Formation of aragonite mesocrystals and implication for biomineralization

GEN-TAO ZHOU,1,2* QI-ZHI YAO,2 JIE NI,1 AND GU JIN2

1CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, P.R. China
2School of Chemistry and Materials, University of Science and Technology of China, Hefei 230026, P.R. China

ABSTRACT

Highly oriented aragonite tablets have been found in the nacre layers of molluscan shell (or mother of pearl). In this article, we show that highly organized aragonite rods can be prepared over a broad range of pH values (1.5 to 6.9) and in the absence of any bio- or organic macromolecules. The organized rods were characterized by XRD, FTIR, FESEM, TEM, SAED, and EDX techniques. FESEM results reveal that the mesoscale aragonite rods are not only assembled with aragonite microrods end-to-end, and side-to-side, but are also partially fused to one another, forming flat, faceted surfaces, i.e., mesocrystal structure. TEM and SAED analyses confirm that the organized rods have the same crystallographic symmetry as single-crystal aragonite, and thus the self-assembly process is energetically favorable. Similar assembly processes also occur for the mineral strontianite of the aragonite group, revealing the occurrence of a general self-assembly process. The driving force controlling the self-assembly process may originate from the inherent anisotropic dipole-dipole interactions between the assembled units. Such dipole interaction may generally occur in biomineralization of nacre layers in molluscan shell, and orchestrate aragonite nanocrystals in an aragonite tablet to coherently orient and array. Furthermore, the dipole-dipole interactions may also contribute to the co-orientation of the aragonite tablets in the same nacreous column. Therefore, our experimental results may provide insight into biomineralization mechanisms. It appears that biological genetic and crystallochemical factors may synergistically operate in biomineralization.

Keywords: Aragonite, mesocrystal, biomineralization, oriented attachment, self-assembly

INTRODUCTION

Classical models describing crystal growth suggest atom-by-atom addition to an existing nucleus or template or via dissolution of unstable phases (metastable polymorphs or small particles) and reprecipitation of the more stable phase, i.e., Ostwald’s rule of stages or ripening. However, an increasing plethora of experimental work and natural observations have revealed that additional particle aggregation-based coarsening mechanisms can operate in certain nanostructured materials and biogenic minerals. This growth process was first highlighted by Banfield’s group, and called “oriented attachment” (Penn et al. 1998a, 1998b; Penn and Banfield 1999; Banfield et al. 2000). They found that anatase and iron oxyhydroxide nanoparticles with sizes of a few nanometers can coalesce together by sharing a single-crystallographic orientation under hydrothermal or biomineralized conditions. This growth process was first highlighted by Banfield’s group, and called “oriented attachment” (Penn et al. 1998a, 1998b; Penn and Banfield 1999; Banfield et al. 2000). They found that anatase and iron oxyhydroxide nanoparticles with sizes of a few nanometers can coalesce together by sharing a single-crystallographic orientation under hydrothermal or biomineralized conditions. In this article, we show that highly organized aragonite rods can be prepared over a broad range of pH values (1.5 to 6.9) and in the absence of any bio- or organic macromolecules. The organized rods were characterized by XRD, FTIR, FESEM, TEM, SAED, and EDX techniques. FESEM results reveal that the mesoscale aragonite rods are not only assembled with aragonite microrods end-to-end, and side-to-side, but are also partially fused to one another, forming flat, faceted surfaces, i.e., mesocrystal structure. TEM and SAED analyses confirm that the organized rods have the same crystallographic symmetry as single-crystal aragonite, and thus the self-assembly process is energetically favorable. Similar assembly processes also occur for the mineral strontianite of the aragonite group, revealing the occurrence of a general self-assembly process. The driving force controlling the self-assembly process may originate from the inherent anisotropic dipole-dipole interactions between the assembled units. Such dipole interaction may generally occur in biomineralization of nacre layers in molluscan shell, and orchestrate aragonite nanocrystals in an aragonite tablet to coherently orient and array. Furthermore, the dipole-dipole interactions may also contribute to the co-orientation of the aragonite tablets in the same nacreous column. Therefore, our experimental results may provide insight into biomineralization mechanisms. It appears that biological genetic and crystallochemical factors may synergistically operate in biomineralization.

Keywords: Aragonite, mesocrystal, biomineralization, oriented attachment, self-assembly

E-mail: gtzhou@ustc.edu.cn

* Corresponding author.