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Polymer-inorganic crystalline nanocomposite materials via nanoparticle occlusion

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Abstract: Efficient occlusion of guest nanoparticles into host single crystals opens up a straightforward and versatile way to construct functional crystalline nanocomposites. This new technique has attracted increasing research interest because it enables the composition, structure and property of the resulting nanocomposites to be well-controlled. In this review article, we aim to provide a comprehensive summary of nanoparticle occlusion within inorganic crystals. First, we summarize recently-developed strategies for the occlusion of various colloidal particles (e.g. diblock copolymer nanoparticles, polymer-modified inorganic nanoparticles, oil droplets, etc.) within host crystals (e.g. $CaCO_3$, ZnO or ZIF-8). Second, new results pertaining to spatially-controlled occlusion and the physical mechanism of nanoparticle occlusion are briefly discussed. Finally, we highlight the physicochemical properties and potential applications of various functional nanocomposite crystals constructed via nanoparticle occlusion and we also offer our perspective on the likely future for this research topic.

1. Introduction

Efficient nanoparticle occlusion within growing inorganic single crystals is rather counter-intuitive because crystallization normally excludes impurities, rather than promoting their inclusion.[1] This nascent research field has attracted increasing attention because it provides a highly convenient route for the preparation of a wide range of nanocomposite materials whereby various types of colloidal systems (e.g. polymeric latexes,[2] diblock copolymer micelles,[3] nano-sized oil droplets,[4] etc.) are incorporated within the inorganic crystalline lattice. The process of nanoparticle occlusion and the structure of the resulting nanocomposite are well-studied. The occurrence of nanoparticle occlusion has to overcome the incompatibility between the guest nanoparticles and host crystals (see **Figure 1**): First, the nanoparticles adsorb at the surface of a *growing* crystal and then they gradually become engulfed during the deposition of further inorganic ions (e.g. Ca^{2+} and CO_3^{2-} in the case of calcite crystals). Second, many guest nanoparticles are distributed throughout the host crystals so they clearly do not act as the nuclei for crystallization. This aspect differentiates such systems from core-shell hybrid materials.[5] Third, the guest nanoparticles are in intimate contact with the crystalline lattice, which nevertheless retains its long-range order. Clearly, nanoparticle occlusion differs significantly from alloying or mechanical blending.[6] There is no doubt that the former approach opens up interesting new avenues for the preparation of novel functional nanocomposite crystals.

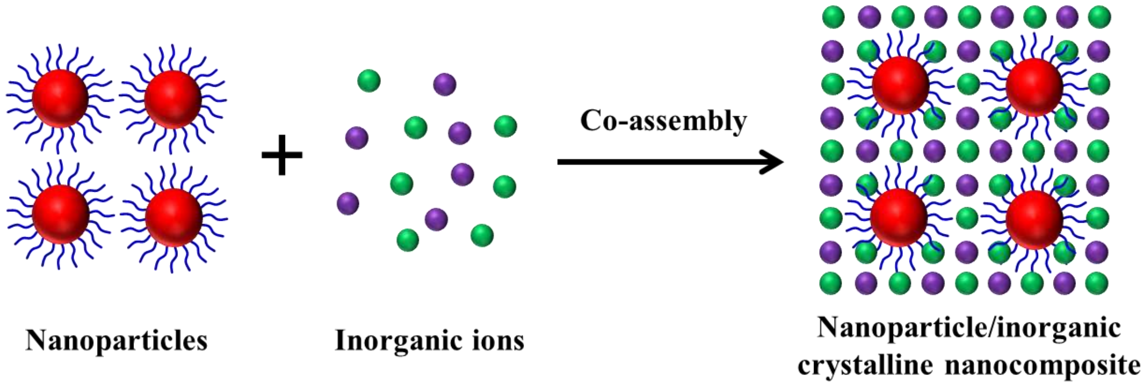

Figure 1. Schematic illustration of the occlusion of sterically-stabilized nanoparticles (e.g. diblock copolymer nanoparticles, polymer-modified inorganic nanoparticles or even polymeric surfactant stabilized nanoemulsions) within inorganic host crystals to produce new crystalline nanocomposite materials.

Such nanocomposite materials are composed of organic/inorganic components. This is analogous to biominerals, which are created by living creatures with nanocomposite structures as well.[7] Intimate interaction between various organic molecules and the inorganic matrix confers superior mechanical properties (e.g. hardness, toughness, etc.) that surpass those of the corresponding geological minerals.[8] Many attempts have been made to mimic the complex structure of biominerals [9] by using either naturally-occurring biopolymers or synthetic water-soluble polymers as additives.[10] However, efficient incorporation of nanoparticles within host crystals has been challenging. Wegner and co-workers added polystyrene latex particles bearing anionic carboxylate surface groups during the formation of ZnO in aqueous media.[11] Scanning electron microscopy (SEM) studies confirmed the porous nature of the ZnO particles, suggesting successful incorporation of the organic component.[12] However, it was not clear whether such latexes were uniformly incorporated throughout the host crystals or merely confined to the surface. Indeed, Qi et al. reported that a similar polystyrene latex was only located at the surface of calcite ($CaCO_3$) crystals.[13] Nevertheless, these pioneering studies were the first to demonstrate the feasibility of the occlusion of organic nanoparticles within inorganic host crystals. In 2010, Meldrum and co-workers used SEM to show that similar polystyrene latex particles bearing high carboxylic acid content could be uniformly distributed throughout calcite crystals.[14]

Over the past eight years, we have exploited recent developments in polymerization-induced self-assembly (PISA)[15] to design a range of well-defined diblock copolymer nanoparticles in order to identify which parameters influence nanoparticle occlusion within host crystals (e.g. calcite, ZnO, etc.).[16] Such studies suggest that the surface chemistry of the guest nanoparticles is the key factor that determines their efficient occlusion.[1a] For example, the precise nature of the anionic character of sterically-stabilized diblock copolymer nanoparticles (e.g. whether they bear carboxylic acid,[16b, 16c] phosphate[16e, 16h] or sulfate groups[16d]) determines their extent of occlusion within calcite crystals. The mean degree of polymerization (DP) of the steric stabilizer chains can also play a vital role in promoting efficient interaction between the nanoparticles and the growing crystal surface.[16c, 16f] Sufficient colloidal stability in the presence of those inorganic ions that form the host crystal (e.g. Ca^{2+} and CO_3^{2-} ions for calcite, etc.) is another important prerequisite for efficient nanoparticle occlusion.[16g] Moreover, the surface density of the steric stabilizer chains and their overall charge can profoundly affect the degree of occlusion.[16b, 16e] Perhaps surprisingly, the particle size and morphology of the guest nanoparticles do not appear to play a decisive role in nanoparticle occlusion.[4, 17]

In this review, we first summarize the strategies that have developed for the incorporation of various nanoparticles into a range of host crystals. Then, we discuss recent developments in achieving spatially-controlled occlusion and identifying nanoparticle occlusion mechanisms, followed by the properties and potential applications of the resulting nanocomposite crystals. Finally, a timely perspective is offered on the likely future of this research field. We hope that this overview will inspire polymer chemists and materials scientists to explore this fascinating route to new functional nanocomposite crystals.

2. Strategies for Nanoparticle Occlusion within Inorganic Crystals

Efficient nanoparticle incorporation must overcome the inherent chemical incompatibility between the organic guest nanoparticles and the inorganic host matrix. Clearly, the surface chemistry of the guest nanoparticles must play a key role in promoting occlusion. In some cases, active occlusion within host crystals can be achieved when using nanoparticles with appropriate surface functionality.[14, 18] However, in some other cases the putative guest is excluded from the growing crystal lattice. Thus, an alternative approach is required for such passive nanoparticles. Various strategies for achieving nanoparticle occlusion are outlined below and their relative advantages and disadvantages are briefly discussed.

