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Short communication

Crystallinity and morphological evolution of hydrothermally synthesized potassium manganese oxide nanowires

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Abstract

Potassium manganese oxide (KMn_8O_{16}) nanowires were synthesized using a customized hydrothermal method and characterized using scanning-electron microscopy, X-ray diffractometry and thermogravimetric analysis to determine the effects of reaction temperatures and molar ratio of reactants on the crystallinity and morphology of the synthesized nanowires. It was established that increasing the stoichiometric portion of potassium precursors increased the average nanowire diameter though such effect was comparatively less prominent in terms of reaction temperature. Deficient supply of potassium inhibited nanowires growth in which only KMn_8O_{16} (cryptomelane) growth orientations of (211), (301) and (600) were observed along with traces of MnO_2, resulting in a wool-like nanowires suspension.

Keywords: B. Electron microscopy; B. Nanocomposites; D. Transition metal oxides; Hydrothermal

1. Introduction

In recent times, there have been tremendous interests on one-dimensional (1D) nanostructures (materials with very high length-to-width ratios) such as nanowires, nanorods and nanotubes. These structures afford good uni-directional conductivity [1] which is evidently useful for electronics applications [2]. There are currently a myriad of methods used to synthesize 1D nanostructures, namely, chemical vapor deposition [3], precursor decomposition, solvothermal, hydrothermal and carbothermal methods [4]. Hydrothermal is a very popular and cost-effective method for such synthesis due to its inherent simplicity in crystallizing materials from aqueous solutions at mild temperatures [5–7].

In two separate studies conducted by Yuan et al. [8,9], hydrothermally synthesized robust and flexible nanowires from potassium oxides and manganese oxides precursors can be further developed to generate free-standing membranes with potential applications in the fields of electronics, catalysis and environmental science. Zhang and co-researchers [10] also synthesized potassium manganese oxide nanobelts using mild hydrothermal conditions and showed that they possessed favorable electrochemical and catalytic properties. Wu and co-researchers [11] recently showed that $K_{2-x}Mn_8O_{16}$ ($x \approx 1$) nanowires possessed high electrochemical capacitance and superior cycling stability implying their tremendous potential application in supercapacitors for electrical storage. Such practical application is nonetheless, less researched and the utilization of potassium manganese oxide nanowires in the

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field of electronics is still in its infancy. One bottleneck frequently associated with industrial application of metal nanowires is the challenge of implementing bulk production and this is no different in the case of the hydrothermal process. This obstacle can, nonetheless, be overcome by implementing an optimized hydrothermal process which forms the crux of the present study.

In this study, one-pot hydrothermal synthesis of potassium manganese oxide nanowires has been conducted in a customized digestion (autoclave) vessel which facilitates production of larger quantities of nanowires compared to conventional and proprietary autoclave vessels. Other novelty of our work is presented in the form of investigation of the effects of reaction temperatures and molar ratio of reactants in a novel hydrothermal vessel designed for both safety and process optimization, which to the best of the authors' knowledge, have not been previously reported. The morphology and crystallinity of the produced nanowires are analyzed via scanning-electron microscopy (SEM) analysis, X-ray diffractometry (XRD) and thermogravimetric analysis (TGA).

2. Experimental

A novel hydrothermal vessel was designed and constructed which consisted of a Teflon®-lined vessel placed in stainless steel (thickness = 5 mm) housing and equipped with a ball valve to facilitate pressure control for safety purposes (Fig. 1). The dimensions of the vessel parts were carefully stipulated to afford ease of handling while maintaining good reaction control inside the vessel. The Teflon® liner (thickness 10 mm) was used to prevent attachment of solids on the vessel wall and avoid cross contamination of the end product. Similarly, the vessel lid was constructed using stainless steel (thickness = 4 mm) and Teflon® (thickness = 10 mm) layers.

