

Oriented Aggregation: Formation and Transformation of Mesocrystal Intermediates Revealed

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Over the past 10 years, oriented aggregation has received increasing attention in the scientific literature.^{1–5} Oriented aggregation is a nonclassical crystal growth mechanism that involves the self-assembly of primary nanocrystals, crystallographic reorganization within the self-assemblies, and conversion to oriented aggregates, which are new secondary crystals.^{3,6} These new secondary structures can be composed of a few to hundreds of primary units. Final oriented aggregates often have symmetry-defying morphologies and can exhibit hierarchical structure. Evidence of crystal growth by oriented aggregation is frequently observed in the synthesis of metal oxides, selenides, and sulfides from initially homogeneous solutions. Recent work has shown that exploiting oriented aggregation can lead to the production of anisotropic nanoparticles (e.g., elongated particles) in high yield and with size control.^{7,8} Oriented aggregation offers the potential to tune material properties by controlling defect concentrations, morphology, and size as well as size distribution.

Recently, Cölfen and Niederberger⁹ defined a “mesocrystal” as a particle composed of primary units in crystallographic registry but without coherent, crystalline material linking them.² In such an object, solvent molecules and/or other species are located in the spaces between the aligned crystallites (Figure 1, top). While the term mesocrystal is not widely accepted, we adopt its usage here. The formation of a mesocrystal has been suggested as a required intermediate step of oriented aggregation.¹⁰ In this state, the primary nanocrystals achieve crystallographic alignment despite spatial separation from one another. This mesocrystal is analogous to the particle–particle outer sphere complex (P•••P) described by the oriented aggregation mechanism of Penn and co-workers,^{3,9} but with the requirement of crystallographic alignment of the primary units. The mesocrystal intermediates eventually fuse into oriented aggregates, which are new single crystals (Figure 1, bottom). The transition from a mesocrystal, which has a substantial inner surface due to the spatial separation between the primary building block crystallites, to a compact single crystal in a solution of saturated D,L-alanine was monitored using time-resolved small angle neutron scattering (SANS) and dynamic light scattering (DLS).¹⁰

Here, we present the first direct observation of mesocrystals with the size and shape similar to those of product oriented aggregates by employing cryogenic transmission electron microscopy (cryo-TEM) to directly image the particles in aqueous suspension. Cryo-TEM enables direct observation of nanoparticles in aqueous suspension by preserving the three-dimensional arrangement of nanoparticles in their native environment through vitrification of water. This technique has been used to study the arrangement of magnetic nanoparticles in a ferrofluid in the presence of a magnetic

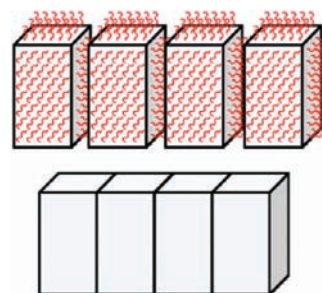


Figure 1. Schematics of a mesocrystal (top) and oriented aggregate (bottom).

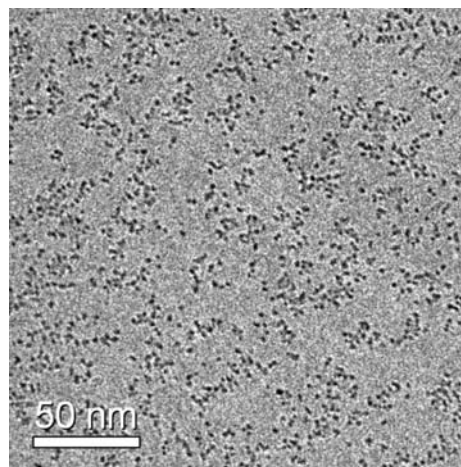


Figure 2. Cryo-TEM image of freshly prepared suspension of ferrihydrite after dialysis (pH 4).

field,¹¹ gold nanoparticle superlattices,¹² and the template-directed growth of calcite crystals from solution.¹³