2.1. Direct Occlusion

Appropriate surface chemistry (e.g. surface charge, surface stabilizer chain length, surface stabilizer chain density, etc.) is the prerequisite for direct nanoparticle occlusion.[1a] For calcite crystals, anionic surface character is important because the surface of the growing calcite is positively charged.[16b] Ionic interactions facilitate the adsorption of guest nanoparticles onto the surface of the growing crystal, which is believed to be the critical first step for nanoparticle occlusion.[19] For ZnO crystals, anionic character similarly promotes nanoparticle occlusion, but it can also cause a significant change in crystal morphology.[12, 16a] Moreover, surface stabilizer chain length and stabilizer chain density are essential for providing interaction sites between the guest nanoparticles and the host calcite crystals, thus promoting efficient nanoparticle occlusion.[16d, 16f] Last but not least, good colloidal stability is vital to ensure the successful occlusion of nanoparticles.[16c]

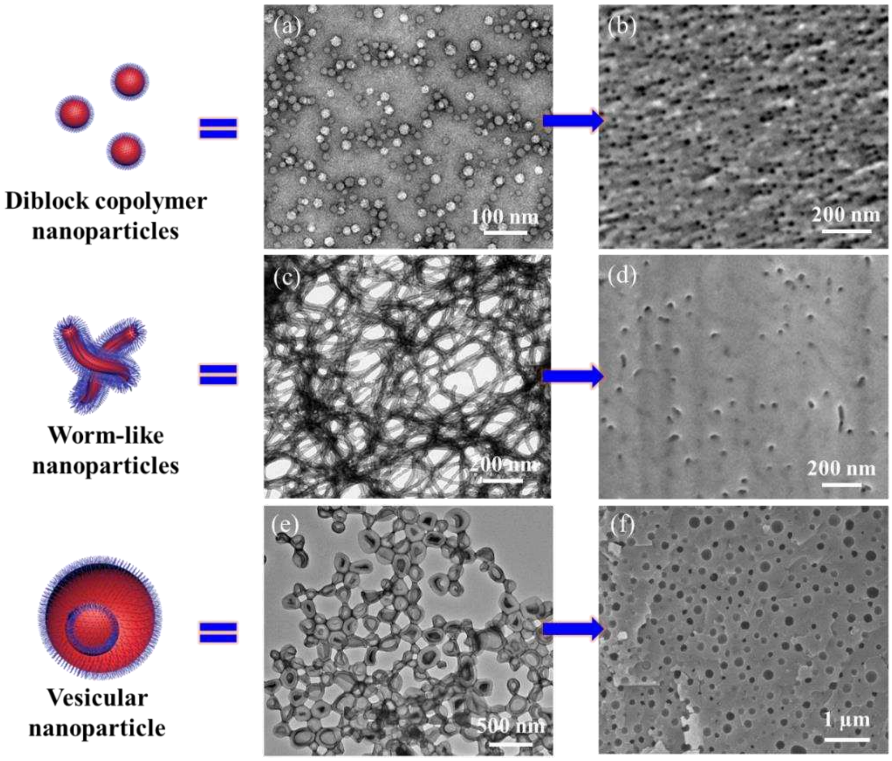

Figure 2. Direct occlusion of three types of diblock copolymer nanoparticles within calcite ($CaCO_3$) crystals. Left, 3D cartoons of spherical, worm-like or vesicular nanoparticles. Middle, representative TEM images. Right, cross-sections of calcite crystals prepared in the presence of the corresponding diblock copolymer nanoparticles (spheres, worms or vesicles). The three diblock copolymer nanoparticles in (a), (c) and (e) are poly(ammonium 2-sulfatoethyl methacrylate)$_{73}$-poly(benzyl methacrylate)$_{300}$, poly(methacrylic acid)$_{71}$-poly(benzyl methacrylate)$_{98}$ and poly(methacrylic acid)$_{73}$-poly(benzyl methacrylate)$_{200}$, respectively.

As mentioned above, occlusion does not appear to be particularly sensitive to the morphology of the guest nanoparticles. For example, PISA enables the convenient synthesis of poly(methacrylic acid)-poly(benzyl methacrylate) nanoparticles in the form of either isotropic spheres or highly anisotropic worms and both species can be efficiently occluded within calcite (see **Figure 2**).[16f, 18]. Moreover, efficient occlusion can be achieved for spherical nanoparticles ranging in size from tens of nm[3, 16b, 16d, 17a, 20] to hundreds of nm[4, 14, 16c, 16e, 16g, 17b] and even up to μm.[18, 21]

2.2. Surface Modification

2.2.1 Post-Modification

As indicated above, the chemical nature of the steric stabilizer chains at the surface of the guest nanoparticles plays a decisive role in dictating nanoparticle occlusion. A wide range of functional inorganic nanoparticles can be modified via so-called ‘grafting from’ or ‘grafting to’ methods.[22] In some cases, inorganic nanoparticles can be readily surface-modified using polymers bearing reactive end-groups. For example, poly(glycerol monomethacrylate)$_{70}$ (G_{70}) chains capped with a dithiobenzoate group can be used to coat gold nanoparticles (AuNPs) in aqueous media. The resulting G_{70}-AuNPs exhibit excellent colloidal stability in the presence of cations such as Zn^{2+} or Ca^{2+}.[17a, 23] This is an important consideration because colloidally unstable nanoparticles cannot be occluded within host crystals. Formation of ZnO or calcite crystals in the presence of such G_{70}-AuNPs nanoparticles leads to their efficient occlusion. It is perhaps worth emphasizing that poly(glycerol monomethacrylate) is a *non-ionic* polymer that had been previously considered to be unlikely to promote occlusion. The successful formation of Au@ZnO nanocomposite crystals is attributed to the *cis*-diol groups within each repeat unit of the G_{70} chains, which are known to chelate with divalent metal cations such as Zn^{2+} (and Ca^{2+}). Such metal ion complexation is believed to drive occlusion of the G_{70}-AuNPs within ZnO[17a] (and calcite[23]). This unexpected finding expands our understanding of occlusion mechanisms and suggests that neutral biomacromolecules could also play a significant role in biomineralization. As shown in **Figure 3**, gold nanoparticles are densely and uniformly distributed within both ZnO (black dots in **Figure 3a** and **3b**) and calcite (white dots in **Figure 3c** and **3d**) host crystals. Under optimized conditions, the extent of G_{70}-AuNPs occlusion can be up to 20 wt.% for ZnO[17a] and 40 wt.% for calcite.[23]

In principle, such surface modification should enable many inorganic nanoparticles to be incorporated into host crystals. However, it can be challenging to control polymer grafting densities on inorganic nanoparticles. Based on our prior studies, this parameter is considered likely to affect the extent of nanoparticle occlusion.[16d]

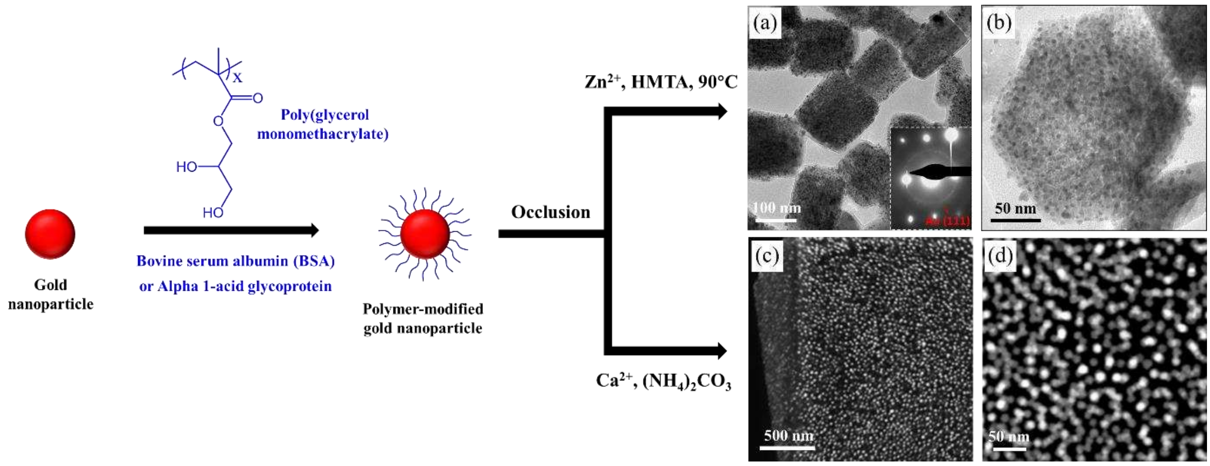

Figure 3. Surface modification of gold nanoparticles using either poly(glycerol monomethacrylate) or bovine serum albumin (BSA) or alpha 1-acid glycoprotein and their occlusion within ZnO rods (a, b) and calcite (c, d).[17a, 23]

