# Mesocrystals — Properties and Applications

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ABSTRACT: Mesocrystals are a new class of nanostructured solid materials, which are most often made of crystallographically oriented nanoparticles. Structural features, properties, and possible applications of mesocrystals are summarized in this paper. Due to their unique structural features and the resulting physical and physicochemical properties, mesocrystals are expected to play a significant role in improving the performance of materials in many applications. These are as diverse as heterogeneous photocatalysts, electrodes, optoelectronics, biomedical materials, hard templates, and lightweight structural materials.
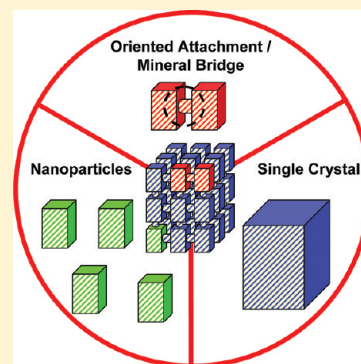
There is immense interest in potential applications of materials with critical dimensions on the order of nanometers. Manipulation of such objects into 1D, 2D, or 3D hierarchical structures with defined morphologies and/or properties is considered as an important step to the successful manufacture of nanodevices. These hierarchical structures may bring in new and collective properties that are different from those of the building units. Self-assembly has been studied for many years and is a feasible and facile way to manipulate nanoparticulate materials into hierarchical structures.

Mesocrystals are a new class of nanostructured solid materials.[1] In 2005, on the basis of detailed studies of the nanostructures and formation mechanisms of some biominerals and their mimetics, Cölfen et al.[2] proposed that the crystal growth of these materials may involve a nonclassical, self-assembly-based crystallization process (Figure 1, the red route).[2−5] The metastable intermediate involved in the process was defined as a "mesocrystal". Mesocrystals represent a new class of nanostructured solid materials, which are made of crystallographically oriented nanoparticles (Figure 1a−d). Although many mesocrystals reported in the literature form via a bottom-up route (Figure 1, the red route), it is still possible to employ other routes to mesocrystals. In previous work, we have shown that anatase TiO_2 mesocrystals can be prepared using NH_4TiOF_3 mesocrystals as precursors via a topotactic reaction.[6,7] Single-crystalline NH_4TiOF_3 materials may also be used as precursors to anatase TiO_2 mesocrystals via a topotactic reaction (Figure 1, the green route),[8] a process that we are working currently. In addition to crystallized materials, amorphous materials are often a good choice for the precursors that are used to prepare mesocrystals. Indeed, biomineralization research has shown that amorphous $CaCO_3$ may be transformed into $CaCO_3$ mesocrystals.[9−11] Hence, the sole criterion of determining whether a material is mesocrystal or not is the unique crystallographically hierarchical structure, not its formation mechanism.

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In the past 6 years, more and more attention has been paid to mesocrystalline materials. An increasing number of papers have been published in the literature. Most of these focused on the characterization of structures and the investigation of formation mechanisms. The results indicate that the structure and formation mechanism of a mesocrystal are related to the shape of the nanoparticle, colloidal stabilization, and vectorial long-range interaction potentials. Surface interaction between the nanoparticles plays a critical role during the formation process of a mesocrystal and may be responsible for the formation of external faces. The reason for the remarkably (almost perfectly in some cases) ordered alignment of nanoparticles is still poorly understood. Special emphasis has been placed on the different possible forces that may drive orientation and assembly between nanoparticles.[4] Diagrams of the four principal possibilities are shown in Figure 1a−d. Only tensorial polarization forces and dipole fields (Figure 1b) have
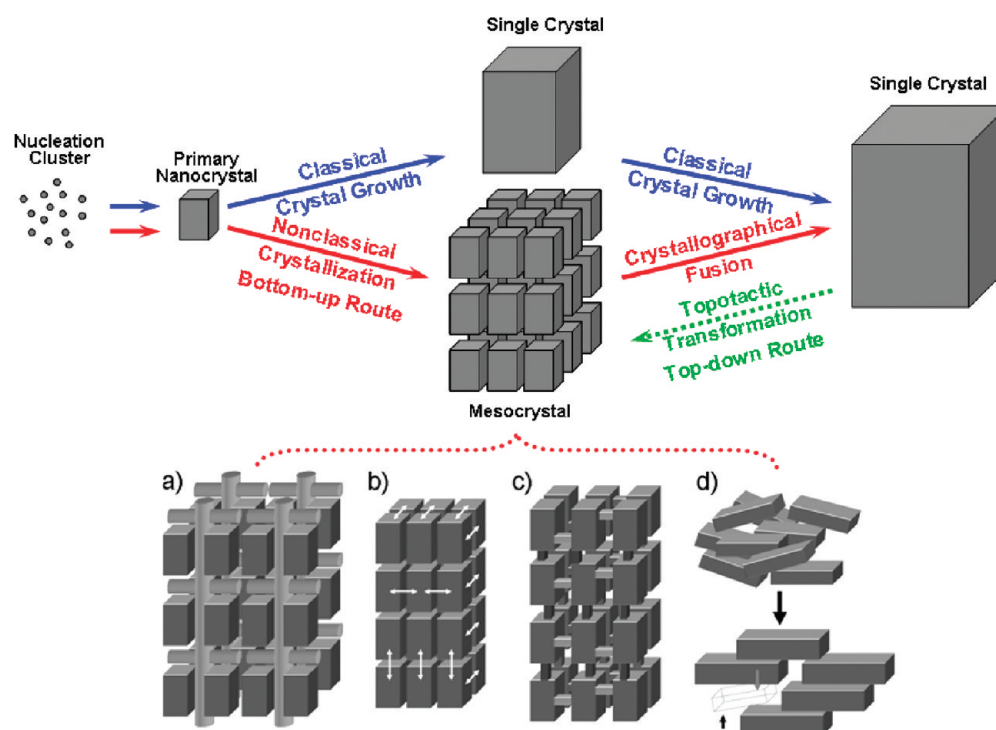
Figure 1. Classical crystallization (blue route) via ion-by-ion addition versus single-crystal formation (red route) by a mesocrystal intermediate made of nanoparticles. (a–d) Illustrative diagrams of the four principal possibilities that could explain the 3D oriented alignment of nanoparticles, (a) by an oriented organic matrix, (b) by physical fields or mutual alignment of identical crystal faces, (c) by epitaxial growth of a nanoparticle employing a mineral bridge connecting the two nanoparticles, and (d) by nanoparticle alignment by spatial constraints. (Reproduced from ref 4 with permission from John Wiley and Sons.)