For our experiments, an aqueous suspension of ferrihydrite nanoparticles was prepared by the controlled hydrolysis of a homogeneous ferric nitrate solution at 45 °C following methods that have been previously published.^{7,14} The dialyzed suspension was diluted to 0.42 g/L ferrihydrite, using $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ as the ferrihydrite chemical formula,¹⁵ and aged at 80 °C, with sampling at various times. The samples were cooled to room temperature prior to vitrification. The time elapsed between sample withdrawal at aging temperature and vitrification was approximately 30 min. Based on our room temperature study (unpublished work), the effect of the 30 min period at room temperature on the aging process is expected to be negligible. Samples were vitrified in liquid ethane using a Vitrobot Mark IV (FEI Company) and cryogenically transferred in liquid nitrogen to the cryo-TEM holder, which was then inserted into the microscope (FEI Tecnai T12 or FEI Tecnai F30 for high resolution). The temperature of the sample was

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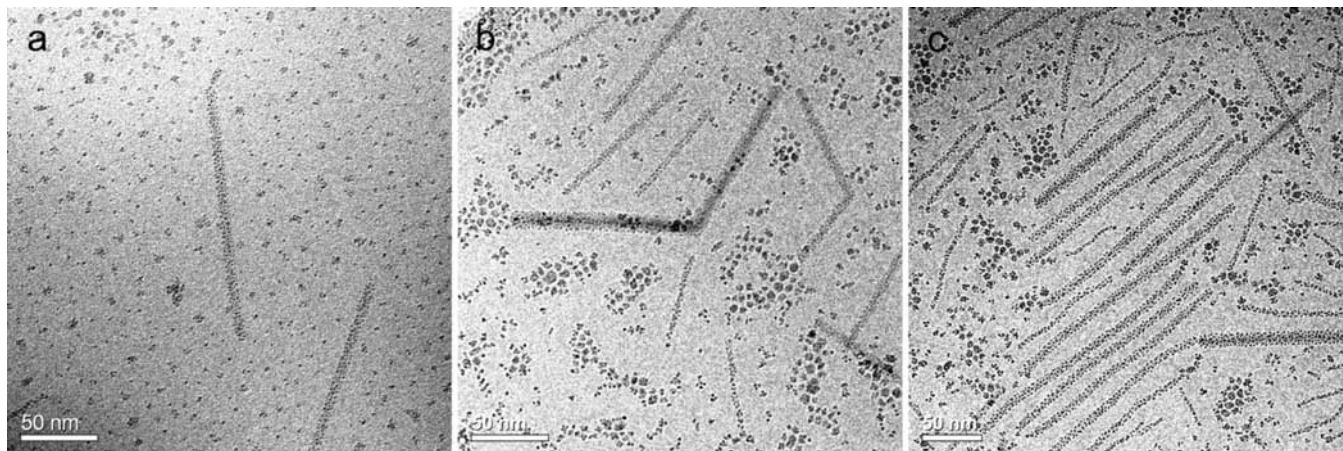


Figure 3. Cryo-TEM images of goethite mesocrystals after (a) 5 days, (b) 10 days, (c) 24 days of aging at 80 °C.

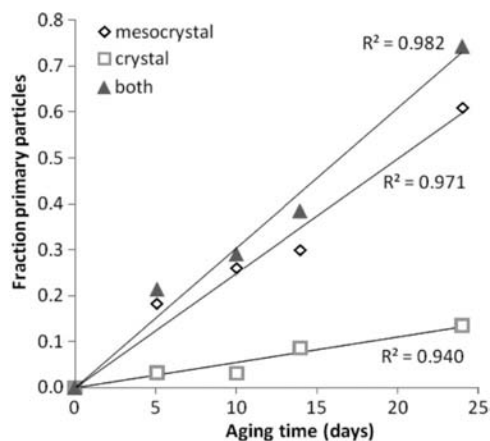


Figure 4. Estimated fraction of primary nanoparticles residing in mesocrystals (◇) and crystals (□) as a function of aging time. Estimates are based on image analysis of 71 cryo-TEM images. (▲) The sum of the fractions of primary particles residing in mesocrystals and crystals.

maintained at approximately -175 °C to prevent crystallization of ice. The goal of this method is to directly observe the nanoparticles as they exist in aqueous suspension. Low dose imaging conditions were employed because the thin film of vitreous water and the iron oxyhydroxide nanocrystals are sensitive to beam damage at the high magnifications required for high-resolution (HR) cryo-TEM.