2.2.2 In Situ Modification

In the case of Fe_3O_4 nanoparticles, surface modification can be achieved during the nanoparticle synthesis.[24] For example, Kulak et al. used reversible addition-fragmentation chain transfer (RAFT) polymerization to prepare double-hydrophilic diblock copolymers, which were subsequently used to produce sterically-stabilized Fe_3O_4 nanoparticles. For example, one of the two blocks can be poly(methacrylic acid) (PMAA), which is known to physically adsorb onto Fe_3O_4. The second block should also be anionic, e.g. either poly(sodium 4-vinylbenzenesulfonate) (PStSNa) or poly(potassium 3-sulfopropyl methacrylate) (PKSPMA), which can each confer electrosteric stabilization. Such anionic blocks not only ensure the colloidal stability of the Fe_3O_4 nanoparticles but also provide specific binding sites for subsequent occlusion. Indeed, such sterically-stabilized Fe_3O_4 nanoparticles can be incorporated into either ZnO or calcite host crystals (see **Figure 4**).[24]

In addition, non-ionic poly(*N*-vinylpyrrolidone) (PNVP) can also act as a steric stabilizer during the synthesis of various inorganic sols, such as Au, Ag or Pt nanoparticles, Fe_3O_4 nanoparticles, and either CdSe or CdTe quantum dots.[25] Such PNVP-decorated nanoparticles can be readily incorporated within metal organic frameworks (MOFs) such as ZIF-8[25] and UiO-66-NH_2[26]. Remarkably, the photocatalytic activity of Pt nanoparticles was significantly enhanced after its occlusion within the host MOFs.[27] Clearly, *in situ* modification is a straightforward and convenient route to sterically-stabilized inorganic nanoparticles. However, addition of such polymers – particularly polyelectrolytes – during the synthesis of the inorganic nanoparticles may affect their size and/or morphology.[28]

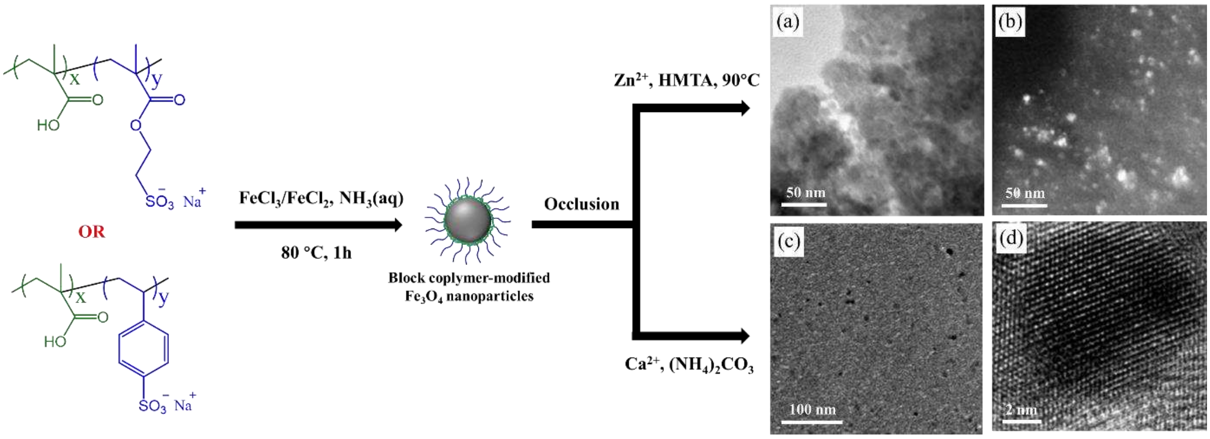

Figure 4. Preparation of anionic diblock copolymer-modified Fe_3O_4 nanoparticles and their occlusion within ZnO (a, b) and calcite (c, d) crystals.

2.3. Gel Entrapment Strategy

Surface modification is an effective way to achieve nanoparticle occlusion within inorganic crystals. However, this strategy is not feasible for all types of nanoparticles. In principle, gel entrapment is an attractive alternative method because it does not require any prior surface treatment.[29] In this approach, nanoparticles are dispersed and physically entrapped within a gel network. *In situ* formation of the host crystals in the presence of such gels inevitably leads to nanoparticle engulfment (see **Figure 5a**). There is no specific surface functionality requirement for the guest nanoparticles. Indeed, many nanoparticles, including gold/magnetite nanoparticles,[30] quantum/polymer dots[31] and microgels[32] have been incorporated into calcite crystals, as reported by Li and co-workers (see **Figure 5**).

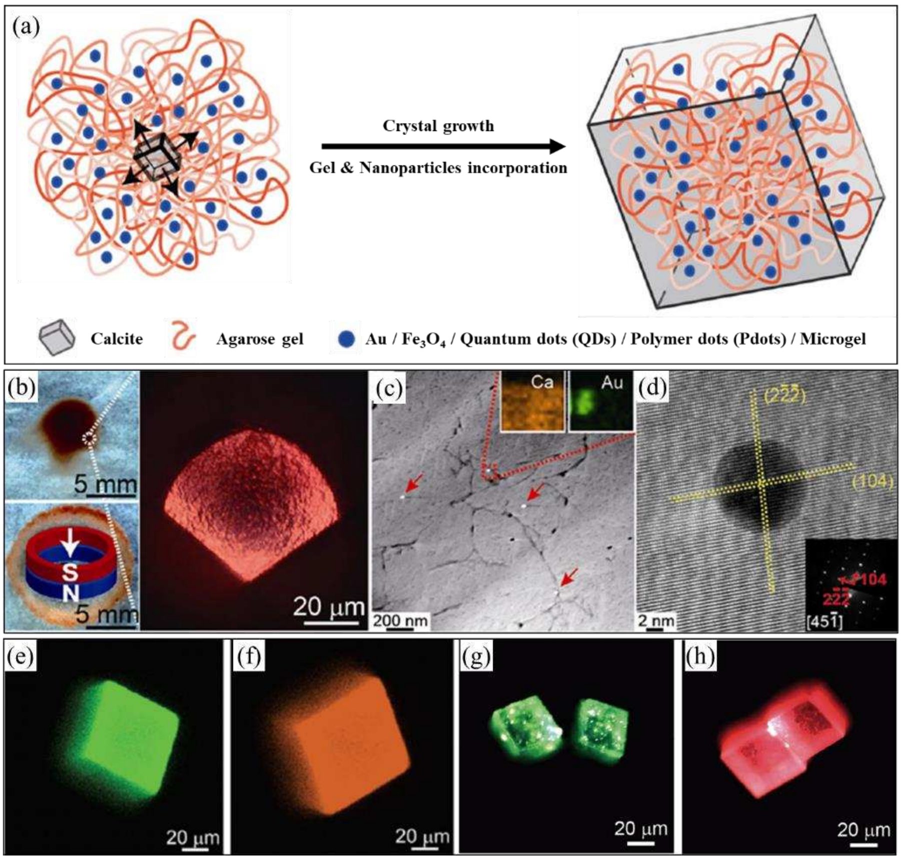

Figure 5. (a) Schematic cartoon showing the incorporation of nanoparticles entrapped within agarose hydrogels into host calcite crystals; (b) photographs showing the response of calcite crystals occluded with both Au nanoparticles and Fe_3O_4 to an external magnetic field; (c) HAADF-STEM image showing a thin section of calcite occluded with ~20 nm Au nanoparticles (white dots), which were identified by EDX as shown in the insets; (d) HRTEM image showing the occlusion of Au nanoparticles within calcite without interruption of the lattice fringes of the host crystal; (e-h) confocal fluorescence images recorded for calcite crystals occluded with various types of quantum dots.

