

Solvent Engineering for Shape-Shifter *Pure Fullerene (C₆₀)*

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Preparation of nano- and microstructures with predetermined morphologies through self-assembly is the key process of the bottom-up approaches to nanotechnology.¹ In particular, construction of shape-defined nanomaterials² of functional nanocarbons such as fullerenes³ could lead to development of photoelectronic devices for ultrahigh information density processing. So far, shape control of nanostructures has been achieved by using the three fundamental strategies of crystallization/precipitation, template synthesis, and amphiphilic assembly. Crystallization and precipitation from appropriate solvents and/or at an interface result in crystals with well-defined shapes as seen in fullerene crystals⁴ such as nanowhiskers.⁵ However, there is usually no flexibility in shape modulation. Template synthesis⁶ produces predesignated structures whose forms are inevitably restricted by the dimensions and forms of the templates. In contrast, self-assembly mainly based on specific amphiphilicity in a surrounding medium results in a selection of morphologies including nanotubes, nanofibers, and microspheres.⁷ For example, assembly of alkyl-tail-attached C₆₀ derivatives in various solvents gives nanofibers, nanosheets, spheres, or flower-like nanoobjects.⁸ Unfortunately, in the latter approach attachment of large functionless groups to the respective functional moieties is always required, and this feature is a distinct disadvantage for applications requiring a high density of functionality. As a useful technique for bottom-up nanotechnology, shape control of *pure* functional molecules remains challenging. Since our finding of microhexagon formation by pure C₆₀ molecules through precipitation from solution,⁹ we have now successfully completed an investigation of solvent engineering for free control of microscopic shapes of pure C₆₀. Here, we report controlled formation of two-dimensional (2D) crystals including hexagons and rhombi and their selective shape shifting (change or growth of crystals) into one-dimensional (1D) rods through solvent-dependent variations of the crystal lattice, *all involving pure C₆₀* (Figure 1).

Interfacial precipitation of C₆₀ by addition of appropriate solvents (6 mL, isopropyl alcohol (IPA) or *tert*-butyl alcohol (TBA)) into saturated C₆₀ solutions (1 mL, benzene, toluene, CCl₄, CS₂, and *m*-xylene)) resulted in various 2D crystals (Figure 2). Scanning electron microscopy (SEM) images clearly demonstrate our control over the edge multiplicity between 3 and 8 of the polygonal nanosheets. Uniformly shaped rhombi (a) and hexagons (b) were obtained at TBA/toluene and IPA/CCl₄ interfaces, respectively, while polygon mixtures (c) were collected from the TBA/benzene interface. The former two cases exhibited a high uniformity in size and thickness of the structures obtained. Shape selection might originate in the dependence of the crystalline lattice obtained on the solvent used, although the detailed mechanism is still under investigation. Transmission electron microscopic (TEM) imaging (d) revealed a thin morphology of the rhombi. Closer TEM imaging

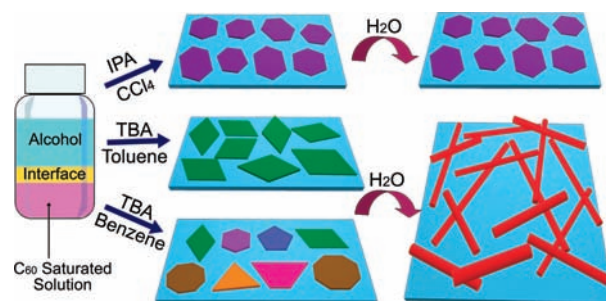


Figure 1. Selective precipitation of fullerene nanosheets and the structural transformation from 2D nanosheets to 1D nanorods.

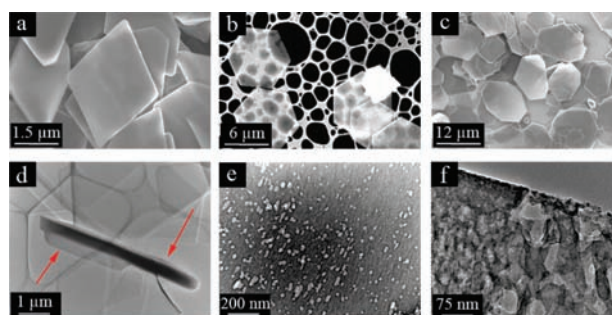


Figure 2. SEM images of 2D C₆₀ micro-objects prepared at (a) TBA/toluene, (b) IPA/CCl₄, and (c) TBA/benzene interfaces. TEM images (d and e) and HR-TEM image (f) of 2D rhombus obtained at TBA/toluene interface.

