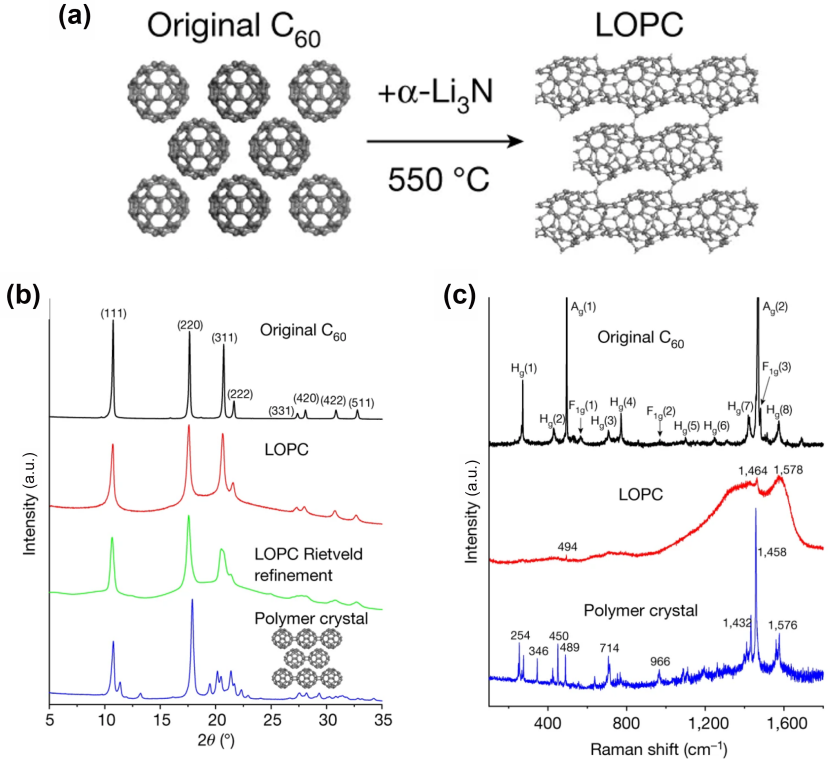

Figure 1 (a) Schematic illustration of the synthesis of the long-range ordered porous carbon material, (b) the X-ray diffraction and (c) the Raman spectra of the long-range ordered porous carbon material, original C_{60} and polymeric C_{60}. Reproduced with permission from Ref. [17], © Pan, F. et al., under exclusive licence to Springer Nature Limited 2023.

fullerenes, such as C_{70}, can be explored as building blocks to construct new carbon materials. And more electron injecting agents beyond α-Li_3N can be investigated to obtain new techniques on synthesizing novel carbon materials. The electron injecting approach may be used to synthesize new materials beyond carbon materials, such as silicon-based clusters [18].

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