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# Microwave-assisted hydrothermal synthesis of coralloid nanostructured nickel hydroxide hydrate and thermal conversion to nickel oxide

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# 1. Introduction

Metal oxides are widely used in the field of heterogeneous catalysis. Nickel oxide (NiO) is one of the most versatile materials among transition metal oxides [1]. Nickel oxide with a variety of morphologies, i.e., nanoparticles, nanotubes, nanowires, nanofibrous, mesoporous, hollow spheres and urchin-like nanostructures has been reported [2–9]. Liu et al. [9] choose urea as a hydrolysiscontrolling agent and polyethylene glycol as a surfactant to obtain an urchin-like nickel oxide. Microwave-assisted hydrothermal synthesis is a convenient and easily controlled technique to prepare nanocrystalline metal oxides within 2-6 min [10,11]. The advantages of this process over the conventional hydrothermal method are: (a) very rapid heating to the required temperature, (b) extremely rapid kinetics of crystallization and (c) possible formation of new meta-stable phases [12]. Microwave irradiation technology has already been applied to industry, family, medical science and extraction or abatement of environmental organic pollution for polycyclic aromatic hydrocarbons (PAHs) [13-15], polychlorinated biphenyls (PCBs) [16], etc. Due to the properties of internal and volumetric heating (dipole rotation and/or ionic conduction), thermal gradients during microwave processing are avoided, providing a uniform environment for reaction. Therefore,

## ABSTRACT

Coralloid nanostructured nickel hydroxide hydrate has been successfully synthesized by a simple microwave-assisted hydrothermal process using nickel sulfate hexahydrate as precursor and urea as hydrolysis-controlling agent. A pure coralloid nanostructured nickel oxide can be obtained from the nickel hydroxide hydrate after calcination at 400 °C. The thermal property, structure and morphology of samples were characterized by thermogravimetry (TG), temperature-programmed reduction (TPR), X-ray (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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microwave heating has shown higher energy efficiency and reaction rates to shorten the reaction time [11,17–19]. The use of microwaves as a source of energy is rapidly becoming more economical and convenient.

Xu et al. [20] synthesize of novel coralloid polyaniline/ BaFe<sub>12</sub>O<sub>19</sub> nanocomposites with outward extending branches having an average diameter in the range of 20–50 nm. The coralloid nanostructures compared to else show specific electrical, magnetic and electromagnetic properties. The coralloid nanostructures may have potential applications in chemical sensors, gas separation, catalysis, microwave absorbing, and magnetoelectric devices. In the application of microwave on the synthesis of nanoporous materials, Tompsett et al. [21] indicate that the precursor of the species can be nucleated to form tiny single crystals under microwave irradiation.

In this study, we report on the application of microwave heating with an autoclave to fabricate coralloid nanostructured nickel oxide. The thermal property, structure and morphology of samples are discussed.

# 2. Experimental

### 2.1. Preparation of coralloid nanostructured materials

In order to prepare coralloid nanostructured nickel hydroxide hydrate as material medium, both nickel sulfate ( $NiSO_4.6H_2O$ ) and urea had been chosen. A mixed solution of 50 ml of 0.6 M  $NiSO_4.6H_2O$  and 2.4 g of urea was transferred to the Teflon container of the double-walled vessel of a microwave system (Milston

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MSD1000, 2.45 GHz, Italy) and irradiated under 500 W microwave for 3 min. The precipitate was then filtered, washed with deionized distilled water, and dried in an oven at 100 °C for 20 h to obtain the as-prepared sample. Then, the as-prepared sample was further calcined separately under air at 300, 400 and 800 °C for 3 h to obtain the black species (assigned as C300, C400 and C800, respectively).

#### 2.2. Characterization techniques

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu  $K_{\alpha 1}$  radiation  $(\lambda = 1.5405 \text{ Å})$  at 40 kV and 30 mA with a scanning speed in  $2\theta$ of 4° min<sup>-1</sup>. The crystallite sizes of nickel hydroxide and nickel oxide were estimated using the Scherrer equation.

The infrared spectra were obtained with a Perkin-Elmer spectrum GX spectrometer in the range of 400–4000 cm<sup>-1</sup>. One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr and subjected to a pressure of 8 tonnes.

Reduction behavior of coralloid nanostructured nickel hydroxide hydrate and nickel oxide was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was heated in a flow of 10% H<sub>2</sub>/N<sub>2</sub> gas mixture at a flow rate of 10 ml min<sup>-1</sup>. During the TPR procedure, the temperature was programmed by 7  $^{\circ}$ C min<sup>-1</sup> heating rate from room temperature to 600 °C.

