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Research Article

Controlled Synthesis of Manganese Dioxide Nanostructures via a Facile Hydrothermal Route

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Manganese dioxide nanostructures with controllable morphological structures and crystalline phases were synthesized via a facile hydrothermal route at low temperatures without using any templates or surfactants. Both the aging duration and aging temperatures were the main synthesis parameters used to influence and control the rate of morphological and structural evolution of MnO_2 nanostructures. MnO_2 nanostructures comprise of spherical nanoparticulate agglomerates and highly amorphous in nature were formed at lower temperature and/or short aging duration. In contrast, MnO_2 nanostructures of sea-urchin-like and nanorods-like morphologies and nanocrystalline in nature were prepared at the combined higher aging temperatures and longer aging durations. These nanostructures underwent notable phase transformation from δ-MnO_2 to α-MnO_2 upon prolonged hydrothermal aging duration and exhibited accelerated rate of phase transformation at higher aging temperature.

1. Introduction

One-dimensional manganese dioxide (MnO_2) nanostructures such as nanorods, nanowires, and nanofibers have generated intense research interests over the past recent years due to their superior optical, electrical, catalytic, magnetic and electrochemical properties [1–3]. Such manganese dioxide nanostructures are of considerable importance in technological applications and have been intensively investigated as promising electrode materials in primary/secondary batteries and electrochemical capacitors due to their excellent electrochemical properties, low-cost, environmentally benign, and ease of preparation [4–7]. Various approaches have been used to fabricate manganese dioxide, such as self-reacting microemulsion [8], precipitation [9], room-temperature solid reaction [10], sonochemical [11], and hydrothermal methods [12]. The hydrothermal method is a powerful synthesis approach for synthesizing various forms of manganese oxides and affords various advantageous features including the use of mild synthesis conditions such as pH and temperature, and a wide range of precursors that can be used.

Various types of inorganic nanowires and nanorods have been synthesized with the aid of templates or catalysts. Templates are being used to confine the growth of crystals, while catalysts may act as energetically favorable sites for the adsorption of reactant molecules [13]. However, the introduction of templates or catalysts to a reaction system is often accompanied by drawbacks such as the need to prepare or select appropriate templates or catalysts. Besides, impurities in the final product may be difficult to be removed, thereby making the overall synthesis process more complicated and costly. As such, any synthetic method without the need to use any catalyst or template is more favorable for the preparation of low-dimensional nanostructures. Recently, a hydrothermal or solvothermal method has been employed to prepare one-dimensional nanoscaled materials, for example, α-MnO_2, without the use of templates or catalysts [14]. This method is superior to traditional methods since no specific and expensive equipment is required for synthesizing nanostructured materials at low temperatures. The hydrothermal preparation of manganese dioxides involved mainly redox reactions of MnO_4^- and/or Mn^{2+} or the phase transformation of granular manganese dioxide precursors [15]. A common approach for the synthesis of single-crystalline α-MnO_2 nanorods was based on the hydrothermal reaction of $MnSO_4$ and $KMnO_4$ [16]. DeGuzman et al. prepared fibrous α-MnO_2 through redox reactions between $KMnO_4$ and $MnSO_4$