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Crystal Growth

Polyhedral Organic Microcrystals: From Cubes to Rhombic Dodecahedra**

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The shape control of symmetric nanocrystals has attracted wide interest in recent years. Not only is the symmetry of the nanocrystals interesting, but they also have potential in tuning the optical, optoelectronic, magnetic, and catalytic properties.[1–3] Tremendous efforts have been directed toward the development of synthetic procedures for inorganic particles with controlled shapes, such as Ag, Au, Pt, PdTe, and Cu_2O.[4–9] Nanostructures or particles in the form of cubes, cuboctahedra, and octahedra have been fabricated by using various approaches, such as changing the precursor ratio in the polyol process, the introduction of inorganic species, and seed-induced growth.[10–13] Despite much success in the synthesis of inorganic nanocrystals, the preparation and shape control of symmetric micro- or nanostructures of small-molecular organic compounds has not yet been reported, although they may offer great variety and flexibility in molecular design and thus tunability in electronic and optical properties.[14–16] Herein, we demonstrate the controlled synthesis of 2,5,8,11-tetra-*tert*-butylperylene (TBPe) particles with cubic, truncated cubic, or rhombic dodecahedral shapes by a simple surfactant-assisted process. More importantly, changes in morphology are accompanied by changes in optical properties.

TBPe is an important organic material with very high fluorescence efficiency, and is widely used in organic optoelectronics.[17] In a typical preparation of TBPe cubes, 1.0 mL of a solution of TBPe in THF (1 mM) was injected into a vigorously stirred solution of Pluronic 123 (P123; 8.3 $\mathrm{g\,L^{-1}}$) in water (5.0 mL) at room temperature. P123 is a triblock polymer with the structure poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) and is a nonionic surfactant. After stirring for 3 minutes, the sample was left standing for stabilization. Figure 1 a shows a scanning electron microscopy (SEM) image of a typical sample of the cubes. The image shows that the cubes or particles have good uniformity, well-defined facets, and sharp edges and corners. The inset shows the corresponding transmission electron microscopy (TEM) image (see also Figure S1 in the Supporting Information). Figure 1 b shows the X-ray diffraction (XRD) spectrum of the sample, and demonstrates that all XRD peaks can be indexed as a body-centered cubic (bcc) structure ($a = b = c = 16.66$ Å, $\alpha = \beta = \gamma = 90°$, space group I_{23}; see Figure S2 in the Supporting Information). Figure 1 c shows the determined unit cell of the structure.[18] The particle shapes were found to be highly sensitive to the solvent composition of the preparation solution, or the solubility of TBPe in the solvent mixtures. By slightly changing the solvent composition, specific polyhedral shapes could be produced in high yields. For example, the volume of THF, in which TBPe is soluble, was increased from 1.0 to 1.5 mL while keeping all other parameters the same. This increase resulted in shape changes from cubes to truncated cubes, then to truncated rhombic dodecahedra, and finally to rhombic dodecahedra (Figure 2 a–e and Table 1 in the Supporting Information). This is the first report of highly symmetric organic crystals by a shape control and evolution process, although these processes have been widely reported for inorganic and metal particles.

In the body-centered cubic (bcc) lattice, the cubes are covered only by {100} planes, while the rhombic dodecahedra are covered by {110} planes, with {110} being the most stable plane in the bcc structure. The particle grows predominantly in either the ⟨100⟩ or ⟨110⟩ direction (Figure 2 g). The final shape of the bcc nanocrystals is mainly determined by the ratio of growth rates in the ⟨100⟩ and ⟨110⟩ direction. Such a growth pattern is similar to that found in inorganic systems,[4,5,19] except that the crystal structures of almost all reported inorganic polyhedral particles have a face-centered cubic (fcc) structure. Since the most stable plane in the fcc lattice is {111} rather than {110}, the resulting inorganic crystal