(e) and high resolution TEM (HRTEM) imaging (f) also demonstrate the presence of numerous pores at the surface of the nanorhombi. We speculate that pore formation occurs by the evaporation of trapped solvent molecules from within the nanorhombi during drying. Interestingly, occasionally nanorhombi were found transformed to 1D structures through rolling up (Figure 2d) probably resulting from the release of high surface energy. Formation of 1D nanostructures (needles and rods) was also confirmed when CS₂ or *m*-xylene were cosolvents with TBA.¹⁰

Although the X-ray diffraction (XRD) patterns (Figure 3A) of pristine C₆₀ powder (a) and the hexagon nanosheet from IPA/CCl₄ (b) can be assigned as fcc¹¹ and hexagonal⁹ crystalline structures, respectively, the rhombus nanosheet from TBA/toluene (c) has a mixed crystalline lattice of fcc ($a = 1.410$ nm) and hexagonal ($a = 2.382$ nm and $c = 1.089$ nm) (Figure 3A). In addition, complete drying upon heating under vacuum does not alter this mixed crystalline structure.¹⁰ Mixed-shaped nanosheets from TBA/benzene also show characteristics of the mixed crystalline lattice.¹⁰ Electron diffraction patterns of these nanosheets¹⁰ confirmed this feature. Raman spectra (Figure 3B)¹⁰ of the nanorhombi prepared in TBA/toluene (c) display a significant shift in the A_g(2) mode peak to

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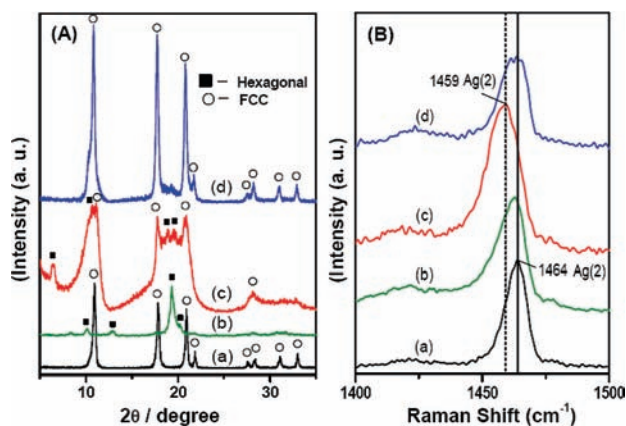


Figure 3. (A) XRD patterns and (B) Raman spectra: (a) C₆₀ powder; (b) hexagonal nanosheets from IPA/CCl₄; (c) rhombus nanosheets from TBA/toluene; (d) nanorods from water treatment of the nanorhombus.

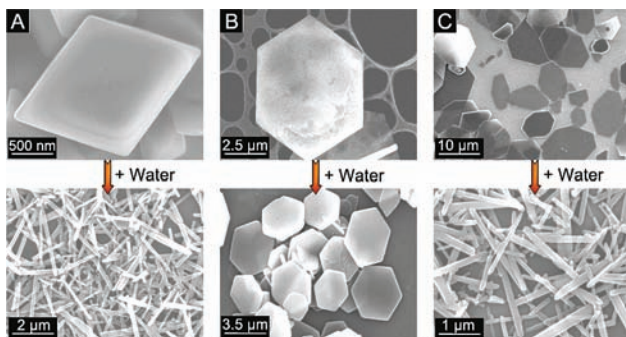


Figure 4. SEM images of structural transformation of 2D fullerene nanosheets upon water treatment: (A) nanorhombus (from TBA/toluene) to nanorod; (B) inert nanohexagon (from IPA/CCl₄); (C) mixed polygon (from TBA/benzene) to nanorod.

1459 cm⁻¹ as compared with that of C₆₀ powder (a) and hexagonal nanosheets (b) (both at 1464 cm⁻¹). The clear presence of the fcc crystalline structure in the nanorhombi indicates the absence of polymerization so that the observed downshift to 1459 cm⁻¹ in the A_g(2) mode can be attributed to the presence of an accumulated strain¹² only present in rhombi nanosheets.

Exposure of these 2D nanosheets to water induced selective transformation into 1D nanorods (Figure 4). Nanorhombi from TBA/toluene (A) and mixed polygons from TBA/benzene (C) were converted to short nanorods upon exposure to water. Approximate matching in size of the nanorhombi (or mixed polygons) and nanorods suggested shape transfer through sheet rolling, which is also implied by the TEM image in Figure 2d. The shape shift is accompanied by changes in the XRD pattern to the fcc lattice (Figure 3A(d)), which is almost identical to the morphologically similar C₆₀ nanowhiskers.⁵ In addition, the Raman A_g(2) peak shifted back to 1464 cm⁻¹ (Figure 3B(d)), suggesting release of structural strains during the shape shift to nanorods. These observations indicate that the metastable nanorhombi which possess a strained mixed crystalline structure metamorphose into the more stable short nanowhisker (nanorods) probably through stimulation by some additional hydrophobic interaction between C₆₀ molecules upon contact with water. In contrast, the stable nanohexagon of a single lattice (and so less strain) does not undergo shape shifting (Figure 4B).

This research clearly demonstrates controlled formation of 2D nanosheets of various shapes (hexagons, rhombi, and mixed

polygons) and selective shape shifting (change or growth of crystals) to nanorods (short nanowhiskers) *all from pure C₆₀ molecules* by very simple solvent treatment. This technically innovative concept based on our findings represents a new methodology in fullerene-based bottom-up nanotechnology.

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Supporting Information Available: Synthetic details and additional characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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