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Supercapacitive Performance of Lithium Doped and Undoped $NiFe_2O_4$ Thin Films by Chemical Deposition Method

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Lithium (Li) doped and undoped $NiFe_2O_4$ thin films for supercapacitor application have been prepared through the chemical deposition method. The Li doped and undoped $NiFe_2O_4$ thin films for structural, morphological and supercapacitive performance have been studied. As the Li doping percentage varies from 1 at. wt.% to 3 at. wt.%, the thickness of $NiFe_2O_4$ thin films increases up to 120 min deposition time, after that slight decrease in thickness was observed. SEM images show randomly grown flake-like structure of Li-$NiFe_2O_4$ thin films. The angle of contact of Li-$NiFe_2O_4$ thin films decreases with increase in Li doping into $NiFe_2O_4$ thin films. The effect of Li doping percentage on supercapacitive performance revealed that as the Li doping percentage is increased from undoped to 3 at. wt.%, the specific capacitance is increased from 314 F/g to 571 F/g.

Key words: Thin film, $NiFe_2O_4$, SEM, supercapacitive performance, XRD

INTRODUCTION

Now-a-days, researchers are focusing on energy storage technology due to fossil fuels, environment pollution, global warming, etc., which offers clean energy. There are several types of electrochemical power systems such as batteries, fuel cells and supercapacitors.[1] Now, the supercapacitor device is capable of storing useful quantities of electricity which can charge very quickly. There are several advantages of supercapacitors, like they have high power density, specific capacitance in several Farads to several hundred Farads, rapid charging—discharging, and charge in seconds, etc. Due to all of these reasons, it directs use for power applications.

There are several materials used for supercapacitor application like MnO_2,[2] CuO,[3] La_2Te_3,[4] RuO_2,[5] etc. These materials have high specific capacitance and using doped $NiFe_2O_4$ films for a supercapacitor is advantageous due to its simple synthesis process and low cost of material. Li-$NiFe_2O_4$ thin films have higher specific capacitance than $NiFe_2O_4$ film, due to this reason we focus on Li doped films. B. Negulescu et al.[6] prepared NiO/$NiFe_2O_4$ bilayer using pulsed laser deposition. Hsiao et al.[7] have studied formation of $NiFe_2O_4$ from plasma induced surface segregation of NiFe and its oxidation during plasma oxidation. Sartale et al.[8] have introduced a novel two step electrochemical route for the deposition of $NiFe_2O_4$ thin films at room temperature. They have prepared $NiFe_2O_4$ thin film by electrochemical oxidation of pre-electrodeposited stoichiometric $NiFe_2$ alloys. Chemical deposition method (CDM) is simple, easy, ecofriendly, cost-effective and less time consuming method for thin films preparation. Due to these reasons we have chosen chemical deposition method (CDM) for preparation of Li doped and undoped $NiFe_2O_4$ thin films for supercapacitor application.

In the present research work, we have prepared undoped and doped Li-$NiFe_2O_4$ thin films for supercapacitor application. In this preparation, we choose a simple CDM method. XRD, SEM, thickness measurement and wettability properties shows,

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prepared undoped and Li doped $NiFe_2O_4$ thin films are a better materials for supercapacitor application and to obtain high specific capacitance.

EXPERIMENTAL DETAILS

Preparation of $NiFe_2O_4$ and Li Doped $NiFe_2O_4$ Thin Films

The source of nickel and ferrous used was 0.1 M $NiCl_2$ and 0.2 M $FeCl_2$ in 1:2 proportion, respectively, and to make it alkaline, aqueous ammonia was added. The pH of the resultant solution was adjusted at 9.5, further $LiCl_4$ is used as doping source (1 at. wt.%, 2 at. wt.% and 3 at. wt.%) and stainless steel was used as the substrate, which was cleaned with chromic acid, followed by rinsing with double-distilled water and finally treated with ultrasonic waves for 20 min. These ultrasonically cleaned substrates were immersed in the chemical bath and the bath was heated. When the bath attained the temperature of 328 K, the precipitation was started in the bath. Later, a similar bath was used for Li doped $NiFe_2O_4$ films. The $NiFe_2O_4$ films were removed after 3 h from the bath, washed with double distilled water and dried in air.

Characterizations

X-ray diffraction (XRD) technique by Philips (PW-3710) diffractometer model with the chromium target (λ = 2.28 Å) in the range of 20°–80° were used to know the structural properties of Li doped and undoped films. The Rame-hart USA equipment with CCD camera contact angle measurements was used for wettability measurements. The surface morphology of thin films was observed via scanning electron microscopy (SEM) of model JEOL-6360. The thickness of thin films was measured by a gravimetric weight difference method through sensitive microbalance. The cyclic voltammetry (CV) measurement were completed using a potentiostat/galvanostat (EG & G PAR 263-A) to define the capacitive properties.