Nanowires were synthesized via a hydrothermal reaction described by Yuan et al. [8,9] and customized for our study. Reactants for this process consisted of 19.1 mmol of potassium sulfate (K_2SO_4), potassium persulphate ($K_2S_2O_8$) and manganese sulfate monohydrate ($MnSO_4.H_2O$) in a ratio of either 1:1:2, 1:2:1 or 2:1:1 in 80 mL of deionized water. The three reactants were purchased from Sigma-Aldrich Malaysia. The resultant homogenous solution was transferred to the hydrothermal vessel. The hydrothermal vessel was placed in a furnace and heated at 250 °C for 4 days. The vessel was subsequently put in a dessicator and allowed to cool to room temperature. The product was suspended in 800 mL deionized water so that a layer of insoluble wool-like solid can be separated from the unreacted raw materials. The suspension was stirred for a day before the solid was decanted and residual suspension filtered. Moisture from the solid was removed by dispersing the solid in a beaker at 90 °C for a day. The effect of reaction temperatures was also investigated in which solution temperature at 200, 230 or 250 °C was stipulated for reactants mol ratio of 1:2:1 because preliminary results indicated that this mol ratio afforded the most consistent morphology and dimensions.

The surface morphology of the synthesized nanowires was analyzed using PHILLIPS XL 20 scanning electron microscopy (SEM) system. X-ray diffractometry (XRD) spectra were obtained using a GBC EMMA diffractometer operating at 2θ step size of 0.01° and speed 1 °/min. Thermal decompositions of the nanowires were investigated using TGA Q50 V20.10 Thermogravimetric Analyzer (TA Instruments, Water LLC) under nitrogen gas flow.

3. Results and discussion

Fig. 2 illustrates SEM micrographs showing the effects of molar ratio and reaction temperature on surface morphology of the nanowires. The yield of the nanowires (> 1 g) is marginally affected by the reaction temperature. Solutions at 1:2:1 and 2:1:1 molar ratios form discernible nanowires while at molar ratio 1:1:2, thick wool-like suspension can be observed enveloping small strands of nanowires, indicating that deficient supply of potassium limits the nanowires growth in the hydrothermal process. Further SEM inspections seem to imply marginal morphological difference between the rest of the nanowires samples whereby temperature does not appear to greatly influence their shapes and forms. A more detailed (quantitative) insight is, therefore, required in this case so that direct comparisons can be made.

Fig. 3 shows the XRD spectra of the potassium manganese oxide nanowires which indicate the effects of reactants molar ratios and temperature on their crystallinity. Closer inspection of each spectrum and peak identification using Inorganic Crystal Structures Database (JCPDS 1999) enables identification of various crystalline orientations. All nanowires samples generally exhibit the mineralogical form of KMn_8O_{16} (cryptomelane-Q) though their relatively 'wide' peaks qualitatively suggest 'small' crystallite sizes. This KMn_8O_{16} system is tetragonal with space group 14/m (87) ($a = 9.84$; $c = 2.85$) (JCPDS-20-0908) detected at 12.6°, 18.0°, 28.8°, 37.6°, 42.0°, 49.8°, 56.2°, 60.0°, 65.5°, 69.1°, 73.0° with (110), (200), (310), (211), (301), (411), (600), (521), (002), (541) and (730) orientations, respectively. Interestingly, MnO_2 (pyrolusite) is also detected at peaks 28.8°, 37.6° and 56.2° (JCPDS-04-0591) [12] together with KMn_8O_{16} while there is essentially no qualitative difference in terms of potassium manganese oxide mineralogy or crystal growth orientations for all nanowires except for the 1:1:2 sample. The 1:1:2 sample is rather peculiar since only KMn_8O_{16} with (211), (301) and (600) orientations are detected while other orientations appear to exist in amorphous state. The distinct wool-like suspension for the 1:1:2 sample observed using SEM (Fig. 2) corroborates this XRD result. This suggests that KMn_8O_{16} growth in the (211), (301) and (600) orientations within the stipulated hydrothermal conditions occur at an initial stage prior to growth in other crystal orientations. Our obtained cryptomelane-based nanowires are somewhat similar to cryptomelane nanowires reported by Yuan et al. [8,9] but fundamental variations in terms of crystal orientations and mineralogy are still apparent. For example, pyrolusite was not detected in their studies, which gave rise to the speculation that the synthesis conditions

