Formation of single-crystallized nanowires of manganese and vanadium oxides by a soft chemical process

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One-dimensional (1D) nanostructures include nanotubes, nanowires, nanorods, nanofibers, nanobelts and nanoribbons. In the past decade, a larger number of 1D structural nanoscale materials have been synthesized using variously synthetic routes, such as chemical reaction[1], template technique[2], and so on. For all of these routes, additional reagents or templates were introduced into the reaction system, As such, the synthetic process is complicated, and might bring about an increase of impurity concentration in the final product. In this study, a simple method was used to synthesize nanowires of manganese and vanadium oxides using only the raw material and water.

Synthesis of nanowires of manganese and vanadium oxides was performed by a soft chemical process [3-4]. In a typical synthesis, 0.15 g commercial γ-MnO_2 or V_2O_4 powder was dispersed into a 15 ml H_2O, then was transferred into a 20 ml autoclave, and kept it in oven at 100 - 200 °C for 1-14 days. The as product was filtered, and died at in air. Finally, the product was characterized by XRD, TGA, SEM and TEM measurements.

Synthesis of single-crystal α- and β-MnO_2

Figure 1A shows the XRD patterns of the raw material and products synthesized at 140, 170 and 200 °C for 3 days. It clearly indicates that diffractions of the products are significantly different from the raw material. As shown in Fig. 1A curves b-d, the crystal phase of the products varied with increasing with increasing temperature, and could be indexed onto α-MnO_2, β-MnO_2 and MnOOH, respectively (JCPDS 44-0141, 24-0735, 74-1632). This result indicates that MnO_2 polymorphic forms can be synthesized by selected-control reaction temperature.

SEM images of α- and β-MnO_2 are shown in Fig. 1B-C and reveal the presence of a larger number of nanowires with a long length. TEM measurement further confirmed the formation of nanowires with a diameter ca. 10-30 nm, as depicted in Fig. 1D-E. High magnification images clearly reveal very crystallized nanowires and the lattice fringes correspond to d-spacing of 0.69 and 0.31 nm for α- and β-MnO_2, respectively.

Synthesis of single-crystal $V_2O_4 \cdot 0.25H_2O$ nanowires

Figure 2A depicts the XRD patterns of the raw material (curve a) and product synthesized at 170 °C for 1, 3, 7, 14 days (curves b-e), respectively. It is notable that a peak at 2θ = 10 ° was observed after the reaction time is more than 3 days, and became more intense with increasing reaction time. This is a characteristic of layered compound, and also was observed in layered hydrate $VO_2 \cdot 1/2H_2O$ and $V_2O_4 \cdot 2H_2O$. This result indicates that the product is a vanadium oxide hydrate $V_2O_4 \cdot nH_2O$ with layered structure. However, all the diffraction peaks can not be indexed onto a vanadium oxide hydrate reported in publications, indicating that the product is a new metastable phase of vanadium oxide hydrate. Using the least-squares method, all the diffraction peaks could be indexed onto the basis of monoclinic symmetry with the lattice parameters a = 16.690 Å, b = 6.200 Å, c = 9.580 Å, and β = 92.20 °. After the product

(synthesized at 200 °C for 3 days) was calcined at 300 °C, the peak at 2θ = 10 ° disappeared (see Fig. 2A curve f), indicating that water of crystallization in product was removed. TG analysis indicates the weight of crystal water is ca. 2.58%, and closes to the theoretical weight of crystal water. Therefore, we suggest that the phase of products is $V_2O_4 \cdot 0.25H_2O$. SEM and TEM images reveal the presence of highly crystallized nanowires.

In order to investigate the formation process of nanowires, a series of the samples were prepared under different reaction conditions and further characterized by XRD, SEM and TEM. Based on the experimental results, the possible formation model of manganese and vanadium oxides was proposed.

References:

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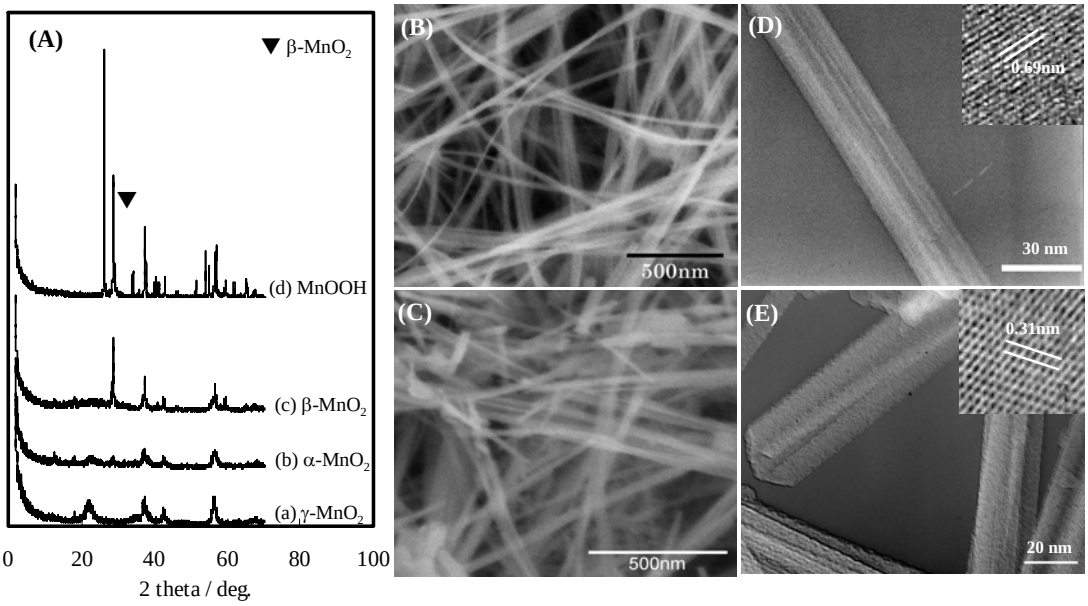

Figure 1 The XRD patterns, SEM and TEM images of manganese oxides obtained at different temperatures.

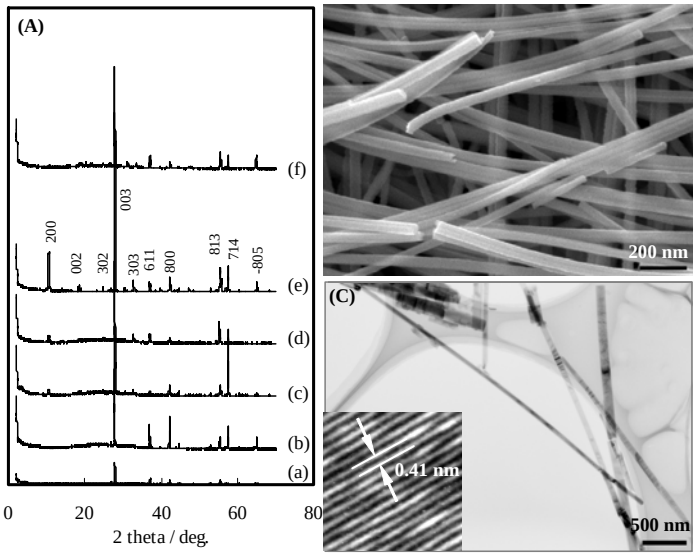

Figure 2 The XRD patterns, SEM and TEM images of vanadium oxide obtained at 170 °C for 14 days.