

Biomimetic Arrays of Oriented Helical ZnO Nanorods and Columns

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Extended helical or chiral nanostructures (helical nanowires, nanofibers, or nanoribbons) are usually associated with biomolecules such as proteins, polypeptides, and their aggregates,¹ but are not common in synthetic materials. Chiral crystal growth of calcium carbonate (calcite) is observed when chiral molecules such as aspartic acid and polyaspartate are used to mediate the mineral growth.^{2,3} Here we report the first synthesis of unusual extended and oriented helical nanostructures in synthetic ceramics. Large arrays of oriented helical ZnO nanorods and columns are formed using simple citrate ions to control the growth behavior of the crystal. ZnO by itself tends to grow into rodlike structures along the $\langle 001 \rangle$ orientation like calcite, but citrate ions specifically adsorb to the (002) surface and force the crystal to grow into plates. The spiral growth of these plates produced the oriented helical nanorods and columns. Unlike calcium carbonate that has been widely studied, ZnO is a wide band gap semiconductor and has useful electronic and optical properties.⁴ The novel structure discussed in this paper could lead to new approaches to control the orientation, the surface area, and the defect structure that are critical for practical applications. Furthermore, the morphology generated in the helical ZnO nanostructure shows remarkable resemblance to the growth morphology of nacreous calcium carbonate in red abalone (gastropod *Haliotis rufescens*), and thus may shed new light on the mineralization of biomaterials.

We used arrays of oriented ZnO rods as the base material to grow the helical structures. The oriented ZnO rod arrays were prepared by controlled nucleation and growth.⁵ To prepare the ZnO rods, ZnO nanoparticles were first deposited on glass substrates. The glass substrates were placed in a solution containing 0.030 M $\text{Zn}(\text{NO}_3)_2$ and 0.030 M hexamethylenetetramine (HMT) and reacted at 60 °C for 3 days. The same procedure was repeated two more times with the addition of a very small amount of sodium citrate (0.00017 M). To grow the helical ZnO nanostructures, the glass substrate containing the oriented ZnO rods was placed in a solution containing 0.030 M $\text{Zn}(\text{NO}_3)_2$, 0.10 M HMT, and 0.0010 M sodium citrate and was reacted at 95 °C for 1 day. Figure 1a shows the scanning electron micrograph (SEM) of oriented fibrous structures grown on the (002) surface of the base ZnO crystals. The large hexagonal surfaces observed in the SEM image are the end (002) surfaces of the ZnO base crystals, indicating good alignment of the ZnO rods. At a higher magnification precisely aligned nanorods on the (002) surface of ZnO crystal are observed (Figure 1b). Panels c and d in Figure 1 indicate that these nanorods were formed from stacking of nanoplates with a uniform thickness of about 15 nm. These nanorods are about 1 μm in height, 500 nm in diameter at the base, and less than 30 nm in diameter at the tip. When the tips of these nanorods are broken off, helical growth features are observed on many nanorods (inserts in Figure 1a). The step height here is about 15 nm. Therefore, we conclude that these nanorods

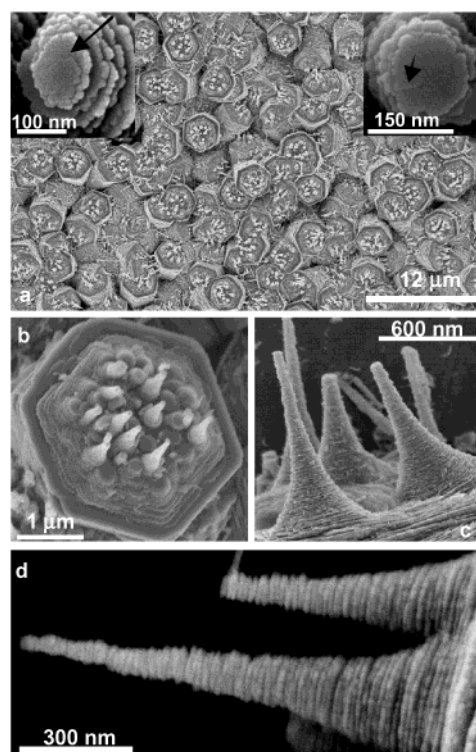


Figure 1. SEM micrographs of helical ZnO nanorods on oriented ZnO crystals. (a) Large arrays of well-aligned helical ZnO nanorods on top of base ZnO rods. (b) Precisely aligned ZnO nanorods on the (002) surface of one ZnO crystal. (c) Tilted high-magnification SEM image of arrays of helical nanorods on one (002) surface. (d) High-magnification SEM image of two long helical ZnO nanorods.

are formed from helical growth of the nanoplates. Furthermore, not only are these nanorods precisely aligned within one ZnO crystal, they are also well aligned across the whole sample because the base ZnO crystals are also aligned.