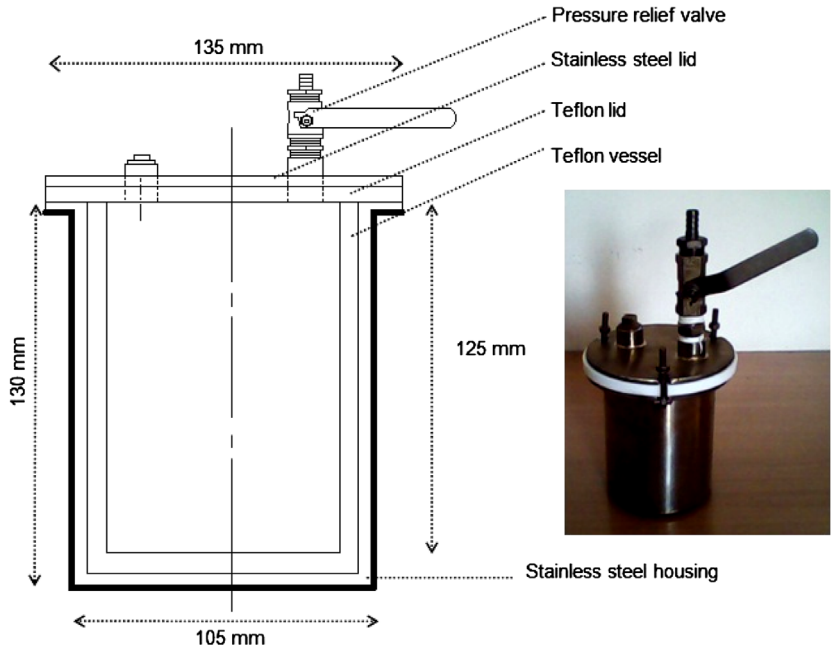

Fig. 1. Schematic diagram of the hydrothermal vessel. Inset shows the actual vessel.