been confirmed, and then only in some selected model systems.[12−17] The other possibilities are still speculative.

Although various mesocrystals such as $CaCO_3$, Fe_3O_4, TiO_2, ZnO, and $Ca_5(PO_4)_3(OH)$ have been successfully synthesized,[5] it is still a challenge to transfer these mesocrystal materials into applications, partly because their formation mechanisms are very complicated and still poorly understood. Moreover, the new physical and physicochemical properties arising from the hierarchical structures are not fully examined. There are few review papers focusing on the properties and applications of mesocrystals. In previous work,[1] we already summarized the possible types of and formation mechanisms of mesocrystals. In this Perspective, we are trying to put more effort into summarizing the properties of mesocrystals and especially detailing recent promising applications.

Because of the unique structural features of mesocrystals, there are different ways to look at these interesting entities. In a bottom-up view, a typical mesocrystal can be regarded as an aggregate of nanoparticles. Some properties belonging to a nanoparticle can be passed to the mesocrystal. One of the properties is the extremely high specific surface area. Inumaru[18] synthesized a $(NH_4)_3PW_{12}O_{40}$ mesocrystal by a homogeneous precipitation method. The BET surface area is close to 81 m^2 g^{-1}, which is comparable to the BET surface area of nanoparticles with a diameter of 12 nm. Mukhopadhyay et al.[19] reported a MgO mesocrystal with a BET surface area of 234 m^2 g^{-1}, comparable to the BET surface area of nanoparticles with a diameter of 6.2 nm. In some applications, mesocrystals can be used as potentially more stable analogues of nanoparticulate materials.

In a top-down view, a typical mesocrystal can be regarded as a single crystal with many nanoscale pores. Some properties belonging to a mesoporous (pore size 2−50 nm) material may

be owned by a mesocrystal. Internal high porosity is often observed in mesocrystals, which originates from unfilled interstices between nanoparticles. Nanoscale pores are visible in many mesocrystals with the help of TEM. The closed intracrystalline pores are good for thermal and dielectric insulation, while the open pores are accessible and good for adsorption and medical delivery. In some applications, mesocrystals can be used as mesoporous materials.

However, high porosity is not an essential feature of a mesocrystal. For some mesocrystals, the nanoscale pores may be occupied by organic/inorganic substances, leading to relatively low porosity. Gilbert et al.[9] suggested that some biominerals may form via amorphous precursors. The amorphous substances can remain in the final products and fully fill the nanoscale pores, leading to a very small specific surface area. The oriented attachment[20,21] (or mineral bridges[11,22]) existing between the nanoparticles is extremely important, which leads to relatively high crystallization degree and may be responsible for some unusual electronic and optical properties. In some applications, mesocrystals can be used as single-crystal materials.

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Mesocrystals are a class of very interesting solid materials. Due to their unique structural features, mesocrystals share some
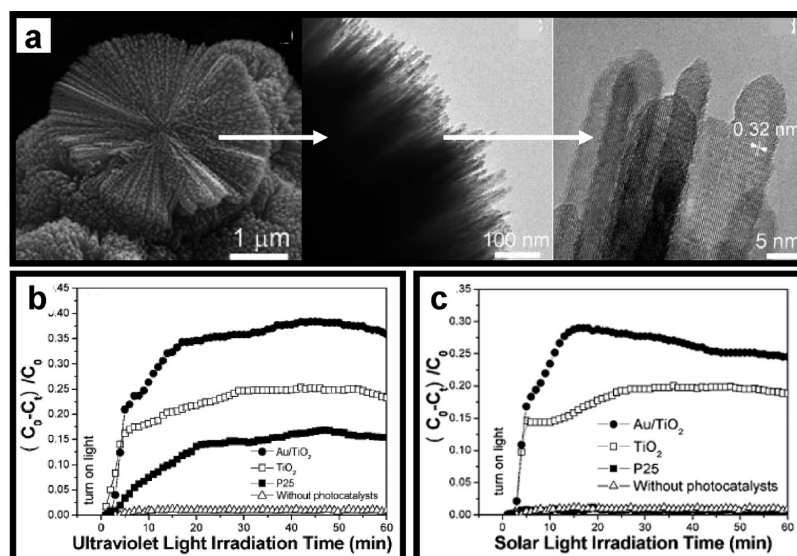
Figure 2. (a) TEM images of the rutile TiO_2 mesocrystals. (b, c) NO removal rate of rutile TiO_2, Au/rutile TiO_2, and P25 under UV light and simulated solar light. (Reproduced from ref 25 with permission from the Royal Society of Chemistry.)

