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# Shape-controlled synthesis of $Ni(OH)_2$/NiO nanowalls by surface reaction of Ni foil in aqueous $NH_4OH$

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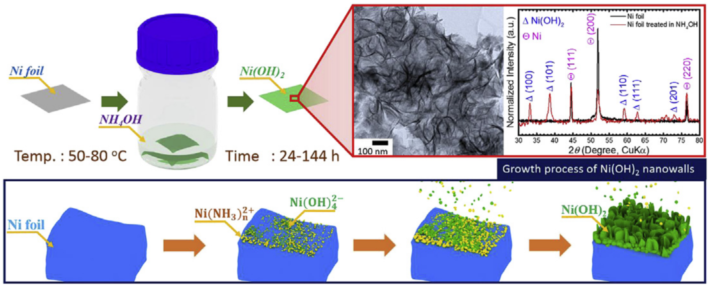
## HIGHLIGHTS

- Uniform $Ni(OH)_2$ nanowalls were synthesized by $NH_4OH$ treatment of the Ni foil.
- The shape/dimension of the wall could be controlled by the treatment temperature/time.
- The growth of $Ni(OH)_2$ nanowalls was faster in a smaller volume of $NH_4OH$.
- The $Ni(OH)_2$ nanowalls could be grown at the treatment temperature of 50–80 °C.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The nanoscale structures of nickel hydroxide and oxide materials attract considerable interest because of their potential application in several fields. This study introduces a facile method to synthesize $Ni(OH)_2$ nanowalls directly on a Ni foil by chemical treatment with an $NH_4OH$ solution. The dimensions and shape of the $Ni(OH)_2$ nanowalls can be easily controlled by changing the temperature (50–90 °C), volume of the $NH_4OH$ solution (25–50 ml), and treatment time (24–144 h). After annealing for 1 h at temperatures below 600 °C, the as-synthesized $Ni(OH)_2$ nanowalls transformed into the corresponding NiO nanostructures, without changes in morphology. The formation of the nanowalls and the influence of the temperature on the morphology of the formed nanostructures were analyzed in terms of the growth mechanism.

## 1. Introduction

Nanoscale metal hydroxides/oxides have attracted significant attention from the scientific community, owing to their low cost and suitability for a wide range of applications [1–5]. Many studies concerning these materials have focused on tailoring their nanoscale morphology by using a variety of synthetic approaches to selectively form nanorods, nanowires, nanoplates, nanoflowers, etc. [6–9]. Recently, well-ordered arrays of metal hydroxide/oxide microstructures and nanostructures were grown directly on metal substrates by simple thermal oxidation [10–13]. Although thermal oxidation can be used to synthesize various metal oxide nanostructures, several problems associated with this method need to be addressed. First, nanostructured metal hydroxides or oxides cannot be formed by heating corresponding metals with low melting temperatures. In addition, the morphology of the nanostructured metal oxide cannot be tailored after the thermal treatment. Several synthesis protocols such as plasma-assisted growth, surface pre-treatment, and hydrothermal-assisted growth have been developed to address these issues [14–16].

Nickel is one of the most abundant elements on Earth; its nanoscale hydroxide and oxide forms are extensively used as supercapacitors, catalysts, electrodes for batteries, gas/biosensors, components of

