Optimization of Nickel Nano Structure Deposition in Alumina Template and Its Utilization as Supercapacitor Electrode

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Abstract. Supercapacitors are consider superior than batteries in terms of cycle life and power delivery which make them more attractive in many applications. Commercially available supercapacitor mostly rely on carbon material which have low capacitance values as compared to nano or micro metal oxides structures. Among metal oxides, nickel oxides with different structures are widely under investigation, but still controlling over the structure is not addressed for supercapacitor application. In this study well controlled one dimensional nano structures were synthesized by using alumina template. Most importantly, full utilization of alumina template was carried out by optimizing growth time of the deposition of nickel wires in 1-D nano-channels of alumina. As prepared nickel nanowires were annealed in air and tested as supercapacitor electrode in potassium hydroxide electrolyte solution. Specific capacitance was calculated to be 380 F/g by cyclic voltammetry at scan rate of 2 mV/s.

1. Introduction
Unique nano-micro structures like porous, hierarchical, hollow etc. are widely investigated due to their superior properties and their utilization in wide variety of application like energy storage and conversion, water treatment, sensor, catalyst and so on. Mostly large surface area and cavities are responsible for their superior properties especially in the application of energy storage devices like batteries and supercapacitor. Supercapacitors have advantage over batteries as they have long cycling life, high power delivering ability, and ecofriendly nature [1-3]. In supercapacitor application, electrode material plays an important role and have large impact on the performance of the device. Carbon material are desirable choice of the electrode material as they have high conductivity and surface area and are abundant available in nature. Activated carbon, graphene, carbon nanotubes and other forms carbon are under investigation but still they suffered low capacitance as due to low surface area utilization as they mainly depend upon physical separation of charges. On the other hand metal oxide nanostructures have high theoretical capacitance as compared to carbon material and they can offer better capacitance values. Ruthenium oxide, copper oxide, nickel oxides, cobalt oxide etc. are sort out as metal oxide due to their oxidation states which promotes the charging activates during charge-discharge process [4-9]. Among above transition metal oxides, Nickel oxide (NiO) has high theoretical value of 2573 F/g in the voltage range of 0.5 V, abundant availability, low toxicity and easy handling make it material of choice for supercapacitor applications [10]. There are different reports of NiO nanostructures synthesized for supercapacitor application which reflects superior nature of material, among which some are highlighted below.

Vijayakumar et al. [11] reported the formation of NiO nanoflakes with the assistance of microwave radiations. In synthesis process nickel nitrate was mixed with cetyltrimethyl ammonium bromide in
were taken by cracking the AAO template with nickel nanowires deposited inside. After cracking the metal taking shape of the nanowires. Thickness of the nanowires is same as the size of the nanochannels of the template while ions of nickel move towards the base of thin film and harden as which was in the range of 147 nm. During the deposition process, liquid electrolyte trae shows the image which reveal nm. After deposition of the nanowires, again cross section of the FESEM was analyzed. Figure 1 (b) shows the image of bare template which shows 1D empty nanochannels with an average size of 200 nanowires, the bare template was broken and cross section of the A

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speed of the rotating holder was adjusted to 5 rpm and deposition was carried out for 360 seconds. After deposition of the thin barrier and seed film, the electrolyte solution was prepared using nickel chloride pentahydrate in deionized water. In 200 ml DI water NiCl$_2$.$5$H$_2$O (0.8M) was added along with boric acid (0.3M) to prepare the electrolyte solution. PH of the solution was adjusted to 3.5. DV voltage supply was used to supply 1.2 V to the system in which nickel strip was used as anode while copper deposited AAO template act as cathode. Optimization of growth of nanostructure was carried out by controlling the deposition time. After deposition, barrier copper layer was removed by wiping out it with nitric acid. As grown nickel 1D nanowires were taken out of the template by dissolving it in 1 M of sodium hydroxide. After dissolving template nanowires were washed with DI water and absolute ethanol and dried in oven. As prepared nanowires were annealed in air using tube furnace. As prepared NiO nanostructures were stored in seal cylinder. Field emission scanning electron microscope was used the morphology, structure and growth of 1D nanostructures. Electrochemical study of the NiO was studied using AutoLab equipped with NOVA software. Slurry of the active material was prepared by mixing 75% of NiO, 15% carbon black and 10% binder. Nickel foam was used as current collector. Before pasting slurry on nickel foam, nickel foam was wished with acetone, ethanol and hydrochloric acid to remove thin oxide layer from its surface. After applying active material on nickel foam, foam was pressed using hydraulic press before testing.

