From Cubes to Dice: Solvent-Regulated Morphology Engineering of Endohedral Fullerene Microcrystals with Anomalous Photoluminescence Enhancement

Jianhua Wu, Xianjun Zhu, Yong Guan, Yujing Wang, Fei Jin, Runnan Guan, Fupin Liu, Muqing Chen, Yangchao Tian, and Shangfeng Yang

Abstract: Despite recent successes in preparing three-dimensional crystals of empty fullerenes, such as C_{60} and C_{70}, 3D endohedral fullerene crystals, and especially hollow nanostructures, have been scarcely reported. A universal approach has now been developed to prepare shape-tunable 3D crystals of several metal nitride clusterfullerenes, including cubes and dice (hollow cubes with holes at the center of each face), which can be readily switched by changing the volume ratio of good (mesitylene) and poor (isopropanol) solvents. X-ray diffraction, soft X-ray nano-computed tomography, and transmission electron microscopy were used to unambiguously identify the interior microstructure of the dice-shaped crystals of Tb_{3}N@C_{80} and especially the depth of the hole at each face, confirming that the dice has a solid center and the holes are not interconnected. Owing to the enhanced light absorption, the dice-shaped crystals exhibit enhanced photoluminescence relative to that of the cubes.

Owing to the unique closed-cage molecular structures, fullerene cages exhibit fascinating physical and chemical properties, rendering promising applications in such functional devices as organic solar cells, light emitting diodes, field effect transistors, and sensors, for which the formation of well-defined molecular assembly is required to achieve high performance. To construct micro- or nano-sized fullerene crystals as ordered molecular assemblies, vapor-driven and solution-driven methods have been developed, affording versatile fullerene crystals with variable morphology, size, and dimension. Among them, three-dimensional (3D) fullerene crystals with polyhedral shapes are of particular interest because of the high symmetry and crystal plane variability. So far, 3D crystals of empty fullerenes, especially C_{60} and C_{70}, have been extensively studied. For instance, in 2010 Choi et al. prepared the first C_{70} cubes via a precipitation method, which showed remarkable increased photoluminescence relative to the powder owing to the increased crystallinity of C_{70} together with the decreased intermolecular interactions. However, 3D crystals of C_{60} have not been reported until very recently by Tsukagoshi and Lu et al., who prepared polyhedral C_{60} microcrystals with variable shapes ranging from parallelepipeds to octahedrons by applying n-heptanol as the poor solvent for the precipitation processes. These studies reveal that, unlike the readily fabricated 1D and 2D fullerene crystals, formation of 3D fullerene crystals is more difficult and sensitively dependent on the type of fullerene.

As a special branch of fullerene chemistry, endohedral fullerene crystals with atoms, ions, or clusters encapsulated in fullerene cages possess even more intriguing properties owing to the intramolecular charge transfer from the encapsulated species to the outer cage. Despite extensive studies on 3D crystals of empty fullerenes, 3D endohedral fullerene crystals, and especially hollow nanostructures with holes in the interior, have been scarcely reported. In 2014 our group reported the first 3D crystals of an endohedral fullerene Sc_{3}N@I_{h}-C_{80}, and found that both cubes and dice (that is, hollow cubes with holes at the center of each face) formed, which can be switched by applying ultrasonication during mixing the good/poor solvents. However, this technique requires a delicate control of the ultrasonicator power and time. Besides, specifically for the dice-shaped crystals which offer larger surface area and consequently enhanced electrocatalytic properties, whether the holes are interconnected aforesaid a hollow center remains an open question.

Herein, we develop a facile and universal approach to prepare shape-tunable (cubes and dice) 3D crystals of several metal nitride clusterfullerenes (NCFs), including M_{3}N@I_{h}-C_{80} (M = Tb, Er, Sc), for which the cubes and dice can be readily switched by changing the volume ratio of good (mesitylene) and poor (isopropanol) solvents. We further use the synchrotron-based soft X-ray nano-computed tomography (Nano-CT) to unambiguously identify the interior microstructure of the dice-shaped Tb_{3}N@C_{80} crystals for the first time. The dependence of photoluminescence (PL) properties of M_{3}N@I_{h}-C_{80} (Tb, Er, Sc) on the crystal shape is also investigated, revealing that the dice-shaped crystals exhibit anomalously enhanced PL relative to that of the cubes.