RESULTS AND DISCUSSION

Structural Properties

XRD patterns of undoped and Li doped annealed $NiFe_2O_4$ films are shown in Fig. 1. The samples were prepared at 0 at. wt.%, 1 at. wt.%, 2 at. wt.% and 3 at. wt.% as (a), (b), (c) and (d) respectively. The crystal structure of $NiFe_2O_4$ is displayed by JCPDS Card No. 10-0325 and oriented along the (311) plane.[9] Other orientations corresponding to (220), (400), and (422) planes are also present with low intensities compared to that of the (311) plane that is observed for film and Δ shows the peaks of stainless steel substrate. Further, when at. wt.% Li doping is increased from 1% to 3% in the bath, the crystallinity of $NiFe_2O_4$ films was decreased. Such a low crystalline or amorphous material is a prime

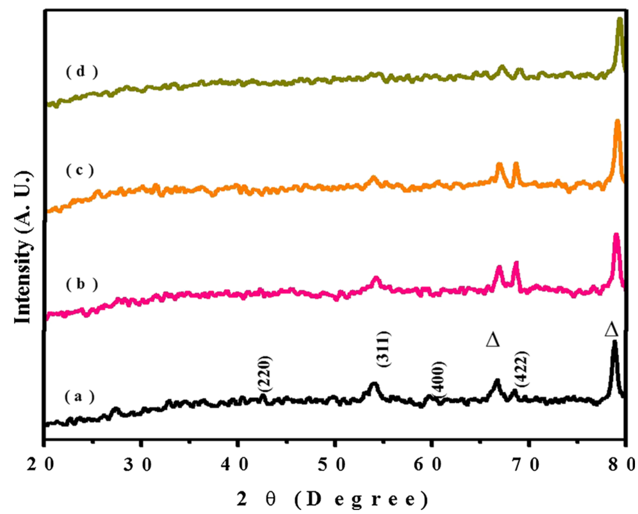

Fig. 1. XRD patterns of (a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.%, and (d) 3 at. wt.% Li doped $NiFe_2O_4$ films.

requirement for supercapacitor application. The small peak intensities in XRD pattern revealed the existence of fine grains (nanocrystalline) with most of the part as amorphous. The XRD patterns of Li doped $NiFe_2O_4$ films are in good agreement with earlier reported results.[10] The crystallite size of deposited films was determined using the well-known Scherer's equation.[11] The crystallite size of undoped $NiFe_2O_4$ film was estimated for highest intensity diffraction peak (311) to be about 39 nm.

Morphological Studies

The surface morphological studies of (a) undoped, (b) 1 at. wt.%, (C) 2 at. wt.%, (d) 3 at. wt.% Li doped $NiFe_2O_4$ films have been carried out from scanning electron micrographs (SEM). The SEM images of undoped and Li doped $NiFe_2O_4$ thin films are shown in Fig. 2a, b, c, and d respectively. The micrograph Fig. 2a shows flake-like structure grown on the substrate observed for undoped $NiFe_2O_4$ film. Figure 2b, c, and d shows Li doping is increased in the NiFe bath, the random types of flake like morphologies are observed. The morphology reported in our outcomes is different than reported results of $NiFe_2O_4$ film.[12,13]

Wettability Measurement

Figure 3a, b, c, and d shows that wettability measurement of Li doped and undoped $NiFe_2O_4$ films onto stainless steel substrates at (a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.%, (d) 3 at. wt.% of Li doping in $NiFe_2O_4$ films. The contact angles are observed to be 38°, 34°, 23°, and 19° respectively. It reveals that the hydrophilicity of the $NiFe_2O_4$ films increases with increase of Li doping percentage in NiFe bath. Decrease in water contact angle for $NiFe_2O_4$ thin film was attributed to the increased porous nature of film. Hence, water contact angle depends not only on the preparation method, but also depends on the doping concentration. The