Figure 2 shows a cryo-TEM image of the freshly prepared suspension of ferrihydrite. In general, this suspension is composed of isolated nanoparticles and relatively dense nanoclusters of a few to several hundred primary nanoparticles. As time progresses, the average number of primary nanoparticles per aggregate increases, and long, thin assemblies composed of primary particles begin to appear, with their number concentration increasing with time. Figure 3 shows representative cryo-TEM images of vitrified samples taken after 5 (Figure 3a), 10 (Figure 3b), and 24 (Figure 3c) days of aging at 80 °C. Image analysis of 71 images using ImageJ software (<http://rsbweb.nih.gov/ij/>) revealed that the fraction of primary particles residing in mesocrystals and crystals steadily increased with aging time (Figure 4). It should be noted that the fraction reported is a minimum estimate of the primary nanoparticles residing in the mesocrystals and finished crystals because the cryo-TEM images are two-dimensional projections of three-dimensional objects.

We hypothesize that these long, thin assemblies are mesocrystals composed of oriented goethite nanocrystals. This hypothesis is consistent with previous results showing that the ferrihydrite nanoparticles first transform to goethite prior to the formation of

oriented aggregates.¹⁴ In addition, the mesocrystals have sizes and shapes similar to those of the final goethite crystals as highlighted in Figure 5. In this figure, the mesocrystals are shown at a higher magnification and the insets are dry-TEM images of goethite nanocrystals grown by oriented aggregation. Figure 5a shows a mesocrystal that has a shape, size, and aspect ratio similar to those of the product goethite nanocrystals (inset of Figure 5a). This image is consistent with the mesocrystal as a precursor to a goethite nanorod. Interestingly, twinned mesocrystals also form (Figure 5b), and the angle between the two arms of the twinned mesocrystal (117.5°) exactly matches that of a twinned goethite crystal¹⁶ (inset of Figure 5b). This observation suggests that each arm of the mesocrystal has the goethite crystal structure and, thus, is composed of goethite nanocrystals that are crystallographically aligned with neighboring nanocrystals. The nanocrystals in the mesocrystals are

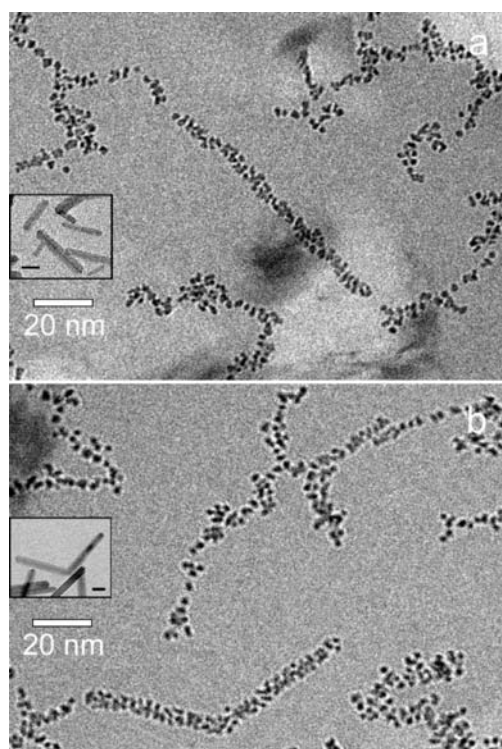


Figure 5. Cryo-TEM images of mesocrystals with size and shape similar to a product goethite nanorod (a) and twin (b) taken after 15 days of aging. Insets are dry-TEM images of product goethite crystals for shape and size comparisons. The scale bars in the insets both correspond to 20 nm.

