

Formation of Highly Ordered Nanostructures by Drying Micrometer Colloidal Droplets

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Materials of interest in solid-state chemistry typically possess a crystalline structure; thus, their functional properties are controlled by the packing of their atoms or ions in three-dimensional space. Similarly, nanoparticles are useful building blocks for nanomaterials, the function of which is determined in part by the spatial structure of the component nanoparticles. Thus, nanoparticles may be used for the construction of periodic and quasiperiodic crystal structures.^{1,2} Many recent research efforts have been devoted to utilizing nanoparticles for the construction of periodic crystal structures.^{3–8} For example, Yin *et al.*⁷ developed a technique to prepare periodic crystal structures of nanoparticles (nanocrystal) in the liquid phase. Talapin *et al.*⁸ used self-assembly of binary nanoparticles to form nanocrystals with forbidden symmetry (quasicrystal). In these prior research efforts, however, the use of organic surfactants has been an essential step in nanoparticle-based crystal preparation, which in turn may reduce the capabilities of the produced nanomaterials (due to the presence of surfactant impurities). As an alternative, drying-mediated self-assembly is a promising method to prepare nanocrystals,^{9–12} as no surfactants are needed.

With regards to desirable morphologies for nanomaterials, high surface area porous or hollow structures are frequently preferred for a wide range of applications.^{13–15} Hollow and porous materials are frequently prepared from a colloidal crystal template on a plate substrate.^{16–18} Most preparation procedures typically consist of three steps: (1) the formation of colloidal crystals, (2) the permeation of voids with a secondary material, and (3) the chemical or thermal re-

ABSTRACT Nanoparticles with well-defined chemical compositions can act as building blocks for the construction of functional structures, such as highly ordered aggregates, as well as porous and hollow aggregates. In this work, a spray-drying technique is used to form a crystal-like structure with nanoparticle building blocks. When spray-drying uniform spherical particles, tightly packed aggregates with either simple or broken symmetries (quasicrystalline) were formed. Using polystyrene (PS) particles with varied zeta potentials as templates, it is also possible to form highly ordered porous and hollow aggregates from inorganic colloidal particles. Essential to the production of quasicrystalline structures is the use of monodisperse colloidal particles in spray drying, as the quasicrystalline form is not achievable when two different sizes of colloidal particles are used in the precursor suspension. With varying colloidal particles sizes, smaller colloidal particles fill the spaces formed between the larger particles, resulting in adjustment of colloidal crystallization. A geometric model that considers the tight packing of several spheres into frustrated clusters (quasicrystal form) with short-range icosahedral symmetry is compared to experimentally produced structures and found to quantitatively explain experimental observations.

KEYWORDS: nanostructured particles · colloidal quasicrystals · crystal-like structure · spray-drying process · porous aggregates · hollow aggregates

moval of colloidal beads. Along these lines, we recently developed an aerosol-assisted spray-drying process, that is, the drying of micrometer droplets consisting of colloidal particles, for the production of nanostructured particles (see Supporting Information Figure S1).^{19–24} The spray drying procedure is described in greater detail in the Experimental Methods section. Briefly, a suspension composed of the desired nanoparticles and organic template nanoparticles (often polystyrene) is atomized and sent into a dryer to remove solvent, and subsequently a furnace, to remove template particles and partially sinter the nanoparticles of interest. After exiting the furnace, the dried, surfactant-free, and solvent-free nanoparticles are embedded in the desired nanostructure and easily collected *via* either filtration or electrostatic precipitation. This process is ideal for the preparation of ordered nanostructures as it (1) relies on spray-drying and therefore does not