In the case of calcite grown in the presence of an agarose hydrogel, the nanoparticle-loaded crystals exhibit a perfect rhombohedral morphology,[29] which suggests that neither the nanoparticles nor the gel affect the crystal habit. Clearly, this gel entrapment strategy is readily applicable to various nanoparticles and can be regarded as rather generic. It is noteworthy that the hydrogel is inevitably occluded into the host crystals along with the occlusion of the entrapped nanoparticles for such strategy.

2.4. 'Trojan Horse' Strategy

In this approach, passive guest nanoparticles are encapsulated within the lumen of diblock copolymer vesicles bearing appropriate surface chemistry. Such vesicles are then employed as a 'Trojan Horse' to deliver the nanoparticles within the desired host crystal.[17b] More specifically, the guest nanoparticles are encapsulated *in situ* during the formation of the diblock copolymer vesicles via polymerization-induced self-assembly (PISA).[15b-d, 33] Thus, the RAFT alcoholic dispersion polymerization of benzyl methacrylate in the presence of an alcoholic silica sol using a poly(methacrylic acid) precursor as the steric stabilizer block leads to the formation of silica-loaded poly(methacrylic acid)-poly(benzyl methacrylate) diblock copolymer vesicles. Silica encapsulation is not particularly efficient, but excess free silica nanoparticles can be readily removed via multiple centrifugation-redispersion cycles. Thereafter, the silica-loaded vesicles are transferred into aqueous solution and the poly(methacrylic acid) undergo ionization to acquire anionic character (see **Figure 6**).[17b] If the poly(methacrylic acid) stabilizer chains are sufficiently long, then successful occlusion within calcite can be achieved.[16c] The vesicle membrane comprises poly(benzyl methacrylate), which is sufficiently hydrophobic to retain small molecule dyes as well as silica nanoparticles. As expected, efficient occlusion of dye-loaded vesicles within calcite confers fluorescence on the host crystals (see **Figure 6**).

This 'Trojan Horse' strategy is more complicated than the gel entrapment strategy. However, the former approach does enable the delivery of small molecules (e.g. fluorescent dyes) into host crystals.

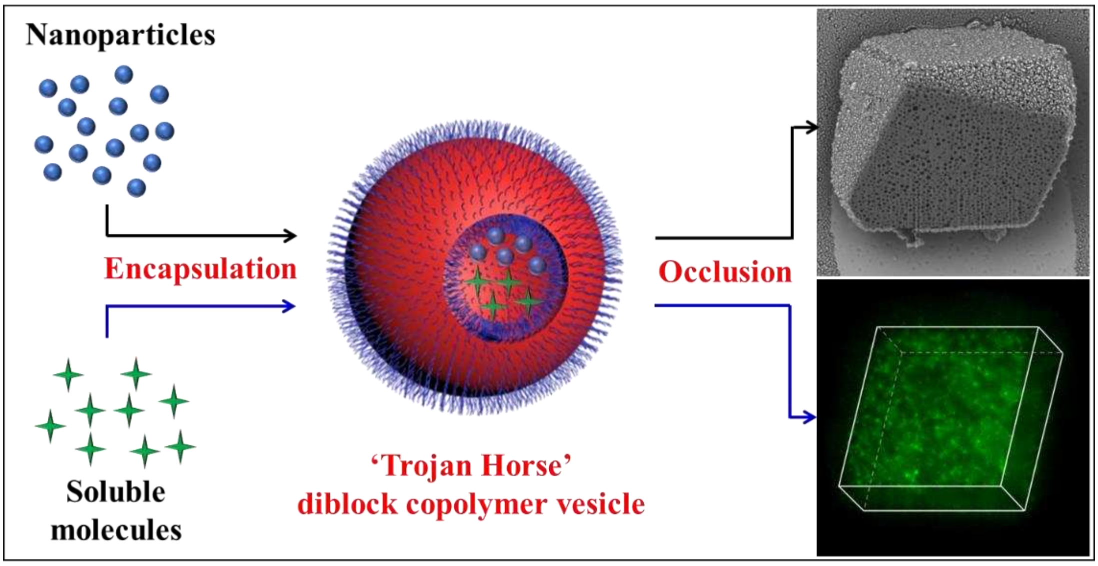

Figure 6. The 'Trojan Horse' occlusion strategy. Schematic representation of the *in situ* encapsulation of either nanoparticles or soluble dye molecules in diblock copolymer vesicles and their subsequent occlusion within calcite crystals.

2.5. Nanoemulsion Strategy

At first sight, one would not expect that oil droplets could be incorporated into an ionic crystal lattice because these two phases are highly incompatible. To tackle this problem, the preparation of very small oil droplets is required.[4] Firstly, a strongly amphiphilic diblock copolymer is prepared in the form of sterically-stabilized nanoparticles via RAFT aqueous emulsion polymerization. These nanoparticles are then used to prepare a relatively coarse oil-in-water Pickering emulsion via high shear homogenization with the model oil of interest (e.g. methyl myristate).[34] Next, this precursor Pickering emulsion is converted into an oil-in-water nanoemulsion by high pressure microfluidization using a commercial LV1 microfluidizer. The high-energy processing conditions leads to *in situ* dissociation of the nanoparticles to afford molecularly-dissolved diblock copolymer chains, which act as a polymeric surfactant for the oil droplets. Thus, the hydrophobic block [e.g. poly(lauryl methacrylate)] is located within the oil phase while the hydrophilic block [e.g. poly(methacrylic acid)] is located in the aqueous phase. Ionization of the latter block produces very fine oil droplets with anionic character and such nanoemulsions can be efficiently occluded within calcite crystals. The overall process is summarized in **Figure 7**.

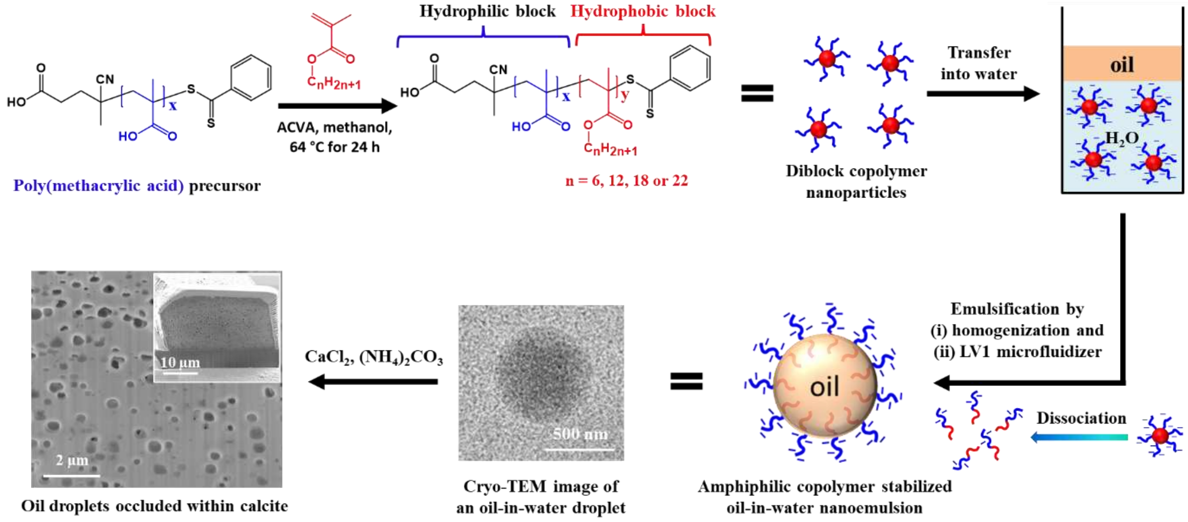

Figure 7. Schematic representation of the synthesis of poly(methacrylic acid)-poly(lauryl methacrylate) diblock copolymer nanoparticles via RAFT-mediated polymerization-induced self-assembly (PISA), the subsequent formation of a nanoemulsion via high-pressure microfluidization processing of a relatively coarse oil-in-water Pickering emulsions (not shown) and the efficient occlusion of the resulting anionic oil droplets within calcite single crystals.

