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# Synthesis and growth mechanism of sponge-like nickel using a hydrothermal method

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ABSTRACT

Sponge-like nickel composed of micro-chains with a diameter of 1–5 μm was selectively synthesized by the hydrothermal method, using sodium hydroxide (NaOH) as the alkaline reagent, aqueous hydrazine as reducing agent and citric acid as a coordination agent. The time-dependent samples prepared at different NaOH concentrations were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectrometer (FTIR). The results showed that the agglomerates of nickel citrate hydrazine complex nanoplates were first precipitated and then reduced to prickly nickel micro-chains at a lower NaOH concentration, which played a role in the further formation of sponge-like nickel. Also, the probable growth mechanism of the sponge-like nickel was proposed. The magnetic properties of sponge-like nickel were studied using a vibrating sample magnetometer. The sponge-like nickel exhibited a ferromagnetic behavior with a saturation magnetization value of 43.8 emu $g^{-1}$ and a coercivity value of 120.7 Oe.

## 1. Introduction

Micro/nanoscale metallic materials have received considerable attention due to their promising applications in diverse areas, including electromagnetic wave absorption materials, hydrogen storage, catalysts, and so on [1–6]. Moreover, the metallic materials may be used as support with active materials to improve the efficiency of reactions [7–11]. Especially in the field of catalyst support, metallic materials with ferromagnetic properties played a role in separation from the reaction medium or in terms of reusability [10,11].

Various approaches have been attempted to synthesize metallic materials such as the chemical vapor synthesis method [12], sputtering/evaporation process [13], the seed-mediated growth method based on the chemical reduction process [10,14], the ultrasound-aided spark discharge process [15], the hydrothermal method [16,17], and the thermal decomposition method [18]. Most of these approaches required only one or two steps. S. Sarkar et al. prepared one-dimensional prickly nickel/gold nanowires by the "bottom up" synthetic approach in aqueous media with an external magnetic field [10]. K. J. Carroll et al. prepared Fe and Ag core/shell nanoparticle using the one-pot method [11]. These procedures usually preferred to fabricate micro- or nano-sized powders. However, the powder-like metallic materials were easily dispersed and suspended in the aqueous media, leading to poor recovering efficiency by magnetic separation. Employing nickel foam as support was an effective way to overcome this problem, but the typical synthesis procedures doing so, including the powder compact foaming process [19] and the electrodeposition process [20], normally involved multiple steps and required the help of templates or pore formers. Consequently, it was expected that the metallic products using as active material supports had an entire structure with micropores, and that they were easily prepared in a one-step and low-cost synthetic procedure.

The hydrothermal method is distinguished from others by its low-cost, simplicity, and easily controlling shape and size of the products by fine-tuning synthesis parameters [21]. Until now, several studies have been devoted to the study of the physical and chemical properties of nickel powders prepared by the hydrothermal method with different morphologies including nanobelts [22], monodispersed spherical nanoparticles [23], nanosheets [24], flower-like particles [16] and sea urchin-like particles [17]. These studies have mainly suggested that nickel powders with a complex surface morphology were generated via

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self-assembly [10,25], depending on the synthesis time, concentration of the acid alkali agents and the type of surfactants or ligands for metallic ions. However, it was still a challenge to prepare the nickel products with an entire structure using hydrothermal method, for example, the sponge-like nickel.

In the present work, the hydrothermal method was employed for preparing the sponge-like nickel products, using citric acid as a ligand for nickel ions and aqueous hydrazine as a reductive agent in an alkaline environment. The probable growth mechanism of the sponge-like nickel product was studied by investigating the effect of hydrothermal treatment time and NaOH concentration on their crystalline sizes and morphologies. In addition, the magnetic properties of the sponge-like nickel and nickel nanoparticles were studied.

## 2. Experimental

### 2.1. Material synthesis

Nickel sulfate hexahydrate ($NiSO_4{\cdot}6H_2O$, ≥98.5%), sodium hydroxide (NaOH, ≥98.0%), citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$, ≥99.5%), aqueous hydrazine ($N_2H_4{\cdot}H_2O$, 80.0%) and ethanol (≥99.0%) were obtained from the Kelong Chemical Reagent Factory, Chendu, China. All chemical solvents and reagents were used in this work without further purification.

In a typical synthesis procedure for preparing sponge-like nickel, $Ni(SO_4)_2{\cdot}6H_2O$ (4.00 g, 0.015 mol) and $C_6H_8O_7{\cdot}H_2O$ (3.17 g, 0.015 mol) were dissolved in 100 ml deionized water. After 20 ml solution was transferred to a Teflon-lined stainless-steel autoclave with 50 ml capacity, 1 ml $N_2H_4{\cdot}H_2O$ and 10 ml NaOH solution (0.50 g) were successively added to a final volume of 30 ml. The autoclave was sealed and hydrothermally treated at 120 °C for 12 h. Subsequently, the stainless-steel autoclaves were cooled to room temperature naturally. The resulting black products and blue precursor precipitates were collected by magnetic separation and centrifugation, respectively, and were washed with distilled water and ethanol in sequence several times. The final products were dried in a vacuum box at 80 °C for 6 h. To investigate the growth process of the nickel samples, the NaOH concentration in the final solution was adjusted to 0.4 mol $L^{-1}$ (0.50 g) and 0.7 mol $L^{-1}$ (0.85 g), respectively, and the hydrothermal treatment times were changed from 0.5 to 12 h. The pH values of the starting solutions at NaOH concentrations of 0.4 mol $L^{-1}$ and 0.7 mol $L^{-1}$ were 12.4 and 13.5, respectively.