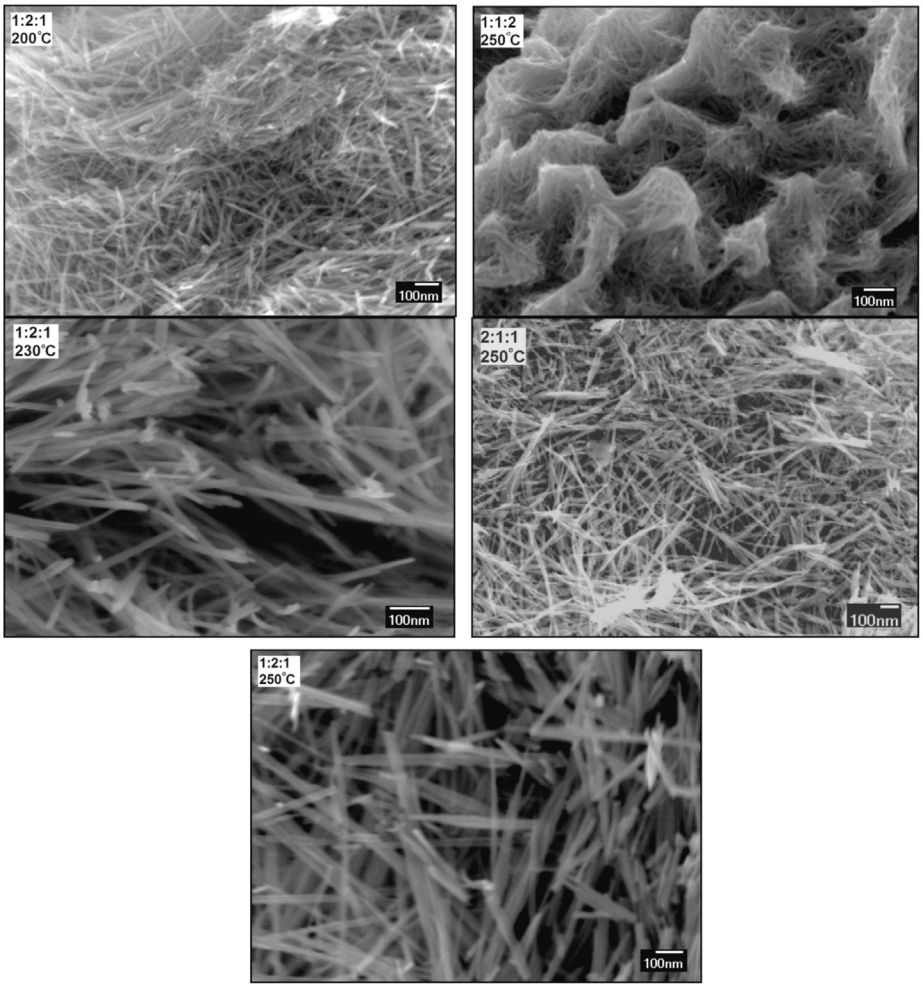

Fig. 2. Micrographs illustrating the effects of molar ratios and reaction temperatures on surface morphology of the nanowires.