This nanoemulsion strategy for oil droplet occlusion is quite general: various oils can be used, including *iso*-hexadecane, styrene, food-grade methyl myristate, sunflower oil or various multicomponent hydrophobic fragrances. Remarkably, the mean oil droplet diameter can be up to 500 nm. In principle, any stable oil droplets bearing suitable surface chemistry can be incorporated into calcite. Moreover, the oil phase can be loaded with hydrophobic small molecules (or nanoparticles). Therefore, such oil droplets can serve as hydrophobic 'Trojan Horses' for delivery of a wide range of water-insoluble small molecules (or oil-dispersible nanoparticles) into host crystals.[4]

3. Spatially-controlled Nanoparticle Occlusion for Patterned Crystals

Efficient incorporation of various types of nanoparticles into host crystals provides access to a wide range of nanocomposite materials. However, manipulating the spatial distribution of nanoparticles within such crystals is a formidable challenge.[35] Green et al. reported that the occlusion of organic additives within calcite exhibited specific intra-sectoral zoning. This is because additives preferentially adsorb to acute step edges during crystal growth.[36] Empirically, we found that the mean degree of polymerization, DP, of the poly(methacrylic acid) stabilizer block plays an important role in determining the spatial distribution of nanoparticles within calcite.[16f] For relatively short poly(methacrylic acid) chains (DP < 30), poly(methacrylic acid)-poly(benzyl methacrylate) nanoparticles are only located at the near-surface layer of calcite crystals; uniform distribution can only be achieved when the poly(methacrylic acid) DP is greater than 50.[16f] In addition, patterned nanoparticle occlusion can be achieved by controlling the crystallization conditions. For example, a rhombohedral single crystal of calcite in which the inner core and outermost layer contain no nanoparticles but the middle layer contains occluded nanoparticles can be grown by adjusting the occlusion conditions (see **Figure 8a-h**).[16g] Similarly, calcite crystals comprising the inverted structure (i.e. nanoparticles located within the crystal core and outermost layer but absent from the middle layer) can also be obtained. Similarly, Jin et al. demonstrated that well-controlled patterned gels within potassium dihydrogen phosphate (KDP) crystals can be produced either by using oscillating crystallization rates or by changing the crystallization media (see **Figure 8i-l**).[37] This approach enables the rational design of single crystals with alternating layers of differing components.

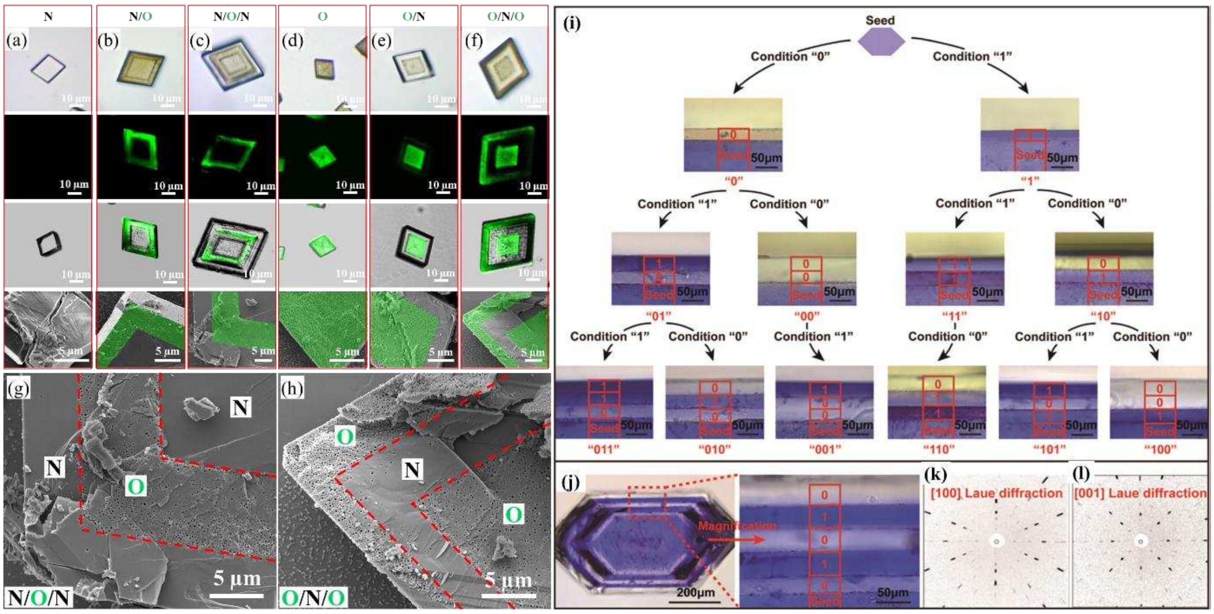

Figure 8. Spatially-controlled occlusion of vesicles (a-h) and gel (i-l) within calcite crystals and potassium dihydrogen phosphate (KDP) crystals, respectively. 'N' and 'O' denote 'no occlusion' and 'occlusion', respectively.

Semiconductor zinc oxide rods grow much faster in the [0001] direction than the $[10\bar{1}0]$ direction, resulting in a twin-like rod structure. Taking advantage of this faceted growth behavior, nanoparticle occlusion within ZnO crystals can either be uniformly distributed throughout the rods or confined to their central regions simply by controlling the nanoparticle dosage. Besides, surface-confined occlusion can also be achieved by simply delaying addition of the nanoparticles.[17a] In principle, such spatially-controlled nanoparticle occlusion enables the internal structure of the host crystals to be engineered.

4. Occlusion Mechanism

Important information regarding the occlusion mechanism has been obtained by *in situ* atomic force microscopy (AFM) studies. Several research groups have reported their findings using this technique.[19, 38] In particular, Estroff and coworkers have gained interesting new insights into the various interaction modes between nanoparticles and growing calcite crystals. During the calcite formation in the presence of nanoparticles, the latter adsorb onto the steps of the growing crystals. Such nanoparticles could then (i) desorb and return to the aqueous continuous phase or (ii) 'hover' over the growing surface, or (iii) be engulfed by the growing steps (see **Figure 9**).[19] Certainly, intimate interaction between the guest nanoparticles and the growing crystals is essential for efficient nanoparticle occlusion. The steric stabilizer chains govern the nature of the interaction between the nanoparticles and the growing inorganic phase, while also ensuring colloidal stability of the nanoparticles in the presence of the inorganic ions (e.g. Ca^{2+} and CO_3^{2-}) under mildly alkaline conditions (e.g. pH 9-10).

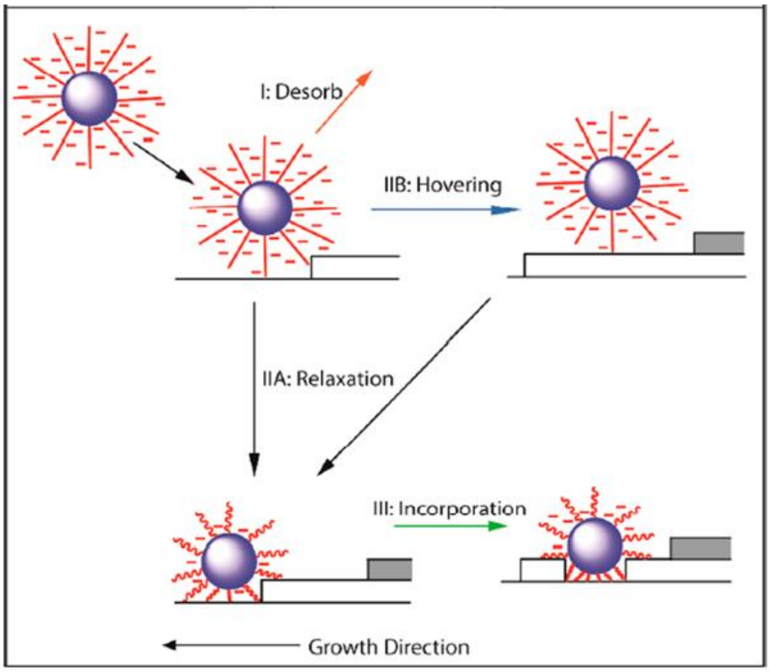

Figure 9. Schematic cartoon illustrating the interaction modes between sterically-stabilized nanoparticles and growing crystals.