similar properties with nanoparticulate, mesoporous, and single-crystal materials. Moreover, mesocrystals possess some unique physical and physicochemical properties that are different from those of the widely used materials, which may give better performance in some applications.

Heterogeneous Catalysts. The heterogeneous catalytic process is mainly related to the adsorption and desorption processes of reactant molecules on the surface of catalysts. Hence, it often requires a large specific surface area, which leads to more unsaturated surface coordination sites that are exposed to the reactant molecules. To a certain extent, many mesocrystals can be regarded as mesoporous materials. It is possible for these mesocrystals to take the place of conventional mesoporous materials in applications related to heterogeneous catalysis.

Zeng et al.[23] synthesized two kinds of CoO and ZnO nanocomposites, CoO/ZnO and $Zn_{1-x}Co_xO/Co_{1-y}Zn_yO$. Both the CoO core and the $Co_{1-y}Zn_yO$ shell are mesocrystalline. The CoO core and $Zn_{1-x}Co_xO/Co_{1-y}Zn_yO$ nanocomposite were used to catalyze the oxidation reaction of CO to CO_2. Both of them show significant catalytic abilities at a temperature as low as 60 °C and increased catalytic abilities at 120−140 °C. Apart from the possible contributions from the zinc dopant, the mesocrystalline attributes may also play an important role. The mesocrystalline structure of the CoO core and the $Co_{1-y}Zn_yO$ shell is responsible for the large specific surface area and leads to the enrichment of hydroxyl groups on the surface, which is beneficial to CO adsorption and thus its oxidation to CO_2.

In addition to small-molecule catalysis, mesocrystals are also good at adsorbing and fixing biomacromolecules, such as enzymes, proteins, and nucleic acids. Tartaj[24] synthesized spherical TiO_2 mesocrystals with mesoporosity and sizes of 50−70 nm. Under optimized conditions, the sample exhibits a very good lysozyme immobilization capability, which is very close to the best reported results for mesoporous silica and carbon.

Heterogeneous Photocatalysts. Heterogeneous photocatalysis is one of the most important, environmentally friendly, and clean chemical technologies in green chemistry. Performance of the photocatalytic reaction is highly related to the specific surface area, crystallite size, and dominant facet of the photocatalyst. Both a high degree of crystallinity and large porosity are needed

for good performance. The good crystallinity leads to faster and more efficient electron transfer. The large porosity results in more active positions to adsorb and react with reactants. Mesocrystals may have better potential than bulk single crystals or nanoparticles in heterogeneous photocatalysis. The above-mentioned anatase TiO_2 mesocrystals by Tartaj[24] not only show a good lysozyme immobilization capability but also are able to photocatalytically degrade organic compounds with the help of UV light. The good photocatalytic ability may be ascribed to the inherent good crystallinity of the TiO_2 mesocrystals, which minimizes the degradation of the properties associated with surfaces. The unique structural features of the TiO_2 mesocrystals make sure that the good crystallinity does not largely undermine the specific surface area.

Another exciting example is the rutile TiO_2 mesocrystals synthesized by Yu et al.[25] using a microwave-assisted hydrothermal method. The TiO_2 mesocrystals are composed of rutile nanowires with an average aspect ratio of 267 (Figure 2a). These mesocrystals show excellent photocatalytic activity and stability in NO removal under UV or simulated solar light irradiation (Figure 2b and c). The Au modification of the TiO_2 mesocrystals can lead to a 50% improvement in photocatalytic performance. The authors ascribed the high photocatalytic ability to the following three factors. First, the rutile TiO_2 nanowires (i.e., the building blocks) have a high aspect ratio, allowing fast charge transport. Second, the TiO_2 mesocrystals (i.e., the built entities) have a large effective surface area, making diffusive transport of photogenerated holes to oxidizable species easier. Finally, the open pores (i.e., interstices between the building blocks) allow efficient penetration of light and diffusion of NO molecules into the photocatalyst. Moreover, the TiO_2 mesocrystals have macroscale dimensions, which make them easier to recycle than the nanoparticulate photocatalytic powders.