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optoelectronic devices, as well as other applications [14,17–23]. Nickel is barely oxidized at room temperature (RT), and is thus considered corrosion-resistant. This is probably the reason why microstructured and nanostructured NiO materials are very difficult to grow by simply heating a Ni metal substrate in air [24]. In 2008, Zhang et al. found that NiO nanowalls can be grown on Ni/stainless steel substrates at 600 °C under oxygen flow [25]. In the same year, Varghese et al. introduced a process to synthesize NiO nanowalls by plasma-assisted thermal oxidation at 600 °C, also under oxygen flow [14]. Another technique used to promote the oxidation of Ni (that is, to improve the efficiency of the formation of NiO nanowalls) consists of generating defects on the Ni surface by physical or chemical methods; this can be achieved by scratching the Ni surface using a knife or sandpaper, or by etching it with an acidic solution [26]. Using a hydrothermal growth process, Yang et al. [16], Zhang et al. [27], and Chen et al. [28] successfully synthesized $Ni(OH)_2$ and NiO nanowalls. Nevertheless, this approach cannot be used for the large-scale synthesis of nanowalls, due to the limited volume of the hydrothermal vessels. In 2011, Soejima et al. synthesized $Cu(OH)_2$/CuO nanobelt arrays by simply soaking a Cu substrate in $NH_4OH$ solution at temperatures lower than 90 °C [29]. Although this method can be potentially scaled up to mass-produce microstructures and nanostructures on metal substrates, further investigations of this approach are still needed.

In this study, $Ni(OH)_2$ nanowalls were synthesized by treating Ni foil in $NH_4OH$ solution. The dimension and shape of the nanowalls could be controlled by changing the treatment temperature and time, as well as the volume of the $NH_4OH$ solution. The dehydration of the as-prepared $Ni(OH)_2$ to NiO was investigated at different annealing temperatures (600–800 °C). In addition, the results were discussed in terms of the growth mechanism of the $Ni(OH)_2$ nanowalls.

## 2. Experimental

$Ni(OH)_2$ nanowalls were synthesized by a simple process, in which a pure nickel foil (thickness 0.1 mm, purity 99.98%, Aldrich) was cut into plates of 20 × 20 $mm^2$ area and then cleaned by sonication in acetone for 10 min. After drying the Ni plates under $N_2$ flow, the plates were placed in 25–50 ml of $NH_4OH$ solution contained in 100 ml Duran laboratory bottles. The bottles were carefully capped and placed in a larger bottle (of total volume 400 ml) filled with 150 ml of distilled water. After carefully covering the cap with aluminum foil, the 400 ml bottle was heated on a hot plate; the reaction temperature was controlled with the help of a proportional integral derivative (PID) temperature controller (the K-type thermocouple was inserted into the reaction vessel and dipped into water). The treatment temperature was varied between 50 and 90 °C at a heating rate of 0.2 °C/min, and different treatments times in the range of 24–144 h (1–6 days) were tested. After the heat treatment, the samples were dried in an oven at 60 °C for 2 h. The dehydration process was carried out in a horizontal furnace. The treated Ni plates were placed in a quartz reactor inside a tube furnace and heated at different temperatures, ranging between 600 and 800 °C, for 1 h. The samples obtained under different treatment conditions are labeled as shown in Table 1.

The as-prepared samples were characterized by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-7610F) operated at an acceleration voltage of 2 kV. The structures of the samples numbered 1–4 in Table 1 were identified by X-ray diffraction (XRD; Xpert-Pro) using Cu Kα radiation (λ = 1.5418 Å). Sample 2 was dispersed on a molybdenum grid for transmission electron microscopy (TEM; Philips Telnai G2F20 S-TWIN) observations.

## 3. Results and discussion

The surface morphology of the Ni foil treated with 25 ml $NH_4OH$ at 60 °C for 24 h (sample Ni60) is shown in Fig. 1. The top-view images (Fig. 1a and b) show that the surface of the foil is covered with dense arrays of nanowalls. The walls are curved, with bent edges, and have an average thickness of 10 nm. Tilted-view images of this sample are presented in Fig. 1c and d. It was found that the nanowalls can be detached using a sticky tape, or separated from the substrate by sonicating in ethanol. FE-SEM images of the extracted nanowalls on a carbon tape and of the treated Ni foil after sonicating in an ultrasonic cleaner for 10 min are presented in Fig. 1e and f, respectively.