[*] J. H. Wu, Y. J. Wang, F. J. Jin, R. N. Guan, F. P. Liu, Dr. M. Q. Chen, Prof. Dr. S. Yang
Hefei National Laboratory for Physical Sciences at Microscale CAS Key Laboratory of Materials for Energy Conversion Department of Materials Science and Engineering, Synergetic Innovation Center of Quantum Information & Quantum Physics University of Science and Technology of China Hefei 230026 (China)
E-mail: sfyang@ustc.edu.cn
Dr. Y. Guan, Prof. Dr. Y. C. Tian
National Synchrotron Radiation Laboratory University of Science and Technology of China Hefei 230029 (China)
E-mail: ychtian@ustc.edu.cn
† These authors contributed equally to this work.
$ Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201905151.
We prepared the 3D crystals of M₃N@C₈₀ (M = Tb, Er, Sc, hereafter the isomeric label is omitted for simplicity) via a liquid–liquid interfacial precipitation (LLIP) method, employing mesitylene and isopropanol as good and poor solvents, respectively (Scheme 1). Briefly, M₃N@C₈₀ microcrystals were first dissolved in mesitylene to obtain a M₃N@C₈₀ solution in mesitylene with an optimized concentration of 0.1 mg mL⁻¹ (see the Supporting Information, Section S1, for details), which was kept under ultrasonication owing to the relatively low solubility of M₃N@C₈₀ in mesitylene. Then a certain volume (1–3 mL) of isopropanol was slowly added into 1 mL M₃N@C₈₀ solution in mesitylene, and the mixture was continuously ultrasonicated for 5 min. The mixture was then kept at room temperature for 12 h without any agitation, and the color of supernatant gradually faded because the fullerene molecules prefer to stack selectively along the <100> and <111> directions. In the present case, while cube-shaped Tb₃N@C₈₀ microcrystals form as well under the mesitylene/isopropanol volume ratio of 1:1, the existence of excessive isopropanol (mesitylene/isopropanol 1:3 (v/v)) in the initial mixture solution leads to increased number of nucleation sites of Tb₃N@C₈₀ molecules, more crystal seeds thus form, and consequently the supply of Tb₃N@C₈₀ solute becomes insufficient; preferential growth of crystal seeds along the <100> and <111> directions occurs according to the principle of crystal growth under shortage of solute. 

As stated in our previous work on ultrasonication-switched formation of dice- and cube-shaped microcrystals of Sc₃N@C₇₀, formation of dice-shaped Sc₃N@C₆₀ microcrystals results from crystal growth under a shortage of solute, which is mainly due to the hindrance of solute diffusion under ultrasonication conditions; consequently the fullerene molecules prefer to stack selectively along the <100> and <111> directions. In the present case, while cube-shaped Tb₃N@C₈₀ microcrystals form as well under the mesitylene/isopropanol volume ratio of 1:1, the existence of excessive isopropanol (mesitylene/isopropanol 1:3 (v/v)) in the initial mixture solution leads to increased number of nucleation sites of Tb₃N@C₈₀ molecules, more crystal seeds thus form, and consequently the supply of Tb₃N@C₈₀ solute becomes insufficient; preferential growth of crystal seeds along the <100> and <111> directions occurs according to the principle of crystal growth under shortage of solute.

When the volume ratio of mesitylene/isopropanol is 1:1, uniform cubic microcrystals with an average size of about 1.2 µm are obtained for the case of Tb₃N@C₈₀ (Figure 1a). Upon decreasing the volume ratio of mesitylene/isopropanol to 1:2, some cubic microcrystals turn into dice-shaped ones with small holes. A further decrease of the volume ratio of mesitylene/isopropanol to 1:2.5 and 1:3 results in uniform dice-shaped microcrystals with larger holes, and a better uniformity is achieved when the volume ratio of mesitylene/isopropanol is set to 1:3 (Figure 1c; Supporting Information, Figure S2). Thus, the optimized volume ratio of mesitylene/isopropanol is determined to be 1:3, under which the average size of the dice-shaped Tb₃N@C₈₀ microcrystals is about 0.8 µm (Supporting Information, Figure S3).