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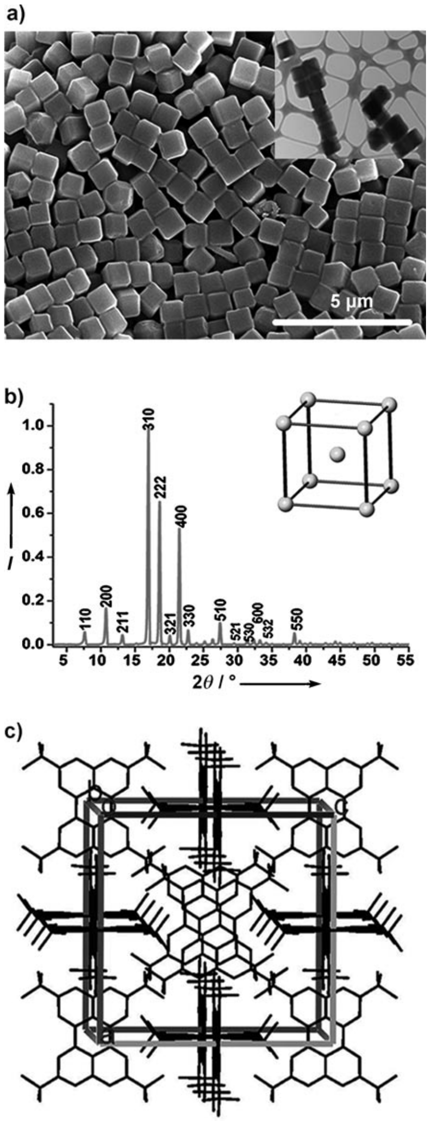

Figure 1. a) SEM image and TEM image (inset) of the TBPe cubes. b) X-ray diffraction pattern and c) unit cell of the crystal structure of the TBPe cubes.

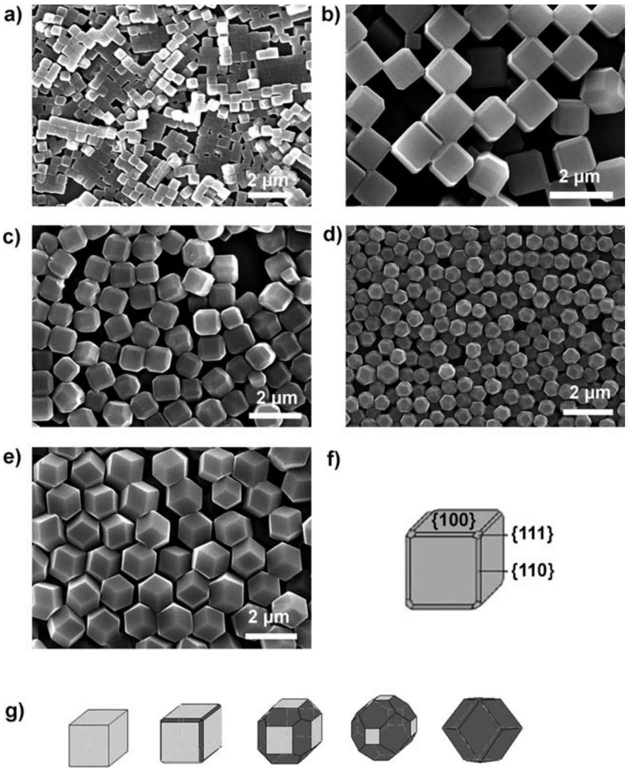

Figure 2. SEM images of TBPe polyhedral particles formed under different conditions. a) Cubes, b) truncated cubes, c) intermediate shape, d) truncated rhombic dodecahedra, e) rhombic dodecahedron. f) Unit cell of the cubic lattice. g) Geometrical particle shapes determined by the ratio of the growth rate in the ⟨100⟩ and ⟨110⟩ directions.

shapes are thus octahedral (enclosed by {111} planes) instead of rhombic dodecahedral.

A detailed growth mechanism is still under investigation. We believe that a change of solvent composition may have the following possible effects in the crystal growth process. Firstly, the change of solubility of TBPe in the solvent system will have a great impact on the supersaturation profile during the nucleation process and the subsequent growth kinetics in different planes. Secondly, a change of solvent composition may also modify the relative order of surface energy by preferential adsorption or desorption of the surfactant on specific crystal surfaces, and thus alter the growth rates along the corresponding directions. The facet with a faster growth rate eventually disappears, while the facet with a slower growth rate will be more exposed on the nanocrystal surface, thus leading to the change of final crystal morphology. In the present system, as more THF is introduced, the growth rate in the ⟨110⟩ direction is reduced and thus more {110} facets are exposed in the crystal surface to ultimately result in rhombic dodecahedra. Thus, the change of solubility of TBPe and the surface-modifying surfactant are believed to play a key role in the shape control and the shape-evolution process.

