J Mater Sci **(2022) 57:1036–1043**

Chemical routes to materials

Synthesis and primary investigation of a novel inorganic gel based on calcium oxalate oligomers

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Received: 21 August 2021
Accepted: 6 November 2021

ABSTRACT

Inspired by inorganic oligomers, we herein develop a novel inorganic gel based on calcium oxalate oligomers, and the crystallization morphology has been studied initially in this paper. The prepared oligomer is translucent gel and can exist stably in ethanol, but in aqueous medium it will change from gel to powder. In the crystallization process, because of the volatile speed of solvent and capping agent TEA at different temperature, CaC_2O_4 oligomer gels (COOGs) exhibited distinct crystallization behavior and morphology. Compared with conventional inorganic crystallization, the crystallization process of the gel at room temperature shows a tendency to gradually extend to the inside of the gel. Moreover, the XRD pattern and SEM images shown that the COOGs achieved distinctly different crystal morphology under different temperature. These provide a preliminary research foundation for the crystallization behavior and control conditions of inorganic gels.

Handling Editor: Andrea de Camargo.

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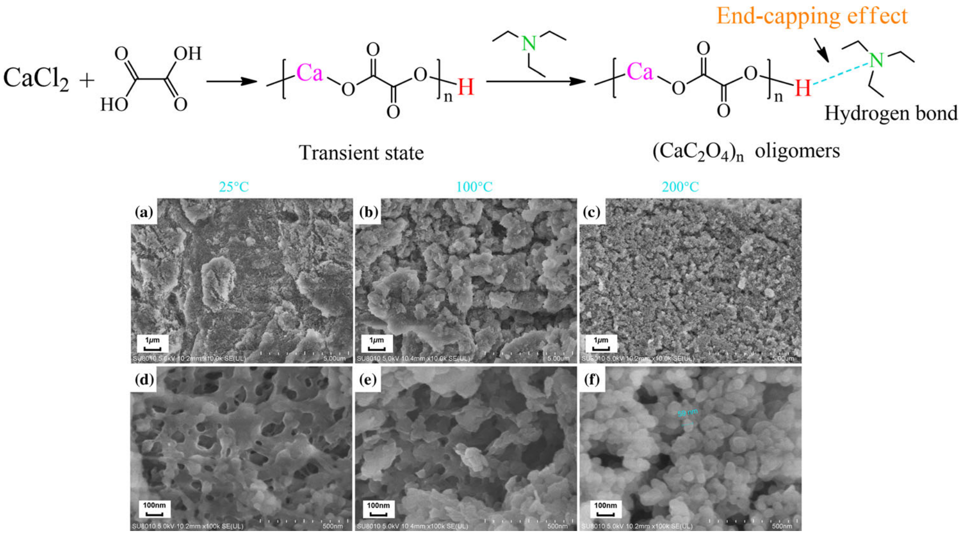
Springer

https://doi.org/10.1007/s10853-021-06705-4

GRAPHICAL ABSTRACT



Introduction

Gels are usually “jellylike” solids with an elastic nature that are used in our daily life, such as in baby diapers, foodstuff, water-retaining agent, solid air fresheners and cosmetics. In recent years, due to diversity structures of gel materials, especially hydrogels, have been continuously explored for their unique and controllable properties and applications in a wide field [1–4]. Conventional hydrogels have found significant applications in adsorbents [5, 6], functional coatings [7, 8], energy and water sustainability [9, 10], desalination [11, 12] and electrolyte of batteries [13, 14]. Besides, due to its biocompatibility, biodegradability, renewability, environmental friendliness and non-toxicity, the application of natural polymers gel in biomedical materials has received extensive attention, including polymer hydrogel bioadhesives [15, 16], drug delivery [17, 18], hydrogel dressings [19, 20], hydrogel-based scaffolds [21, 22], etc. Meanwhile, the potential application of gel materials is also being continuously explored. It is convenient to tune network structure, the electrochemical performances, mechanical properties and biofunctionalities of conductive hydrogels over a very wide range. More importantly, upon external stimuli, gels can take up or lose water and thus change their volumes or shapes, and even achieve shape memory and recovery functions, which known as stimulus-responsive materials or smart materials [23–25]. And the properties (toughness, stretchability and fluidity) of gels can be modulated during synthesis, enabling the application of gelatinous materials to achieve unique performances and diverse functionalities to various promising fields, such as wearable sensors [26, 27], flexible energy storage devices [28], biocatalytic monitoring and regulation [29], humane–machine interfaces [30, 31] and 3D/4D printing [32, 33].

