Study of Ultra capacitor Electrodes Based On Metal / Metal-Oxide Core/Shell Nano-Heterostructures

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ABSTRACT

This study deals with the fabrication technique used for novel nano-heterostructures (NHs) and to study their electrochemical properties as Ultra capacitor electrodes. The Ni/NiO core/shell and Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures Ultra capacitor electrodes offer the desired properties of macroporosity to allow facile flow of electrolyte, thereby reducing device resistance and nanoporosity with large surface area to allow the kinetics of faster reaction. Here the three different electrode configuration, Ni/NiO core/shell and Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures Ultra capacitor electrodes is studied which exhibites specific capacitances, at a constant current density , high energy , power density , good capacitance retention and long cyclicality. The remarkable electrochemical property of the large surface area nano-heterostructures is described based on the effective nano-architectural design of the electrode with the coexistence of the highly redox active materials at the surface supported by highly conducting metal channel at the core for faster charge transport.

Keywords: Nanostructures, Electrodeposition, core-shell, Renewable Energy, Ultra capacitors.

INTRODUCTION

Diminishing reserves of fossil fuels and severe impacts of burning fossil fuels both on human beings and environment have been increasingly driving the world towards the development of clean and sustainable energy. Transforming natural energy, such as wind, tide, and solar energies can generate large amount of clean and sustainable energy. The development of energy storage devices is extremely important to store the harvested energy for wide applications. Nowadays, ultra capacitors are exhibiting wide applications in electric vehicles, pacemakers, consumer electronic devices and so on. Recently, redox-active transition-metal oxides (TMOs) such as RuO_2, MnO_2, Fe_2O_3, NiO and Co_3O_4 are being described as the emerging electrode materials for Ultra capacitors (UCs) because of their high specific capacitances and excellent reversibility [1,2]. In this context, selections of specific materials as well as the proper nano-engineering design of the electrode are very effective. As the high cost of RuO_2 limits its practical applications, among the other TMOs, Co_3O_4 and NiO could have been an ideal alternative for the UCs electrode because of their high theoretical capacitances, availability, stability and relatively low cost. It is also well studied that the nano-architectures with large active surface area, short ion transport pathway and better electronic conductivity could improve the performance of UCs[4,5]. The unique nano-architecture of the hybrid metal oxides can be used as anticipation with higher specific capacitance as well as high energy and power density of the Co_3O_4 and NiO based UCs. The Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell NHs have redox active oxides with large active surface to serve as the electrode. The thin mixed-oxide layer will provide the short ion transport path, whereas the metal alloy core will act as the fast electron conducting channel to the current collector.

METHODOLOGY

The electrode containing high density ordered arrays of 1D Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures can be designed and studied with the help of controlled high temperature oxidation of Ni and Co-Ni nanowires which are grown via template assisted electrodeposition technique by using the highly ordered nanoporous anodic aluminium oxide (AAO) as a template [6]. The unique feature of this technique is that individual nano-heterostructure in the electrode has its own contact with the current collector (Au), which results the enhanced charge transfer kinetics[7,8]. Materials characterization should be done by field emission scanning electron microscopy (FESEM), energy-dispersive x-ray spectroscopy (EDS), transmission electron microscopy (TEM), and energy filtered TEM (EFTEM)[10]. The electrochemical properties of the samples can be obtained by cyclic voltammetry (CV) and galvanostatic (GV) charge/discharge tests by using software controlled conventional three-electrode electrochemical cell [11].

RESULTS AND DISCUSSION

The field emission scanning electron microscopy (FESEM) image of the Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures (NHs), have uniform diameter which indicates that the surface of NHs are very rough and porous, which will increase the active surface area of the electrodes. the energy-dispersive x-ray spectroscopy (EDS) spectrum confirms the presence of Ni and O in the Ni/NiO core/shell NHs, Co, Ni and O in the Co-Ni/Co_3O_4-NiO core/shell NHs. The transmission electron microscopy (TEM) micrograph of Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell NHs, gives the formation the uniform nano-layer. The energy filtered TEM (EFTEM) micrographs of the Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell NHs, indicates the formation of a good quality NHs with uniform chemical composition. Electrochemical properties of the Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures electrode can be obtained by cyclic voltammetry (CV) and galvanostatic (GV) charge/discharge method by using a three-electrode system, where the nano-heterostructures as working electrode should be dipped in 1 M KOH aqueous solution at room temperature.