The photoluminescence (PL) properties of the polyhedral particles were subsequently investigated. Figure 3 shows that similar-sized TBPe particles of different shapes exhibit different PL spectral features. Curve fitting reveals that all the spectra consist of three peaks at 472 nm, 495 nm, and 530 nm.[20] As the particles change from cubes to rhombic dodecahedra, the peak at 495 nm becomes increasingly more intense relative to that at 472 nm. The cause of the morphology-dependent optical properties is not entirely clear, however, because of the limited penetration depth of the light source, the phenomenon may be due to the different surface states on the crystal facets, which have a different effect on the PL characteristics.[21]

The size of the particles can be easily tuned by simply varying the surfactant concentration. For example, rhombic dodecahedron particles with sizes of 2.5 µm, 1.8 µm, 1.2 µm, and 800 nm could be prepared by using surfactant concentrations of 8.3, 4.2, 2.1, and 1.0 $\mathrm{g\,L^{-1}}$, respectively (see Figure S3 in the Supporting Information). By taking advantage of the unique particle shape in the presence of surfactant, we successfully assembled the truncated rhombic dodecahe-

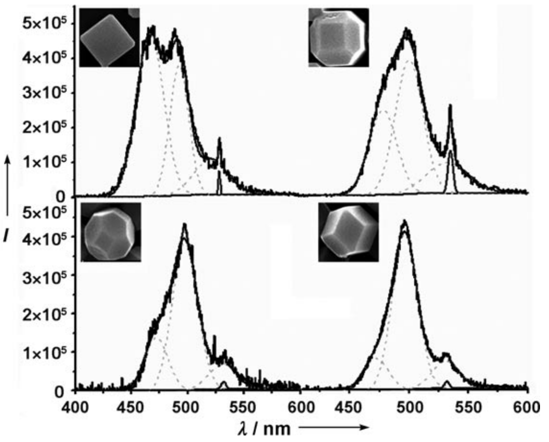

Figure 3. Photoluminescence spectra of TBPe particles with different shapes. The sharp peak at around 532 nm comes from the double-frequency signal of the laser source used in the measurement

dron crystals into a large-area close-packed film, as shown in Figure 4. Such films may have potential application in photonic crystals[10,22] and gas sensors.[23–24]

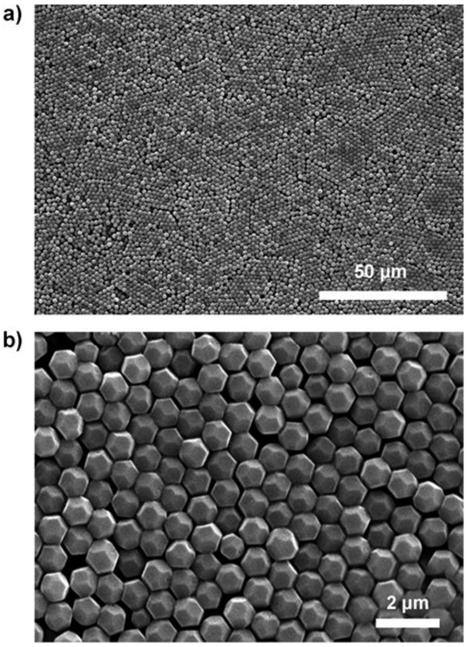

Figure 4. SEM images of the as-assembled large area close-packed film of truncated rhombic dodecahedron particles.

In conclusion, we have achieved the controlled synthesis of crystalline TBPe particles with various high-symmetry morphologies ranging from cubes through truncated cubes and truncated rhombic dodecahedra to rhombic dodecahedra. The morphological control was realized by changing the solvent composition or solubility of TBPe with the assistance of a surfactant, which altered the growth rate in the ⟨100⟩ direction relative to that in the ⟨110⟩ direction. Significantly, changes in particle morphology induced distinctive changes in optical properties. We have reported the first preparation of organic crystals with controlled shapes and high symmetry. The present findings offer guidelines for developing high-symmetry organic micro- and nanostructures, which may have optical and pharmaceutical applications.

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