Gelatinous materials are mainly cross-linked networks with 3D hierarchical structures. Organic molecules are more likely to obtain such structures through natural molecular extraction and artificial synthesis and modification. In the whole family, polymeric superabsorbent and biomacromolecular gels are the main category, such as polysaccharides, silicone, cellulose-based materials and polypeptide [34, 35]. In addition, composite gels have attracted extensive attention due to their high strength and various composite methods. This kind of gel mainly consists of metal nanoparticle–hydrogel composites system [36–38]. However, compared with organic macromolecular gels, the types and applications of inorganic gels are relatively narrow, such as mineral inorganic gels, sodium alginate-based hydrogel and ferric hydroxide colloid. At present, inorganic gels are mainly used as thickeners and suspension stabilizers. Further investigation of inorganic gelatinous materials is still under way.

Gels are mainly designed and synthesized by chemical and physical methods based on chemical bonds and intermolecular interaction [39, 40]. Recently, based on classic inorganic and polymer chemistry, an innovation concept of cross-linking ionic oligomers was proposed by Tang. et al. [41]. As protonated carbonates can form hydrogen bond (H-bond) with tertiary amine group, they found that a capping effect was generated during the synthetic process of calcium carbonate. Ionic oligomer gel (cross-linking $CaCO_3$ oligomers) was produced by using ethanol as the solvent and triethylamine as the capping agent. Pure monolithic calcium carbonate can be obtained under the conditions of controlling the removal of ethanol and triethylamine of the gels, which shows potential application in fields such as enamel repair and dental restorations. In addition, they further studied the calcium phosphate [$Ca_3(PO_4)_2$] oligomer gel and its organic–inorganic hybrid properties after being composited with polymer materials, showing broad application potential in the field of biomimetic materials [42–44].

In recent years, a series of new gel materials are continuously being developed and investigated. As an inorganic substance widely present in plant tissue cells and animal bodies, there has no research of synthesis and properties on calcium oxalate (CaC_2O_4) gels [45]. In this work, according to the research on $CaCO_3$ and $Ca_3(PO_4)_2$ oligomers, CaC_2O_4 oligomer gels (COOGs) was chemically synthesized. The results show that the obtained gels were stable in ethanol but instable in water. Moreover, after crystallization at room temperature, the gels showed complicated crystal behaviors. Meanwhile, by utilizing X-ray diffraction (XRD) and scanning electron microscope (SEM), different micromorphology has been found for the gels crystallized at different temperatures due to the escape rate of TEA and the solvent. And based on the preliminary microscopic morphology analysis, the higher the temperature, the smaller and more uniform the crystal unit obtained.

Experimental section

Materials

$CaCl_2·2H_2O$ (99.9%) and TEA (99.5%) were purchased from Aladdin Biochemical Technology Co., Ltd. Oxalic acid (99.0%) and ethanol (99.7%) were procured from Maclean Biochemical Technologies Co., Ltd. Deionized water was prepared in laboratory. No further purification was performed before all chemicals use.

Preparation of CaC_2O_4 oligomer gels

CaC_2O_4 oligomer gels is prepared following the method described by Tang et al.[41]. In brief, 960 mg of $CaCl_2·2H_2O$ was dissolved in 120 mL ethanol under magnetic stirring to form a clear alcoholic solution. Afterward, a total of 18 mL of TEA was added to the above solution under stirring for 30 min at room temperature (RT). The alcoholic solution (1.08 g of $H_2C_2O_4$ dissolved in 9 mL of ethanol) was then added slowly under magnetic stirring for 12 h at RT. The gels were obtained by centrifugation at 8000 rpm and washed with ethanol three times to remove the residual TEA.