### 2.2. Characterization

XRD analysis was carried out on a Regaku SmartLab diffractmeter with Cu-Kα radiation (λ = 1.54060 Å), employing a scanning rate of 0.05 deg/s at 2θ ranging from 20° to 80°. The X-ray tube was powered using an acceleration voltage of 45 kV and a current of 200 mA. The average crystallite size was calculated by the Scherer equation, using Jade 9 software. The diffraction pattern from the line broadening of a standard silicon materials was collected to determine the instrumental broadening. The instrumental corrected broadening corresponding to each diffraction peak of Ni was calculated using the relation, $ß_{hkl} = [(ß^2_{hkl})_{Measured} - (ß^2_{hkl})_{Instrumental}]^{1/2}$, where $ß_{hkl}$ is the integral half width. The scanning electron microscopy (SEM) images and energy disperse epectroscopy (EDS) spectrum were obtained with a JEOL JSM-7800F field emission scanning electron microscope and Oxford X-Max$^N$, respectively. The Fourier-transform infrared (FT-IR) spectroscopy

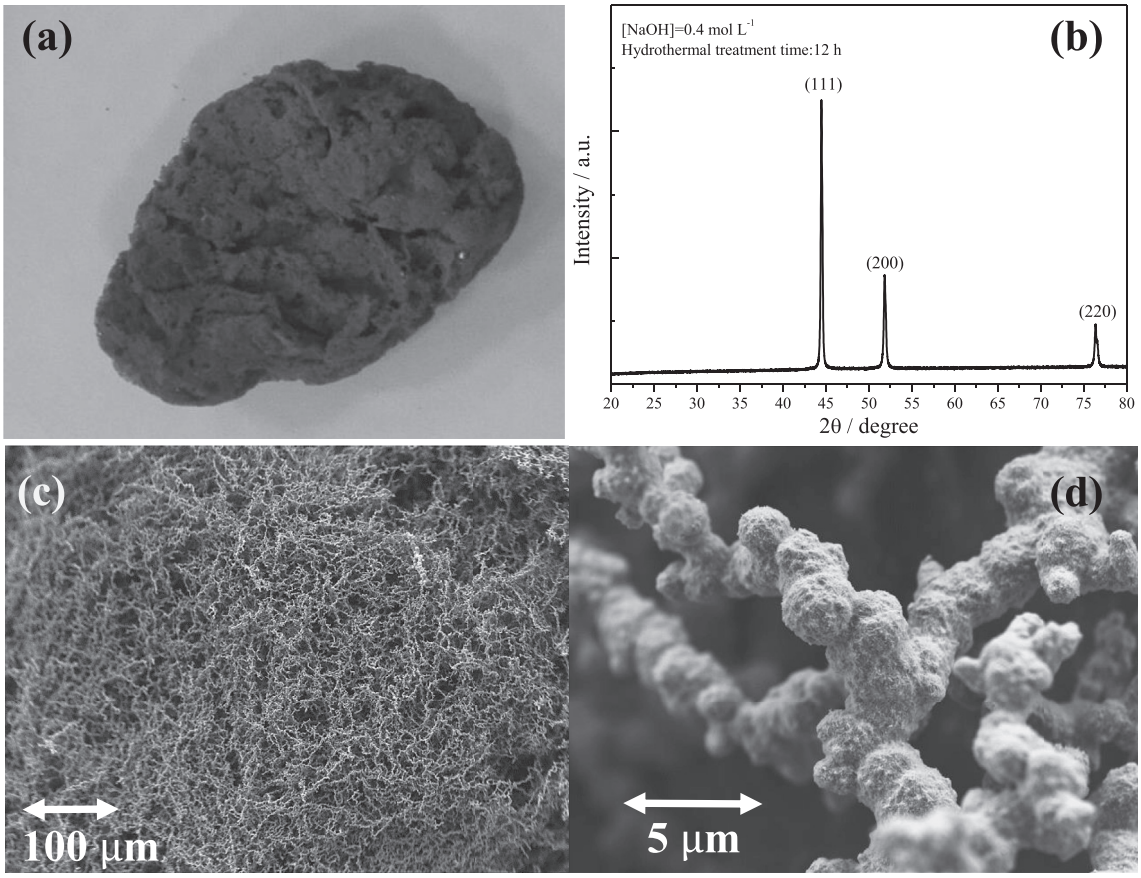


**Fig. 1.** (a) Digital image, (b) XRD pattern, (c) and (d) SEM images of sponge-like nickel sample prepared by hydrothermal treatment with a NaOH concentration of 0.4 mol $L^{-1}$ for 12 h.