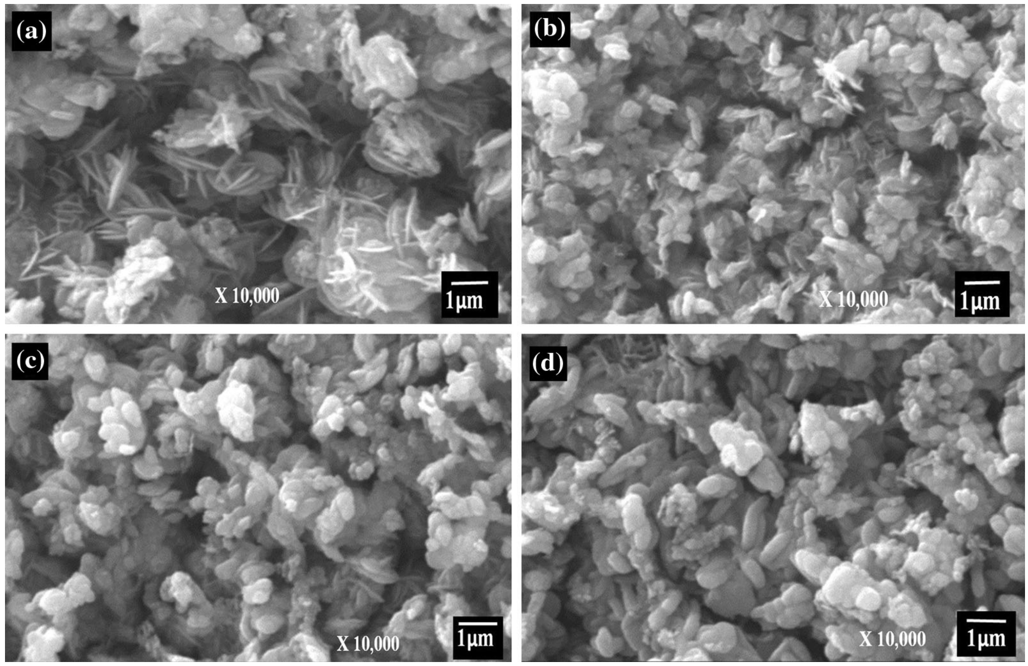

Fig. 2. SEM images of (a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.%, and (d) 3 at. wt.% Li doped $NiFe_2O_4$ films at × 10000 magnifications.

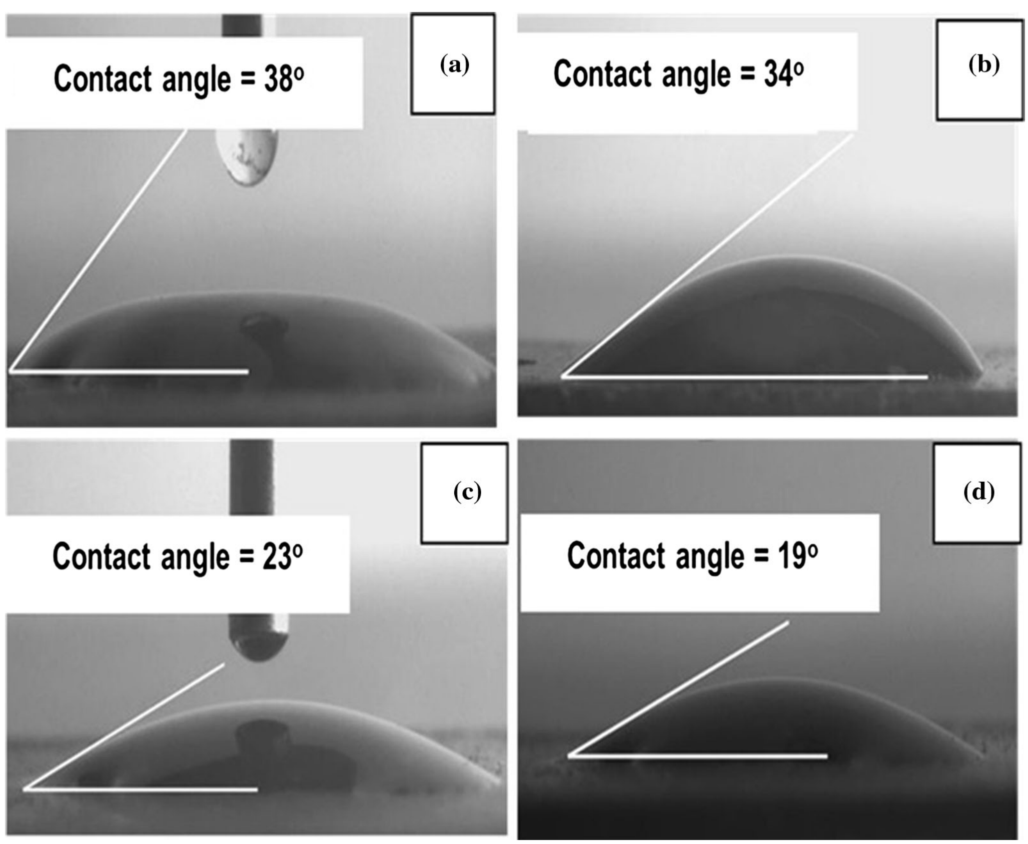

Fig. 3. Contact angle images of (a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.%, (d) 3 at. wt.% Li doped $NiFe_2O_4$ films.