Characterization

X-ray diffraction (XRD) spectra of the powder samples after drying were performed using an Ultima IV X-ray diffractometer with a Cu Kα beam (40 kV, 40 mA) in θ–2θ scans of 5 ~ 80° (0.02 Å step size, 50 s/step). The morphologies of crystallized gels were examined with a field emission scanning electron microscope (SU8010 Hitachi), which is operated at an operating voltage of 5.0 kV for SEM observations.

Results and discussion

The calcium oxalate oligomer gels (COOGs) is prepared by the method as shown in Fig. 1. In the process of synthesis, the end-capping effect of TEA on the CaC_2O_4 achieved low molecular weights oligomers with cross-linked structures. These gelatinous CaC_2O_4 oligomers derived from the intermolecular H-bond between triethylamine (TEA) and transient state of CaC_2O_4 (N···H) (Fig. 1a). Since the amount of

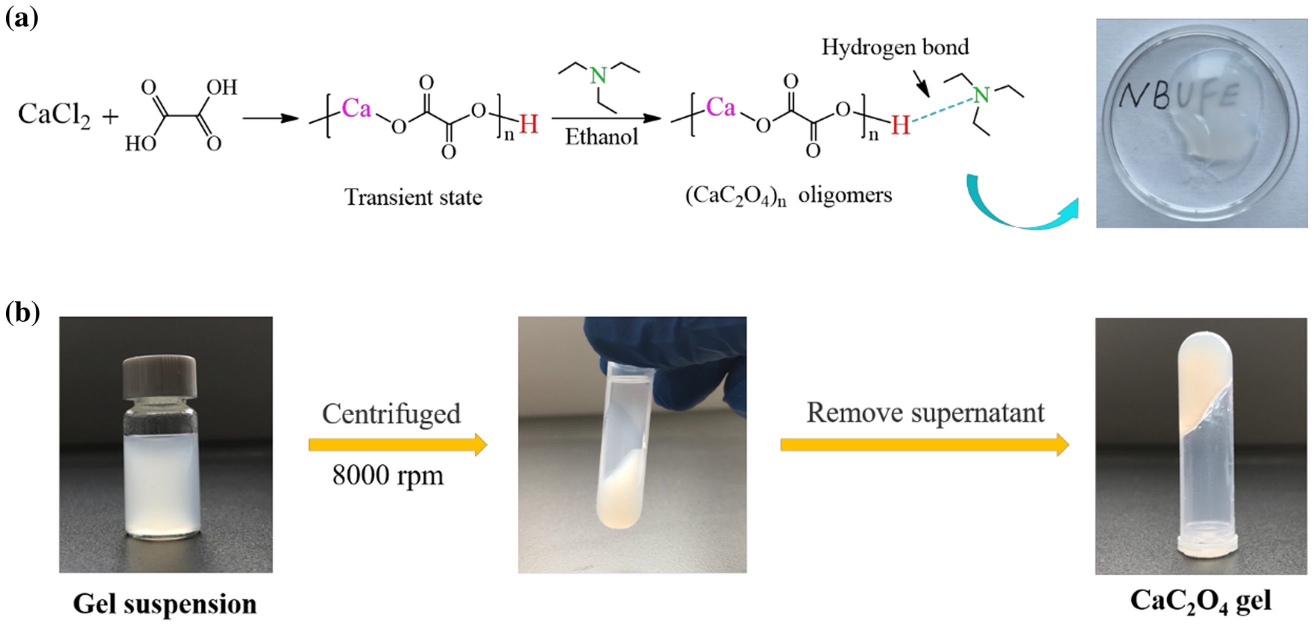
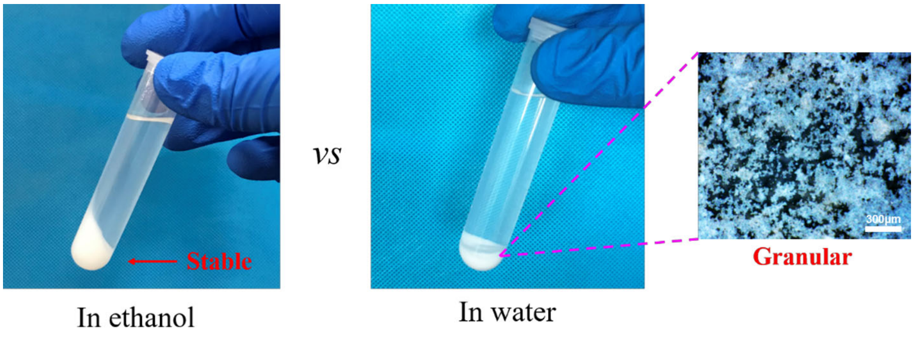


