

Frame Stability of Tunnel-Structured Cryptomelane Nanofibers: The Role of Tunnel Cations - DTU Orbit (09/11/2017)

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The role of tunnel K⁺ ions on the growth and stability of tunnel-structured cryptomelane-type MnO₂ nanofibers (denoted as cryptomelane nanofibers hereafter) has been discussed by means of X-ray diffraction and electron microscopy. Cryptomelane nanofibers with typical diameters of 20–80 nm and lengths of 1–6 μm have been synthesized by means of a simple hydrothermal reaction of KMnO₄ and MnSO₄ aqueous solutions at 140 °C. The growth of cryptomelane nanofibers under hydrothermal conditions follows a dissolution–recrystallization process and involves a morphological transformation from a layered precursor to the tunnel-structured cryptomelane, in which the K⁺ ions play important roles in templating and stabilizing the tunneled framework. The presence of tunnel K⁺ ions also enhances the frame stability of the cryptomelane nanofibers at elevated temperatures. The formation of a layered K_xMn₂O₄ ($x \approx 0.26$) with a hexagonal phase structure has been observed at about 900 °C. The transformation from tunneled cryptomelane to layered K_xMn₂O₄ also follows the dissolution–recrystallization growth mechanism, in which the diffusion of K⁺ ions at high temperatures represents a critical process. The topological correlation between the tunneled and layered MnO₂ materials might provide useful information for the synthesis of MnO₂ nanomaterials with controlled microstructures for different applications.

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