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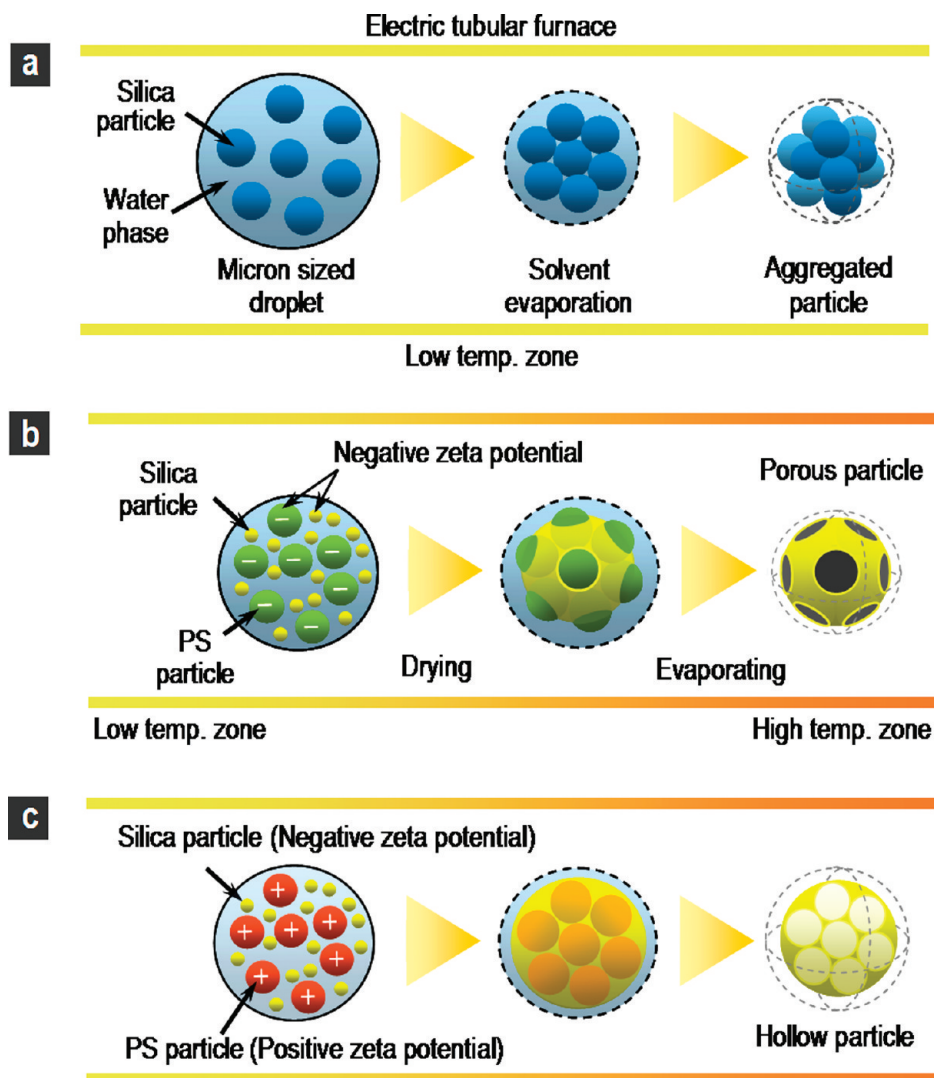


Figure 1. A schematic illustration of particle formation on the surface of charged colloidal particles: (a) large silica aggregates produced by negative zeta potentials on silica colloids, (b) porous aggregates produced by negative zeta potentials on silica and PS colloids, and (c) hollow aggregates produced by oppositely charged silica and PS colloids.

require the use of surfactants and (2) can be used to produce highly desirable hollow and porous nanostructures. However, a detailed examination of the preparation of aggregate, porous, and hollow aggregates, all of which are attainable *via* spray-drying, has not been performed hitherto. The objective of this study therefore is to investigate in detail the formation of highly ordered nanostructured forms, namely aggregate, porous, and hollow aggregates by means of spray-drying technology. Specifically, our investigation focuses on the effects of nanoparticle size distribution and template particle physicochemical properties on symmetry formation in the produced nanomaterials, including the formation of tetrahedrons, cubes, isohedrons or 5-, 8-, 10-, 12- or >12-sided structures which are spherical, porous, or hollow. A theoretical approach that considers tight packing of several spheres (small aggregates) into a crystalline structure as well as a forbidden symmetry

(or quasicrystal form) is also developed and related to observed nanostructured materials.

RESULTS AND DISCUSSION

Preparation of Highly Ordered Aggregate, Porous, and Hollow Aggregates by Spray-Drying. In spray-drying, the spherical packing of uniform (monodisperse) colloidal particles in a dried droplet determines the final form of the aggregate particles.²⁵ To examine the results of nanoparticle packing in spray-drying without the use of template particles, uniform silica colloidal particles (100 nm in diameter)²⁶ were used alone in the spray drying precursor suspension. Figure 1a shows a schematic diagram of self-assembly of silica colloidal spheres inside a droplet during the spray drying process. In this study, the droplets generated by an ultrasonic nebulizer (1.7 MHz) had a mean diameter of approximately 4.8 μm and a geometrical standard deviation around 1.38.²⁵ The droplet size and the concentration of colloidal silica