Figure 1 **a** Schematic illustration of the preparation process conditions and the capping strategy for producing CaC_2O_4 oligomer gels; **b** optical photographs of the original CaC_2O_4 oligomer suspension and the prepared gels after centrifugation.

triethylamine added in the reaction system is greatly excessive, the pH value of the reaction system can be kept stable throughout the process. In addition, in order to prevent the influence of triethylamine volatilization on the reaction, the entire reaction system process is kept in a closed system. As shown in Figure S1, the prepared COOGs present a uniform gel dispersion system. After standing for 12 h, the state of liquid–gel layering gradually appeared. Through centrifugal separation, the COOGs has a characteristic of viscoelasticity and translucence (Fig. 1b). By investigating the stability of the COOGs dispersing in ethanol and water, we found that it shows different state changes over time, respectively. The results indicated that the gels could maintain a stable gel state for a long time (over three months) in ethanol. However, it exhibited an entirely different change of form in water for 24 h. As shown in Fig. 2, COOGs is gradually degraded into fine particles in aqueous medium, which obviously shows very poor stability than in ethanol.

After the TEA is volatilized, the "locking" effect becomes weaker or disappears. The inorganic gel will crystallize gradually and form a block structure, and this process is not reversible. Generally, the crystallization of inorganic materials is an extremely complicated process. Here, we initially explored the crystalline morphology of the gel after centrifugation and its dispersion at room temperature. By observing the macroscopic and microcosmic photographs of the crystal of CaC_2O_4 oligomer gels suspension, due to the different volatilization rates of triethylamine and solvent in the gel dispersion at different locations, complex crystallization phenomena also occur in

Figure 2 State of CaC_2O_4 oligomer gels dispersed in ethanol and water, and the optical microscopy photographs of the collapsed gels in water.



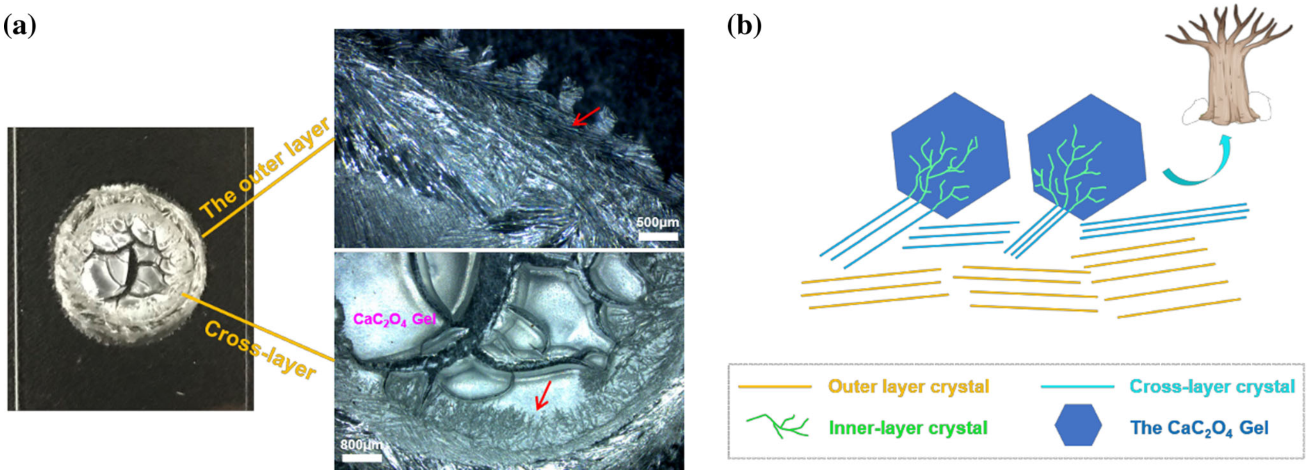


Figure 3 (**a**) Macroscopic and microcosmic photographs of the incomplete crystal of CaC_2O_4 oligomer gels; (**b**) schematic illustration of the centrifuged CaC_2O_4 oligomer gels' crystal morphology at room temperature.

