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Synthesis of Co_3O_4 nanowires on nickel foam by a novel microwave-assisted template-free method

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ABSTRACT

Spinel cobalt oxide (Co_3O_4) nanowires grown on Ni foam are successfully synthesized using a novel microwave-assisted template-free method. The effect of reaction temperature, concentration of reactants, and reaction time on the morphology and crystalline structures of the prepared nanowires is studied. The present work has demonstrated that uniform Co_3O_4 nanowires with diameters of 500–580 nm and lengths of 6–8 μm can be synthesized under proper reaction condition. Moreover, the proposed microwave-assisted template-free method can significantly reduce reaction time, increase reaction efficiency, and provide better control over the geometry of the nanostructures.

1. Introduction

Cobalt oxide (Co_3O_4) has shown excellent electrochemical properties and has been widely adopted in many applications such as heterogeneous catalysis [1,2] as well as in sensors [3], electronic devices [4], fuel cells [5], and advanced lithium ion battery electrode [6–8]. Over the past few years, the synthesis and functionalization of nano-sized Co_3O_4 with different forms have attracted considerable interest. Among these different forms, the one-dimensional Co_3O_4 nanowires, which are emerging as a novel and powerful class of material, have received increasing attention owing to their homogeneous nanostructures, easy to control hierarchical organization, efficient mass transfer, and large surface area [9,10]. These unique properties pose significant positive impact on the improvement of their catalytic performance. Therefore, extensive efforts have been devoted to the study of Co_3O_4 nanowires. To prepare these nanostructured materials with excellent properties, several methods have been proposed, such as template-directed synthesis method [11,12], direct oxidation method [13], and template-free method [14]. In the template-directed synthesis method [11,12], the right choice of the suitable porous materials as templates should be adhered to because failure to do so will inevitably complicate the synthetic procedures. Moreover, the use of the templates limits the dimensions of nanowires. Variation in the dimension requirement will require a new template, increasing the complexity of the preparation procedure. Furthermore, the nanowires prepared by this method easily form undesirable aggregated structures after the removal of polymers from the templates. This lowers their catalytic performance. In the direct oxidation method [13], direct oxygenation of pure cobalt foils requires high temperatures (480–520 °C), long reaction times (10–12 h), and expensive specialized apparatus. Thus, this method is not an ideal choice for the fabrication of nanowires as well. Compared with the template-directed synthesis and direct oxidation methods, the template-free method is considerably simpler and can result in uniform nanostructures. However, the conventionally used oven heating requires long reaction time and large energy input, making the template-free method costly. Consequently, the search for a simpler and more efficient method continues as driven by the need to save on time and energy.

Recently, microwave radiation has been found to increase the rate of solution-phase reactions through the high dielectric loss of polar solvents resulting from the provided microwave energy. Based on this, the current work proposes a microwave-assisted template-free synthesis method for the preparation of Co_3O_4 nanowires on nickel (Ni) foam. Ni foam possesses good mechanical property, thermostability, and high conductivity. Thus, it can be rapidly heated to high temperature to ensure the complete reaction in a short period of time. Moreover, the relatively large surface area and pore size of Ni foam can facilitate the growth of nanowires in a large area. Hence, we selected Ni foam as the substrate for the growth of nanowires. We also investigated the effect of reaction temperature, concentration of reactants, and reaction time on the morphology and crystalline structure of the

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prepared Co_3O_4 nanowires. The results demonstrate that the microwave-assisted method has the advantages of time efficiency and low energy consumption, more convenient operation, and better control of the nanostructured geometry.

2. Experimental

A microwave-assisted template-free method was utilized for the growth of self-supported Co_3O_4 nanowire arrays on Ni foam. Pretreatment of Ni foam sheets, measuring 1 cm × 1 cm with pore density of 110 PPI and with a mass density of 320 g/m^2 (Artenano Company Limited, Hong Kong) consisted of the following: degreasing by immersion in acetone for 10 min; etching with dilute HCl (6.0 mol/L) for 15 min, and rinsing with distilled water. Subsequently, Ni foam was soaked in $NiCl_2$ (0.1 mmol/L) for 4 h, rinsed with distilled water, and dried. After the pretreatment of Ni foam, the precursor for the growth of Co_3O_4 nanowires was prepared. To explore the optimal conditions, different amounts of Co $(NO_3)_2$ and NH_4NO_3 (see Table 1) were dissolved in aqueous ammonia solution (12 wt%) and mixed homogeneously under vigorous stirring for 10 min at room temperature. The resultant mixture, together with the pretreated Ni foam, was loaded into the microwave digestion system (MDS-6, Sineo Microwave Chemical Technology Co. Ltd.), and microwave-irradiated with 600 W at 70–100 °C for 1–4 h. After the microwave-assisted thermal reaction, the prepared nanowires grown on Ni foam were dried at room temperature and calcined at 300 °C for 2 h. For comparison, the conventional hydrothermal method was also employed in the present work for the synthesis of Co_3O_4 nanostructures with oven heating. Different samples and their corresponding conditions are summarized in Table 1. The morphology of all prepared nanowire arrays was observed by a scanning electron microscopy (SEM, JEOL JSM-5600) at 20 kV. X-ray diffraction (XRD) patterns were obtained on a Siemens D500 diffractometer with the step of 0.02° using Cu Kα (λ=0.1542 nm) radiation at 40 kV and 30 mA.