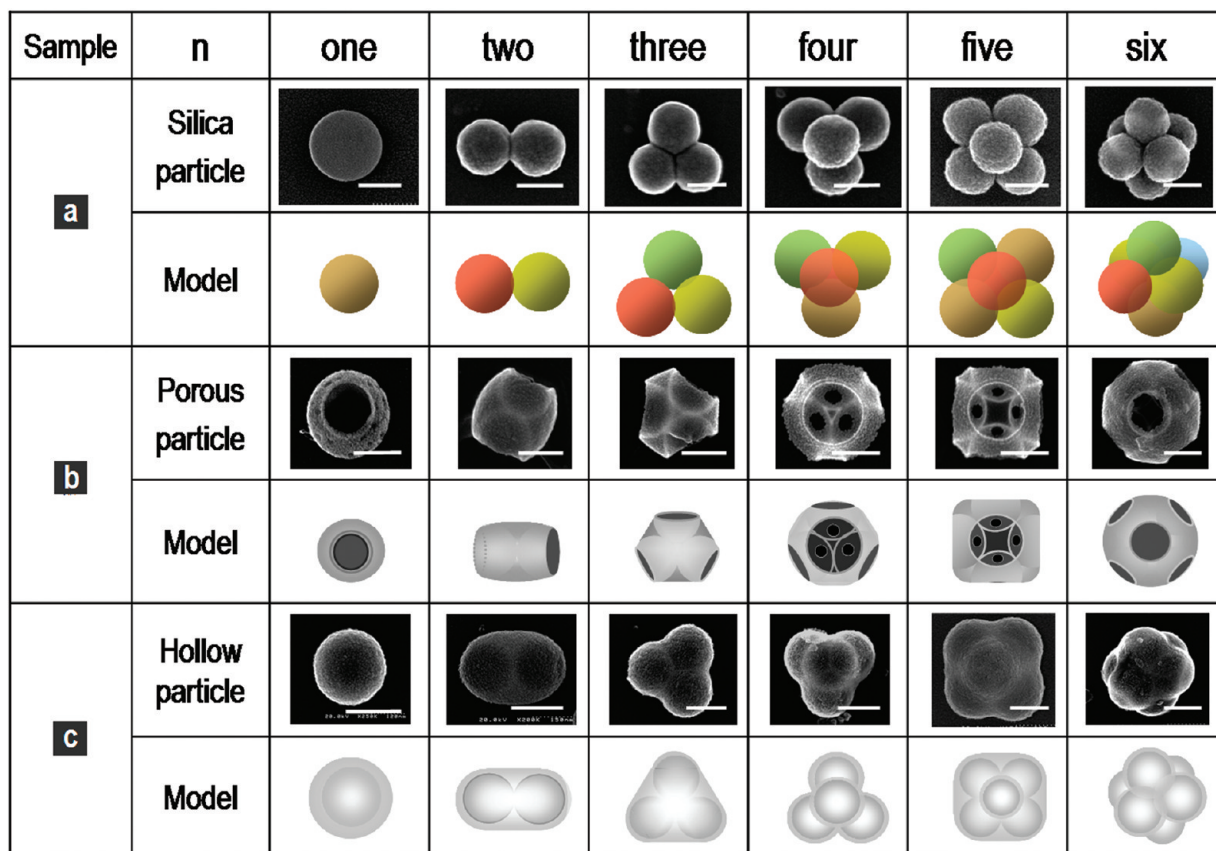


Figure 2. Scanning electron micrographs and schematic models of (a) aggregated particles of 100 nm silica for $n = 1-6$ and scale bars are 100 nm, (b) porous aggregates of 5 nm silica for $n = 1-6$ and scale bars are 150 nm, and (c) hollow aggregates of 5 nm silica for $n = 1-6$ and scale bars are 200 nm.

spheres in the droplet were the main factors controlling the number of spheres in the aggregates and the aggregate size; thus, in spray-drying the observed distribution of number of silica spheres per aggregate is reflective of the nebulized droplet size distribution.

Field emission scanning electron microscope (FE-SEM) images of various aggregated silica particles generated with a silica nanoparticle concentration of 0.05 wt % are shown in Figure 2a. Using a controlled separation procedure, highly ordered aggregate particles with a small numbers of primary silica spheres, that is, one, two, three, four, five, or six silica particles, were obtained. This result indicates that the formation of packing spheres with simple symmetry can result from spray-drying droplets consisting of uniform colloidal spheres. Previously, a similar formation of packing spheres from colloidal particles in a water-in-oil emulsion procedure was reported. However, to the best of our knowledge, this is the first report of using the spray-drying methodology to form highly ordered aggregate particles (sphere packing) having topological symmetry. Additionally, unlike the liquid phase process, in which the size classification of particles is difficult to perform, the spray-drying process occurred in the gas phase, allowing the size classification of the prepared particles to be easily performed using an aerosol impactor or a differential mobility analyzer (DMA).

