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Nacre-like calcium carbonate controlled by ionic liquid/graphene oxide composite template

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A B S T R A C T

Nacre-like calcium carbonate nanostructures have been mediated by an ionic liquid (IL)-graphene oxide (GO) composite template. The resultant crystals were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, and X-ray powder diffractometry (XRD). The results showed that either 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) or graphene oxide can act as a soft template for calcium carbonate formation with unusual morphologies. Based on the time-dependent morphology changes of calcium carbonate particles, it is concluded that nacre-like calcium carbonate nanostructures can be formed gradually utilizing [BMIM]BF_4/GO composite template. During the process of calcium carbonate formation, [BMIM]BF_4 acted not only as solvents but also as morphology templates for the fabrication of calcium carbonate materials with nacre-like morphology. Based on the observations, the possible mechanisms were also discussed.

1. Introduction

Ionic liquids (ILs) are organic salts with polar character and low melting point (<100 °C). They are thermally and chemically stable and have a practically non-detectable vapor pressure. Their non-volatile nature allows for easy recycling after usage and, thus, endows them with high ranking in the realm of green chemistry [1,2]. For this reason, they are considered as green solvents which can meet the demands of environmental protection [3] as opposed to traditional volatile organic compounds. ILs have been explored as environmentally benign reaction media for the production of inorganic materials. Interestingly, ILs sometimes can act not only as solvents but also as reactants and morphology templates for the fabrication of inorganic materials with new or improved properties [4–9].

At the same time, graphene oxide (GO) has attracted wide interests of researchers because of its unique physicochemical and structural properties. GO sheets have one atom thickness and two-dimensional structure with negatively charged edges, high specific surface area and mechanical strength, which endow them excellent performances in mediating the mineralization of $CaCO_3$. Thus, GO sheets as additives can greatly reduce the interfacial Gibbs energy of $CaCO_3$/GO composite crystal formation as compared to the application of other molecular templates according to an empirical equation proposed by Nielsen [10,11]. The functional groups of GO can also act as interfacial linkers and facilitate the stress transfer from the polymer matrix to GO. Some materials have been induced by GO, such as metals [12], semi-conductors [13], $CaCO_3$ [10,14] and hydroxyapatite (HAP) [15–17]. In particular, these GO/$CaCO_3$ (HAP) inorganic hybrid materials have excellent biocompatibility and mechanical properties. In the meantime, six widely used methods for graphene oxide preparation have been reported, such as modified Hummer method, exfoliating carbon nanotube method, chemical vapor deposition (CVD) method [18], et al. Cytotoxicity and biocompatibility of graphene oxide have also been evaluated. Y Chang et al. found GO with no obvious cytotoxicity on A549, MCF7 or SKBR3 cells when GO was prepared with the modified Hummer's method [19–21].

In addition, GO paper [22], GO-PVA, and PMMA polymer nanocomposites [23] can been formed with nacre-like structure through hydrogen bonding. Synthesis of nanomaterials with ultra-strong mechanical property greatly broadens the space for the preparation of special materials with graphene oxide. Strong electrostatic/chemical interaction between ILs and GO improves the dispersion of GO, as well as enhanced performance of matrixes induced by the introductions of ILs into functional composites and give rise to a wider range of GO applications [24–26]. Also, the combination of IL and GO provides an effective platform for the nucleation and growth of $CaCO_3$ micro/nanoparticles.

It is well known to all that natural nacre has a unique combination of remarkable strength and toughness and is often described as “brick-and-mortar” structure. The unique structure is attributed to its hierarchical nano/microscale structure and precise inorganic–organic interface [27,28]. In this article, we put forward the synthesis of the nacre-like $CaCO_3$ nanocomposites by using gas diffusion method-

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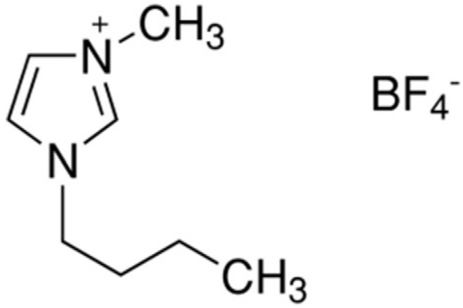


Scheme 1. Chemical structure of the IL employed.

assisted [BMIM]BF_4/GO composite template under room temperature. To precipitate $CaCO_3$, $CaCl_2$ and $(NH_4)_2CO_3$ are selected as the sources of calcium and CO_2, respectively. The use of $(NH_4)_2CO_3$ instead of CO_2 allows the reaction medium to maintain at a neutral or weakly basic pH caused by the dissolution of ammonia. In comparison to previous studies, this article develops a facile strategy to fabricate the nacre-like calcium carbonate materials in green solvent. Furthermore, it develops a new opportunity for the formation of calcium carbonate with superior function and morphology.

