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Advanced asymmetric supercapacitor with $NiCo_2O_4$ nanoparticles and nanowires electrodes: A comparative morphological hierarchy

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ABSTRACT

In the present work, hydrothermal and wet chemical methods are adopted to fabricate $NiCo_2O_4$ nanowires (NiCo-NW) and $NiCo_2O_4$ nanoparticles (NiCo-NP) respectively. Owing to the mesoporous nature of these subunits, fast and convenient electron-ion transport and redox reaction, NiCo-NW achieves excellent electrochemical performance. Structure and microstructural characterizations of these samples are carried out by analyzing X-ray diffraction data employing the Rietveld method of structure refinement method and analyzing HRTEM, FESEM images and FTIR spectra. The low dimensional NiCo-NP is found to provide superior electrochemical performance than the NiCo-NW (~13 nm) due to its smaller particle size (~9 nm). This porous structure effectively helps in better transport of ions in the electrolyte. It manifests high specific capacitance 1066.03 F g^{-1} and enormous areal capacitance up to 5.96 F cm^{-2} whereas NiCo-NW exhibits specific capacitance up to 880.72 F g^{-1} and high areal capacitance of 4.93 F cm^{-2}. An asymmetric supercapacitor (ASC) has been fabricated with NiCo-NP and activated carbon as positive and negative electrodes respectively in 1 M Na_2SO_4 electrolyte medium. This device offers maximum specific energy 59.56 Wh Kg^{-1} and maximum power density 3403 W kg^{-1} with a high energy density of 4.197 Wh Kg^{-1} and shows excellent cyclic stability.

1. Introduction

In recent years, enormous attention has been drawn to develop novel materials and devices for the new renewable and sustainable energy sources with high efficiency, high reliability and high energy density. The supercapacitor has been used massively in last few decades as a green energy storage device combining the features of the conventional capacitor (high power density, long cycling life) and rechargeable batteries (high energy density) [1–8]. Based on the charge storage mechanism supercapacitors are of two types: (i) electric double-layer capacitor(EDLC), and (ii) pseudocapacitors. For EDLCs electric energy is stored by separation of charge in Helmholtz double-layer and for pseudocapacitor storage of electric energy is achieved by a faradaic redox reaction with charge transfer [8–10]. Various carbonaceous materials like activated carbon, CNT, graphene are being used as electrode materials for EDLCs for their higher surface area with a porous surface and electrically intercalated networks. EDLCs show high power density, better cycle life than pseudocapacitor but possess very low specific capacitance. However, due to fast multi electro-redox reaction, pseudocapacitors possess higher specific capacitance, higher energy density than observed in EDLCs [11,12], but it leads to deficient cycle stability because of redox reaction like a battery.

The primary focus of the present work is to improve cell voltage and energy density by developing an ASC device in which (EDLC) electrode has been used as the negative electrode and redox-active transition metal oxides as a positive electrode. The maximum operating voltage in the cell system can be reached by using different potential windows of the two-electrode system. Primarily, activated carbon has been used as the negative electrode and transition metal oxides as a positive electrode. So, the main focus of ASC is to develop better metal oxides for advanced positive electrode [3,13].

Various metal oxides and hydroxides with their variable valence states had been widely used for electrode materials in pseudocapacitors [14,15]. Attempts had been made to prepare inexpensive metal oxides like Co_3O_4 [16,17], NiO [10,18], MnO_2 [19], V_2O_5 [20], Fe_2O_3 [21] for high theoretical capacitance and low toxicity. Both Ni and Co-based materials were considered to be the most admirable

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Enhanced electrochemical properties of Co_3O_4 with morphological hierarchy for energy storage application: A comparative study with different electrolytes

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ABSTRACT

A facile hydrothermal route synthesizes Co_3O_4 nanocrystals with urchin spine-like morphology. Structure and microstructural characterizations of the sample are carried out. Electrochemical properties have been explored in the presence of different electrolytes. In order to find out the best electrolyte, three electrolytes (Na_2SO_4, NaOH and Na_2SO_4 with Hq) of fixed concentration (1 M) are used to record the cyclic voltammetry data. In the presence of Na_2SO_4 as an electrolyte, specific capacitance becomes 218 F g^{-1}, possibly because of low ionic conductivity of SO_4^{2-}, higher charge transfer resistance. When NaOH and Na_2SO_4 (with Hq) are used as electrolytes, high specific capacitances of 1720 F g^{-1} and 2433 F g^{-1} respectively are obtained due to extra pseudocapacitive effect of redox reaction. It is worth noting that the semicircle diameter in the EIS plot is highest for Na_2SO_4 and lowest for Na_2SO_4 (with Hq) electrolyte. The R_{ct} value depends on the type of electrode and the interaction between electrolyte ions with the electrode.