In addition to TiO_2, other substances have also been made into mesocrystal architectures and used as photocatalysts. Xue et al. reported[26] a successful synthesis of BiOBr microspheres (Figure 3a) made of mesocrystal nanosheets. These microspheres show excellent adsorption and photocatalytic ability (Figure 3b−d), which are partly ascribed to the large specific surface area of the nanosheets. The unusual hierarchical
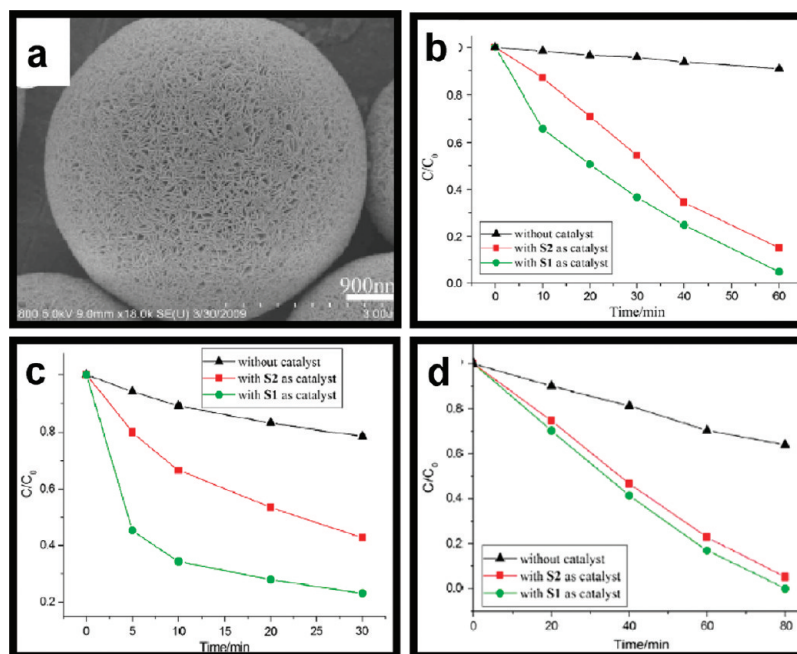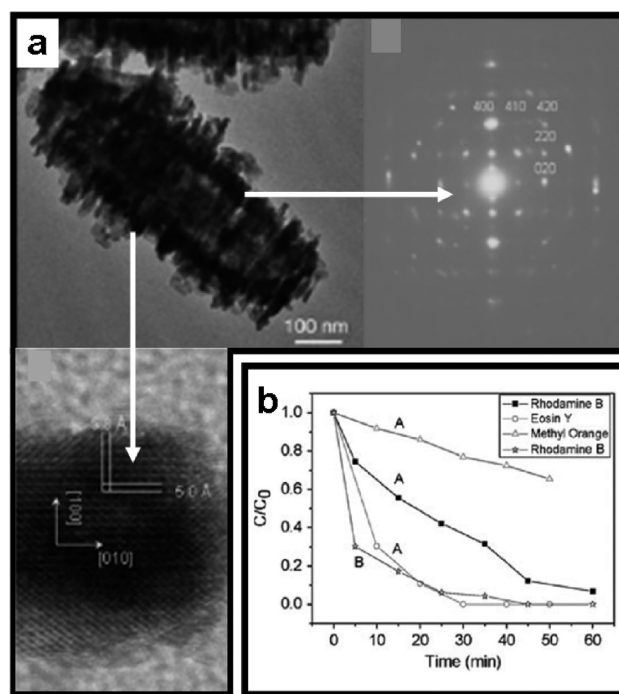
Figure 3. (a) TEM images and SAED pattern of the BiOBr microspheres (S1) composed of mesocrystal nanosheets. Photodegradation efficiencies of methyl orange (b), rhodamine B (c), and phenol (d) as a function of irradiation time. S1 and S2 represent the samples prepared with and without oleic acid respectively. (Reproduced from ref 26 with permission from Elsevier.)

structure of the microspheres puts thousands of the mesocrystal nanosheets together and therefore leads to a large number of unsaturated surface coordination sites, which are exposed to the pollutant molecules in solution and have strong adsorption capacity. The unique structural features allow the more efficient transport of reactant molecules to the active sites and therefore promote the performance of the BiOBr microspheres as photocatalysts. The relatively high crystallinity of the BiOBr nanosheets may also play an important role by facilitating the transfer of electrons and holes and thus the degradation of pollutants. Pancake-like $Fe_2(MoO_4)_3$ mesocrystals[27] also show excellent photocatalytic ability in the degradation of bromopyrogallol red.

In some cases, selective photocatalytic ability was also achieved. As a semiconductor, with a band gap at around 3.12 eV, $AgIn(WO_4)_2$ has proven to possess high photocatalytic activity under UV light. Yu et al.[28] synthesized $AgIn(WO_4)_2$ mesocrystals (Figure 4a) by a microwave method. The mesocrystals are made of two parts, an olive-like core and a striated pattern of outgrowths that are vertical to the core. The photocatalytic experiments indicate that the photodegradation process of eosin Y is much faster than that of rhodamine B or methyl orange (Figure 4b), suggesting a selective photocatalytic ability. The selectivity may be ascribed to the special interaction between the organic molecules and the surfaces of the outgrowths.