As mentioned earlier, in the spray-drying process, the size and morphology of the obtained aggregate particles depend on the solid concentration in the precursor and the droplet size. If the colloidal silica concentration in the precursor is increased, the spray dried particles will have a large number of primary silica particles. Figure 3a shows FE-SEM images of various aggregated silica spheres derived from a precursor with a silica concentration of 0.1 wt %. Aggregates with different numbers of primary silica particles, $n = 4, 13, \sim 14, \sim 27, \sim 35$, were obtained using a controlled separation procedure. The product aggregates were classified by the DMA. The DMA classifies the relationship between electrical mobility and mobility equivalent diameter of particles. As shown in Figure 3, when $n = 13$ or more, distortions in the pattern/symmetry of colloidal silica packing spheres were observed. This kind of structure is also called a frustrated cluster or quasicrystal. By definition, quasicrystals are symmetry-forbidden; however, the crystals are thermodynamically stable and possess unique physical properties.²⁷⁻²⁹ Quasicrystals are different from periodic crystals in that they possess a rotational symmetry incompatible with periodicity. In the next section of this paper, a detailed theoretical approach will be introduced to explain the formation of ordered colloidal packing spheres and the formation of

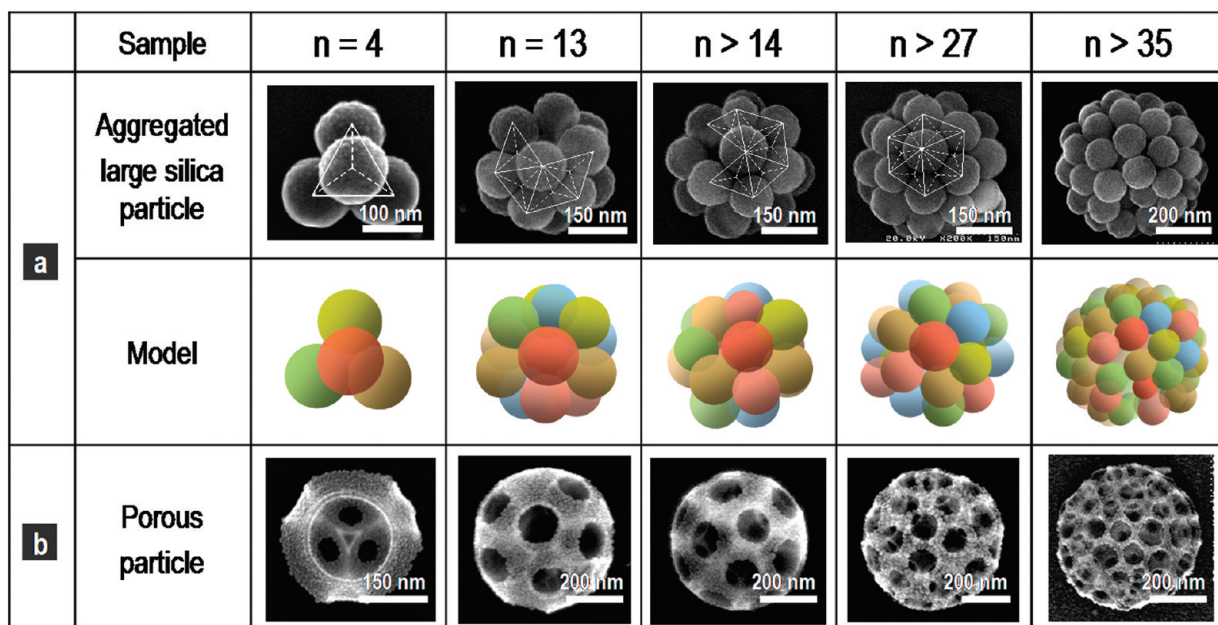


Figure 3. Scanning electron micrographs and schematic models of large silica aggregates and mesoporous silica aggregates produced in the spray-drying process.

frustrated clusters (quasicrystals) that occurred after the drying of droplets consisting of colloidal spheres.

