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Gas assisted in situ biomimetic mineralization of bacterial cellulose/calcium carbonate bio composites by bacterial

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ABSTRACT

Biomineralization inspired process to produce polymer of desired need is a promising approach in the field of research. In the present work, the bacterial cellulose (BC) based nanocomposites with a 3D network were synthesized via a biological route by choosing the calcium salt of primary metabolites (calcium gluconate) as the carbon source. The BC based composites were characterized by employing with Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). During the preparation of nanocomposites, the calcium ions embedded on the cellulose fibrils were served as the nucleation center and calcium carbonate was deposited into BC network in the assistance of CO_2. The uniform distribution of embedded objects on the cellulose nanofibers between internal and external was achieved. The exploitation of organisms for inorganic growth, shape and self-assembling explores new opportunities to the design of original nanostructures.

1. Introduction

Nature provides a rich toolbox for living organisms to create gradients in material considering the innumerable chemical, structural and geometrical variables that can be adapted [1–3]. Biological materials are generally composites with spatially heterogeneous and tunable properties [4]. The bio mineralized structures synthesized by organisms, such as nacre [5, 6], stony coral [7,8] and bone, and play crucial role in maintaining their soft bodies, protecting them from predators or storing inorganic ions. Inspired by the biomineralizing organisms, the skeletal organic matrix (SOM) secreted by the animal plays the important roles in biomineralization process of the coral through evolution [8]. The relation between the mineral phase and the SOM across different spatial scales is mutually reinforcing. Hierarchically porous structures are of key importance to allow adaptation to constant environmental changes [9].

As a new class of composites produced by living organisms including microorganisms, cell and bacterial, bio composites have attracted great attention [10]. The living organisms are considered to be a micro-factory as they are able to ingest small molecules from the environment for its growth. The bio composites with complex nanoarchitecture are often obtained by the product of cellular or extracellular reactions mechanisms.

Bacterial cellulose (BC) harvests a specific interest in the field of biogenic materials as the main extracellular polymeric sections (EPS) secreted by bacteria belonging to the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina* [11,12]. Meanwhile, the metabolic pattern of cellulose producing bacteria indicated that weak acids such as gluconic acid, lactic acid and acetic acid are accumulated first and were consumed subsequently during the fermentation processes [13–16]. It has been proved that gluconic acid can be used as a sole carbon source for BC production [13]. BC with intrinsically 3D structure has untra-fine structure and sufficient mechanical strength and is believed to be the most striking features which distinguishes BC from other natural polymers [17–19]. Commonly a bio-inspired approach has been used to fabricate the BC based composites through microbial fermentation, such as the carbon nanotube (CNT) [20], grapheme oxide (GO) [21,22], calcium carbonate ($CaCO_3$) [23], et al. However, this method cannot work well while the BC pellicle is thick, due to the small pores restricts the uniform distribution of embedded objects between internal and external. The biogenic incorporation of bulk matter is challenging during the in-situ biosynthesis, once the intrinsically 3D structure with small pore is formed [24].

In this work, novel bionic method was exploited to replicate nacre features into artificial structural materials by adding calcium gluconic to mimic the living environment of nacre. The preliminary results showed that the secreted organic extracellular matrix (BC) is embedded with calcium ions during the fermentation process, of which is thought to the initiation of mineralization. The granules phase formed on the

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