We studied the crystal structures of the cube- and dice-shaped Tb₃N@C₈₀ microcrystals by powder X-ray diffraction (XRD). For cubic Tb₃N@C₈₀ microcrystals, only one intense diffraction peak with a d-spacing of 10.9 Å, which can be indexed as the (100) plane based on a simple cubic structure, is observed in its XRD pattern (Figure 1b). However, in the XRD pattern of dice-shaped Tb₃N@C₈₀ microcrystals, two intense diffraction peaks with a d-spacing of 10.9 Å and 3.35 Å, indexed as (100) and (310) planes, respectively, are observed. For the latter peak, a shoulder diffraction peak with a d-spacing of 3.34 Å correlated to the (311) plane is also detected. Of note, the full-width at half-maximum (FWHM) value of the intense (100) peak of dice-shaped Tb₃N@C₈₀ microcrystals is larger than that of cubic Tb₃N@C₈₀ microcrystals, suggesting lower crystallinity of dice-shaped Tb₃N@C₈₀ microcrystals (Supporting Information, Figure S4).
To compare the morphologies of the cube- and dice-shaped Tb,N@C₈₀ microcrystals more clearly, we carried out transmission electron microscopic (TEM) characterizations. While a solid cubic structure can be clearly seen in the low-magnification TEM image of cubic Tb,N@C₈₀ microcrystals (Figure 1c), in the TEM image of dice-shaped Tb,N@C₈₀ microcrystals, the center looks obviously thinner than the four blades (Figure 1g), confirming its dice shape. Besides, the four blades along the square diagonal are nearly symmetrical, indicating the holes on the six facets of the cube are in the centers of the facets. Furthermore, the high-resolution TEM (HR-TEM) images of both cube- and dice-shaped Tb,N@C₈₀ microcrystals show clear lattice fringes with the distance between two adjacent planes of 10.9 Å (Figures 1d,h), which can be assigned to the (100) crystalline plane. These results coincide with those obtained from XRD study.

An intriguing question is whether the holes on the six facets of the cube are interconnected for dice-shaped Tb,N@C₈₀ microcrystals. To identify the interior microstructure of the dice-shaped of Tb,N@C₈₀ crystals, we employed the synchrotron-based soft X-ray nano-computed tomography (Nano-CT), which is advantageous in terms of high penetrating depth and thus enables observation of the interior microstructure of material.[13] The 3D morphologies of a dice-shaped Tb,N@C₈₀ microcrystal in different views are illustrated in Figure 2a (for a movie of the 3D structure, see the Supporting Information, Movie S1), revealing clearly the existence of holes on the six facets, which are not interconnected. Moreover, according to the computed tomography model (Figure 2b), the depth of the hole and the thickness of the solid center can be obtained, confirming that the holes are not interconnected, with the penetration ratio of the hole being in the range of 61.7% –75.8% (Supporting Information, Table S1). To our knowledge, this is the first time that the interior microstructure of the dice-shaped fullerene crystals is determined unambiguously.

To examine whether this solvent-regulated morphology engineering method is applicable for other NCFs, we changed the fullerene to two analogous NCFs M,N@C₆₀ (M = Er, Sc), which were dissolved in mesitylene as the starting solution for crystal growth. Following the same procedure used for Tb,N@C₈₀, we find that cubic- and dice-shaped crystals of M,N@C₆₀ (M = Er, Sc) can be readily manipulated by changing the mesitylene/isopropanol volume ratio from 1:1 to 1:3 as well (Supporting Information, Figure S5). This indicates the universality of our method in selective preparation of cube-/dice-shaped fullerene crystals. Compared to the ultrasonication-switched method for preparing dice- and cube-shaped Sc,N@C₈₀ microcrystals reported previously,[10] the solvent-regulated method developed in the present work is much more facile since no external energy is needed to switch the morphology of the as-grown crystals.