**Table 1**
Sample labels corresponding to different preparation conditions.

| Sample label | $NH_4OH$ treatment conditions | | | Annealing temperature (°C) |
|---|---|---|---|---|
| | Temperature (°C) | Time (h) | $NH_4OH$ volume (ml) | |
| Ni60 | 60 | 24 | 25 | – |
| Ni60-600 | 60 | 24 | 25 | 600 |
| Ni60-700 | 60 | 24 | 25 | 700 |
| Ni60-800 | 60 | 24 | 25 | 800 |
| Ni50 | 50 | 24 | 25 | – |
| Ni60R | 60 | 24 | 25 | – |
| Ni70 | 70 | 24 | 25 | – |
| Ni80 | 80 | 24 | 25 | – |
| Ni90 | 90 | 24 | 25 | – |
| Ni70-48h | 70 | 48 | 25 | – |
| Ni50-144h | 50 | 144 | 25 | – |
| Ni70-50L | 70 | 24 | 50 | – |
| Ni70-V | 70 | 24 | $NH_3$ vapor | – |

In a previous study based on thermogravimetric analysis, El-Kemary et al. reported that $Ni(OH)_2$ can be transformed to NiO at 400 °C [30]. In addition, Spinner and Mustain claimed that the decomposition of $Ni(OH)_2$ to NiO in air is partially and fully completed at 500 and 600 °C, respectively [31]. In this study, the Ni60 sample was dehydrated at 600–800 °C for 1 h to inspect its structural and morphological changes. The XRD patterns of samples Ni60, Ni60-600, Ni60-700, and Ni60-800 are shown in Fig. 2a, b, 2c, and 2d, respectively. Both $Ni(OH)_2$ and Ni phases are observed in sample Ni60 (Fig. 2a). The three peaks at $2\theta$ values of 44.5°, 51.8°, and 76.4° correspond to the (111), (200), and (220) planes of Ni, respectively [JCPDS file No. 00-004-0850, cubic structure, space group *Fm*–3m (225)]. In addition, three additional peaks at $2\theta$ values of 19.3°, 33.1°, and 38.5° can be assigned to the (001), (100), and (101) planes of $Ni(OH)_2$ [JCPDS file No. 00-014-0117, hexagonal structure, space group *P*–3*m*1 (164)]. The XRD patterns of the Ni foil before and after the ammonia treatment are shown in Fig. S1 (Supplementary Information). Based on the ratio between the three diffusion peaks of Ni in these spectra, the preferred etching surface of the Ni foil in the ammonia soaking treatment is expected to be the (200) surface. When the Ni60 sample is treated at 600–800 °C for 1 h, the $Ni(OH)_2$ phase completely transforms into the NiO phase. Thus, in addition to the peaks originating from Ni, observed in the Ni60-600, Ni60-700, and Ni60-800 samples (Fig. 1b–d), further diffraction peaks located at 37.2°, 43.3°, 62.9°, and 79.4° can be assigned to the (111), (200), (220), and (222) planes of NiO [JCPDS file No. 00-047-1049, cubic structure, space group *Fm*–3m (225)]. No other impurity phases are observed in the XRD patterns. The crystallite sizes of NiO in samples Ni60-600, Ni60-700, and Ni60-800, calculated using the Scherrer equation [32] with the $2\theta$ value of 37.2°, are 2.4, 3.2, and 4.1 nm, respectively. This indicates that the crystallite size of NiO increases with the annealing temperature. Moreover, the structural transformation from hexagonal $Ni(OH)_2$ to cubic NiO may change the wall-like shape into a different morphology.

The surface morphologies of the samples annealed at 600, 700, and 800 °C are displayed in Fig. 3, which shows that the morphology of the sample treated at 600 °C for 1 h is similar to that of sample Ni60 (Fig. 3a and b). When the annealing temperature is increased to 700 °C, the nanowalls are replaced by uniform nanoparticles (Fig. 3c and d). At a higher annealing temperature (800 °C), the nanowalls completely disappear and the sample surface is fully covered by grains with non-