Electrode Materials. Similar to the photocatalytic materials, the performance of electrode materials is highly related to specific surface area and the degree of crystallinity. Pang et al.[29] synthesized $W_{18}O_{49}$ mesocrystals, which have a regular hexagonal shape and are made of highly ordered ultrathin nanowires (Figure 5a). Due to the high surface-to-volume ratio and small grain size of the nanowires (i.e., the basic building blocks), the $W_{18}O_{49}$ mesocrystals possess good electrochemical properties (Figure 5b and c), a fast electron−proton transfer rate, good stability, and large pseudocapacitive capacitance. The average specific

Figure 4. (a) TEM images and SAED pattern of a typical $AgIn(WO_4)_2$ mesocrystal. (b) Photocatalytic degradation of different organic dyes with $AgIn(WO_4)_2$ mesocrystals. (Reproduced from ref 28 with permission from the Royal Society of Chemistry.)

capacitance of the $W_{18}O_{49}$ mesocrystals can reach 579 F g^{-1} at a scan rate of 20 mV s^{-1} and 491 F g^{-1} at 200 mV s^{-1}, potentially making them advantageous in supercapacitors.

Mesocrystals can also be used in lithium ion batteries as either anode or cathode materials. Qi et al.[30] synthesized anatase TiO_2 mesocrystals, which are made of [001]-oriented anatase nanoparticles (Figure 6a) and exhibit remarkable
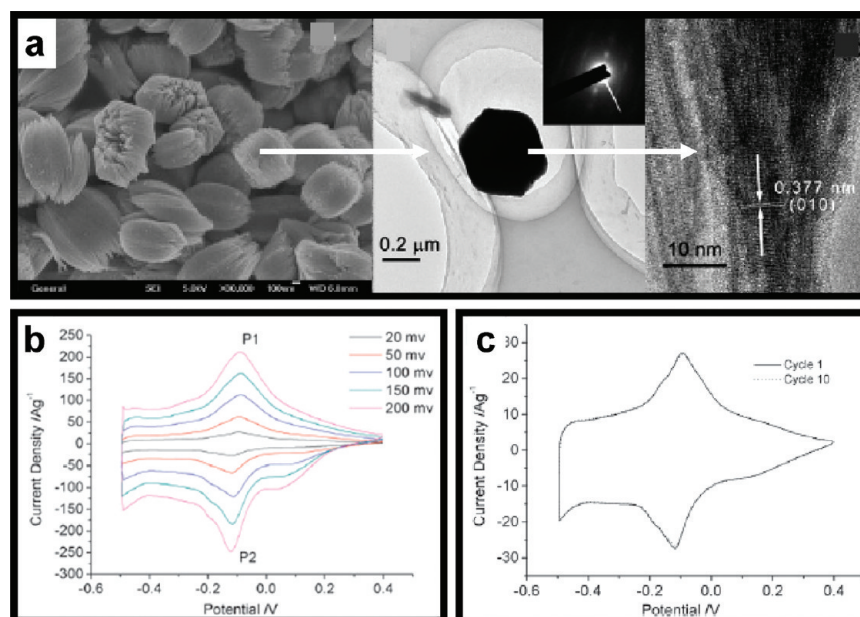
Figure 5. (a) TEM images and SAED pattern of the $W_{18}O_{49}$ mesocrystals. (b) Cyclic voltammetry of the mesocrystals. (c) Comparative voltammograms between the 1st and the 10th cycle voltammograms. (Reproduced from ref 29 with permission from the Royal Society of Chemistry.)
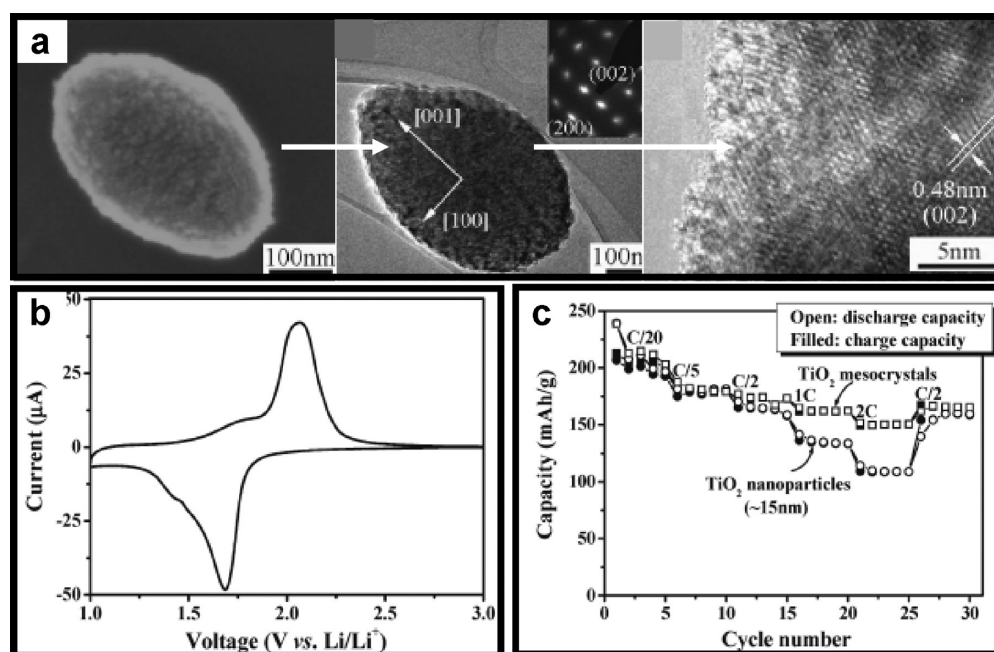
Figure 6. (a) TEM images and SAED pattern of the anatase TiO_2 mesocrystals. (b) Cyclic voltammograms of the TiO_2 mesocrystals. (c) Rate capability of nanoporous mesocrystals and nanocrystals of anatase TiO_2 from C/20 to 2 C (1 C = 170 mA g^{-1}) for five cycles. (Reproduced from ref 30.)

