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Pulsed Reverse Potential Electrodeposition of Carbon-Free Ni/NiO Nanocomposite Thin Film Electrode for Energy Storage Supercapacitor Electrodes

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Abstract: A combined cyclic voltammetry and pulse reverse potential electrodeposition technique has been used to synthesize carbon-free Ni/NiO nanocomposite thin film supercapacitor electrode. The structural and morphological analyses have revealed the presence of crystalline phases of both Ni and NiO in the form of nanospheres of size ~50 nm. The electrochemical analysis of the Ni/NiOna nocomposite electrode has shown a remarkable performance by delivering a high specific capacitance of 2000 Fg^{-1} at an applied current load of 1 Ag^{-1} and a capacitance retention of 98.6%, after over 800 cycles under a high current load of 20 Ag^{-1}.

Keywords: electrodeposition; pulse reverse potential (PRP); Ni/NiO nanocomposite; supercapacitor electrode; high capacitance retention; energy storage

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1. Introduction

Supercapacitors (SCs) have received much attention as important energy storage devices in recent times as a result of their high-power densities and longer cycle life compared to batteries, and high energy densities compared to dielectric capacitors [1]. Based on their charge storage mechanism, SCs can be classified as electric double-layer capacitors (EDLCs) or pseudocapacitors (PCs). PCs are known to provide higher specific capacitance and energy density than EDLCs due to the multiple oxidation states of their electroactive materials, which favour fast faradaic reactions [2–4]. Transition metal oxides such as NiO [1] RuO_2 [3], Co_3O_4 [5] and MnO_2 [4] are mainly used as PC electrode materials. Among them, NiO has received much attention in the past few years because of its low cost, environmental friendliness, and high theoretical specific capacitance (2573 F/g) [1]. Nanostructured NiO coatings have also been found to be useful in other types of applications such as the one recently reported by Yu-Ling Hsieh et al. in bioapplications [6].

In this work, we report a novel approach of electrodeposition technique that combines the modes of cyclic voltammetry (CV) and pulse reverse potential (PRP) to deposit a carbon-free conducting Ni/NiO nanocomposite thin film supercapacitor on a chemically inert conducting Ti- substrate.

2. Experimental Section

The carbon-free Ni/NiO nanocomposite thin film was deposited on Ti-substrate by CV in a potential range of −1.4 to +1.0 V vs. Ag/AgCl at a scan rate of 20 mVs^{-1} for 2 cycles, followed by pulse reverse potential (PRP) of 60 cycles of width of 1 s for the duration of 60 s. The minimum and the maximum of pulse heights were chosen to be −1.4 V and +1 V, respectively. The details of this deposition mechanism can be found in the Supplementary Data S1. The electrolyte solutions, namely, 0.1 M $NiSO_4 \cdot 6H_2O$ and 0.2 M $NaClO_4 \cdot H_2O$ of pH of 4.5, were used for the deposition of the Ni/NiO nanocomposite thin

film. The deposition process was conducted in a standard three-electrode glass cell with a platinum wire, Ti-substrate and Ag/AgCl as the counter, working and reference electrodes, respectively. After electrodeposition, the as-prepared carbon-free Ni/NiO nanocomposite thin film electrode was rinsed in deionized water and dried on a hot plate at 100 °C for 10 h in air before performing physical and electrochemical tests. The morphological and elemental analyses of the carbon-free Ni/NiO nanocomposite thin film were studied by a scanning electron microscope (SEM, JEOL JSM-6480 LV, Japan), equipped with the function of energy-dispersive X-ray spectroscopy (EDX). The X-ray diffraction (XRD) analyses were carried out by Bruker D8 Discover system. The electrochemical properties (cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) were evaluated using Solartron SI1287 electrochemical workstation (Solartron, Gastonia, NC, USA) in a 1 M KOH aqueous solution.