The preparation of porous and hollow aggregates was performed based on the above results. Highly ordered porous and hollow aggregates were produced by drying droplets consisting of two different colloids: 5 nm silica and 200 or 230 nm polystyrene (PS) colloids. If the signs of the zeta potentials of the two colloids are the same, porous aggregates were prepared, and if the zeta potentials were of opposite sign, hollow aggregates were formed. The porous and hollow structure formations resulting from the same- and opposite-signed zeta potential colloids are shown in Figure 1 panels b and c, respectively. In the first step of the process, colloidal mixtures of silica and PS colloids were sprayed onto a reactor. Depending on the concentration and zeta potentials, particles within the droplets became organized, with the PS particles defining the final structure of the product. Voids between the PS particles were filled with silica nanoparticles, and the solvent present in the multiphase droplets was evaporated in the reactor, producing a powder composite composed of silica and PS particles. The PS nanoparticles were decomposed in the high-temperature zone of the reactor, yielding porous or hollow silica aggregates.

Figure 2b shows FE-SEM images of the final structures of highly ordered porous aggregates derived from a precursor containing a mixture of silica 0.05 wt % and PS 1.0 wt % colloidal particles. Product particles with different numbers of PS particles in the droplet, that is, $n = 1, 2, 3, 4, 5$, and 6, were obtained using a controlled separation procedure. Similar to the aggregate particles derived from the uniform colloids, nanostructured porous aggregates with periodic crystal sym-

metry could be obtained. We believe that these kinds of porous structures can be used in many applications including basic research, catalysis, chromatography, filtration, electro-optics, and controlled drug release.

The preparation of hollow aggregates by the same method is shown in Figure 1c. The formation of hollow-structure aggregates, which differs from that of porous aggregates, is described in detail in the following. A mixture of negatively charged silica colloids and positively charged PS colloids was used as the precursor. During the evaporation of a droplet, the negatively charged silica particles tended to be attracted toward the positively charged PS particles' surfaces, resulting in PS particles coated with silica nanoparticles. After the drying process, a solid system of silica and PS composite particles was formed. These particles were carried into the higher temperature zone of the furnace, where the PS particles evaporated, creating a hollow space inside the silica nanoparticle shells. Similar to the previous experimental result, crystal-like nanostructured hollow aggregates were obtained. The morphologies of the hollow nanoclusters for $n = 1-6$ are shown in Figure 2c. These hollow aggregates might be applied in drugs, cosmetics, inks, pigments, or chemical reagents³⁰ because of their excellent properties, including low density, high specific surface area, adsorption capacity, and ability to encapsulate.³¹ To the best of our knowledge, this is the first report of one-step formation of highly ordered porous and hollow structures using simple symmetry and small numbers of template particles.

Figure 3b shows the resulting porous aggregates consisting of large numbers of template particles ($n > 13$). Unlike the aggregate packing spheres with $n > 13$,

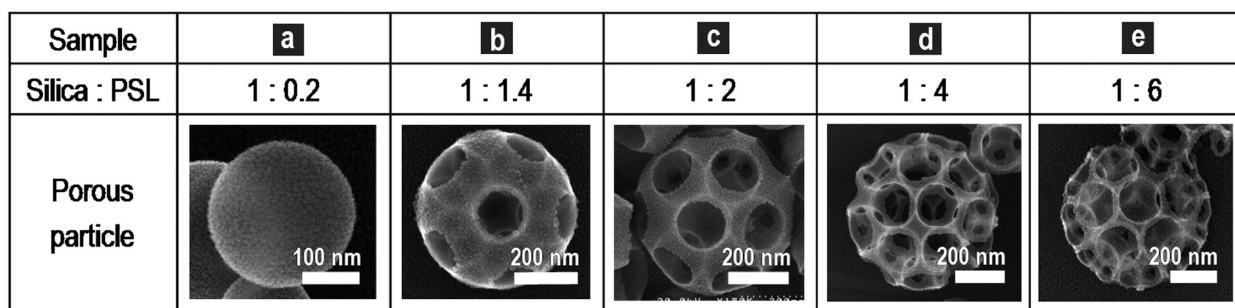


Figure 4. Scanning electron micrographs of porous aggregates produced with various concentration ratios; the concentration ratios of silica to PS colloids are (a) 1:0.2, (b) 1:1.4, (c) 1:2, (d) 1:4, and (e) 1:6.

which exhibited distortion symmetry, no distortion symmetries (quasicrystal forms) were observed in the porous aggregates. The quasicrystal form that was observed in aggregate particles may disappear when using two differently sized colloidal particles. It is possible that the smaller colloidal silica particles fixed/adjusted the colloidal crystallization when they filled the spaces formed by the larger PS particles.