1. Introduction

Nowadays, one of the primary focuses of the scientific community is to harvest new sustainable energy materials to cope up with the continuous changes in the global climate. The demand for energy, however, is increasing day by day. It becomes very urgent for a scientist to develop new renewable energy sources with high power and better efficiency. It is now well known that supercapacitors have emerged as an alternative energy storage device with better efficiency than a rechargeable battery [1,2]. Supercapacitors exhibit higher energy efficiency, excellent reversibility, higher energy density than a conventional capacitor. Generally, supercapacitors can be classified into three types based on the charge storage mechanism: (i) electrical double-layer capacitor (EDLC), (ii) pseudocapacitors, and (iii) hybrid system. The energy storage mechanism in the electrochemical capacitor is of two types: faradaic and non-faradaic. The non-faradaic reaction arises in the EDLC due to ion adsorption at the electrode/electrolyte [3]. Various carbonaceous materials such as activated carbon, carbon nanotube (CNT), graphene oxide belong to the EDLCs. Such carbonaceous materials possess a large surface area with a porous surface with the interlaced network [4]. However, EDLCs cannot fulfill the requirement for the peak power assistance in the vehicle since EDLC offers low energy density. Instead, the faradaic pseudocapacitors are based on the fast reversible redox reaction within electroactive materials on the electrode, and its energy density is at least one order of magnitude higher than EDLCs [3,4].

In contrast, various inexpensive transition metal oxides such as Co_3O_4 [1,5–8], NiO [4,9], MnO_2 [10], and Fe_3O_4 [11], $NiCo_2O_4$ [12] are mainly used as electrode materials for pseudocapacitors. They provide enhanced electrochemical performance over EDLCs because of their higher specific capacitance generating from rapid and productive redox reaction. Finding cheap material with superior pseudocapacitive performance has thus attracted enormous attention. Among all these transition metal oxides, Co_3O_4 has been studied extensively for its supercapacitor application due to its high surface area, easily tunable surface area, multiple oxidation states and tunable structural properties. The Co_3O_4 is a p-type direct optical bandgap semiconductor that shows the high theoretical capacity, excellent corrosion stability and can act as

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Article

Ultrastable Asymmetric Supercapacitor Device with Chemically Derived and Mechanically Activated $NiCo_2O_4$

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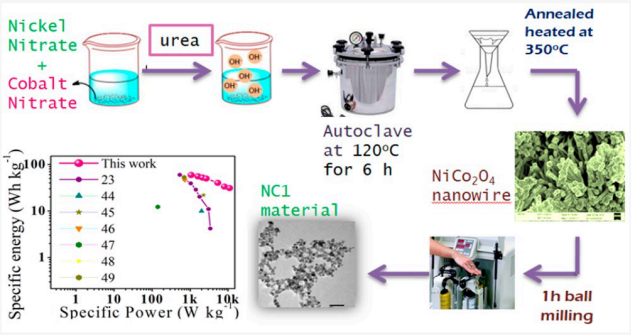
ABSTRACT: We report the effect of mechanical alloying on the chemically synthesized $NiCo_2O_4$ nanowire for better electrochemical performance. The nickel cobaltite nanowires (NC) were successfully synthesized via the hydrothermal method without any surfactant. Then they were milled for 1 h (NC1) and 2 h (NC2) to boost the electrochemical performance. The structural and microstructural parameters, shape, size, and morphology of these samples are revealed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM) techniques. The Brunauer–Emmett–Teller (BET) characterization and Barrett–Joyner–Halenda (BJH) model reveal that the NC1 sample offers the highest specific surface area among all three samples with its one-dimensional mesoporous structure (pore diameter, ~7 nm). The NC1 sample displays an excellent specific capacitance and rate capability (1234 F g^{-1} at a scan rate of 2 mV s^{-1}). However, upon further milling (2 h) the electrochemical performance of the sample decays rapidly due to an increase in particle size and reduction in specific surface area. A remarkable specific capacity of 1196 F g^{-1} is achieved in the 1 h milled sample at the lowest current density of 12 A g^{-1}, and at 40 A g^{-1} and 129.2 F g^{-1} specific capacitance can be retained. We further demonstrate an asymmetric device based on the NC1 sample as a positive electrode, which produces an excellent energy density of 59.221 Wh kg^{-1} at a power density of 1065.4 W kg^{-1}. The assembled device can attain an outstanding power density of 10.992 kW kg^{-1} at an enormous high current density of 13.33 A g^{-1} and demonstrates an excellent cyclic performance of 91.7% retention after 5000 cycles.