different areas (Figure S2). Compared with the dispersion, the gel after centrifugation preferentially crystallizes from the outside, and the area adjacent to the crystal and the gel exhibits the phenomenon of extending into the latter (Fig. 3a). This phenomenon is like the continuous extension and growth of the branches of a tree in the bud (Fig. 3b).

Considering that the increase in the temperature can accelerate the speed of the solvent ethanol and triethylamine in the gel, further exploration was focus on the influence of temperature on the crystalline properties of the inorganic gel. XRD pattern of the COOGs crystallized at 25, 100 and 200 °C is shown in Fig. 4. According to the XRD pattern, the crystalline products at the above three different temperatures are calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$). The diffraction peaks at the interplanar spacing d = 0.595, 0.364, 0.297 and 0.235 nm are attributed to the (101), (020), (202) and (130) crystal planes of $CaC_2O_4 \cdot H_2O$, respectively. The results show that, in comparison, the intensity of the diffraction peak of the (101) crystal plane has an obvious tendency to increase with the increase in the temperature. The calculated crystallite size at different temperature was 92.1, 11.6 and 35.6 nm, respectively. The change in the strength of the crystal plane may cause the crystal micromorphology to change significantly with the external temperature.

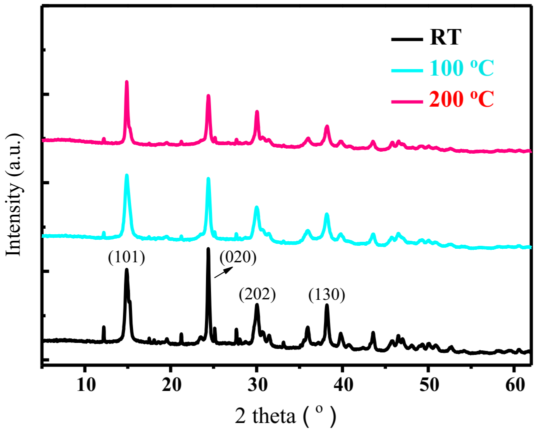


Figure 4 XRD pattern of the CaC_2O_4 oligomer gels crystallized at different temperature.

In order to further explore whether the morphology of the obtained gel crystals is controllable, the microscopic morphology of the COOGs at different external temperatures was further observed. Here, we observed the SEM images of the COOGs crystallized at 25, 100 and 200 °C, respectively. As shown in Fig. 5a, COOGs crystallized at room temperature exhibited a layered closely packed structure. By observing the spectrum under further magnification, we can clearly see that the small crystals are combined with each other in a three-dimensional cross-linking manner. Each of the crystals is of irregular shapes and the size is about 100–200 nm (Figure S3a, Fig. 5d). When increasing the crystallization temperature to 100 °C, it shows a layered stacked structure ether, but it is different from the structure at room temperature (Fig. 5b). The most significant difference is that large aggregates appear between the crystals, and smaller crystals that are tightly bound to each other begin to appear, which leads to defects in the layered stacking, and the cross-linked network

