Synthesis of Porous Nickel Oxide Nanofiber

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Porous nickel oxide (NiO) nanofibers, structured with and composed of linearly oriented NiO nanoparticles, were synthesized via a simple method using a solution containing ethanol, H_2O, $NiCl_2$, and P123 (Pluronic P123, a triblock copolymer $H(OCH_2CH_2)_{20}(OCH(CH_3)CH_2)_{70}(OCH_2)_{20}OH$). By adjusting the concentration of P123, this method allows for the control of the fiber morphology and the nanoparticle size.

NiO is a desirable material for p-type transparent conducting films because it is a p-type semiconductor with a band-gap energy in the range of 3.6 to 4.0 eV.[1,2] By enlarging the specific surface area, NiO has been used in electronic capacitors[3] and as antiferromagnetic nanoparticles.[4] It has also been used as an electrode in dye-sensitized solar cells.[5] In order to control the size of NiO particles, various synthetic approaches have been reported.[3,4,6] In recent years, nanotubes of inorganic semiconductors such as CeO_2,[7] ZnO[8] and CuO[9] have been attracting interest because of their unique properties such as one dimensional continuity united with a high specific surface area. For example, TiO_2 nanotubes increased the efficiency of dye-sensitized solar cells when used as n-type electrodes instead of layered TiO_2 nanoparticles,[10] presumably because the electron conductivity was increased by the continuity of the nanotubes.

In the present study, we have developed a simple synthetic approach for NiO nanofibers by calcination of a NiO precursor film prepared with ethanol, H_2O, $NiCl_2$ and P123. P123 is a surfactant frequently used as a template for preparing crack-free TiO_2 films.[11–13] P123 has been used for the first time as a template for preparing p-type inorganic semiconductors. Although the preparation of single crystal nanorods of $Ni(OH)_2$ under harsh conditions using an ammonia solution has been previously reported,[14] our method is unique in being able to control the morphology of the nanofibers without complicated synthetic methods or harsh preparation conditions. Details of the synthesis are as follows: $NiCl_2$ (1.0 g) was dissolved in 2.0 g of distilled water, 4.0 g of ethanol was then added, and finally, a specific quantity of P123 (0.12, 0.5, 1.0, 1.5, and 2.0 g) was dissolved in the mixed solution under room temperature and atmospheric pressure conditions. The solution was stirred for 1–2 h. The NiO film precursor was obtained by spin coating a 4-cm^2 ITO glass (Nippon Soda Co. Ltd., E-020) surface with the solution at 300 rpm for 3 s and then at 2000 rpm for 10 s, at room temperature. The ITO was immersed for 2 h in an alkali bath for obtaining a hydrophilic surface prior to spin coating. Differential scanning calorimetric analysis (DSC, Rigaku, DSC8230) of the precursor films was carried out in air at a heating rate of 10 °C/min in order to determine suitable calcining conditions. Finally, the precursor film was calcined to obtain NiO film. Characterization of the NiO film was then conducted. X-ray diffraction (XRD, Rigaku, CN4148B2, 40 kV, 30 mA) patterns of the samples were obtained using Cu Kα radiation. The morphology of the NiO film was examined using a field emission scanning electron microscope (FE-SEM, Hitachi Co. Ltd., S-5000).

The results of DSC measurements are shown in Figure 1. Ethanol and H_2O were removed from the sample under vacuum. The broad endothermic peak centered at below 100 °C is due to the rapid removal of ethanol, H_2O, and HCl. The endothermic peak centered at 200 °C corresponds to the decomposition of P123, as described in ref 13. Some residual organic matter was removed at between 250 and 340 °C. On the basis of the DSC measurements, the calcination of the NiO precursor was performed in air at 500 °C for 30 min.

Figure 2 shows the XRD patterns of the NiO film prepared from solution containing different amounts of P123 (0.12, 0.5, 1.0, 1.5, and 2.0 g). The diffraction patterns were in good agreement with the JCPDS card, confirming the formation of NiO.[15] The particle diameters were estimated using Scherrer's equation to be 80–50 nm, 38, 33, and 30 nm, respectively, for 0.12, 0.5,

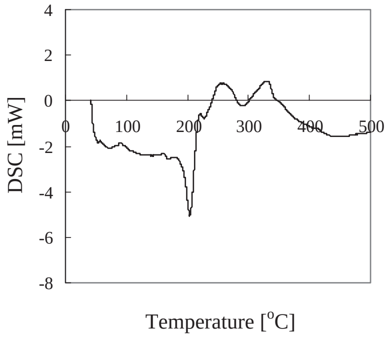

Figure 1. DSC curve of porous NiO nanofiber precursors. The amount of P123 is 1.0 g.