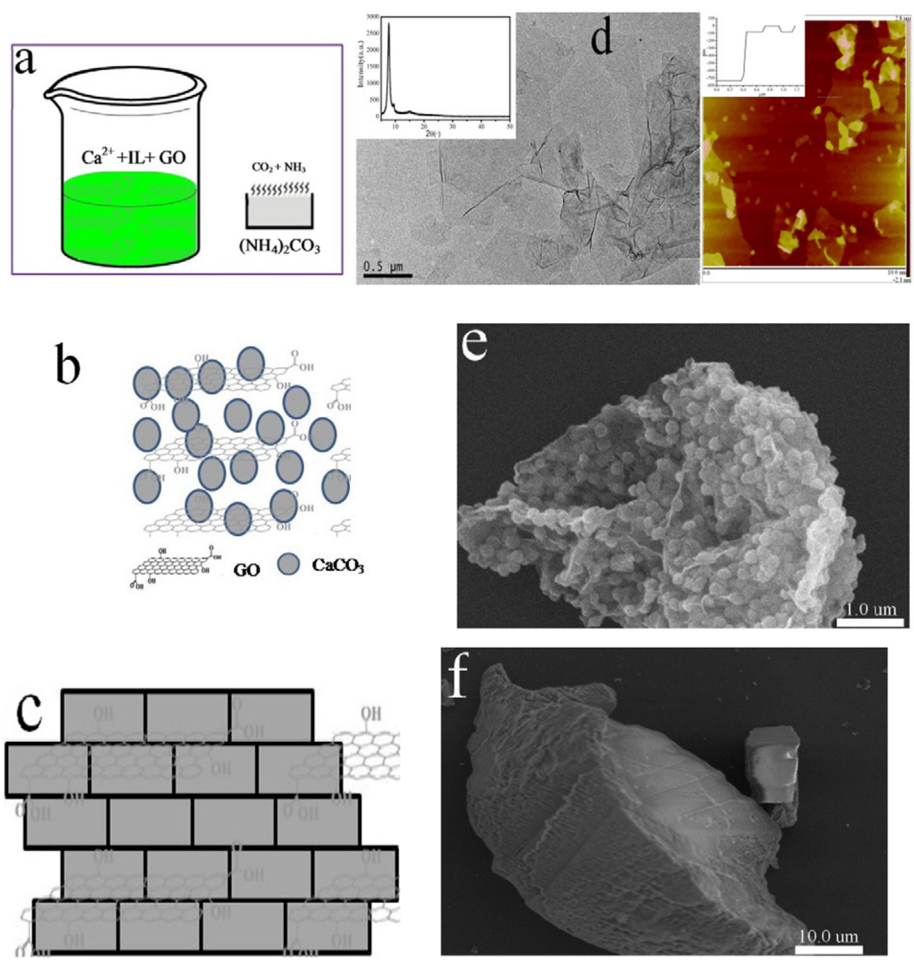
2. Experiment

2.1. Preparation of graphene oxide

Graphene oxide was synthesized from graphite by a modified Hummers method [29,30]. Briefly, natural graphite (1.0 g), $NaNO_3$ (0.75 g) and concentrated H_2SO_4 (75.0 mL) were added into $KMnO_4$ (3.0 g) gradually with stirring and cooled in order to keep the temperature below 5 °C for 1 h. Then, the ice bath was removed and the solution was kept stirring at room temperature. Five days later, distilled water (140.0 mL) was slowly added. After 1 h, this reaction was transferred to a 98 °C water bath and stirred for 2 h. Then, 30% H_2O_2 solution (10.0 mL) was added and kept stirring for 2 h. The mixture was centrifuged and washed successively with 1.0 mol/L HCl aqueous solution and Milli-Q water several times until the pH of the supernatant was ~7. The bright yellow graphite oxide powder was dried in a vacuum oven less than 40 °C for 24 h.

2.2. Synthesis of $CaCO_3$ in ionic liquid/graphene oxide solutions

Anhydrous calcium chloride ($CaCl_2$) and ammonium carbonate ($(NH_4)_2CO_3$) were obtained commercially and were of pure analytical grade. All reagents above were used without further purification. Double-distilled water was employed in all experiments. The ionic



Scheme 2. Illustration of the formation of the nacre-like $CaCO_3$. The steps describe (a) mineralization of $CaCO_3$ in the presence of [BMIM]BF_4/GO composite template and $CaCl_2$ by CO_2 gas diffusion method, (b) calcium carbonate particles grown on graphene oxide template, and (c) their conversion to nacre-like $CaCO_3$ materials with time prolonged. Images in the right column show (d) TEM of GO sheets used for this study (inset: XRD patterns analysis) and AFM image of GO sheets (inset: height line),(e) SEM images of GO-wrapped $CaCO_3$ microspheres, and (f) SEM images of $CaCO_3$ microspheres induced by [BMIM]BF_4/GO composite template.