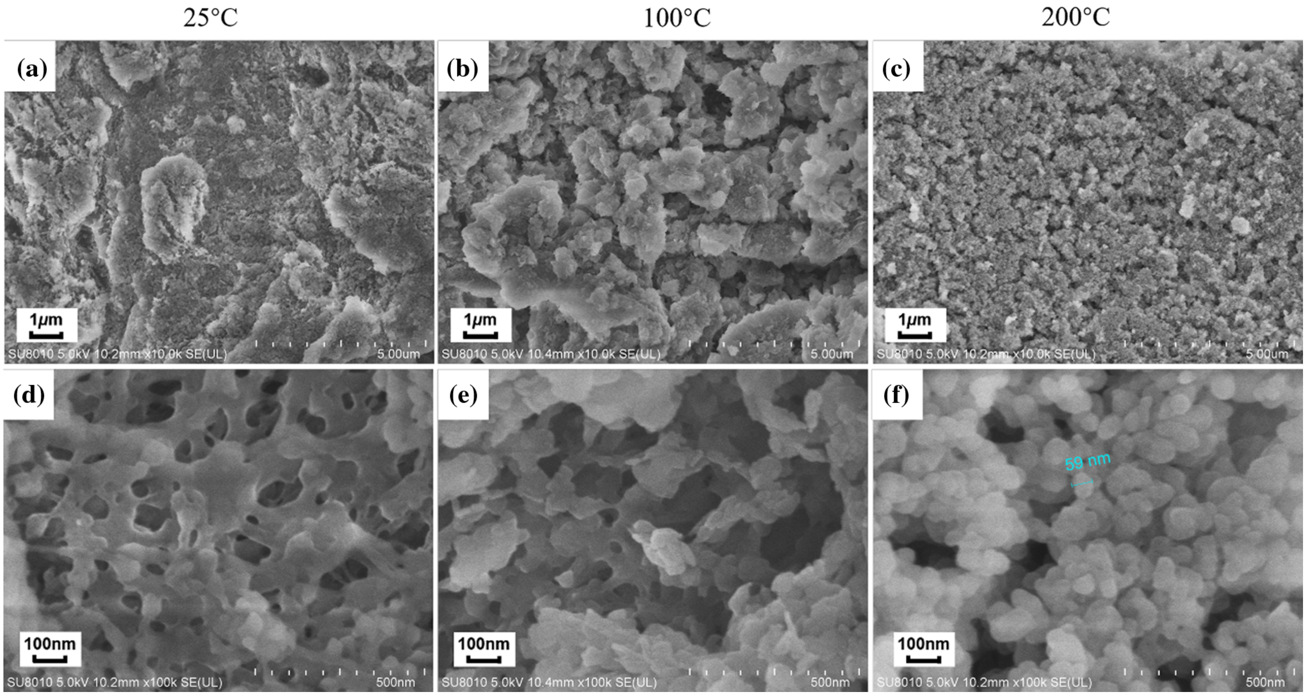


Figure 5 Different microscopic sizes of SEM images of the CaC_2O_4 oligomer gels crystallized at different temperature: 25 °C (**a**, **d**), 100 °C (**b**, **e**) and 200 °C (**c**, **f**).

structure is gradually broken (Figure S3b, Fig. 5e). Compared with the former, the gel at a higher temperature of 200 °C exhibits a special structure that is smaller in size, tightly arranged with each other and evenly arranged (Fig. 5c, Figure S3c). The particle size was reduced to 50–100 nm. The cross-linked network structure has disappeared, replaced by nanoscale spherical crystal units that are closely arranged and independent of each other (Fig. 5f). The above shows that relatively high temperatures tend to make the crystal units more tightly bound, and the crystal units become smaller and more uniformly arranged, which corresponds to the crystal plane intensity change of the 020 in the XRD pattern. Besides, temperature is an important and simple way to achieve the different crystal morphology of CaC_2O_4 oligomer gels.

Conclusions

In this work, the triethylamine (TEA)-stabilized inorganic CaC_2O_4 oligomer gels (COOGs) are prepared through a simple synthesis method. This study indicates that the calcium oxalate oligomers can be achieved by capping effect in inorganic synthesis process as previously studied calcium carbonate and calcium phosphate oligomers. The prepared oligomer is translucent gel, and the gels are much less stable when they are dissolved in water than in ethanol. In addition, by controlling the external temperature, XRD and SEM analysis found that the crystalline micromorphology of the COOGs exhibits unique morphological characteristics.

Acknowledgements

"Research Start-Up Fund of NBUFE (1320200911)" is greatly acknowledged for their financial support.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary Information: The online version contains supplementary material available at https://doi.org/10.1007/s10853-021-06705-4.

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