Figure 4 panels a–e show the morphologies of porous silica aggregates derived from a precursor with various ratios of silica to PS colloidal particle concentrations. The concentration ratios of silica to PS colloids were 1:0.2, 1:1.4, 1:2, 1:4, and 1:6, respectively. When a small amount of PS colloid is present in a droplet, a nearly regular configuration of holes located at isogonal distances is obtained. When the concentration of silica is low and the number of PS colloid particles is high, the structure of the porous aggregate is not regular. As the number of PS colloid particles in a droplet increased (a higher concentration of precursor PS particles), the potential of the PS colloid dominated over that of the silica colloid, and the number of silica colloid particles per PS decreased. The results indicate that the nanostructures were developed primarily in the porous particle space, and a stable configuration of porous aggregates was observed. The slow movement of PS particles into an equilibrium position was governed by a constrained Hamiltonian system, indicating that the highlighted formation conditions were predominant.

Packing of Spheres in a Droplet: Topological Approach. The formation of ordered structures within a droplet is the basis of the following methodology and is directly related to symmetry. The concept of symmetry plays a significant role in the natural sciences and is particularly important in the description of crystal forms as the basis of the mathematical classification of crystal lattices. The role of symmetry in crystalline structures has recently been developed, producing a less intuitive theory with deeper mathematical significance. Symmetry has been recognized as an invariant property and a basic law of physical systems, and the role of symmetry in the production of nanostructured materials is presented below. Theoretical considerations are related to

the problem of sphere packing and environments in Penrose tilings.

In close packing of nanoparticles, equidimensional spheres are formed in Euclidean space, and clusters of spheres with weak contact points are used as a basis set. A set $\{S\} = \{(S_1, p_1), \dots, (S_N, p_N)\}$ of N nonintersecting spheres (S_i, p_i) with a common radius r centered at p_i is considered a nanocluster if a sphere (S_j, p_j) exists at a distance of $(p_i, p_j) = 2r$ for each sphere in the set (S_i, p_i) . These two spheres are considered in contact. A nanocluster is connected in an ordered sequence if spheres $\{(S_{11}, p_{12}), \dots, (S_{1k}, p_{1k}), (S_{11}, p_{11}) = (S_i, p_i), (S_{1k}, p_{1k}) = (S_j, p_j)\}$ exist at a distance $(p_{1n}, p_{1(n+1)}) = 2r, n = 1, \dots, k - 1$ for every two spheres $(S_i, p_i), (S_j, p_j)$. All spheres in contact with (S_i, p_i) are considered in the vicinity (O_{Si}) of a sphere (S_i, p_i) .

A nanocluster is considered weakly tetrahedral if three spheres $(S_{12}, p_{12}), (S_{13}, p_{13}), (S_{14}, p_{14})$ exist at a distance of $(p_{1k}, p_{1l}) = 2r$ for $1 \leq k, l \leq 4$ for each sphere in the set (S_{11}, p_{11}) . A tetrahedral system of four spheres (Figure 5a) is denoted as T . A nanocluster is considered tetrahedral if an ordered chain $\{T_{il}\}_{i=1, \dots, k}$ exists for every two tetrahedra T_{i1} and T_{ik} such that T_{in} and $T_{i(n+1)}$ possess a common face at $n = 1, \dots, k - 1$ (Figure 5b, Figure 5c).

A tetrahedron is the basic unit of close packing of identical spheres. However, small distortions associated with tetrahedral packing become apparent when 20 tetrahedra combine to form a 13-sphere icosahedron. When symmetrically arranged around a central sphere, the 12 remaining spheres of an icosahedron are not perfectly packed into a tetrahedral cluster because the distance, a , between the center of the spheres (with a surface-sphere of radius $2r$) is larger than $2r$, the distance between the spheres and the center.^{32,33} The elementary properties of an icosahedron are expressed by the relation $a = 8r/(10 + 2\sqrt{5})^{1/2}$.

If 12 spheres are packed tightly around a central sphere, the icosahedral symmetry is broken, and cracks between symmetrical arrangements coalesce into a large void (Figure 5d). This free space is not large enough to accommodate another sphere but is an important source of degeneracy in dense (random) packing of identical spheres in Euclidean space. The addition