3. Results and Discussion

Figure 1a shows the XRD spectrum of the carbon-free Ni/NiO nanocomposite thin film deposited on a Ti-substrate and the inset shows the deconvoluted peak observed around 44.5°. The diffraction spectrum shows two small peaks of (111) and (200) at 2θs of 36.5° and 42.1°, respectively, which can be assigned to the cubic NiO structure with lattice constant a = 4.1717 Å, corresponding well with the standard crystallographic data for NiO (JCPDS Card:# 65-5745). The deconvoluted peak in the inset shows the presence of a metallic Ni(111) peak at 2θ of 44.5°. The truncated peaks corresponding to Ti are assigned by an asterisk (*) symbol in the main graph. The Ti peak has also been labelled as B in the inset. The calculated mean crystallite sizes of NiO and Ni using Scherrer's equation are found to be 7 and 5 nm, respectively. The broad and low intensity XRD peaks of Ni and NiO can be attributed to the amorphous nature and to the small size of the Ni and NiO nanostructures [7,8]. Similar small size NiO crystallites of 5.6 nm have been reported by Atalay et al. on NiO nanostructures deposited by chemical precipitation onto fungi substrates [8]. The distribution of the small nanosize crystallites of Ni and NiO in the composite thin film can contribute to the large specific surface area [9].

Figure 1b shows the SEM image of the Ti substrate presenting a smooth surface. However, the SEM image in Figure 1c shows the morphology of the as-deposited carbon-free Ni/NiO composite thin film, revealing a porous interconnected nanospherical structure. Figure 1c confirms a uniform distribution of loosely packed nanospherical particles with an average size of ~50 nm, randomly deposited within and between the pores, indicating complete deposition coverage. The particle size (~50 nm) distribution was confirmed by image analysis as presented in the Supplementary Data (S2). The EDX spectrum in Figure 1d shows the peaks of O and Ni in addition to the substrate peaks of Ti indicating the formation of NiO nanostructures with an adequate Ni/O ratio of 1.5.