NiO nanoflakes. NiO nanoflakes exhibit capacitance of 401 F/g at 0.5 mA/cm$^2$ current density. Chai et al. [12] reported the formation of flower-like NiO using hydrothermal synthesis method. In synthesis process nickel chloride with the hexamethylenetetramine and transferred to autoclave and treated hydrothermally for 4 hours in heated oven at 180°C. As prepared product was washed and annealed at 300°C to synthesis flower like NiO. These nanostructure showed capacitance of 340 F/g. Qiu et al. [13] reported the synthesis of NiO nanoparticles on graphene sheets. In synthesis process graphene sheets, nickel nitrate and urea were added together to form homogenous suspension. Suspension was heated for 180 mints at temperature of 90°C. As prepared material was washed and annealed at 450°C to get NiO@Graphene. The capacitance was calculated using charge and discharge test which showed capacitance of 1098 F/g.

Although the NiO can achieve better capacitance but still control over structure and morphology is need to be addressed. In this study anodized alumina template (AAO) was used to synthesize 1D NiO nanostructures with well controlled diameter and length while as synthesized nanostructures were further used as electrode material. The Detail methodology of this work is given in below section.

2. Methodology

The For the preparation of NiO 1D nanostructures, whatman AAO template with 200 nm and thickness 60 µm. Advantage of the templates is that it can provide open nanochannels for depositing metal based structure with regular morphology and controlled thickness. Firstly AAO template was coated with coated with metal thin film to close it from one end and at the same time provide a conductive base for the growth of nanostructures. DC Sputtering was used to deposit inexpensive copper metal film as it can be sputter easy and also later on can be removed easily for further processing of AAO template. Deposition was carried out at room temperature to avoid damage to the template while argon gas flow was maintain at 100 sccm to avoid the oxidation of the film. Speed of the rotating holder was adjusted to 5 rpm and deposition was carried out for 360 seconds. After deposition of the NiO 1D nanostructures, whatman AAO template with 200 nm and thickness 60 µm. Advantage of the templates is that it can provide open nanochannels for depositing metal based structure with regular morphology and controlled thickness. Firstly AAO template was coated with coated with metal thin film to close it from one end and at the same time provide a conductive base for the growth of nanostructures. DC Sputtering was used to deposit inexpensive copper metal film as it can be sputter easy and also later on can be removed easily for further processing of AAO template. Deposition was carried out at room temperature to avoid damage to the template while argon gas flow was maintain at 100 sccm to avoid the oxidation of the film. Speed of the rotating holder was adjusted to 5 rpm and deposition was carried out for 360 seconds. After deposition of the thin barrier and seed film, the electrolyte solution was prepared using nickel chloride pentahydrate in deionized water. In 200 ml DI water NiCl$_2$.5H$_2$O (0.8M) was added along with boric acid (0.3M) to prepare the electrolyte solution. PH of the solution was adjusted to 3.5. DV voltage supply was used to supply 1.2 V to the system in which nickel strip was used as anode while copper deposited AAO template act as cathode. Optimization of growth of nanostructure was carried out by controlling the deposition time. After deposition, barrier copper layer was removed by wiping out it with nitric acid. As grown nickel 1D nanowires were taken out of the template by dissolving it in 1 M of sodium hydroxide. After dissolving template nanowires were washed with DI water and absolute ethanol and dried in oven. As prepared nanowires were annealed in air using tube furnace. As prepared NiO nanostructures were stored in seal cylinder. Field emission scanning electron microscope was used the morphology, structure and growth of 1D nanostructures. Electrochemical study of the NiO was studied using AutoLab equipped with NOVA software. Slurry of the active material was prepared by mixing 75% of NiO, 15% carbon black and 10% binder. Nickel foam was used as current collector. Before pasting slurry on nickel foam, nickel foam was wished with acetone, ethanol and hydrochloric acid to remove thin oxide layer from its surface. After applying active material on nickel foam, foam was pressed using hydraulic press before testing.