crystalline-phase stability and improved performance as anode materials for lithium ion batteries. The pure anatase phase can be retained even after being sintered at 900 °C. The crystalline-phase stability has been ascribed to the crystallographically oriented arrangement and infusion between the TiO_2 nanoparticles, which leads to the decrease of the interfacial nucleation sites for the rutile phase. The oriented arrangement and infusion are also responsible for the decrease of the grain boundaries between the TiO_2 nanoparticles and thus the facile electronic conduction and fast Li ion transport between the electrolyte and the mesocryatal electrode, which leads to the better rate in the TiO_2 mesocrystals than that in TiO_2

nanocrystals at high current rate (Figure 6b and c). The uniformly porous structure of the mesocrystals can facilitate their contact with the electrolyte and hence is also advantageous to the fast Li ion transport. The TiO_2 mesocrystals are able to deliver specific discharge capacities of 164.9 and 151.7 mA·h g^{-1} at 1 and 2 C, which are larger than that of the reported TiO_2 hollow spheres and comparable with that of the reported mesoporous spheres.

Niederberger et al.[31] synthesized $LiFePO_4$ mesocrystals, which are built of slightly elongated nanoparticles of about 100 nm. The $LiFePO_4$ mesocrystals exhibit high discharge capacities of ~150 mA·h g^{-1} and very stable cycling

Figure 7. (a) Morphology-dependent PL spectra of AgIn(WO$_4$)$_2$ materials. (b) The excitation spectra of the AgIn(WO$_4$)$_2$ materials using 560 nm as the emission wavelength. Samplez 1−5 present the samples prepared at different initial concentrations of the precursors. The number of outgrowths of the AgIn(WO$_4$)$_2$ mesocrystals decreases from sample 1 to 5. (Reproduced from ref 32 with permission from Springer.)

performances. The LiFePO$_4$ mesocrystals also show an excellent rate capacity (81%) even after ∼50 cycles and up to a discharge rate of 4 C. The authors did not clarify the relationship between the unique structural features and the performance of the LiFePO$_4$ mesocrystals and only suggested that there may be a relationship between them.

Optoelectronic Materials. The optoelectronic properties of semiconductors are highly dependent on their structural features. As a group of novel nanostructured materials, mesocrystals are expected to exhibit some interesting and synergetic optoelectronic properties. In addition to the photocatalytic ability, the above-mentioned AgIn(WO$_4$)$_2$ mesocrystals[32] (Figure 4a) also show interesting white emission when irradiated by visible light and are a good choice for optoelectronic materials. Their photoluminescence intensities can be modulated by the number of outgrowths on the core (Figure 7). The larger the number of outgrowths, the stronger the resultant emission intensity. The high surface-to-volume ratios are responsible for electron−hole recombination, leading to a large reorganization in the local charge distribution and thus the strong vibronic transitions and broad emission bands. The high surface-to-volume ratio is also responsible for the efficient and fast trapping of photogenerated holes at surface sites for radiative recombination of charge carriers.

Chu et al.[33] synthesized ZnO mesocrystal microspheres with a core−shell structure in which the densely packed hexagonal nanoplates are vertical to the sphere core. The ZnO mesocrystals show strong mechanical resonance and radiative emission at ∼0.36 THz under continuous green wave laser irradiation. The quantum efficiency of converting the incident power into terahertz radiation is about 33%, which is comparable with existing terahertz-emitting materials. The mechanical resonance and radiation originate from the coherent vibration of the hexagonal ZnO nanoplates (i.e., the basic building blocks), which are induced by the laser irradiation.

Xu et al.[34] prepared vertical nanowall arrays of Co-doped ZnO mesocrystals on p-Si plates. The resultant n-Zn$_{1−x}$Co$_x$O nanowall/p-Si heterojunction exhibits a well-defined and reliable rectifying ability. The turn-on voltage can be tuned by the Co^{2+} concentration. Moreover, the pn heterojunction is very stable. The rectifying performance can remain unchanged for over 3 months. The Co-doped ZnO mesocrystals have large specific surface area, which is advantageous to the application in the sensor field.

In addition to inorganic mesocrystals, the optoelectronic properties of the mesocrystals composed of small organic molecules were investigated. Cölfen et al.[35] synthesized

ultralong mesocrystal belts of 3,4,9,10-perylenetetracarboxylic acid potassium salt (PTCAPS). These mesocrystal belts are made of nanoparticles, whose {001} faces are stabilized by polymer complexation (Figure 8b and c). The PTCAPS

Figure 8. (a) I−V curves measured on PTCAPS belts deposited across a pair of gold electrodes separated by 70 μm, (A) in air and (B) under a saturated vapor of hydrazine. The inset shows the I−V curve measured for the reference PTCAPS single crystal under a saturated vapor of hydrazine. (b) Equilibrium morphology of PTCAPS calculated under vacuum by MS modeling. (Reproduced from ref 35.)

mesocrystal belts show a remarkably high electronic conductivity in the doped state (Figure 8a), which may benefit from the wirelike π−π interactions along the [020] long axis of the belts. In the presence of electron donors, the extended π-electron delocalization along the belts leads to the remarkably high electronic conductivity along the long axis, which is much higher than that of the corresponding single crystal. These mesocrystal belts will have some interesting applications in new types of optoelectronic devices.