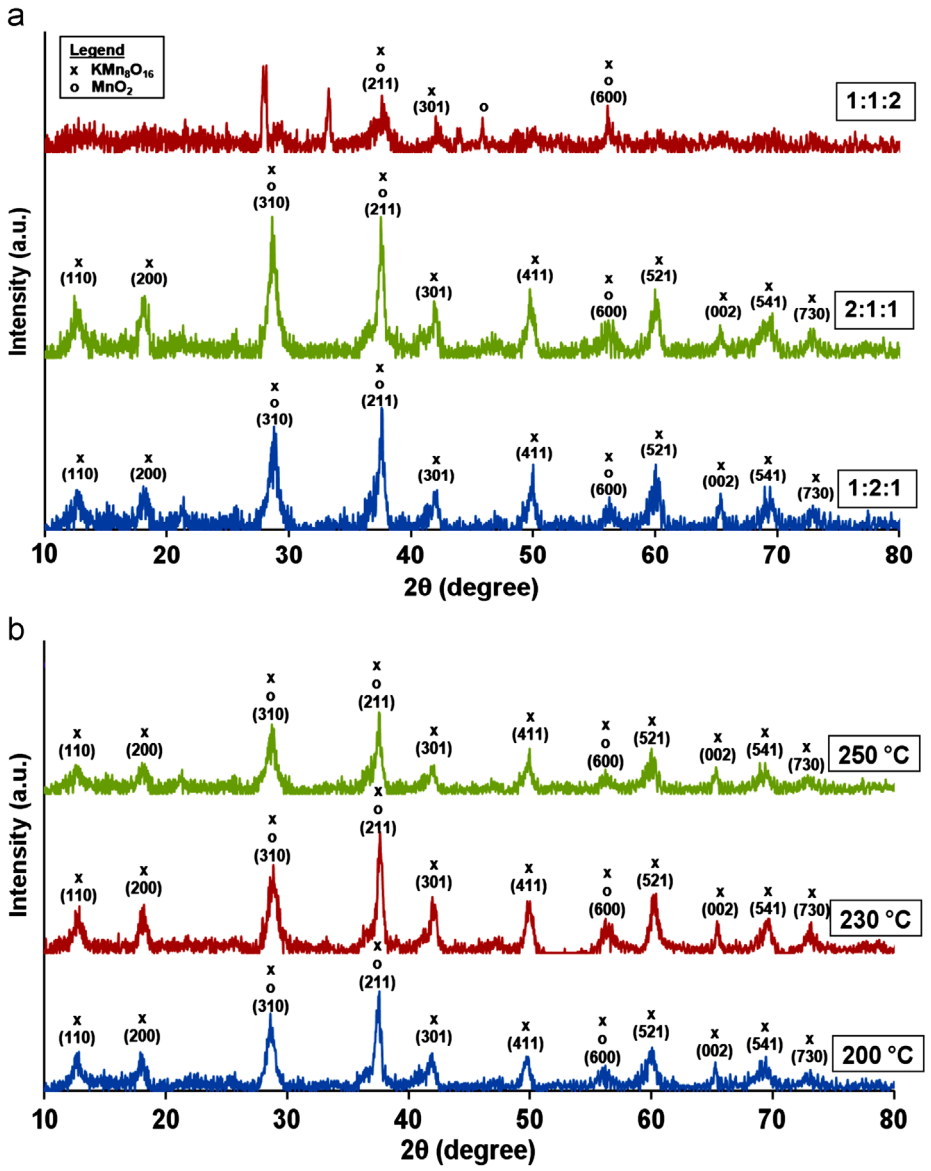

Fig. 3. Effects of (a) reactants molar ratios (temperature = 250 °C); and (b) reaction temperatures (molar ratio = 1:2:1) on the crystallinity of potassium manganese oxide nanowires.

in our study induced its growth together with KMn_8O_{16}. The co-existence of both cryptomelane and pyrolusite in 1D nanostructures was also reported by Qiu and co-researchers [13] whereby it was possible that an increase in potassium concentration stimulated the integration of K^+ into manganese oxide and single phase cryptomelane could be formed.

Based on the XRD spectrum for each sample, the crystallite size (D) of nanowire was determined by using the quintessential Debye–Scherrer formula:

$$D = \frac{K\lambda}{B\cos\theta} \quad (1)$$

where λ is the wavelength of the X-ray source which is 0.15406 nm for this measurement, 2θ is the position of main diffraction peak, B is the full-width-half-maximum (FWHM) of the peak and K is a constant depending on the shape of the material. The typical value of K is 0.9. The main XRD peak of KMn_8O_{16}/MnO_2 (211) at 37.6° was selected for this determination due to its prominence which afforded good size representation. Table 1 shows the estimated D values which markedly indicate that the crystalline size of nanowire increases with temperature which is in good agreement with SEM observations. This is possibly attributed to the high energy supply from high synthesis temperature which enhanced nucleation and crystallite growth [14]. Correspondingly, the 1:1:2 (250 °C) sample possesses the smallest crystallite size among all samples; this further strengthens our previous discussion on the anomalous nature of the 1:1:2 sample. Increasing the stoichiometric portion of potassium precursors clearly increases the average nanowire diameter though such effect is not as apparent in terms of reaction temperature. It has been suggested that smaller crystal size is generally obtained at lower temperature [15] and this seems to be the case in our study. In addition, a higher temperature is

Table 1
Effects of (a) reactants molar ratios; and (b) reaction temperatures reactants on the crystallite size of nanowire.

Sample	2θ (211)	$2\theta_1$	$2\theta_2$	B (°)	B (radians)	θ	D (nm)
1:2:1 (200 °C)	37.62/90	37.28	37.82	0.27	0.00471	18.81	31.1
1:2:1 (230 °C)	37.66/110	37.44	37.92	0.24	0.00419	18.83	35.0
1:2:1 (250 °C)	37.66/74	37.32	37.78	0.23	0.00401	18.83	36.6
1:1:2 (250 °C)	37.60/33	36.92	37.92	0.5	0.00872	18.80	17.0
2:1:1 (250 °C)	37.52/82	37.34	37.76	0.21	0.00366	18.76	40.0