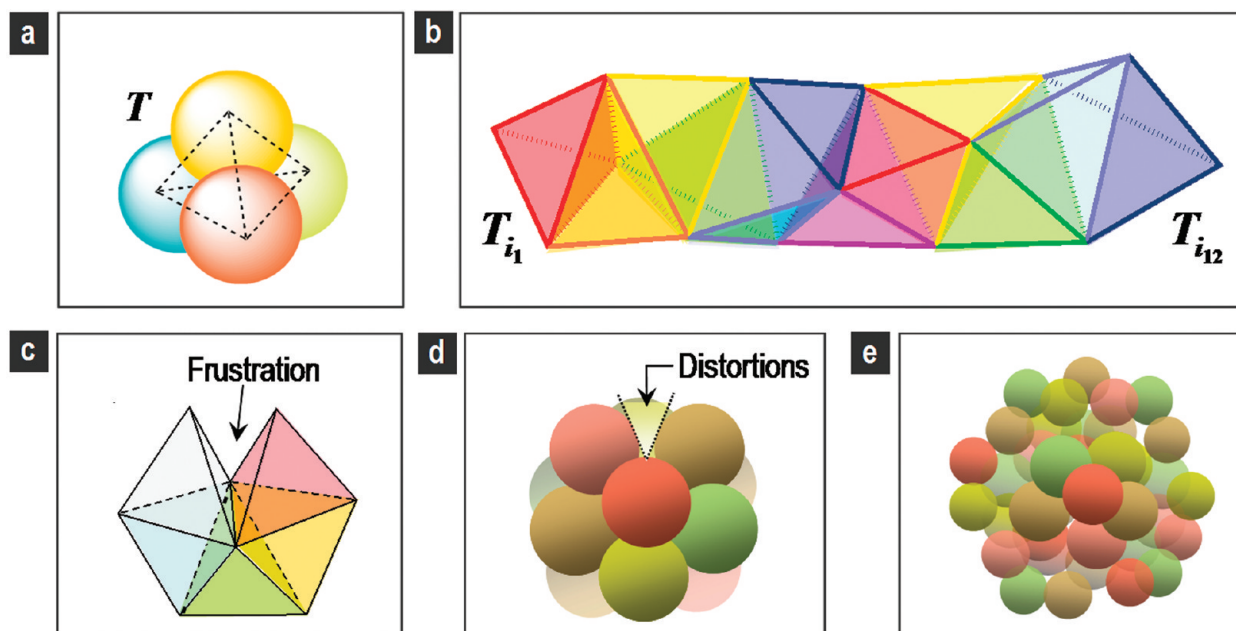


Figure 5. (a) Tightly packed tetrahedron unit; (b) tetrahedral chain cluster – Coxeter spiral; (c) tetrahedral cluster bracelet with distortion; (d) icosahedral packing with a homogeneous distribution of distortions; (e) cracks in the outer shell.

of spheres to the cluster enlarges the unpacked space and causes cracks between spheres in the outermost shell to become progressively larger (Figure 5e).

The above theoretical finding can explain the formation of colloidal sphere packing obtained in the experiments. Moreover, the distortion symmetry (quasicrystal form) of colloidal silica packing spheres with primary particle number $n = 13$ (Figure 3a) was confirmed by this theoretical result. Also, as shown in Figure 3a, greater numbers of primary particles ($n > 13$) resulted in a greater disordering of spheres. The quasicrystalline form that was observed in aggregate particles disappeared in the prepared porous aggregates (Figure 3b), as two differently sized colloidal particles were used in the precursor. It may be that the smaller colloidal silica particles filled the spaces formed between the larger spherical particles, resulting in the fixing/adjustment of the larger spheres' crystallization during evaporation of the droplet.

CONCLUSION

Aerosol-assisted spray-drying is a useful method for the production of crystal-like nanoparticles with a desired morphology and symmetry. In the case of uniform colloidal spheres, the formation of tightly packed spheres (aggregate particles) with simple symmetry as well as broken symmetry (quasicrystal) form was ob-

served. Highly ordered porous and hollow nanostructured particles were produced with the addition of template PS particles and with control of the zeta potential of the colloids. The template particles were used for skeleton formation by organizing silica particles around a PS core. The final structure of the porous and hollow crystal-like particles depends on the initial concentration of particles, the particle size and the zeta potentials of the silica and PS particles. A theoretical approach that considered tight packing of several spheres into frustrated clusters (quasicrystal form) with short-range icosahedral symmetry was investigated, confirming the mechanism of structure formation in the experiment. The quasicrystalline form that was observed in aggregate particles disappeared when two differently sized colloidal particles were used in the precursor, as smaller colloidal silica particles filled the spaces formed between the PS particles. This resulted in the fixing/adjustment of the PS crystallization during the evaporation of droplets. This methodology could be extended to produce nanoparticles with different chemical compositions. The resulting nanostructures may possess functional properties applicable to catalysis, chromatography, sensors, electro-optics, controlled drug release, and integrated reaction-separation processes, as well as many other applications.

