Conversion of Conventional NiO Powders into Nanostructures by a Simple Chemical Method

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We report the synthesis of nanostructured nickel oxide and nickel hydroxide from conventional NiO powders onto different substrates by a chemical method which simply involves dissolving and decomposition steps. Scanning electron microscope (SEM) observations have revealed various morphologies of the nanostructures on different substrates. With the described method, no impurity residue will remain on the substrates, hence requiring no additional washing and separation processing.

Nanostructured materials have attracted much attention mainly due to their novel properties that may not be present in bulk materials.[1–4] As important functional materials that can be widely used as catalyst,[5–8] battery electrode materials,[9–11] and chemical sensors,[12] nickel oxide (NiO) and nickel hydroxide ($Ni(OH)_2$) have been extensively investigated. Several forms of nanostructures of NiO and $Ni(OH)_2$, including nanoparticles,[13] nanorods,[14] and nanorings,[15] have been successfully synthesized under high pressures at high temperatures in autoclaves through hydrothermal method. There are still extensive efforts to develop these nanostructures via simple and low-cost processing. In this communication we report a simple and convenient chemical method by which nanostructured NiO and $Ni(OH)_2$ can be obtained from conventional NiO powders. These nanomaterials were intentionally synthesized on substrates because we believe that, compared with free standing ones (such as nanoparticles), the nanostructures on appropriate substrates are one step closer for making practical devices.

In our work, nanostructures of $Ni(OH)_2$ and NiO were converted from conventional NiO powders by a process as follows: 0.8-g nickel oxide black (BDH Chem. Ltd., UK) was dissolved in 100 mL of 25% aqueous ammonia (International Laboratory, USA). After 24 h of dissolving, the solution turned to a light blue color. The solution was then dip coated on fused quartz and conventional sodium glass substrate, respectively, followed by a baking at 100 °C for 10 h in an oven. Finally, the samples were annealed at different temperatures.

The dissolving of the raw NiO powders in ammonia is expessed in Eq 1. The evaporation process at 100 °C produces $Ni(OH)_2$ by decomposing the products in Eq 1. Upon annealing at higher temperatures, $Ni(OH)_2$ further decomposes into NiO.

$$NiO + 6NH_3 + H_2O \rightarrow Ni(NH_3)_6^{2+} + 2OH^- \tag{1}$$

X-ray diffraction (XRD) and scanning electron microscope (SEM) were employed to pursue the microstructure and phase information of the reaction products. Figure 1 shows a representative SEM image of $Ni(OH)_2$ grown on a piece of sodium glass substrate. Two obviously different morphologies are observed. Dispersing all over the substrate (the dark areas in Figure 1) is a two-dimensional network, consisting of grass-fiber-like nanostructures (about 10-nm thick and 200-nm long for each fiber). An enlarged picture of such structure is shown in the bottom-left inset of Figure 1. In the other areas (the brighter ones) are the coralloid-ball-like structures with ≈500 nm in diameter. An enlarged picture of such structures is shown in the upper-left inset of Figure 1. We believe the coralloid balls are actually the aggregations of the grass-fiber-like nanostructures.

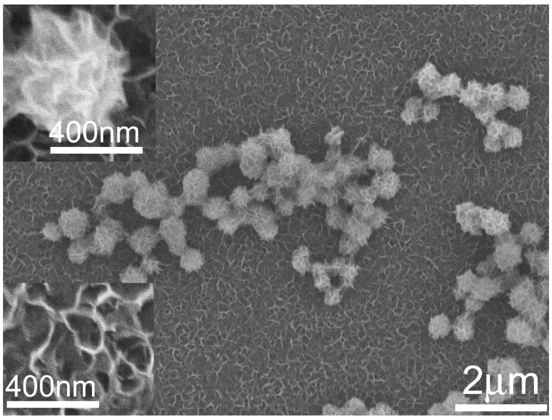


Figure 1. SEM image of the as-prepared $Ni(OH)_2$ on glass substrate. The upper-left inset shows the coralloid-ball-like nanostructures and the bottom-left inset shows the grass-fiber-like nanostructures.

Figure 2 shows the XRD pattern of the as-prepared nickel hydroxide on glass substrate. With reference to JCPDS Card # 74-2075, all the peaks in Figure 2 are identified to be from hexagonal $Ni(OH)_2$. It is interesting to note that the (001) peak is much broader than the (100) peak. For nanostructures, such broadening reflects the decrease in crystallite size according to Scherer's equation,

$$L = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

where L is the crystallite size, λ is the wavelength of the X-ray radiation (Cu $K\alpha = 0.15418$ nm), K is usually taken as 0.89, β is the line width at half-maximum height after subtraction of equipment broadening, and θ is diffraction angle. In our experiments, the equipment broadening is about 0.3 degree. The line width at half-maximum of peak (001) is 6.05 degree after we separate the left shoulder peak of an unknown phase, and that of peak (100) is 0.47 degree. Thus, it can be estimated that along the 001-direction, the crystallite size is ≈2 nm while along 100-direction, it is ≈50 nm. Noticing such sizes are much smaller than the geometric sizes of the "fiber," we may reasonably assume that each "fiber" itself is polycrystalline. Moreover, the intensity ratio of (001) over (100) in Figure 2 is ≈100:76, while the "standard"