INTRODUCTION

Due to the rapid growth of portable energy storage systems, mobile systems, and other electronic gadgets, the main interest of scientists in these fields is to develop advanced new generation high energy and power density devices.[1−3] Various transparent energy storage systems are used in commercial and industrial areas. A supercapacitor can be recognized as an efficient, clean energy storage candidate due to its excellent cycle life, high power density, and better cycle stability. Typically, the charge storage mechanism of a supercapacitor is of two types: one is the capacitive type and the other is the pseudocapacitive type. Generally, the charge storage process of the capacitive type is an electric double-layer capacitor that relies on electrostatic charge storage separation of ions at the electron electrolyte interface.[4,5]

In contrast, in a pseudocapacitor, capacitance is produced by a fast multielectron faradaic surface redox reaction. The capacitance performance is much better than the electric double-layer capacitor (EDLC), especially in energy density. Several transition metal oxides (NiO, $NiCo_2O_4$, $CoFe_2O_4$, MnO_2, and Co_3O_4) and sulfides are vastly used and studied as positive electrodes for their different pseudocapacitive nature.[6−10] The binary oxides manifest extraordinary electrochemical performance than a single metal oxide because of their redox reaction between valence states, large electrode–electrolyte contact surfaces, and many defects, which improves pseudocapacitance as well as the energy density of the material.[11−13] The crucial parameters which regulate the electrochemical performance are the porosity, particle size, specific surface area, oxygen vacancy, and surface defects. Scientists these days try to incorporate an optimized amount of oxygen vacancy and surface defects to balance the electrochemical performance of the material in a well-mannered way.[14−16] Since metal oxide with a higher oxygen vacancy ensures a higher CV current and higher positive potential, forming an oxygen vacancy becomes one of the main choices for getting higher electrochemical performance by an easy and economical technique. In metal oxides or ceramics with

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Superior photocatalytic performance and photo disinfection of bacteria of solvothermally synthesized mesoporous La-doped CeO_2 under simulated visible light irradiation for wastewater treatment

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ABSTRACT

A simple, cost-effective, and facile solvothermal approach has been adopted to synthesize mesoporous CeO_2 nanostructures with varying La-doping (2, 4, and 6 mol%) concentrations. Photocatalytic and antibacterial performances are investigated against the inactivation of *Escherichia coli* and *Bacillus licheniformis* bacteria cells. Structural and microstructural characterizations of La-doped CeO_2 nanostructures are performed by analyzing X-ray diffraction (XRD) data employing the Rietveld refinement method, scanning electron (SEM) and transmission electron microscopy (TEM) images, Brunauer–Emmett–Teller (BET), energy-dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS) spectra. Among three doped samples, the 4 mol% La-doped CeO_2 (LCe4) has exhibited high oxygen and Ce^{3+} concentrations, high microstrain, small crystallite size, and lowest band gap energy, as are revealed by the analysis of XPS, UV–VIS absorption spectra, photoluminescence (PL) spectra, and Rietveld refinement result. The LCe4 sample with the highest number of oxygen vacancies and high surface area shows superior photocatalytic activity (~95% Rhodamin B (RhB) degradation in 130 min, ~70% Methylene Blue (MB) degradation within 30 min, and ~95% phenol degradation in 180 min under solar radiation). It shows a striking photo-disinfection effect and enhanced antibacterial activity (almost identical to a pure drug) against gram-positive and gram-negative bacteria under visible light irradiation. This novel disinfection and catalytic property of the LCe4 sample is attributed to the mesoporous structure of materials and surface activity, which lowers the electron-hole recombination rate and transports more photogenerated electrons and holes. The nanostructured mesoporous LCe4 material has been used as an effective visible light-activated photocatalyst and photo disinfection for treating wastewater containing organic dyes and gram-negative and gram-positive bacteria.