EXPERIMENTAL METHODS

Chemicals and Materials. Two sizes of silica colloidal particles (5 and 100 nm in diameter, Nissan Chemical Industry, Co., Japan) were purchased. Polystyrene latex (100 and 200 nm in diameter) was purchased from Japan Synthetic Rubber, Japan (JSR). All chemicals and reagents were used as received.

Experimental Setup. Figure S1 shows the experimental setup for the spray-drying technique used in this study. After suspension of the silica and/or PS colloids in water, the method consists of three steps: the generation of droplets, the formation of a particle in an electric furnace, and the collection of the generated particles. The experimental procedure has been explained in de-

tail in a previous investigation.³⁴ An ultrasonic nebulizer (1.7 MHz, NE-U17, Omron, Co. Ltd., Tokyo, Japan) was used as a droplet generator. A homemade cyclone connector was used to obtain monodispersed droplets with a regular size distribution by removing large droplets from the spray stream.²⁵

Synthesis of Large Aggregated Structure Particles. Spherical silica colloids, with a homogeneous colloidal size of 100 nm, were used as the precursor in the generation of aggregated silica particle structures. To preserve the particle size, the as-prepared colloidal silica nanoparticles were diluted with ultrapure water to obtain colloidal silica nanoparticle precursors at a concentration of 0.05 and 0.1 wt %. The colloidal precursor was atomized using an ultrasonic nebulizer to generate droplets. The droplets were carried out in nitrogen gas at a flow rate of 1.2 L/min and were introduced into a 120 °C electric tubular furnace, where water was removed from the suspension. Aggregated structures of large silica particles were prepared as a result.

Preparation of Porous Structure Aggregates. Porous structure aggregates were prepared using a mixture of silica and PS colloids as the precursor. The precursor, consisting of negatively charged silica colloidal particles (5 nm in diameter, ζ potential = -20 mV) as the main material and negatively charged PS colloidal particles (200 nm in diameter, ζ potential = -40 mV) as the templating material, was diluted with ultrapure water. The ζ potential was measured with an electrophoretic light-scattering instrument (ELS-8000, Photal Otsuka Electronics, Osaka, Japan) to determine the particles' surface charges. The samples of porous aggregates were prepared using the precursor of 10 mL of the 0.05 wt % colloidal silica nanoparticles with 1 mL of 1 wt % PS particles. Droplets of the precursor were generated by atomizing and carried by nitrogen gas at a flow rate of 0.75 L/min. An electric tubular furnace consisting of low- and high-temperature zones from 120 to 600 °C was used as the particle generator. The generated droplets were carried through the low-temperature zone of the furnace, where water was removed from the suspension. As a result, silica and PS composite particles were formed as dry composites. After the composite particles were carried into the high temperature zone of the furnace, the PS evaporated, yielding a collection of voids. Thus, porous aggregates were obtained from the spray-drying process.

Preparation of Hollow Structure Aggregates. Hollow structure aggregates were produced using silica and PS particles with different surface charges. The precursor, consisting of negatively charged colloidal silica particles (5 nm in diameter, ζ potential = -20 mV) and positively charged colloidal PS particles (230 nm in diameter, ζ potential = +40 mV, prepared in our laboratory³⁵), was diluted with ultrapure water. The hollow aggregates were prepared using a precursor of 10 mL of the 0.05 wt % colloidal silica nanoparticles with 1 mL of 1 wt % colloidal PS particles. The sprayed droplets were carried by nitrogen at a flow rate of 0.75 L/min and introduced into an electric furnace. In the low-temperature zone, 120 °C, the droplets shrunk due to water evaporation, and a solid system of silica and PS particles was formed. These particles were introduced into the high-temperature zone at 600 °C, where the PS particles evaporated. At this point, the final hollow structure aggregates were formed.

Structure Observation and Classification. The generated particles leaving the furnace were then introduced into an Am-241 neutralizer and charged before introducing the DMA. The DMA (model 3081, TSI Inc., USA) classifies the charged particles to monodisperse particles of a known particle electrical mobility diameter. Propagated particles were collected on a quartz filter for 30 min. The structure and morphology of the resultant particles were examined by field emission scanning electron microscopy (FE-SEM, S-5000, Hitachi Ltd., Tokyo, Japan) operating at 20 kV.

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Supporting Information Available: Figure S1: The spray-drying process with an ultrasonic nebulizer used as the atomizer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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