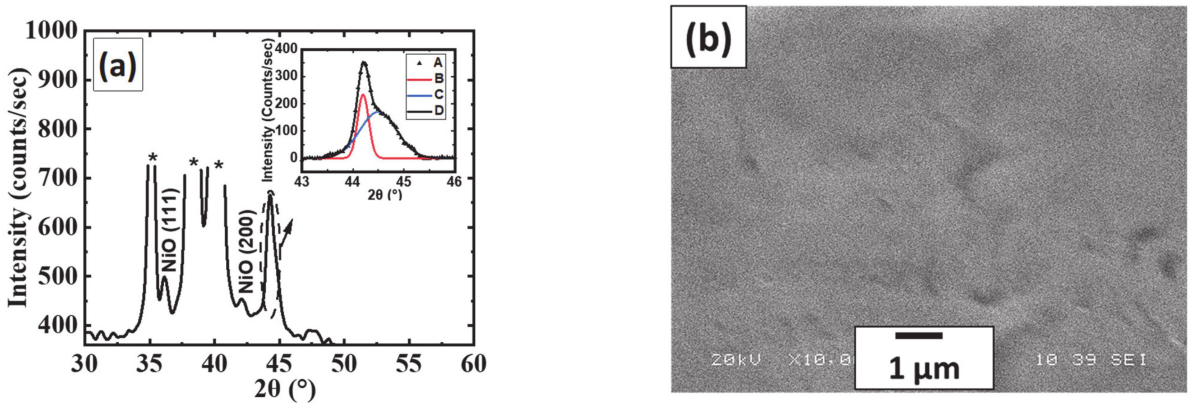


Figure 1. *Cont.*

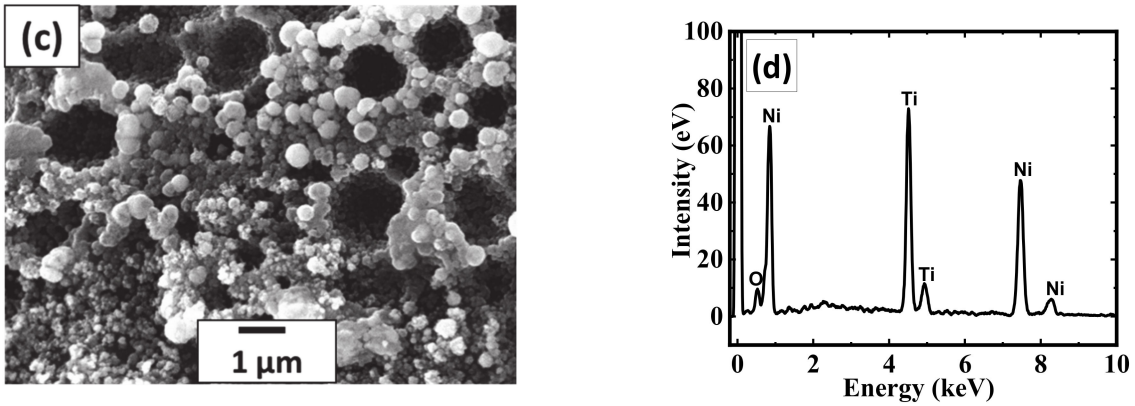


Figure 1. (**a**) XRD spectrum of the carbon-free Ni/NiO nanocomposite thin film on Ti-substrate. Table 200. C-fitted peak of Ni (111), D-smoothened data, (**b**,**c**) SEM images of Ti-substrate and carbon-free Ni/NiO nanocomposite thin film (**d**) EDX spectrum corresponding to Figure 1 (**c**).

The electrochemical and energy storage properties of the carbon-free Ni/NiO nanocomposite thin film electrode were studied and have been presented in Figure 2. The Nyquist plots and the polarization curves of the Ni/NiO coating on the Ti substrate as well as on Ti substrate can also be found in Figure S3a,b of the Supplementary Data. The CV curve of the bare Ti-substrate in Figure 2a shows a horizontal line that signifies no capacitance behavior arising from Ti-substrate. Interestingly, on the carbon-free Ni/NiO nanocomposite thin film, an oxidation peak is observed at +0.55 V, which is related to Ni oxidation state from Ni(II) to Ni(III) where NiO is oxidized to NiOOH and a reduction peak at +0.35 V is related to the reduction of NiOOH to NiO. This is a typical faradaic pseudocapacitive behavior for NiO and these reduction and oxidation peaks correspond to the reversible reaction following redox reaction [10]:

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (1)$$

Apart from CV, galvanostatic charge–discharge (GCD) was performed at different current densities and has been presented in Figure 2b. The specific capacitances of the carbon-free Ni/NiO nanocomposite thin film electrode have been calculated to be 2000, 1820, 1770, 1640 and 1440 Fg^{-1} at the respective current densities of 1, 2, 3, 4, and 5 Ag^{-1}. These values, revealing high energy storage capacities, are much higher than previously reported values on Ni based energy storage materials [1,11]. For example, Joaquin et al. reported 755 Fg^{-1} at 1 Ag^{-1} on electrophoretic deposited core shell nanowire arrays of Ni/NiO [12] while Navale et al. reported 458 Fg^{-1} at 1 Ag^{-1} corresponding to potentiostatic electrodeposited NiO thin films on stainless steel [11]. However, Farrukh et al. have previously reported a similar high capacitance value of 2093 F/g on their NiO nanotubes electrochemically deposited on anodized aluminium (AAO) [13]. The large specific capacitance of our carbon-free Ni/NiO composite thin film electrode may be attributable to the nanostructured morphology of the electrode composed of nanospherical structures of Ni/NiO contributing to increased surface area, as evident from the SEM images in Figure 1c. Such a high surface area oriented morphology arising from the nanospherical patterns could be responsible for the high capacitive behavior of the Ni/NiO thin film electrode. This behavior could be attributed to better accessibility of the electrolyte to the surface of electrode to facilitate the Faradic reaction as presented in Equation (1) [13,14].

