



Communication

Assessing the synergy effect of additive and matrix on single-crystal growth: Morphological revolution resulted from gel-mediated enhancement on CIT-calcite interaction



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ABSTRACT

It is well known that in biomineralization, the inorganic solids crystallized in the presence of organic phases, which are generally recognized as additives and matrix, leading to the crystal morphology modification. However, the synergy effects of both soluble additive and insoluble matrix on regulating the morphology of synthetic single-crystals are less studied. Here, we examine the morphological revolution of calcite single crystals induced by the additive, citrate (CIT), or/and the matrix, agarose gel network. The agarose gel matrix is inert to the crystal morphology in the sense that the agarose gel-grown calcite crystals maintain in characteristic rhombohedra. In contrast, CIT additives are active in crystal morphology modification and crystals begin to exhibit curved rough surfaces when grown in solution with the concentration of CIT coated Au nanoparticles ([CIT-Au NPs]) of more than 2.25 mg/mL. Interestingly, once agarose gel and CIT-Au NPs are simultaneously introduced, the curved morphological feature emerges at a much lower [CIT-Au NPs] of around 0.2 mg/mL. Increasing the gel concentrations further reduce the [CIT-Au NPs] needed to trigger calcite morphological modification, suggesting that the gel networks reduce the CIT diffusion and thereby enhance the kinetic effects of CIT on crystallization. As such, this work may have implications for understanding the mechanism of hierarchical biominerals construction and provide rational strategy to control single-crystal morphologies.

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Crystalline materials with designed morphologies are intensively demanded towards their specific structural, mechanical, optical and optoelectronic properties [1–4]. In nature, organisms exert exact control over biomineralization, resulting in inorganic/organic hybrid single-crystals (e.g., sea urchins and *Atrina rigida* and *Pinna nobilis*) with their structures and morphologies regulated to realize optimized functions from a materials chemistry perspective [5–8]. It is widely believed that biological minerals are endowed with a remarkable range of morphologies through the crystallization in the presence of various organic phases including soluble additives and insoluble matrix, spurring investigations of biomimetic morphogenesis in the sense of introducing additives and/or matrix to control the nucleation, growth, and alignment of single-crystal [9–13].

In recent years, the chemical compositions and complex structures of additives and matrix have been tremendously

broadened to affect the crystallization kinetically [14–23]. The inorganic ions, such as Mg^{2+} , Li^+ and SO_4^{2-} , have been demonstrated to be incorporated into the lattice of calcite, thus influencing the morphology of calcite crystals [24–26]. Especially, relevant investigations revealed that the Mg^{2+} is preferentially adsorbed onto the surface of growing calcite and inserted inside the step edge in molecular scale [27]. Together with the mechanism of stabilizing the amorphous precursor phase, Mg^{2+} effectively control the morphology of calcite [28]. Apart from inorganic ions, the organic components including amino acids [29–31], peptides [32,33], diblock copolymers [34] as well as proteins [35] also contributed to shape crystals while acquiring the in-depth understanding of crystal-additive interactions. In these cases, the crystal shape is generally controlled by step-specific interactions between flexible impurities and individual step edges incorporated in preexisting crystal faces [36]. Particularly, the electrostatic adsorption between functional groups and growing surface [37], accompanied with the helical configuration [33] of organic additives are also of significance in recognizing specific crystal plane to control the crystal growth.

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In addition to the additives, the insoluble matrix can also regulate the morphologies of crystal, especially generating the complex internal structure. The calcite single-crystal crystallized in the presence of polymer membranes, formed by templating sea urchin skeletal plates, exhibited sponge-like morphologies [38]. Furthermore, the ordered three dimensional (3D) matrix, such as ordered structured colloidal crystals [39] and gyroid structured block copolymer [40], were introduced to endow the calcite single-crystal with correspondingly specific internal structure, respectively. Moreover, the gels matrix as random polymer networks were widely demonstrated to affect the crystal morphology, as the nucleation and crystal growth could be controlled in a hydrogel medium through the diffusion-controlled effect [41–44]. In a silica gel, the crystals were shaped into sheet and helical morphologies originating from the adsorption of silicate anions [45,46]. In gelatin matrix, the as-grown calcite in ellipsoidal shape and the vaterite with porous hexagonal columns were obtained [47,48]. As to the agarose gels, the calcite crystallized inside resulted in star-like [49] and spherical shapes [44] under controlled growth conditions. Particularly, the combination of gel matrix and soluble polymeric components [50] or even the inorganic nanoparticles [51,52] could induce the crystal morphological transformation. Spurred by these unique phenomena, it is desired to know, whether or not the additives cooperate with matrix to govern the morphological revolution of single-crystal. Although a wide range of crystal-shaping effects and mechanisms were investigated, the synergistic effects of additives together with matrix in controlling crystal morphology were less frequently considered. Here, we shaped calcite single-crystal using citrate (CIT) introduced agarose gel media to address this issue (Fig. 1). By monitoring the morphological revolution of as-grown calcite, the mechanism of gel-mediated enhancement on CIT-calcite interaction has been identified.