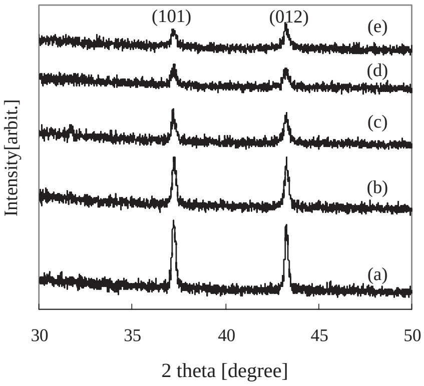

Figure 2. XRD patterns of porous NiO nanofiber on glass. The amount of P123 is (a) 0.12 g, (b) 0.5 g, (c) 1.0 g, (d) 1.5 g, and (e) 2.0 g. Calcination temperature is 500 °C for 30 min.

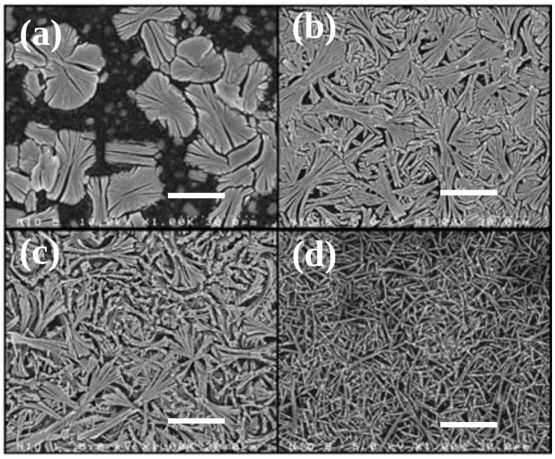

Figure 3. FE-SEM micrograph of porous NiO nanofiber on ITO. The amount of P123 is (a) 0.12 g, (b) 0.5 g, (c) 1.0 g, (d) 2.0 g. Scale bar and magnification is 24 µm and × 1000. Calcination temperature is 500 °C for 30 min.

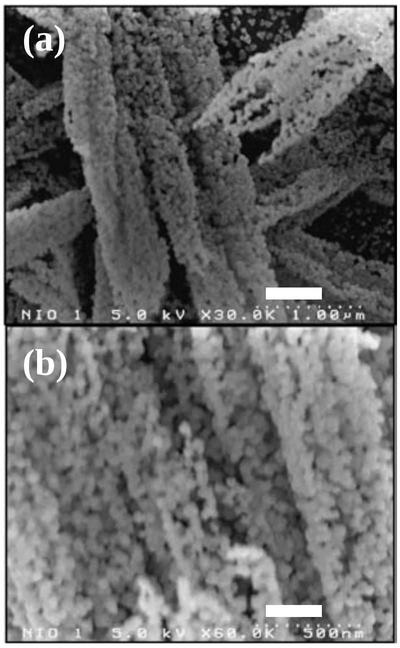

Figure 4. FE-SEM micrograph of porous NiO nanofiber on ITO. The amount of P123 is 1.0 g, Scale bar and magnification is (a) 500 nm and × 30000, (b) 250 nm and × 60000. Calcination temperature is 500 °C for 30 min.

1.5, and 2.0 g of P123. This result indicates that the diameter of NiO nanoparticles can be controlled by adjusting the amount of P123 in the precursor solution.

The FE-SEM micrographs of the NiO films (Figures 3 and 4) revealed a unique NiO morphology, namely a porous nanofiber structure. The morphology of NiO was dramatically changed with increasing concentration of P123. The morphology shown in Figure 3d indicates fiber growth in random directions, while Figures 3a and 3b indicate growth from a certain central point. These results imply that P123 in the sample solution formed micelles and functioned as a template,[12–14] and the size and shape of the micelle changed with an increase in the concentration of P123. Interestingly, fibers with a fairly high aspect ratio, with lengths of 20–50 µm and diameters of 300–500 nm, were formed. Furthermore, it was confirmed using the SEM micrograph that a single fiber consisted of many nanoparticles with diameters of 30–50 nm, as shown in Figure 4. The diameters of the nanoparticles are consistent with the particle diameters obtained from the XRD data. The nanoparticles were seen to be linearly connected and shaped into fibers. When the nanoparticles diameter is 30 nm, the calculated surface area is $28.7\,\mathrm{m^2/g}$ for the nanofibers constituted with nanoparticles, our nanofibers with nanoparticle, therefore, should have a higher specific surface area than the calculated nanofibers without nanoparticle ($1.9\,\mathrm{m^2/g}$), which is advantageous for dye-molecular adsorption or surface electronic charging. In spite of being porous, good electrical conductivity is expected for the porous NiO nanofiber film since it has better continuity than an unconnected packing of nanoparticles.

In conclusion, we obtained porous NiO nanofibers consisting of NiO nanoparticles using a simple synthetic procedure, the spin coating of a P123–NiCl$_2$–H$_2$O–ethanol solution followed by calcination.

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