Transmission electron microscopy studies suggest that there is no distinct 'polymer' layer between the sterically-stabilized guest nanoparticles and the host inorganic crystals.[3, 17a, 18, 23, 24b] This is perhaps not surprising because the stabilizer chains are not densely packed at the surface of the nanoparticles and presumably crystal growth can penetrate this polymer layer, resulting in intimate contact with the nanoparticle cores. This interpretation is supported by high resolution TEM examination of a cross-section of ZnO crystals containing G_{70}-AuNPs.[17a]

The host crystals must exert a compression force on the nanoparticles during their occlusion. Several research groups have reported experimental evidence for such compression. For example, diblock copolymer micelles became elongated during their occlusion within calcite as evidenced by both TEM and *in situ* AFM.[3, 19a] Similarly, oil droplets became distinctly non-spherical during their occlusion within calcite.[4] Such changes in morphology for these relatively soft guest nanoparticles are attributed to compressive forces arising from the growing steps. In contrast, no change in morphology was observed after the occlusion of relatively hard polystyrene latexes[14] or polymer-modified gold nanoparticles.[17a] In principle, the occlusion mechanism for nanoparticles may shed new light on the mechanism for biomineralization, which involves the incorporation of various biopolymers into the host crystal.

5. Properties and Potential Applications

Efficient nanoparticle occlusion leads to the formation of a new class of nanocomposite crystals. Both the composition and structure of such materials can be readily adjusted either by combining differing guest/host pairs or by optimizing synthetic protocols. Hence this new approach offers considerable potential for the preparation of bespoke functional materials. Indeed, the intimate combination of various components may lead to emergent properties. For example, incorporation of either amino acids or gel into semiconductors such as ZnO or PbI_2 can be exploited to tune band-gaps.[39] Calcite crystals that contain diblock copolymer micelles exhibit superior hardness and fracture toughness compared to pure calcite (see **Figure 10a-d**).[3] This is because efficient occlusion introduces internal organic-inorganic interfaces, which are responsible for the enhanced mechanical properties.[3]

Occlusion of functional guest molecules or nanoparticles can confer the host crystals with new properties. For example, incorporation of dye-loaded vesicles can produce fluorescent calcite crystals (**Figure 10e**).[16c, 17b] Interestingly, incorporation of quantum dots (QDs) or polymer dots (so-called Pdots) into calcite crystals can enhance their photostability and prolong their fluorescence lifetime (**Figure 10f**).[31] In addition, magnetic host crystals can be prepared via occlusion of magnetite nanoparticles.[24]

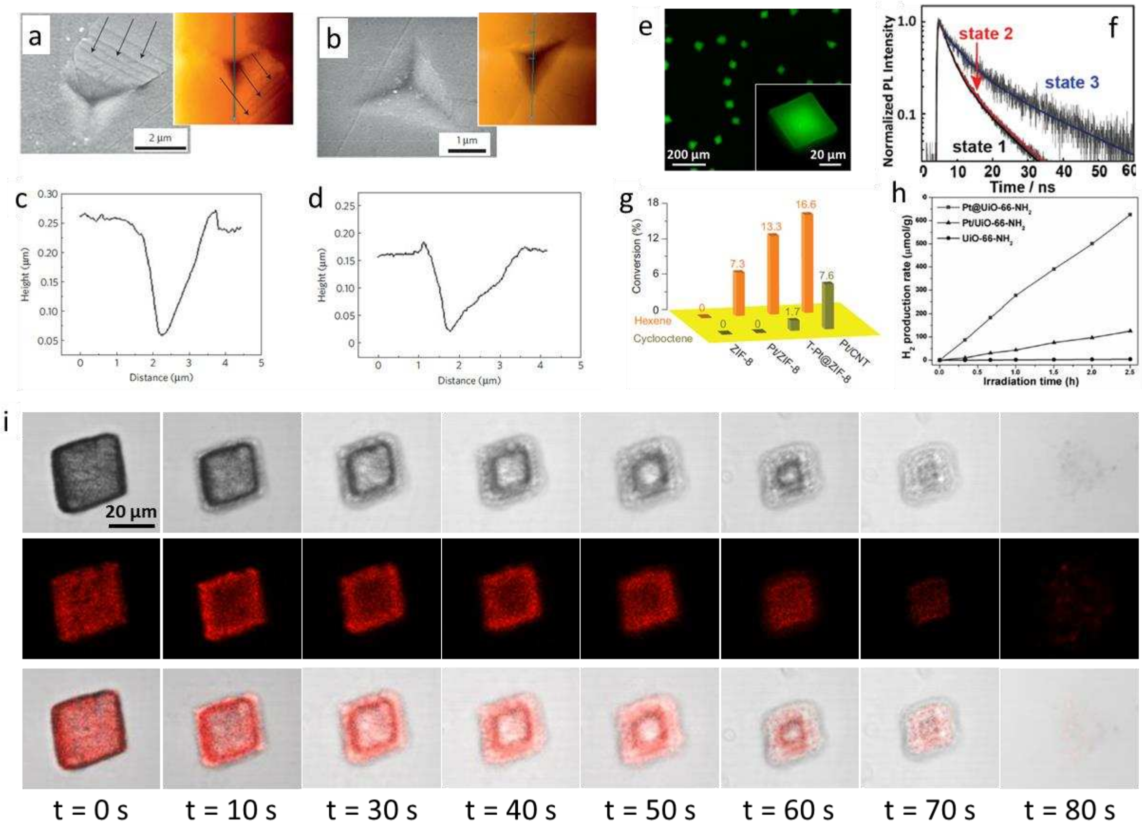

Figure 10. Occlusion of nanoparticles within inorganic crystals leads to enhanced properties and new potential applications. (a-d) Nanoindentation tests on pure calcite and micelle-loaded calcite crystals; (e) fluorescent microscopy image of calcite crystals containing fluorescent vesicles; (f) transient photoluminescence spectra of quantum dots in solution (stage 1), trapped in gel (stage 2) and occluded within calcite (stage 3); (g) hydrogenation of *n*-hexene and *cis*-cyclooctene recorded for Pt/ZIF-8 nanocomposites; (h) photocatalytic properties recorded for various samples; (i) *in situ* monitoring of acid-triggered release of oil droplets occluded within calcite crystals.

Moreover, metal-organic frameworks (MOFs) can also be used as host crystals. The highly porous structure of MOFs is beneficial for enhanced catalytic properties. For example, Lu et al. reported that encapsulation of Pt nanoparticles within a zeolitic imidazolate framework (ZIF-8) resulted in unique catalytic regioselectivity.[25] This study showed that platinum nanoparticles alone can catalyze the hydrogenation of both *n*-hexene and *trans*-2-hexene without selectivity. However, the same platinum nanoparticles occluded within ZIF-8 catalyzed *n*-hexene but remained completely inactive towards *trans*-2-hexene (see **Figure 10g**). However, the mechanism governing this interesting observation remains unclear at present.[25] In addition, the Jiang research group has demonstrated that photocatalytic hydrogen production activity is related to the precise location of platinum nanoparticles within UiO-66-NH_2 crystals. The platinum nanoparticles located within such crystals exhibit superior performance compared to those located at the crystal surface (see **Figure 10h**).[26]

In the case of pH-sensitive crystals, controlled release of the occluded cargo can be achieved. For example, oil droplet-loaded calcite crystals remain stable when stored in neutral or alkaline solution but lowering the solution pH leads to acid etching of the crystals and gradual release of the oil droplets (see **Figure 10i**). In principle, hydrophobic drugs could be loaded into such biocompatible calcite crystals, with acid-triggered release occurring on exposure to a low local pH (e.g. in the stomach).[4]

6. Summary and Outlook

A wide range of colloidal systems, including polymeric latexes, diblock copolymer nanoparticles, inorganic nanoparticles and even oil droplets, can be readily incorporated into various host crystals (e.g. calcite, zinc oxide or ZIF-8). The key requirement is to ensure that the surface of the guest particles contains a suitable functional polymeric stabilizer, which not only ensures colloidal stability but also promotes intimate host-guest interactions.

