



Anions bonded on the supramolecular hydrogel surface as the growth center of biominerals

Naien Shi, Gui Yin, Min Han, Zheng Xu*

State Key Laboratory of Coordination Chemistry, National Laboratory of Solid State Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

In this work, a supramolecular hydrogel formed from *N,N,N'*-tris(3-pyridyl)-trimesic amide was reported to serve as the matrix for the growth of biominerals. The organic hydrogel scaffold contains nitrogen heterocyclic ring and amide groups that can bind anions of the mineral (specially here, carbonate ions and phosphate ions) through hydrogen bonding interactions and act as the biomineralization active sites for growing biominerals. Calcium carbonate nucleated on the site of the hydrogel fiber where carbonate ions bonded and left obvious hydrogel fiber prints on the obtained product. Calcium phosphate grew into curved platelike nanostructures along the hydrogel fibrous network. XRD pattern and FT-IR spectra confirmed the formation of minerals on the hydrogel. The results indicate that the hydrogen bonding interaction can provide strong enough binding force for the growth of the minerals on organic scaffolds. Our finding extends the organic scaffolds into biodegradable small molecule hydrogels and also extends the growth centers of the minerals from conventional carboxylate groups binding Ca^{2+} to amide and pyridyl groups binding PO_4^{3-} .

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1. Introduction

Calcium phosphate is one of the most important minerals “processed” by living organisms [1]. As the lifespan of mankind increases, the repair and graft of broken bones become more and more important [2]. In order to synthesize artificial bone materials with strong mechanical strength and high affinity to natural bones, researchers have been attempting to integrate organic scaffolds and calcium phosphate together [3–7]. Up to now, the complicated interactions of the biomolecule-mineral nucleus have not yet been well understood [8]. It is generally accepted that the protein-based organic scaffold is a key factor for controlling the growth of minerals in natural bones [3]. As we know, many kinds of amino acids in the organic scaffolds of natural bones contain nitrogen heterocyclic ring and amide groups (Pro and His, etc.), therefore the role of nitrogen heterocyclic ring and amide groups in biomineralization process is a crucial issue. Whereas the specific sites of the organic scaffolds reported previously are the carboxylate groups, which strongly bound to calcium ions via electrostatic interactions to form growth centers of calcium phosphate [3–7,9]. Here, we select a supramolecular hydrogel containing amide and pyridyl group as the organic scaffold, adopting hydrogen bonds to bind

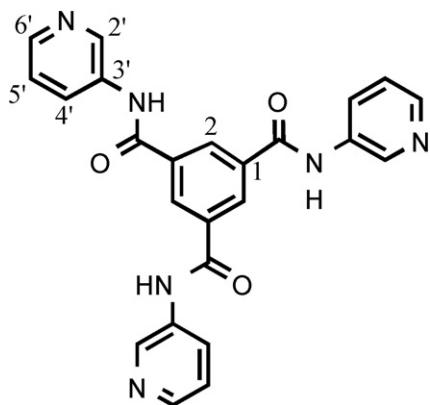
anions of the mineral to study the growth of calcium phosphate. The gel is composed of *N,N,N'*-tris(3-pyridyl)-trimesic amide (Scheme 1) [10,11], which exclude the role of carboxylate groups. By alternatively adding phosphorous source Na_3PO_4 and calcium source CaCl_2 , respectively, calcium phosphate was formed and grew into curved platelike nanostructures along the hydrogel fibrous network. It demonstrates that nitrogen heterocyclic ring and amide in the organic scaffolds can provide site-specific nucleation centers through hydrogen bonds ($\text{P}-\text{OH} \cdots \text{N}$; $\text{P}-\text{O} \cdots \text{N}-\text{H}$). Additionally, to the best of our knowledge, there are few works on the preparation of calcium phosphate nanostructures using supramolecular hydrogel as organic scaffold [12]. It may pave a way to the design of novel organic scaffolds which are not only high affinity to biominerals but also biodegradable.

2. Experimental

2.1. Synthesis of the gelator of trimesic amide

Trimesic acid (5 g, 23.8 mmol) was put into SOCl_2 (10 mL) in the presence of DMF (0.2 mL) and stirred for 1 h at room temperature, then refluxed for 6 h until all reacted, followed by removing the solvent and dried in vacuum until the solvent was completely removed, then trimesic chloride was obtained as a solid at room temperature. Next, adding trimesic chloride (0.92 g, 3.4 mmol) into freshly distilled anhydrous THF (20 mL) containing 3-pyridylamine

* Corresponding author. Tel.: +86 25 83593133; fax: +86 25 83594502.
E-mail address: zhengxu@netra.nju.edu.cn (Z. Xu).



Scheme 1. Chemical structure of the amide.

(1.00 g, 10.6 mmol) and pyridine (1.5 mL), the crude product was afforded as a precipitate. It was washed by diethyl ether, water and hot methanol, respectively, and dried in vacuum. The final product was obtained as a white solid (1.19 g, 80%). ESI MS m/z (%): 439.1 ($M+1$, 100%). $^1\text{H NMR}/\delta$ (ppm): 11.24 (s, 3H, NH), 9.20 (d, 3H, H-2'), 8.91 (s, 3H, H-2,4,6), 8.50 (dd, H-6'), 8.48 (ddd, H-4'), 7.67 (dd, H-5').