The Ag/AgCl and Pt can be used as reference and counter electrodes, respectively.The redox peaks for all scan rates are associated with the surface or near surface based Faradic reactions. The equations are:

$Co_3O_4 + H_2O + OH^- \leftrightarrow 3CoOOH + e^-$

$NiO + OH^- \leftrightarrow NiOOH + e^-$

The charging process involves the oxidization of Co^{2+} and Ni^{2+} into Co^{3+} and Ni^{3+}, respectively, with the movement of the corresponding electrons towards the current collector (Au) through the electrode; while discharging involves subsequent reduction of metal ions from +3 state to +2 state followed by the electron transport in reverse direction. The increase of current with increasing scan rate is quite obvious because during fast scanning diffusion layer cannot extend far from the electrode surface, thus facilitating higher electrolyte flux towards the electrode leading to higher value of current which is in contrary to the case at lower scan rates where the large width of the diffusion layer significantly reduces the electrolyte flux and hence the current. The energy and power densities can be calculated by the respective formulas. The energy density of the Ni/NiO and Co-Ni/Co_3O_4-NiO. core/shell NHs electrode decreases . The Ni/NiO and Co-Ni/Co3O4-NiO core/shell NHs also exhibit excellent electrochemical cycling stability. Such high stability of the electrode can be accounted for the higher mechanical integrity which can sustain significant structural distortion during repetitive charging/discharging process and also non-dissolution of active material within the electrolyte.

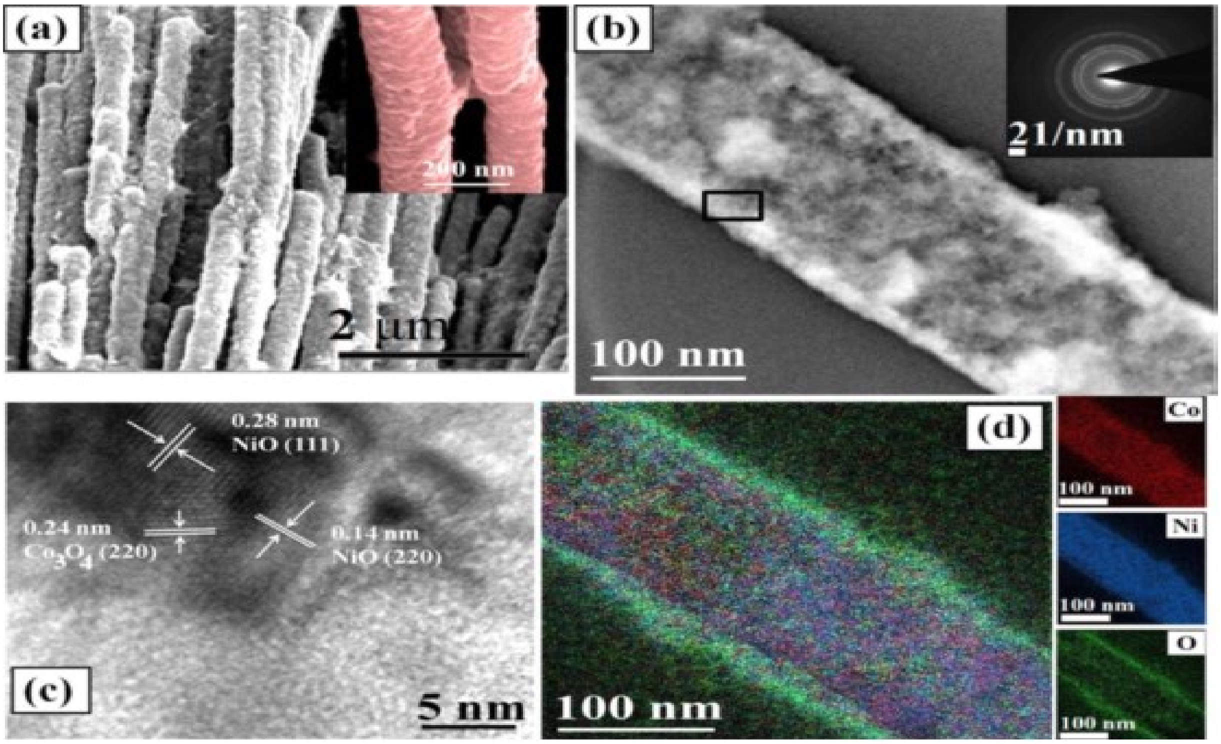

Figure 1. (a) FESEM micrographs, (b) TEM and SAED pattern ,(c) HRTEM image, and (d) EFTEM micrographs of the Co-Ni/Co3O4-NiO core/shell nano-heterostructures[9]

CONCLUSION

In conclusion, Ni/NiO and Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures with remarkable ultra capacitance properties can be achieved. The nano-heterostructures can be fabricated by combining simple electrochemical deposition of Ni and CoNi nanowires followed by controlled oxidation. The unique nano-architectural design of the nano-heterostructures electrode having a large rough surface area coupled with the presence of highly redox active materials with short ion diffusion path can be grown on the highly conducting metal channel facilitating the faster charge transport helps to achieve enhanced electrochemical properties suitable for the ultra capacitor applications.

Conflicts of interest: The authors stated that no conflicts of interest.

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