3. Result and Discussion

Morphology of the grown nickel nanowires was studied using FESEM. Before deposition of nanowires, the bare template was broken and cross section of the AAO was investigated. Figure 1 (a) shows the image of bare template which shows 1D empty nanochannels with an average size of 200 nm. After deposition of the nanowires, again cross section of the FESEM was analyzed. Figure 1 (b) shows the image which reveals the formation of nanowires. These nanowires originated from the thin film which was deposited using DC sputtering. Thickness of the thin film was measured using FESEM which was in the range of 147 nm. During the deposition process, liquid electrolyte traveled in the 1D nanochannels of the template while ions of nickel move towards the base of thin film and harden as metal taking shape of the nanowires. Thickness of the nanowires is same as the size of the nanochannels.

Figure 2 shows the growth of the nickel nanowires, deposited at different timing. These images were taken by cracking the AAO template with nickel nanowires deposited inside. After cracking the
AAO template the samples were loaded in FESEM and measurement was taken at same condition for all samples.

After optimization of growth, nickel nanowires were taken out of AAO template for further processing. In first step thin copper barrier layer was removed by wiping it with concentrate nitric acid using cotton buds. After removing barrier layer templates were dissolved in 1 M of NaOH. Small amount of NaOH was taken in the beakers and templates were soaked. After dissolving templates nickel nanowires were washed with deionized water and ethanol to clean it from remaining NaOH. Nickel nanowires were further oxides using furnace in air to form NiO nanostructures. NiO nanostructures were further transferred into electrode and tested for supercapacitive properties.

Cyclic voltammetry was performed for electrodes in the range of 0 V to 0.45 V at room temperature. Different voltages in the range of 2 mV/s to 75 mV/s were applied for scanning of electrodes. In figure 3 (a) two very distinct peaks of currents were observed in the cathodic and anodic parts of sweep. These peaks are refer to pseudocapacitance features of the material and are entirely different than the double layer capacitance behavior [14]. These peaks are result of oxidation and reduction reaction between electrolyte and active material. This redox reaction can be explained by following equation [15].

\[
NiO + OH^- \leftrightarrow NiOOH + e^- 
\]

Figure 1. (a) FESEM image of bare AAO template showing open 1D nanochannels (b) FESEM image of nanowires in AAO template.
The intensity of the peak was amplified with the increasing scan rate from 2 mV/s to 75 mV/s and the same time redox pair presence was also corresponding to the reversible behavior of the electrode material.

Figure 3(b) shows the capacitance values of the electrode at different scan rates. The capacitance of different scan was calculated using following equation:

\[
C_s = \frac{\int (V_2 - V_1) dV}{m V (V_1 - V_2)}
\]

(1)

Where \( C_s \) is specific capacitance, \( V_1 \) and \( V_2 \) are upper and lower potential of the scan, \( V \) is scan rate, \( m \) is the mass loading and \( I(V) \) is current at two potential. The capacitance calculated at different scan rate 2 mV/s, 5mV/s, 10 mV/s, 25 mV/s, 50 mV/s and 75 mV/s are 380 F/g, 286 F/g, 249 F/g, 217 F/g, 194 F/g and 179 F/g, respectively. At low scan rate high capacitance values were observed which is due to the fact that at low scan ions can get sufficient interval to interact with active material.

4. Conclusions

In this research work we report the growth of nickel nanowire using 1D nanochannel alumina template. Template preparation along with deposition process was discussed. Deposition process was optimized for the full utilization of the template. 1D nanowires were further oxidized to form NiO for utilizing them in supercapacitor. Cyclic voltammetry scan at 2 mV/s showed that NiO electrode can
achieve the capacitance of 380 F/g. Such abundant available nickel metal showing good performance as electrode material can further by better option for using it as part of supercapacitor device.

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