First, we investigated the influence of agarose gels (Fig. 1a) or CIT exerted on calcite morphologies, respectively. On one hand, calcite crystals were grown at a fixed concentration (5 mmol/L) of Ca^{2+} using the ammonium carbonate method as previously reported [53,54]. Initially, we imaged the morphologies of calcite crystals grown in

agarose gels by scanning electron microscopy (SEM). As the agarose concentration increased from 1 w/v% to 3 w/v%, calcite crystals retained the characteristic rhombohedral morphology (Figs. 1d and g), consistent with the previous reports [53,55–56]. On the other hand, we introduced the 20 nm CIT coated Au nanoparticles (CIT-Au NPs) to investigate the interaction between CIT additive and calcite crystal (Fig. 1b). Rhombohedral morphology was retained as the calcite crystallized in aqueous solution containing 0.5 mg/mL CIT-Au NPs (CIT-Au NPs) (Fig. 1e). However, when the concentration of CIT-Au NPs ([CIT-Au NPs]) reached 3 mg/mL, the as-grown crystals exhibited curved rough surfaces that are approximately parallel to the c-axis, capping with smooth rhombohedral planes (Fig. 1h). According to previous investigations, the caps were identified as {104} faces, and the newly-occurred irregular curved surfaces were generated by the step growth inhibition originating from CIT adsorption at {104} steps [57]. In addition, CIT could contact with the surface carbonate simultaneously, by virtue of its hydroxylic group [58]. In this way, CIT selectively favors the faces of calcite crystals to affect the crystal growth process, and further regulates the crystal morphology. Therefore, the agarose gel matrix is inert to the crystal morphology, while the CIT additives are active in crystal morphology modification as the [CIT-Au NPs] is high.

Next, agarose gels and CIT-Au NPs were both introduced into the crystallization media through crystallizing in agarose gels containing dispersed CIT-Au NPs (Fig. 1c). When the [CIT-Au NPs] was 0.1 mg/mL in gel, the as-grown crystals showed the characteristic rhombohedral morphology (Fig. 1f). Conversely, as [CIT-Au NPs] in agarose gels was increased to 2 mg/mL, the crystals showed the curved morphological features (Fig. 1i), demonstrating that CIT-Au NPs could shape the calcite crystal in either solution or agarose gel media.

Furthermore, a closer examination of how the simultaneously introduced agarose gel and CIT-Au NPs affect the calcite morphology was performed. As a control experiment, the crystallization in the presence of CIT-Au NPs in solution, instead of gel media, was first examined. Representative SEM images of calcite crystals grown in CIT-Au NPs aqueous solution are shown in Figs. 2a,c,e. The crystals grown in 0.5 mg/mL CIT-Au NPs solution maintained in characteristic rhombohedra (Fig. 2a), while the calcite crystals in 2.25 mg/mL CIT-Au NPs solution began to exhibit rough, curved surfaces (Fig. 2c). With the increase of [CIT-Au NPs] from 2.25 mg/mL to 4 mg/mL, the number of curved calcite crystals progressively increased. These results are consistent with the previous study where the increasing [CIT] led to remarkable influence on calcite growth, favoring the formation of irregular vicinal faces [59]. Then we grew calcite inside agarose gels (1 w/v%) containing CIT-Au NPs and examine the morphologies of crystal (Figs. 2b,d,f). In sharp contrast, at an extremely low [CIT-Au NPs] of 0.2 mg/mL in agarose gel, the curved morphological feature of calcite crystals emerged (Fig. 2d). Similar to the crystals grown in CIT-Au NPs solutions, the calcite crystallized in the presence of agarose gel and CIT-Au NPs exhibited an increase in the number of curved crystals as the [CIT-Au NPs] increased from 0.1 mg/mL to 4 mg/mL. To acquire an accurate evaluation of morphologies change, the ratio of curved crystal (RCC) was defined as the ratio of the curved crystals' number to the total number of crystals. And the RCC were plotted as a function of [CIT-Au NPs] with lines fitted by the logistic regression model (Fig. 2g) [60]. We subsequently used the fitted curve to calculate its x-intercept termed as the "critical [CIT-Au NPs]" where the [CIT-Au NPs] triggers the calcite morphological revolution with statistical significance. For CIT-Au NPs in agarose gel, the critical [CIT-Au NPs] was 0.0813 mg/mL, while for CIT-Au NPs in solution, the critical [CIT-Au NPs] was 0.826 mg/mL. The logistic fitting curves reconfirmed that the introduction of agarose gel media significantly reduced the [CIT-Au NPs] to transform calcite morphology.

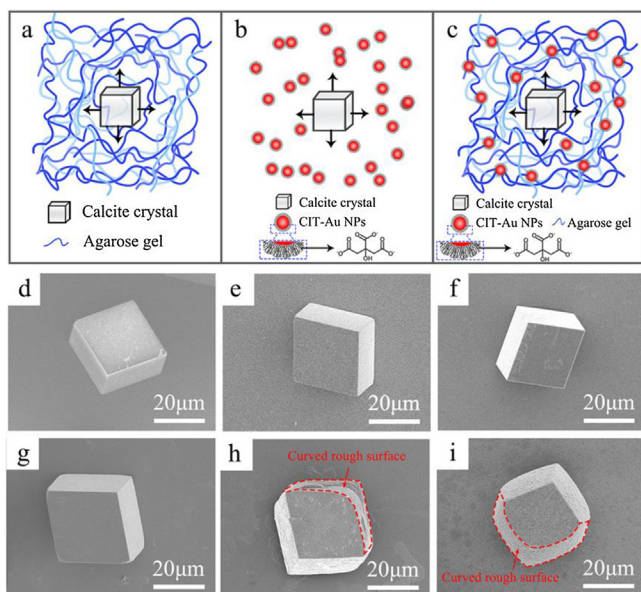


Fig. 1. Schematic diagram of the calcite crystals grown in (a) agarose gel; (b) CIT-Au NPs solution; (c) agarose gel containing CIT-Au NPs. (d–i) SEM images of calcite crystals grown in varied media: (d) 1 w/v% agarose gels; (g) 3 w/v% agarose gels; (e) 0.5 mg/mL CIT-Au NPs solution; (h) 3 mg/mL CIT-Au NPs solution; (f, i) 1 w/v% agarose gels containing CIT-Au NPs (f) 0.1 mg/mL and (i) 2 mg/mL CIT-Au NPs. The red dashed lines highlight the curved rough surface.

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