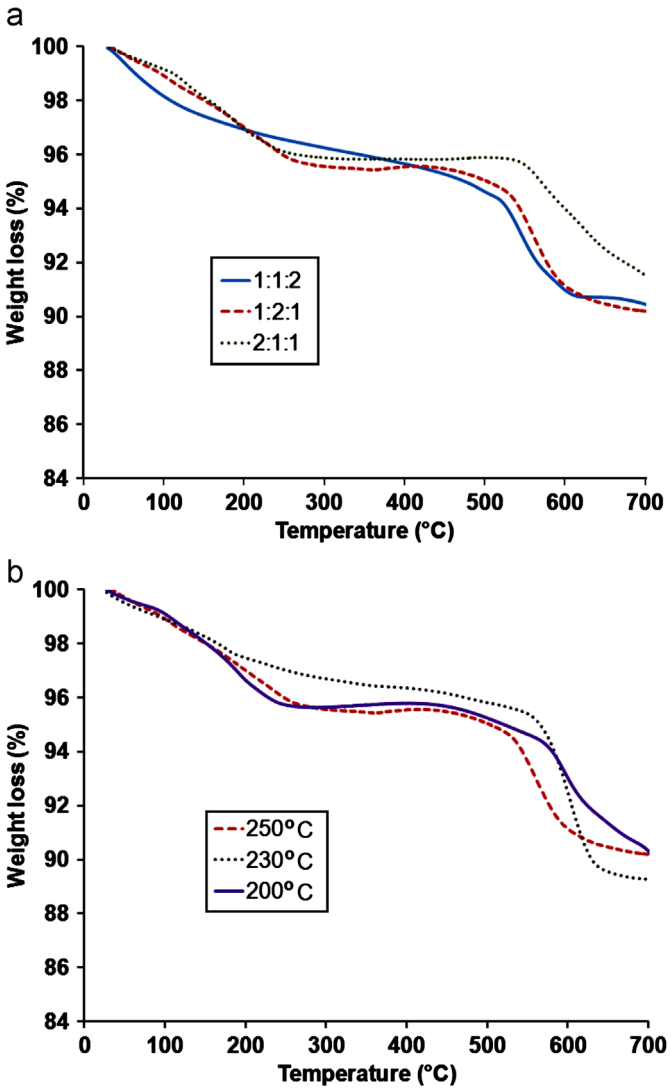

Fig. 4. Effects of (a) reactants molar ratios (temperature = 250 °C); and (b) reaction temperatures (molar ratio = 1:2:1) on the thermal stabilities of potassium manganese oxide nanowires.

preferable for the anisotropic growth of crystal, and results in a product with higher aspect ratios [15].

TGA analysis results (Fig. 4) seem to indicate that neither reactant molar ratio nor temperature has significant effect on the thermal stabilities of the nanowires. The thermal decomposition curves exhibit the archetypal two-stage decomposition process whereby the first stage involves removal of sorbed water (up to 250 °C) while the substantial weight loss at the latter stage (*ca* 520–620 °C) can be possibly attributed to transformation of the cryptomelane phase into manganese oxide [9].

4. Conclusions

KMn_8O_{16} nanowires exhibiting various crystal growth orientations have been synthesized using a customized hydrothermal method and characterized using SEM and XRD. MnO_2 is also detected as a mineralogical component in the nanowires. Increasing the stoichiometric portion of potassium precursors increases the average nanowire diameter though such effect is comparatively marginal in terms of reaction temperature. The anomalous 1:1:2 sample indicates that deficient supply of potassium limits nanowires growth to which only cryptomelane growth orientations of (211), (301) and (600) are observed, resulting in a wool-like nanowires suspension. The customized hydrothermal method reported here is envisioned to be useful for process engineers aiming for optimized systems to realize enhanced production of 1D nanostructures for applications in the fields of catalysis or electronics.

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