As extensively reported for empty fullerenes C₆₀ and C₇₀, upon formation of microstructures, photoluminescence (PL) is enhanced relative to that of the fullerene powder owing to the improved crystallinity.[12] This stimulated us to investigate the PL properties of cube- and dice-shaped crystals of M,N@C₆₀ (M = Tb, Er, Sc) powder, cube, and dice, indicating that the PL intensity of M,N@C₆₀ powder is dramatically enhanced for M,N@C₆₀ cube, and a further PL enhancement is observed for M,N@C₆₀ dice. Similar to the cases of empty fullerenes C₆₀/C₇₀ and an endohedral fullerene Lu₆@C₇₀, PL enhancement of M,N@C₆₀ cube relative to that of M,N@C₆₀ powder is understandable based on the improved crystallinity of the cube.[5c,12c,13] However, surprisingly the PL intensity of M,N@C₆₀ dice is even more stronger than that of cube, despite of the decreased crystallinity according to XRD results as discussed above. Interestingly, such an anomalous PL enhancement effect is observed for all three NCFs, suggesting that it is originated from the microstructure of the crystals and independent on the nature of NCF molecule. To our knowledge, this phenomenon has never been reported for empty and endohedral fullerene microcrystals, and the detailed PL enhancement mechanism is unclear yet. A plausible interpretation is that the dice-shaped crystals enable enhanced excitation light absorption owing to the light-trapping effect induced by the holes (Supporting Information, Figure S6).

We also carried out time-resolved PL (TRPL) studies to compare the PL dynamics of M,N@C₆₀ (M = Tb, Er, Sc) powder, cube, and dice. According to the fitted time constants obtained from a biexponential decay (Supporting Information, Table S2), the time constants of the main components of M,N@C₆₀ (M = Tb, Er, Sc) dice and cubes are all larger than those of the corresponding powders, and the M,N@C₆₀ (M = Tb, Er, Sc) dice exhibit the largest time constants, suggesting the slowest fluorescence quenching as a result of inhibited nonradiative relaxation.[7,14] These results are consistent with the highest steady-state PL intensities of M,N@C₆₀ (M = Tb, Er, Sc) dice as discussed above.

In summary, we develop a universal approach to prepare 3D cube- and dice-shaped microcrystals of several NCFs M,N@C₆₀ (M = Tb, Er, Sc), with the morphology readily regulated by changing the volume ratio of good (mesitylene) and poor (isopropanol) solvents. The interior microstructure of the dice-shaped of Tb,N@C₈₀ crystals was investigated by the synchrotron-based soft X-ray nano-computed tomography (Nano-CT) for the first time, confirming that the dice has a solid center and the holes are not interconnected. The dice-shaped M,N@C₆₀ (M = Tb, Er, Sc) crystals exhibit anomalously enhanced PL relative to those of the cubes due to...
presumably to the enhanced excitation light absorption. Our solvent-regulated shape engineering method is facile and effective in tuning the PL properties of fullerene microcrystals, offering new opportunity in the applications of fullerenes in optoelectronic devices.

Acknowledgements

We thank Professor Hualing Zeng (University of Science and Technology of China) for technical assistance on PL measurements. This work was supported by the National Key Research and Development Program of China (nos. 2017YFA0402800, 2017YFA0402904), National Natural Science Foundation of China (nos. 51572254, 11775224).

Conflict of interest

The authors declare no conflict of interest.

Keywords: clusterfullerenes · endohedral fullerenes · interfacial precipitation · metal nitrides · photoluminescence


Figure 3. a)–c) Steady-state and d)–f) time-resolved PL spectra of M3N@C80 (M = Tb, Er, Sc) powder (black), cubes (blue), and dice (red). TRPL spectra were measured at λ = 580 nm (λex = 532 nm).


Manuscript received: April 25, 2019
Accepted manuscript online: May 27, 2019
Version of record online: ■ ■ ■ ■ ■

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A roll of the dice: A universal approach to prepare shape-tunable 3D crystals of several metal nitride clusterfullerenes (NCFs), including cubes and dice, which can be readily switched by changing the volume ratio of good (mesitylene) and poor (isopropanol) solvents. The dice-shaped crystals exhibit anomalously enhanced photoluminescence (PL) relative to that of the cubes.