hydrophilic type surface is required for improved supercapacitive performance of thin film samples.[14]

Capacitive Performance Studies

The capacitive properties of Li doped and undoped $NiFe_2O_4$ electrodes can be calculated from the cyclic voltammetry (CV) curve at a scanning rate using the following equation.[15]

$$C = \frac{I}{(\mathrm{d}V/\mathrm{d}t)}, \quad (1)$$

where I is the average current in ampere and $\mathrm{d}v/\mathrm{d}t$ is the scanning rate in volt/s.

In the present study, cyclic voltammograms were obtained at sweep rates ranging from 10 mV/s to 200 mV/s in different concentrations of electrolyte and the resulting capacitance was calculated.

The aqueous electrolytes like NaOH, KOH, NaCl, Na_2SO_4 and Na_2SO_3 with 1.0 M molar concentrations have been tested for Li doped and undoped $NiFe_2O_4$ film electrodes. Figure 4 showed the typical cyclic voltamograms of CDM deposited (a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.%, and (d) 3 at. wt.% Li doped $NiFe_2O_4$ films on stainless steel substrate at the scan rate of 10 mV/Sec. The maximum capacitance as compare to other electrolytes for Li doped and undoped $NiFe_2O_4$ electrodes is obtained for 1.0 M Na_2SO_3 electrolyte.

The capacitive performance of CDM deposited Li doped and undoped $NiFe_2O_4$ electrodes were carried out in Na_2SO_3 electrolyte. The effect of Li doping percentage on supercapacitor performance revealed that as the Li doping percentage increased from [(a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.% and (d) 3 at. wt.%] the current under the curve is increased and also specific capacitance is enhanced from 314 F/g to 571 F/g. The maximum specific capacitance of 571 F/g is achieved for 3 at. wt.% Li doped $NiFe_2O_4$ film electrode at the scan rate of 10 mV/s.

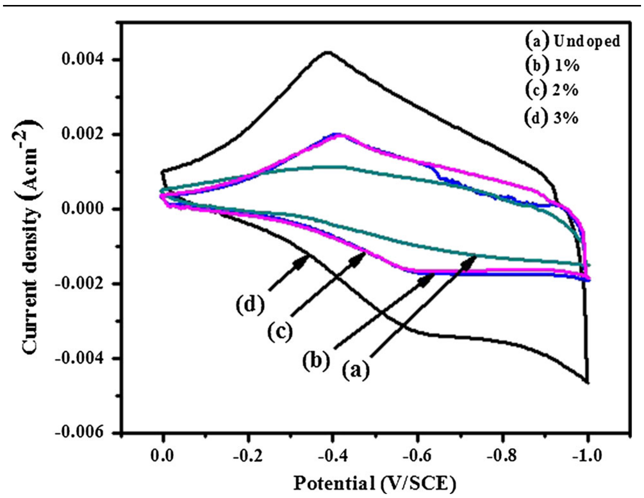

Fig. 4. The cyclic voltammogram of (a) undoped, (b) 1 at. wt.%, (c) 2 at. wt.%, and (d) 3 at. wt.%, Li doped $NiFe_2O_4$ films.

The specific capacitance of Li doped and undoped $NiFe_2O_4$ thin films are (a) 314 F/g, (b) 386 F/g, (c) 468 F/g and (d) 571 F/g respectively. The undoped $NiFe_2O_4$ thin films display more specific capacitance than previously reported results.[16] In the present work, we have used lithium chloride in a NiFe bath for energy enhancement due to lithium properties.[17] It means Li doping is used in the bath to increase the supercapacitive performance of thin films.[18]

CONCLUSIONS

XRD patterns of Li doped and undoped $NiFe_2O_4$ thin films show crystalline to amorphous nature which is a key requirement for supercapacitor application. The crystallite size of undoped $NiFe_2O_4$ thin films for a characteristic peak is found to be 39 nm that is nanocrystalline in nature. The SEM images show randomly oriented flakes-like structure of $NiFe_2O_4$ thin films. The wettability studies display a hydrophilic nature with contact angle 38° to 19° respectively. The samples prepared at 3 at. wt.% Li doping shows maximum specific capacitance 571 F/g and after that with increase in doping % of Li, specific capacitance of film is decreased. It means the results show Li doping is superior for supercapacitor applications.

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