Thermal gravimetric analysis (TG/DTG) was carried out using a Seiko SSC5000 TG system. The mass of the sample was 10 mg and the heating rate was maintained by 10 °C min<sup>-1</sup>. The temperature was raised from room temperature to 800 °C under an airflow with a rate of 100 ml min $^{-1}$ .

Transmission electron micrographs (TEM) were taken on a PHILIPS (CM-200) microscope at an accelerating voltage of 200 kV. The samples for TEM were prepared by ultrasonic dispersing of the powder catalysts in ethanol, which was then deposited and dried on a holey carbon film on a copper grid.

The surface morphology of coralloid nanostructured nickel hydroxide hydrate and nickel oxide were observed by means of a scanning electron microscope (JSM-6330TF) operated at 10 kV.

## 3. Results and discussion

The SEM and TEM images of the as-prepared sample are shown in Fig. 1. From our observation of the present SEM image (Fig. 1(a)), the as-prepared sample possesses coralloid nanostructures with the length varying from 2 to 3 µm. The TEM images (Fig. 1(b) and (c)) show the assemblies of nanostructures. Detailed observation finds that the nanostructures consist of sheets or plates with nanoscale dimensions. The plates with high aspect ratio are ascertained to grow radial from the core particles. Fig. 2 presents a schematic diagram for the formation of coralloid architecture using the microwave-assisted hydrothermal method mentioned above. The proposed mechanism involves a sequence of steps: nucleation of nickel precursor and urea to form tiny particles, growth of tiny particles by aggregation to form sheets or plates, self-assembly and overlap of sheets or plates to form coralloid nanostructure. Because of the existence of NCO, CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup> groups, we believe that electrostatic and hydrogen bonds is the main driving forces for self-assembly to form coralloid nickel hydroxide hydrate.

The SEM of NiO nanostructures (Fig. 3(a)) can be obtained by the heat treatment of the coralloid nanostructured nickel hydroxide hydrate. The TEM images (Fig. 3(b) and (c)) show that the NiO nanostructures are stable and remain sheets or plates with a diameter of about  $2-3 \,\mu$ m.

Fig. 4 shows the TG curve for the thermal decomposition of asprepared sample under airflow (100 ml min<sup>-1</sup>). Four weight loss regions (assigned as D1, D2, D3 and D4) are observed. Prior to

Fig. 1. SEM and TEM images of the as-prepared: (a)  $5000\times$ , (b)  $20,000\times$  and (c) 40.000×.

250 °C, the gradual weight loss should come from the desorbed water on the as-prepared sample surface in the heating process. The weight loss of 14% in step D2 is mainly caused by the dehydroxylation of nickel hydroxide hydrate, 3Ni(OH)<sub>2</sub>·xH<sub>2</sub>O, to 3NiO·xH<sub>2</sub>O (comparison with the theoretical weight loss, the stoichiometry of *x* approaches 2.0):

$$3Ni(OH)_2 \cdot 2H_2O \rightarrow 3NiO \cdot 2H_2O + 3H_2O \tag{1}$$

The weight loss of 3% and 6% in steps D3 and D4 exhibit only a tardy weight loss probably due to the further removal of chemisorbed and occluded water through the conversion of Ni(OH)<sub>2</sub> to NiO.







Fig. 2. Schematic explanation of the formation of coralloid nanostructure.

Fig. 5 shows the XRD patterns of the as-prepared and calcined sample. All of the detectable peak positions and relative intensities are consisted from those of the  $3Ni(OH)_2 \cdot 2H_2O$  (Fig. 5(a)) and nickel oxide (Fig. 5(b) and (c)) phases. The as-prepared sample



Fig. 3. SEM and TEM images of the C400: (a)  $5000\times$ , (b)  $20,000\times$  and (c)  $100,000\times$ .

(Fig. 5(a)) indicates that all the diffraction peaks can be perfectly indexed [ICCD card, no. 22-0444,  $3Ni(OH)_2 \cdot 2H_2O$ ], consisting of a nickel hydroxide hydrate. The XRD pattern of the C300 sample (Fig. 5(b)) presents a weak peak around 13° (comes from (0 0 1) plane of  $3Ni(OH)_2 \cdot 2H_2O$  phase). As the calcined temperature reaches above 400 °C, the (0 0 1) plane of  $3Ni(OH)_2 \cdot 2H_2O$  is not observed (Fig. 5(c)). The results show that the  $3Ni(OH)_2 \cdot 2H_2O$  is converted completely into nickel oxide [ICCD card, no. 47-1049, NiO] after calcination above 400 °C.