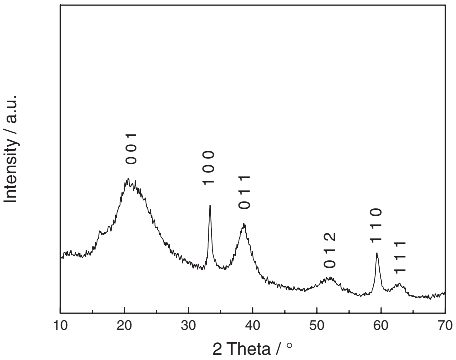
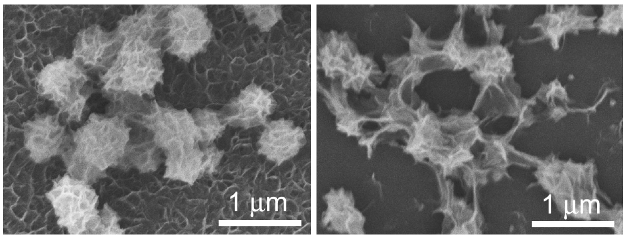


Figure 2. X-ray diffraction of the as-prepared $Ni(OH)_2$.

number is 100:28 in the JCPDS card, indicating that the growth of $Ni(OH)_2$ has a preference along the in-plane direction.

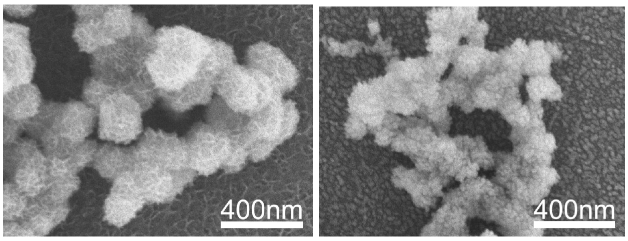
There are several factors to control the nanostructures, such as the concentration of Ni^{2+} complex solution, the thickness of the complex solution film on the substrate and the properties of the substrate itself. On the sodium glass, very dilute complex solution and small thickness of the complex solution film favor the formation of the grass-fiber-like nanostructures; while solution of relatively high concentrations and relatively big thickness lead to the coralloid-ball-like structures. On quartz substrate, only the coralloid-ball-like structures can be formed from dilute and thin complex solution film. Figure 3 shows the SEM images of $Ni(OH)_2$ on conventional glass (Figure 3a) and fused quartz (Figure 3b). $Ni(OH)_2$ on the fused quartz does not have the grass-fiber-like networks and its coralloid balls are not rounded in shape and contain less solid compared to the nanostructures grown on glass. We believe the different morphologies originated from different wetting status of the solutions on the two substrates in the process.

The effect of annealing on the nanostructures was also investigated. After annealing at 300 °C for 4 h, the material on glass was found to be slightly different from that before the thermal treatment. As shown in Figure 4a, the annealing has led to a noticeable size reduction in both the coralloid balls and the fibers, which must be related to the dehydration when $Ni(OH)_2$ was converted to NiO during the annealing treatment. X-ray diffraction shown in Figure 5a reveals that the heat-treated material is amorphous. The small peaks at 37.5° and 43.0° indicate a crystallized phase (halite) has started to form. Further annealing of the sample at 800 °C for 4 h has led the sample to exhibit a nanoparticle-like morphology with a particle size ≈10 nm in diameter, as shown in Figure 4b. The material has turned into the halite structure completely. The XRD peaks in Figure 5b are identified to come from cubic NiO (with reference to JCPDS Card # 78-0643). Such particle size implies that the nanostructure has a very large specific surface area and thus the material is expected to be highly chemically active in terms of the adsorbing ability, catalytic activity, and accessible ability for battery electrode.



(a) (b)

Figure 3. $Ni(OH)_2$ nanostructures on (a) conventional glass substrate, (b) fused quartz.



(a) (b)

Figure 4. SEM images of the nanostructures after annealing at (a) 300 °C, (b) 800 °C.

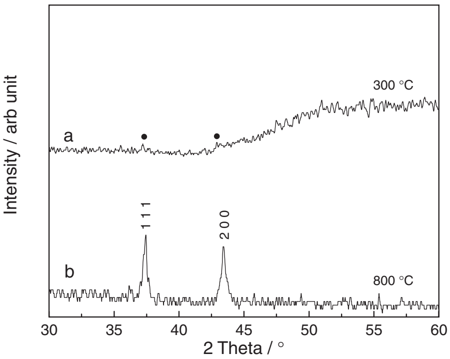


Figure 5. XRD patterns of the sample annealed at different temperatures.

In summary, $Ni(OH)_2$ and NiO nanostructures were fabricated on different substrates by a simple chemical method. The influence of thermal treatment and substrate on the phase and morphology of the materials was investigated. The resulting nanostructures are expected to be highly chemically active.

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