Biomedical Materials. Due in part to similarities with biominerals in living organisms, nanostructured materials have been widely used as biomedical materials, such as tissue engineering scaffolds and drug carriers. As a class of novel nanostructured materials, possible applications of mesocrystals have also been tentatively examined.

Due to their biocompatibility and stability under physiological conditions, water-soluble Fe$_3$O$_4$ nanoparticles with superparamagnetic properties have been widely used as targeting transporters in biomedical applications. In order to make them water-soluble, the sizes of the Fe$_3$O$_4$ nanocrystals have to be very small. However, when their sizes are as small as 10 nm, it becomes very hard to separate and control Fe$_3$O$_4$ nanocrystals using a magnetic field due to a very low magnetization. Increasing the size of Fe$_3$O$_4$ nanocrystals can increase their saturation magnetization. The superparamagnetic−ferromagnetic transition occurs at a domain size of ∼30 nm for Fe$_3$O$_4$, which limits the

possible useful size of F_3O_4.[4] Yin et al.[36] developed a method to prepare F_3O_4 mesocrystals, which may solve the problems and is able to increase magnetization while retaining the super-paramagnetic properties of F_3O_4 nanoparticles. The Fe_3O_4 mesocrystals are monodisperse, well-controlled between 30 to 180 nm, and composed of crystallographically oriented Fe_3O_4 nanocrystals with sizes from 6 to 10 nm. The Fe_3O_4 mesocrystals remain superparamagnetism even though their size exceeds 30 nm. The unique structural features of the Fe_3O_4 mesocrystals play a very important role as their magnetization is much higher than that of individual Fe_3O_4 nanocrystals. The Fe_3O_4 mesocrystals are ideal candidates as targeting transporters for medical applications, such as drug delivery, bioseparation, and magnetic resonance imaging.

In addition to using mesocrystals as targeting transporters in medial applications, the individual drug ingredients can also be fabricated into a mesocrystal form. Lee et al.[37] prepared mesocrystals of racemic (R,S)-($\pm$)-sodium ibuprofen dihydrate via a bioinspired method. The mesocrystals are well-faceted, highly separated, and composed of almost perfectly aligned nanoplates. The dissolution rate of the mesocrystals is quicker than that of its conventional counterpart. This mesocrystal architecture may provide a new paradigm in formulation design for the pharmaceutical industry.

Imai et al.[38] tried to repair the broken prismatic layer of seashell that was partially etched. The mesocrystal, macroscopic morphology, and specific crystallographic orientation could be reproduced in the repaired part (Figure 9). The authors
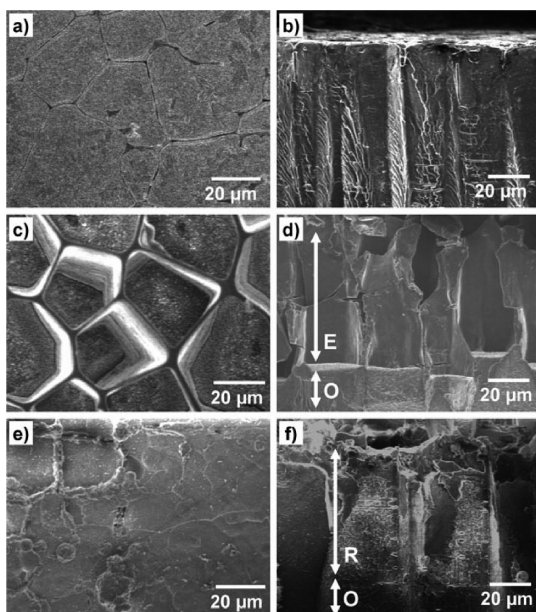
Figure 9. FESEM images of the prismatic layer of seashell during the different stages of the repairing procedure, (a, b) the original prismatic layer, (c, d) the partially etched layer. and (e, f) the regenerated layer. The left (a, c, e) and right (b, d, f) panels correspond to the top views and cross-sectional images, respectively. O = original part, E = etched part, and R = repaired part. (Reproduced from ref 38 with permission from John Wiley and Sons.)

suggested that organic macromolecules play important roles in the repairing process. The soluble macromolecules control the formation of the mesocrystals through the epitaxial growth from the original part. The insoluble macromolecule provides the confined space that leads to the macroscopic shape. Tooth enamel is the hardest biominerals in the human body and can

be regarded as a mesocrystal made of highly hierarchical and regularly oriented hydroxyapatite nanocrystals. Enamel loss is one of the most common tooth diseases and is difficult to restore. A lot of work[12–14] has been directed toward repairing damaged enamel. However, few methods are able to restore the unique enamel prism structure. That gives enamel extreme hardness. The approach Imai et al. proposed to repair the prismatic layer of seashell in vitro may also be extended to repair tooth enamel in vivo perfectly.