Fig. 6 shows the TPR profiles of the as-prepared and calcined sample. Aside from the slight reduction peak at 297  $^{\circ}$ C (this peak perhaps is attributable to the reduction of nickel oxide that comes from the dehydration of the as-prepared sample, see Fig. 4), the



Fig. 4. TG curve for the thermal decomposition of as-prepared sample under airflow.



Fig. 5. XRD patterns of the samples: (a) as-prepared, (b) C300 and (c) C400.



Fig. 6. TPR profiles of the samples: (a) as-prepared, (b) C300 and (c) C400.

reductive signal of nickel hydroxide hydrate in TPR (Fig. 6(a)) shows an overlap around 336 and 370 °C according to Eq. (2):

 $3Ni(OH)_2 \cdot 2H_2O + 3H_2 \rightarrow 3Ni + 8H_2O$  (2)

Fig. 6(c) shows the reductive signal of the C400 sample that presents one-step reduction around 329 °C. According to our previous report [22], the pure coralloid nanostructured nickel oxide is reduced directly into Ni according to Eq. (3):

$$NiO + H_2 \rightarrow Ni + H_2O \tag{3}$$

The different shape of the TPR profile obtained for C300 (Fig. 6(b)) is probably due to the mixture of two solid phases (the XRD measurement reveals the existence of  $3Ni(OH)_2 \cdot 2H_2O$  and NiO) that affect the shape of the reduction profile. The peak around 312 °C is the reduction of nickel oxide and the peak at 330 °C comes from the reduction of nickel hydroxide.

In order to understand the crystallographic sites occupation and the cationic jumps along the phase transition of nickel oxide, the IR absorption spectra are measured for nickel hydroxide hydrate and nickel oxide. Fig. 7 shows the IR absorption spectra of the asprepared and calcined sample. The spectrum of coralloid nanostructured nickel hydroxide hydrate (Fig. 7(a)) presents a



Fig. 7. IR spectra of the samples: (a) as-prepared, (b) C300 and (c) C400.



**Fig. 8.** SEM image of the C800 (50,000×).

strong band at 2200  $cm^{-1}$  (attributed to the  $\nu_{a\,(\text{NCO})}$  mode), a weak band appearing at 1396 cm<sup>-1</sup> (due to the  $v_{s (NCO)}$  mode) and broader band around 645 cm<sup>-1</sup> (due to the  $\delta_{(NCO)}$  mode) [23,24]. The prominent band at 1033–1123 cm<sup>-1</sup> is typical of SO<sub>4</sub><sup>2–</sup> ions. The absorption band at 490 cm<sup>-1</sup> and 600–645 cm<sup>-1</sup> indicate that the as-prepared sample is Ni-O stretching vibration mode and deformational Ni–OH mode. The C300 spectrum (Fig. 7(b)) displays a series of weak peaks around 2200, 1396, 1123, 1033 and  $645 \text{ cm}^{-1}$  that confirms the mixed phased existing in C300 sample. The broad peak around  $3500 \text{ cm}^{-1}$ , corresponding to –OH, is also decreased in intensity. This means that the NCO and  $CO_3^{2-}$  are almost removed while still containing some hydroxyl group that comes from the adsorbed water after calcinations at 400 °C (Fig. 7(c)). The NCO and  $CO_3^{2-}$  seem assisted sheets or plates with nanoscale dimensions growth on 3Ni(OH)<sub>2</sub>·2H<sub>2</sub>O nanoparticles and the formation of coralloid nanostructured.

The plates with nanostructured morphology are completely destroyed after heat treatment approaching 800 °C (Fig. 8). The water of crystallization on the plate nanostructure compound influences the particle morphology of the final nickel oxides. In comparison with the thermal analysis of TG (Fig. 4), the water of crystallization can escape as the temperature reaches above 700 °C. The results further confirm the various morphologies between C400 and C800 samples.

The coralloid nanostructured nickel oxide is similar to the urchin-like nanostructures that might exhibit some novel properties, which in turn can lead to new and important applications in cell (high electric capacitance) and catalysis (hydrogenation reaction) [9,25,26].

# 4. Conclusion

We have successfully synthesized the coralloid nanostructured nickel hydroxide hydrate through a rapid microwave-hydrothermal process. The pure coralloid-like nanostructured nickel oxide can be obtained from the calcination of nickel hydroxide hydrate at 400 °C. XRD, SEM, TEM, IR and TPR analysis shows that nickel oxide has apparent coralloid nanostructures and remains sheets or plates with nanoscale dimensions with length 2–3  $\mu$ m.

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