Over the past decade or so, it has become apparent that the direct incorporation of nanoparticles during the formation of inorganic host crystals offers a versatile route for the rational design of new crystalline nanocomposite materials with adjustable chemical compositions and tunable physical properties. However, this fascinating sub-field remains in its infancy. In particular, the following topics/questions should be addressed. (1) nanoparticle occlusion experiments reported in the literature are almost exclusively performed in aqueous media. However, many crystals can also be grown in non-aqueous media.[40] Can new design rules be developed to promote occlusion under such conditions? (2) To date, the focus has been on single-component nanoparticle occlusion. If binary (or ternary) mixtures of nanoparticles are used this is likely to result in competitive occlusion. However, it may also enable co-operative (synergistic) occlusion to be achieved under some circumstances. For such experiments it will be important to be able to distinguish between the various types of occluding nanoparticles (e.g. on the basis of differences in size, shape or perhaps fluorescent labels). This approach is potentially attractive because it offers the possibility of constructing complex multifunctional nanocomposite crystals in a single step. (3) The occlusion of nanoparticles within crystals is much easier to characterize compared to the incorporation of soluble macromolecules. Given this intrinsic advantage, can nanoparticle occlusion provide us with a deeper understanding of the mechanism of formation of naturally-occurring biominerals? (4) It is now well-established that crystalline nanocomposites can be constructed via nanoparticle occlusion. However, the composition-structure-function relationships for such nanocomposites have not yet been elucidated. In particular, further systematic studies of how microscopic structure affects macroscopic properties are highly desirable.

Nanoparticle occlusion within inorganic crystals is an inherently interdisciplinary research field that involves polymer chemistry, colloid science, materials science and crystal engineering. We are confident that it has an important role to play in the rational design and synthesis of new materials with multiple components and functionality.

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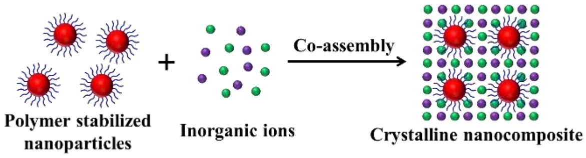
Nanoparticle occlusion within host crystals provides a straightforward yet efficient route for the rational design and preparation of novel nanocomposite materials. This review article summarizes the recent developments in this research field, including strategies for nanoparticle occlusion, spatially-controlled/patterned nanoparticle occlusion, nanoparticle occlusion mechanism(s), physicochemical properties of the resulting nanoparticle@crystal nanocomposites, and potential applications for these new materials.

Yin Ning*, Steven P. Armes* and Dan Li

Polymer-inorganic crystalline nanocomposite materials via nanoparticle occlusion



References

[1] a) Y. Ning, S. P. Armes, *Acc. Chem. Res.*, **2020**, *53*, 1176; b) J. Ren, Y. Liu, H. Li, *J. Polym. Sci.*, **2021**, *doi.org/10.1002/pol.20210408*; c) Y. Liu, L. Chen, W. Liu, T. Ye, H. Chen, H. Li, *Polym. Adv. Technol.*, **2014**, *25*, 1189.

[2] G. Wegner, M. M. Demir, M. Faatz, K. Gorna, R. Munoz-Espi, B. Guillemet, F. Gröhn, *Macromol. Res.*, **2007**, *15*, 95.

[3] Y.-Y. Kim, K. Ganesan, P. Yang, A. N. Kulak, S. Borukhin, S. Pechook, L. Ribeiro, R. Kröger, S. J. Eichhorn, S. P. Armes, *Nat. Mater.*, **2011**, *10*, 890.

[4] Y. Ning, F. C. Meldrum, S. P. Armes, *Chem. Sci.*, **2019**, *10*, 8964.

[5] R. Ghosh Chaudhuri, S. Paria, *Chem. Rev.*, **2012**, *112*, 2373.

[6] a) J. R. Davis, Alloying: understanding the basics, ASM International **2001**; b) C. Suryanarayana, *Prog. Mater. Sci.*, **2001**, *46*, 1.

[7] S. Mann, Biomineralization: principles and concepts in bioinorganic materials chemistry, Oxford University Press, Oxford, **2001**.

[8] a) S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum, N. J. Reeves, *Science*, **1993**, *261*, 1286; b) P. Gilbert, M. Abrecht, B. H. Frazer, Geochemistry, *Rev. Mineral. Geochem.*, **2005**, *59*, 157.

[9] L.-B. Mao, H.-L. Gao, H.-B. Yao, L. Liu, H. Cölfen, G. Liu, S.-M. Chen, S.-K. Li, Y.-X. Yan, Y.-Y. Liu, *Science*, **2016**, *354*, 107.

[10] a) S. H. Yu, H. Cölfen, J. Hartmann, M. Antonietti, *Adv. Funct. Mater.*, **2002**, *12*, 541; b) S.-H. Yu, H. Cölfen, *J. Mater. Chem.*, **2004**, *14*, 2124; c) A. G. Shtukenberg, M. D. Ward, B. Kahr, *Chem. Rev.*, **2017**, *117*, 14042.

[11] a) G. Wegner, P. Baum, M. Müller, J. Norwig, K. Landfester, *Macromol. Symp.*, **2001**, *175*, 349; b) R. Muñoz-Espí, G. Jeschke, I. Lieberwirth, C. M. Gomez, G. Wegner, *J. Phys. Chem. B*, **2007**, *111*, 697; c) R. Muñoz-Espí, A. Chandra, G. Wegner, design, *Cryst. Growth & Des.*, **2007**, *7*, 1584.

[12] R. Muñoz ‐ Espí, Y. Qi, I. Lieberwirth, C. M. Gómez, G. Wegner, *Chem. Eur. J*, **2006**, *12*, 118.

[13] C. Lu, L. Qi, H. Cong, X. Wang, J. Yang, L. Yang, D. Zhang, J. Ma, W. Cao, *Chem. Mater.*, **2005**, *17*, 5218.

[14] Y. Y. Kim, L. Ribeiro, F. Maillot, O. Ward, S. J. Eichhorn, F. C. Meldrum, *Adv. Mater.*, **2010**, *22*, 2082.

[15] a) S. L. Canning, G. N. Smith, S. P. Armes, **2016**, *49*, 1985; b) N. J. Warren, S. P. Armes, *J. Am. Chem. Soc.*, **2014**, *136*, 10174; c) E. J. Cornel, J. Jiang, S. Chen, J. Du, *CCS Chem.*, **2021**, *3*, 2104; d) F. D'Agosto, J. Rieger, M. Lansalot, *Angew. Chem. Int. Ed.*, **2020**, *59*, 8368; e) M. J. Derry, L. A. Fielding, S. P. Armes, *Prog. Polym. Sci.*, **2016**, *52*, 1; f) X. Wang, Z. An, *Macromol. Rapid Commun.*, **2019**, *40*, 1800325.