2.2. Preparation of the hydrogel containing Na_2CO_3 and the mineralization of CaCO_3 using the organic hydrogel

The hydrogel was prepared in 2:1:1 EtOH/ H_2O / Na_2CO_3 (0.02 M) aqueous solution (v/v) with the trimesic amide concentration of 0.6 wt%. Then it was heated to all dissolved and left stand to obtain Na_2CO_3 -hydrogel composite gel. For the mineralization of CaCO_3 , the Na_2CO_3 -hydrogel composite gel was immersed in CaCl_2 aqueous solution (0.02 M) for 2 days to ensure complete reaction. The obtained CaCO_3 product can be separated by repeatedly washing with hot EtOH/ H_2O mixed solvent.

2.3. Preparation of hydrogel/calcium phosphate composite

Firstly, the hydrogel was prepared in 1:1 water/ethanol (v/v) mixed solvent at a concentration of 0.6 wt%, and was heated to 90°C to a transparent sol. Then it was quickly poured into a culture dish and was allowed to cool in a refrigerator ($T = 15^\circ\text{C}$). Then 6 mL aqueous solution of Na_3PO_4 (0.02 M) was added in it and immersed for 1 day. Removing Na_3PO_4 solution, CaCl_2 aqueous solution (6 mL, 0.02 M) was added in and immersed for another 1 day to react completely with the adsorbed Na_3PO_4 . Finally, the obtained product was washed by deionized water. Took a piece of the sample carefully in order to avoid breaking, and then allowed it to evaporate in air and dried in vacuum for further SEM measurement.

2.4. Measurements

FT-IR spectra were recorded on a Bruker Vector.22 FT-IR spectrophotometer at a resolution of 2 cm^{-1} in KBr pellets. NMR spectroscopy was collected on AVANCE DAX-500 (Bruker, Sweden) 500 MHz superconducting nuclear magnetic resonance spectrometer. ESIMS result was obtained on LCQTM electrospray ionization mass spectrometer (Finnigan, American). X-ray powder diffraction patterns were performed on X'Pert Pro X-ray Diffractometer (PANalytical, Herland). SEM images were taken on a JEOL JSM-5610LV Scanning Electron Microscope. The sample of xerogel is obtained by evaporating the solvent to be dried in air. The samples were further sputtered a layer of platinum for SEM characterization.

3. Results and discussion

Firstly, the microstructure of the organic supramolecular hydrogel scaffold is illustrated. Supramolecular gel is attracting more and more interests in the past few years, because of its potential application in biology arising from its special biodegradability as compared to polymer gels [13–15]. During the gelation, the small organic molecular gelators self-assemble into fibrous aggregates with a meshlike structure that holds a large amount of solvents by interfacial tension and supramolecular interactions [16,17]. Here, trimesic amide molecules self-assemble into one-dimensional fibrous structure through intermolecular $\text{N-H}\cdots\text{Py}$ hydrogen bonds (Py stands for pyridyl group) [10,11]. SEM image of the hydrogel (Fig. 1a) shows that a large quantity of long fibers (50 nm in diameter) tangled together. In order to study the possibility of the trimesic amide hydrogel as the scaffold for biomineralization via hydrogen bonding interactions, we choose the growth of CaCO_3 and CaPO_4 as examples. Firstly, the growth of CaCO_3 on the hydrogel fibers is studied. After mixing the hydrogel and carbonaceous source Na_2CO_3 homogeneously, the diameter of corresponding fibrils enhanced to 500–1000 nm (Fig. 1b), which was much larger than that of the amide hydrogel. ESI-MS result of the Na_2CO_3 -hydrogel composite shows no carboxylate groups (data not shown), which implies that the trimesic amide molecules are not hydrolyzed. The influence of carboxylate on the biomineralization of calcium phosphate can be excluded.

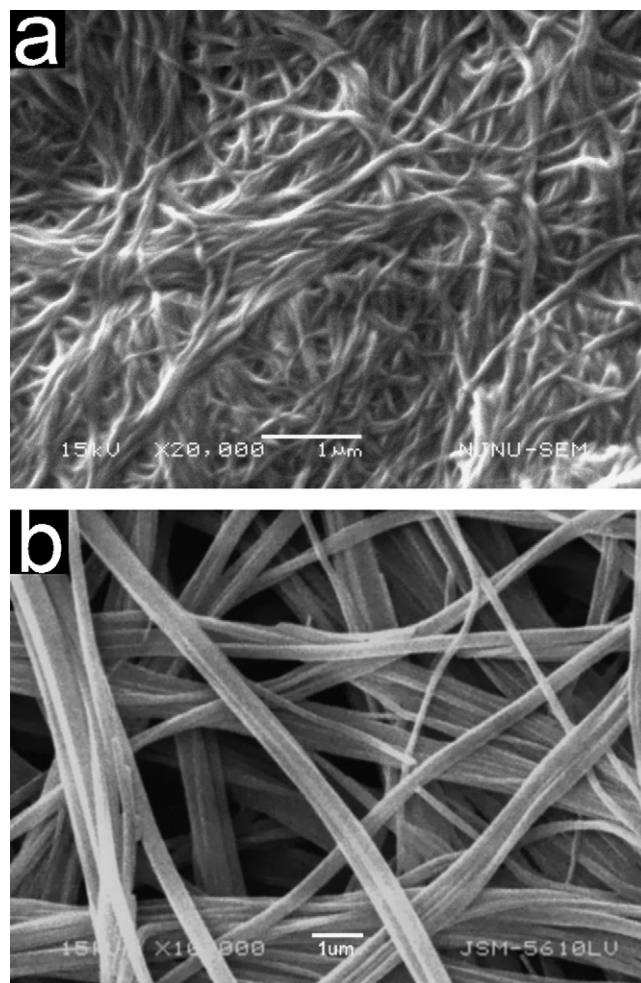


Fig. 1. SEM images of xerogel (a) EtOH/ H_2O gel and (b) EtOH/ H_2O gel containing Na_2CO_3 .

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