Hard Templates. Mesoporous materials are often used as hard templates for synthesized nanoparticles or nanostructured materials. Due to the similarity between mesoporous materials and mesocrystals, mesocrystals can also be used as hard templates. Li et al.[39] synthesized a Au nanoflake film, which is replicated from peptide mesocrystals. The film can give rise to useful and remarkable surface-enhanced Raman spectroscopy properties. The method is very facile and may lead to a new paradigm in the design of efficient substrates for active Raman spectroscopy.

Lightweight Structural Materials. From the origination of the mesocrystal concept, we know that there are a number of biominerals which can be classified as mesocrystals. In fact, Nature already exhibits potentially exciting applications for mesocrystals, such as providing structural materials that are hard as well as light. One strategy, which can be deduced from biominerals such as sea urchin skeleton and nacre, is the brick and mortar principle.[40] These biominerals have improved mechanical properties due to the optimized organization of the organic and inorganic nanoscale building blocks. A directional freeze-drying method[41,42] has been largely explored to prepare a lamellar porous structure, which simulates the structure of nacre on a micrometer scale. However, at the nanometer scale, approaches involving mesocrystals still present the best opportunity.

In conclusion, increasing efforts has been put onto transferring mesocrystals into various applications. Some results are very exciting. However, most of the research is at discovery by trial and error rather than driven by systematic principles. There are still several problems that should be resolved before mesocrystalline materials become widely used:

(1) An unambiguous classification of mesocrystals is needed. The classification should be based on the difference of structural features because different hierarchical structures mean different physical or physicochemical properties. Tentative suggestions[1] have been made, where the mesocrystal has been divided into three classes.

(2) Intensive research on formation mechanisms of various mesocrystals is also needed, which will lead to synthetic methods with good reproducibility. Self-assembly is a good strategy to prepare mesocrystals; however, sometimes, the process is hard to control. Minor change of synthesis conditions may lead to totally different products. For this reason, novel and non-self-assembly will be a beneficial supplement, such as topotactic transformation.

(3) Another problem is the shortage of research on the synergetic properties arising from the crystallographically ordered nanoparticles. High performance and good results in many cases are usually ascribed to the contribution of the properties from the individual nanoparticles. The roles that the interaction between the individual nanoparticles plays are less investigated

626

dx.doi.org/10.1021/jz2015742 | *J. Phys. Chem. Lett.* 2012, 3, 620–628

and discussed. However, the interaction is very important in telling us whether a mesocrystal is a better choice for a certain application than another material. In the future work on the properties of mesocrystals, it would be better to synthesize the corresponding nanoparticulate and single-crystal counterparts and clarify the difference between the properties of the family.

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Mesocrystals are, in terms of our understanding, a new class of hierarchically nanostructured solid materials. They are composed of crystallographically oriented nanoparticles and in fact widely exist in natural and synthetic materials. The nanoparticles are glued together by inorganic or organic linkers. Due to their unique structural features, mesocrystals have many physical and physicochemical properties that are different from those of usual nanoparticulate materials and single-crystal materials and therefore are expected to provide better performance in some applications.

In a bottom-up view, a mesocrystal is made of nanoparticles. Many properties belonging to the nanoparticles, such as the shape, specific surface areas, photocatalytic activity, superparamagnetism, photoluminescence behavior, and so forth, will be passed to the mesocrystal. If the fusion sites (i.e., oriented attachments/mineral bridges) between the nanoparticles are very few, the properties of the individual nanoparticles will largely determine the properties of a mesocrystal, which has been proved in many experiments summarized in this paper. In this case, the new properties arising from the synergetic effects may not be distinct. Some properties may be additive, such as the magnetism in the Fe_3O_4 case.[36] If there are many fusion sites between the nanoparticles, the crystallization degree increases and may lead to some new and synergetic properties that are highly related to the crystallized parts of the mesocrystals, such as the transport behaviors of electrons, ions, holes, and so forth. This kind of mesocrystals is needed in applications like photocatalysis, solar energy, energy storage, and optoelectronics. However, there is a balance between the crystallinity and specific surface area of a mesocrystal that needs to be optimized for each application and thus presents an ongoing challenge.

In a top-down view, a mesocrystal can be regarded as a bulk single crystal, where some components are replaced by an inorganic/organic substance to form a network structure. Due to their hierarchically structured and organic/inorganic hybrid features, it should be easy to give multiple functions to these materials, such as color, magnetism, electroconductivity by using doping, or composite technologies. The modification on the composite may largely increase the performance of a mesocrystal on a certain application. Another advantage of a mesocrystal is the relatively large size, which makes it easier to be handled and even potentially recycled in some applications, such as heterogeneous catalysis or photocatalysis. Their large size is also a benefit to biomedical application because it may decrease the public concerns about the safety of nanodimensional materials. In conclusion, research on mesocrystals is in its infancy stage, and a lot of problems are waiting to be resolved. However, according to the results from the literature, there will be an important position for mesocrystals in many applications.

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Notes
The authors declare no competing financial interest.

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