[16] a) Y. Ning, L. Fielding, T. Andrews, D. Growney, S. Armes, *Nanoscale*, **2015**, *7*, 6691; b) Y. Ning, L. A. Fielding, K. E. Doncom, N. J. Penfold, A. N. Kulak, H. Matsuoka, S. P. Armes, *ACS Macro Lett.*, **2016**, *5*, 311; c) Y. Ning, L. Han, M. J. Derry, F. C. Meldrum, S. P. Armes, *J. Am. Chem. Soc.*, **2019**, *141*, 2557; d) Y. Ning, L. A. Fielding, L. P. Ratcliffe, Y.-W. Wang, F. C. Meldrum, S. P. Armes, *J. Am. Chem. Soc.*, **2016**, *138*, 11734; e) M. Douverne, Y. Ning, A. Tatani, F. C. Meldrum, S. P. Armes, *Angew. Chem. Int. Ed.*, **2019**, *58*, 8692; f) Y. Ning, L. Han, M. Douverne, N. J. Penfold, M. J. Derry, F. C. Meldrum, S. P. Armes, *J. Am. Chem. Soc.*, **2019**, *141*, 2481; g) Y. Ning, Y. Han, L. Han, M. J. Derry, S. P. Armes, *Angew. Chem. Int. Ed.*, **2020**, *59*, 17966; h) A. Hanisch, P. Yang, A. N. Kulak, L. A. Fielding, F. C. Meldrum, S. P. Armes, *Macromolecules*, **2016**, *49*, 192.

[17] a) Y. Ning, L. A. Fielding, J. Nutter, A. N. Kulak, F. C. Meldrum, S. P. Armes, *Angew. Chem. Int. Ed.*, **2019**, *58*, 4302; b) Y. Ning, D. J. Whitaker, C. J. Mable, M. J. Derry, N. J. Penfold, A. N. Kulak, D. C. Green, F. C. Meldrum, S. P. Armes, *Chem. Sci.*, **2018**, *9*, 8396; c)

O. Nahi, A. N. Kulak, T. Kress, Y.-Y. Kim, O. G. Grendal, M. J. Duer, O. J. Cayre, F. C. Meldrum, *Chem. Sci.*, **2021**, *12*, 9839.

[18] Y. Y. Kim, M. Semsarilar, J. D. Carloni, K. R. Cho, A. N. Kulak, I. Polishchuk, C. T. Hendley IV, P. J. Smeets, L. A. Fielding, B. Pokroy, *Adv. Funct. Mater.*, **2016**, *26*, 1382.

[19] a) K. R. Cho, Y.-Y. Kim, P. Yang, W. Cai, H. Pan, A. N. Kulak, J. L. Lau, P. Kulshreshtha, S. P. Armes, F. C. Meldrum, *Nat. Commun.*, **2016**, *7*, 10187; b) C. T. Hendley IV, L. A. Fielding, E. R. Jones, A. J. Ryan, S. P. Armes, L. A. Estroff, *J. Am. Chem. Soc.*, **2018**, *140*, 7936.

[20] G. Magnabosco, I. Polishchuk, F. Palomba, E. Rampazzo, L. Prodi, J. Aizenberg, B. Pokroy, G. J. C. G. Falini, Design, *Cryst. Growth Des.*, **2019**, *19*, 4429.

[21] M. Zhang, H. Ping, W. Fang, F. Wan, H. Xie, Z. Zou, Z. Fu, *J. Mater. Chem. B*, **2020**, *8*, 9269.

[22] S. Minko, Grafting on solid surfaces:"grafting to" and "grafting from" methods, Polymer surfaces and interfaces, Springer2008, pp. 215.

[23] Y.-Y. Kim, R. Darkins, A. Broad, A. N. Kulak, M. A. Holden, O. Nahi, S. P. Armes, C. C. Tang, R. F. Thompson, F. Marin, *Nat. Commun.*, **2019**, *10*, 5682.

[24] a) A. N. Kulak, R. Grimes, Y.-Y. Kim, M. Semsarilar, C. Anduix-Canto, O. Cespedes, S. P. Armes, F. C. Meldrum, *Chem. Mater.*, **2016**, *28*, 7528; b) A. N. Kulak, M. Semsarilar, Y.-Y. Kim, J. Ihli, L. A. Fielding, O. Cespedes, S. P. Armes, F. C. Meldrum, *Chem. Sci.*, **2014**, *5*, 738.

[25] G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, *Nat. Chem.*, **2012**, *4*, 310.

[26] J. D. Xiao, Q. Shang, Y. Xiong, Q. Zhang, Y. Luo, S. H. Yu, H. L. Jiang, *Angew. Chem. Int. Ed.*, **2016**, *55*, 9389.

[27] K. Sun, M. Liu, J. Pei, D. Li, C. Ding, K. Wu, H.-L. Jiang, *Angew. Chem. Int. Ed.*, **2020**, *59*, 22749.

[28] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, *Prog. Polym. Sci.*, **2013**, *38*, 1232.

[29] H. Li, H. L. Xin, D. A. Muller, L. A. Estroff, *Science*, **2009**, *326*, 1244.

[30] Y. Liu, W. Yuan, Y. Shi, X. Chen, Y. Wang, H. Chen, H. Li, *Angew. Chem. Int. Ed.*, **2014**, *53*, 4127.

[31] Y. Liu, H. Zang, L. Wang, W. Fu, W. Yuan, J. Wu, X. Jin, J. Han, C. Wu, Y. Wang, *Chem. Mater.*, **2016**, *28*, 7537.

[32] X. Jin, J. Xue, D. H. Kang, Y. Liu, J. Ren, Q. Wen, D. Hu, Y. Yu, W. Yang, B. Du, *Giant*, **2020**, *3*, 100023.

[33] a) C. Liu, C.-Y. Hong, C.-Y. Pan, *Polym. Chem.*, **2020**, *11*, 3673; b) A. Blanazs, J. Madsen, G. Battaglia, A. J. Ryan, S. P. Armes, *J. Am. Chem. Soc.*, **2011**, *133*, 16581.

[34] a) Y. Ning, Y. Yang, C. Wang, T. Ngai, Z. Tong, *Chem. Commun.*, **2013**, *49*, 8761; b) Y. Ning, C. Wang, T. Ngai, Z. Tong, *Langmuir*, **2013**, *29*, 5138.

[35] J. Ihli, M. A. Levenstein, Y.-Y. Kim, K. Wakonig, Y. Ning, A. Tatani, A. N. Kulak, D. C. Green, M. Holler, S. P. Armes, *Chem. Sci.*, **2020**, *11*, 355.

[36] D. C. Green, J. Ihli, P. D. Thornton, M. A. Holden, B. Marzec, Y.-Y. Kim, A. N. Kulak, M. A. Levenstein, C. Tang, C. Lynch, S. E. D. Webb, C. J. Tynan, F. C. Meldrum, *Nat. Commun.*, **2016**, *7*, 13524.

[37] X. Jin, L. Chen, Y. Liu, T. Ye, C. Hu, J. Ren, H. Chen, H. J. T. J. o. P. C. C. Li, *J. Phys. Chem. C*, **2019**, *123*, 13147.

[38] a) J. Chi, W. Zhang, C. V. Putnis, L. Wang, *Cryst. Growth & Des.*, **2021**, *21*, 2398; b) J. Chi, W. Zhang, L. Wang, C. V. Putnis, *Environ. Sci. Technol.*, **2019**, *53*, 8097; c) M. K. Choudhary, R. Jain, J. D. Rimer, *PNAS*, **2020**, *117*, 28632; d) L. Wang, C. V. Putnis, *Acc. Chem. Res.*, **2020**, *53*, 1196; e) J. Chi, Y. Yin, W. Zhang, C. V. Putnis, L. Wang, *Environ. Sci: Nano*, **2021**, *8*, 2855.

[39] a) A. Brif, G. Ankonina, C. Drathen, B. Pokroy, *Adv. Mater.*, **2014**, *26*, 477; b) C. Hu, T. Ye, Y. Liu, J. Ren, X. Jin, H. Chen, H. Li, *Mater. Chem. Front.*, **2018**, *2*, 362.
[40] a) R. Boistelle, J. P. Astier, *J. Cryst. Growth*, **1988**, *90*, 14; b) J. W. Mullin, Crystallization, Elsevier**2001**.