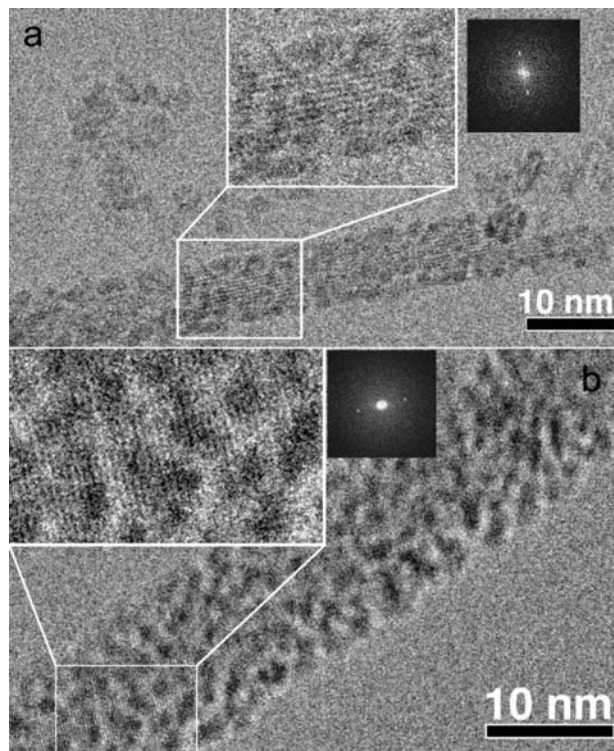


Figure 6. High resolution cryo-TEM images of mesocrystal intermediates showing lattice fringes that correspond to (a) (110) planes and (b) (021) planes of goethite. Samples were taken after 14 days of aging.

spatially separated from one another by a fraction of 1 nm despite the absence of added surfactants. It seems reasonable to assume that the interface contains solvent molecules (in this case, water).

The best evidence supporting the above hypothesis is the combination of the high-resolution cryo-TEM images shown in Figure 6, the lower magnification images shown in Figures 3 and 5, and observations of mesocrystal break-up during sublimation of the vitreous water with extended exposure to the electron beam. The representative, high-resolution images of Figure 6a and b clearly show the mesocrystals are composed of crystalline primary units that are crystallographically aligned with respect to one another and are elongated parallel to the *c* crystallographic axis of goethite. The lattice fringes, which span the entire length of the mesocrystal, correspond to the (110) and (021) planes in goethite, with *d*-spacings of 4.18 Å and 2.58 Å, respectively, and as highlighted by the Fast Fourier Transforms of the images. The lower magnification images (Figures 3 and 5), which are taken at greater defocus, confirm the spatial separation between the primary particles. Finally, as the vitreous water sublimates, the mesocrystals inside the vitreous water were observed to lose their rod-like appearance and break apart

into individual primary particles. These primary building-block particles then moved along with the retreating edge of the vitreous water until contacting the amorphous carbon support film.

The above observations strongly support the hypothesis that the mesocrystals are composed of oriented goethite nanocrystals. Moreover, it is consistent with the previous results by Burleson and Penn,¹⁴ showing that the phase transformation from ferrihydrite to goethite precedes the formation of the oriented aggregate. Finally, high-resolution cryo- and dry-TEM images of single crystalline oriented aggregates of goethite presented in Figures S1 and S2, respectively, show that the crystal orientation was preserved upon mesocrystal fusion into single crystalline products while still in the dispersed state.

These results support the supposition that the mesocrystal is a necessary precursor to the single-crystal oriented aggregate, support a multistep mechanism for oriented aggregation,² and represent a fundamental step forward in our understanding of the oriented aggregation crystal growth mechanism.

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Supporting Information Available: Detailed experimental procedure, high-resolution cryo and dry TEM images of single crystalline oriented aggregates are provided. This material is available free-of-charge via the Internet at <http://pubs.acs.org>.

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