3. Results and discussion

In the proposed microwave-assisted template-free method, the reaction temperature, concentrations of reactants, and

Table 1
Summary of the synthesis conditions and the corresponding sizes of Co_3O_4 nanowires.

Sample	Temperature(°C)	Concentration (mol/L)			Time(h)	Co_3O_4 nanowire size	
		Cobalt nitrate	Ammonium nitrate	Ammonia		Diameter(nm)	Length(μm)
1	70	0.2	0.1	6	3	/	/
2	90	0.2	0.1	6	3	500–580	6–8
3	100	0.2	0.1	6	3	/	/
4	90	0.1	0.05	3	3	/	/
5	90	0.3	0.15	9	3	1000–3000	11–15
6	90	0.2	0.1	6	1	370–450	4–5
7	90	0.2	0.1	6	2	400–550	6–8
8	90	0.2	0.2	6	4	500–580	6–8
9(oven)	90	0.1	0.1	3	12	/	/

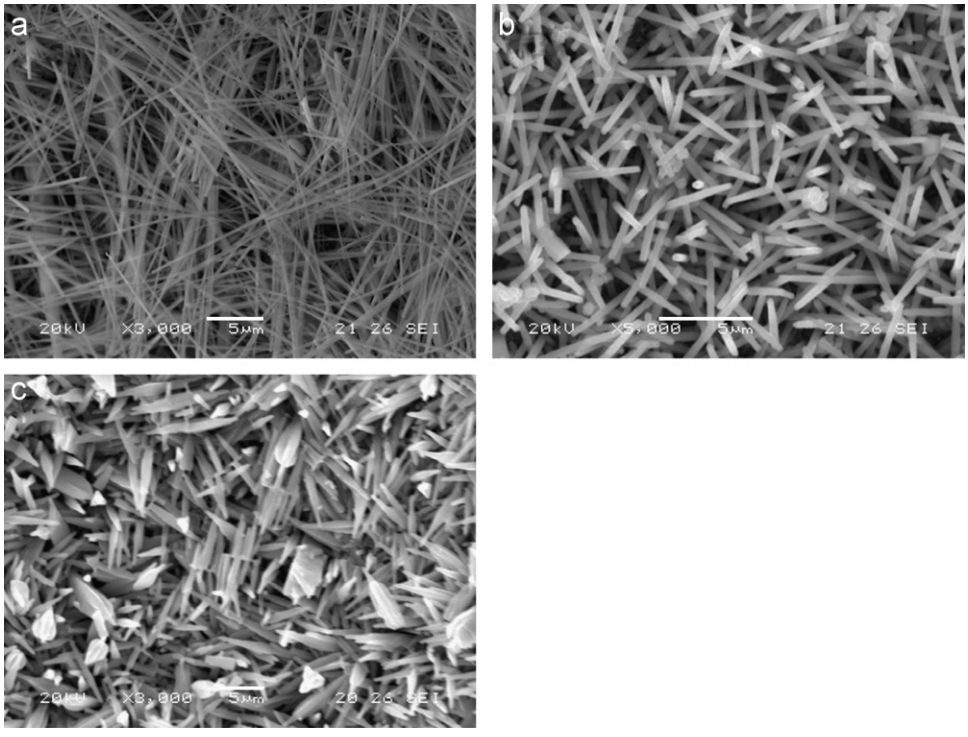

Fig. 1. Scanning electron microscopy (SEM) images of Co_3O_4 nanostructures synthesized at different temperatures: (a) 70 °C (sample 1), (b) 90 °C (sample 2), (c) 100 °C (sample 3).