The helical rod and column structures reported in this study are remarkably similar to the growth patterns of the nacreous calcium carbonate. In the early stage of growth of the nacreous layer of red abalone, large arrays of aligned calcium carbonate columns made of thin aragonite nanoplates are first observed.

Figure 2 shows the similarity of SEM images of the helical ZnO nanocolumns (Figure 2a) and the growth tip of a young abalone shell containing oriented columns of aragonite nanoplates (Figure 2b). Furthermore, when we performed a secondary growth on the helical nanorods, aligned and well-defined nanoplates are formed, as in nacre. Panels c, d, and e of Figure 2 show that the side-width growth of the ZnO nanoplates leads to hexagonal ZnO plates that begin to overlap with one another. The helical growth behavior now becomes clearly visible on top of the columns (inserts in Figure 2c).

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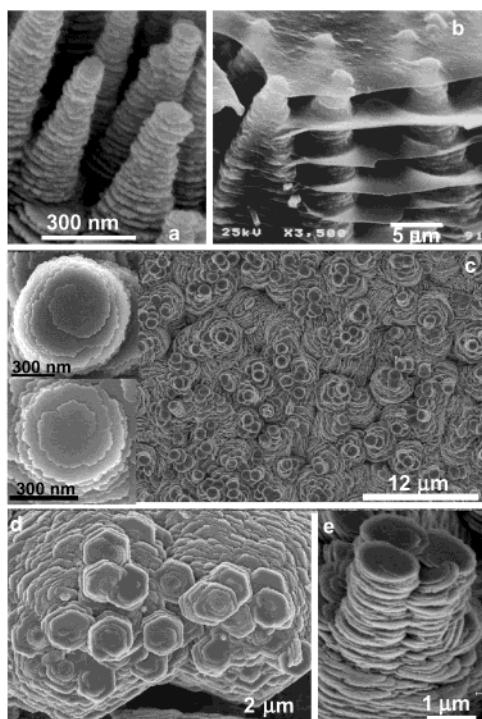


Figure 2. Comparison of ZnO helical structures with nacre. (a) High-magnification image of oriented ZnO helical columns. (b) Nacreous calcium carbonate columns and layers near the growth tip of a young abalone. (c) Large-area view of the helical columns. (Inset) Top view of the helical structure. (d) High-magnification of the surfaces of the helical columns showing well-defined hexagonal platelike structures. (e) Layered structures in the helical ZnO columns.

In the literature most theories for biomineralization of nacre emphasize the role of the organic phases,^{6,7} whether these organic phases function as simple physical compartments or act to control nucleation or to terminate crystal growth by surface poisoning. In contrast a mineral-bridge mechanism was recently proposed in which the aragonite plates continuously grow from one layer to another through a central pore channel that connects the adjacent layers.⁸ In the mineral-bridging mechanism the role of the organic template in controlling the nucleation events as well as the crystal orientation is diminished (but not eliminated). Our results suggest that we can grow similar biomimetic structures in synthetic ceramics through a different helical growth mechanism. Here the column structures made of nanoplates grow continuously from one layer to another in a helical fashion, but an organic templating membrane

is not required to grow the oriented and aligned nanoplates. The oriented structure and the morphology are direct results of the helical growth pattern. In fact helical growth rings were also revealed on the surface of the nacreous aragonite plates in earlier studies,⁹ implying that helical growth might play some role in the formation of organized nacreous calcium carbonate.

However, the organic species still play critical roles. The organic species associated with the membranes revealed in Figure 2b at least dictate whether the platelike aragonite or column-like calcite will form in shells.^{6,10} In our study, ZnO tends to grow long rod structures without the citrate ions. Results in the literature as well as from our own calculations suggest that citrate ions strongly bind to the Zn atoms on the (002) surfaces. We have shown that the citrate ion binding has a strong inhibiting effect on the growth of (002) surfaces. With citrate ions fat hexagonal ZnO crystals, rather than long hexagonal rods, are produced. A higher citrate concentration leads to the formation of fine ZnO nanoplates. The helical growth of these nanoplates produces the extended helical nanostructure reported in this work.

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