Figure 2c shows the long-term galvanostatic cycling performance of our Ni/NiO composite electrode. The capacitance retention of our electrode over 800 cycles at a high current density of 20 Ag^{-1} is 97.4%. The inset of Figure 2c shows the specific capacitance performance during the last eight charge–discharge cycles.

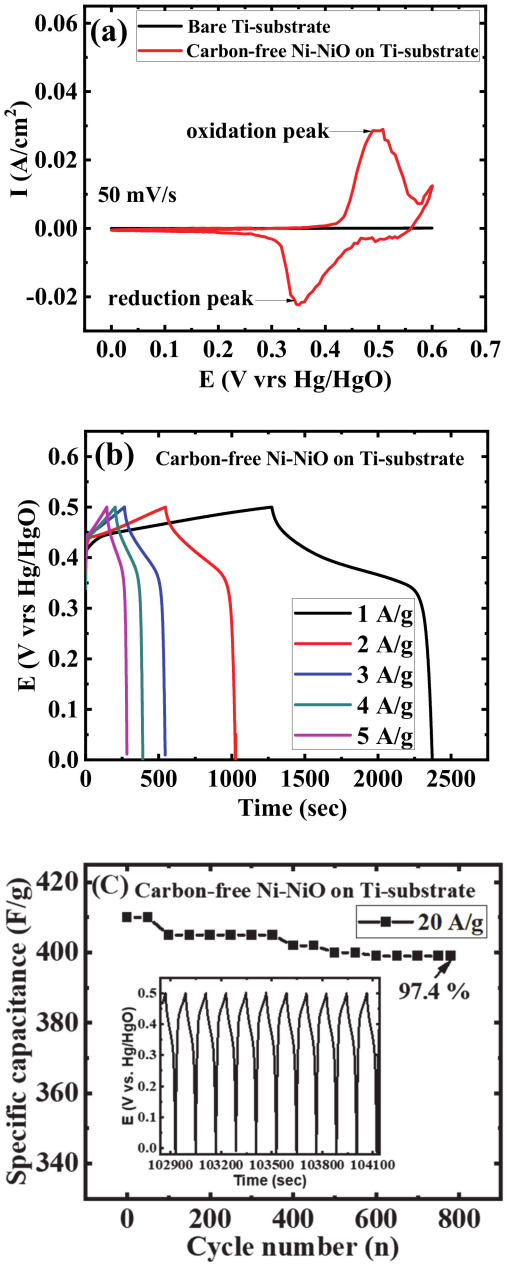


Figure 2. (**a**) CV curves of Ti-substrate and the carbon-free Ni/NiO nanocomposite thin film on Ti-substrate; (**b**) Charge–discharge curves of one cycle at different current densities; (**c**) Cycling performance after 400 cycles at 20 A/g.

4. Conclusions

Carbon-free Ni/NiO nanocomposite thin film supercapacitor electrode material composed of nanospherical features of size ~50 nm has been synthesized and deposited on a Ti substrate surface by a simple combined cyclic voltammetry and pulse reverse electrodeposition technique. A very high specific capacitance of 2000 Fg^{-1} at a current density of 1 Ag^{-1} with an excellent galvanostatic cycling stability over 800 cycles has been achieved on our Ni/NiO electrodes, presenting great potential for a long-term supercapacitive application.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/coatings11070780/s1, Figure S1: Deposition profiles of carbon-free Ni/NiO nanocomposite thin film on Ti-substrate: (a) Cyclic voltammetry (CV) followed by (b) Pulse reverse potential (PRP); Figure S2: (a) SEM image (b,c) Particle size distribution of the Carbon-free Ni/NiO nanocomposite thin film on Ti-substrate; Figure S3: (a) Nyquist plots and (b) polarization curves of Ni/NiO coating on Ti substrate and pristine Ti substrate (inset shows the Nyquist plot of Ni/NiO coating on Ti).

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Conflicts of Interest: The authors declare no conflict of interest.

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