1. Introduction

Water pollution from mixing hazardous materials and heavy metals has become a serious global issue. Because of water pollution, various water-born diseases become vulnerable to humanity in most developing countries due to the lack of adequate purifier systems like UV radiation and chlorofication, particularly in rural areas. Thus, the availability of purified drinking water becomes a critical issue for the increasing population. Photocatalytic degradation of pollutants is a facile green chemical, sustainable and cost-effective method to remove contaminants from wastewater containing organic dyes [1–3].

CeO_2 is considered one of the most abundant rare earth oxides frequently used in electrochemical cells, energy storage and optical devices, photocatalysis, and as a biomaterial. CeO_2 is an n-type semiconductor material with various chemical and physical properties, like pollutant elimination with non-toxicity [5–7]. The main feature of CeO_2 is the transformation of the Ce^{4+} to Ce^{3+} valence state, which causes oxygen vacancies and a high stoichiometry deviation, consequentially increasing visible light absorbance [4–8]. Various reports on CeO_2 as a photocatalyst with different morphologies, like nanocube, nanowire, and nanodisc, using different templates are available. The present study intends to develop CeO_2 nanomaterials with an optimum mesoporous structure and

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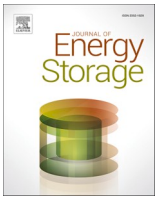

Research Paper

Mn-doped $NiWO_4$ quantum dots with superior electrochemical and conductivity performance for energy storage application

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ABSTRACT

Monoclinic amorphous $Ni_{1-x}Mn_xWO_4$ (x = 0.00, 0.02) compounds have been successfully synthesized by hydrothermal technique for achieving better capacitive and conductive performances. Different characterization techniques like X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible (UV–Vis) and photoluminescence (PL) spectroscopy have been employed to investigate their structural, microstructural, and optical properties. Mn-ion incorporation in the $NiWO_4$ lattice reduces the particle size of the sample to ~4.5 nm, compared to the pure undoped $NiWO_4$ sample (~18 nm), confirmed from the transmission electron microscopy image and Brunauer–Emmett–Teller analyses (BET). Tauc plot of $Ni_{0.98}Mn_{0.02}WO_4$ sample exhibits a significant increase in bandgap energy, compared to pure undoped $NiWO_4$ sample due to the quantum confinement effect. The electrochemical performance of electrodes made with these materials has been revealed by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) properties and electrochemical impedance spectroscopy (EIS). Moreover, the addition of 2 % Mn in $NiWO_4$ causes an increase in specific surface area (117.390 m^2/g) due to the reduced particle size of the material, resulting in excellent specific capacitance of 463 F g^{-1} at 0.5 A g^{-1} current density. The detailed charge storage mechanism for the improvement of conductivity and electrochemical performance of the Mn-doped $NiWO_4$ has been revealed in different studies. An asymmetric supercapacitor device (ASC) has been fabricated using Mn-doped $NiWO_4$ electrode material as positive electrode. The device shows superior cyclic stability upto 5000 cycles, can retain 88.4 % of its initial value.

1. Introduction

Electrochemical storage devices such as supercapacitors, fuel cells, and Li-ion batteries are more sustainable clean energies to deal with the global warming issues [1–3]. Among all three renewable energy sources, a supercapacitor is more promising than Li-ion batteries due to its fast charging, longer recyclability, better power density, and easy maintenance. Supercapacitors are classified into two categories, (i) electric double-layer capacitors (EDLC) and (ii) pseudocapacitors [2–5]. Researchers are continuously trying to improve the energy density of supercapacitors without hampering their power density and cycle life. Pseudocapacitor materials store more energy than an electric double-layer capacitor.

For this reason, various binary and ternary metal hybrid oxides with different morphologies were synthesized for supercapacitor applications [6,7]. However, some drawbacks of using metal oxides in electrochemical applications include poor conductivity, low energy density, and poor cycle stability [8,9]. It has been revealed from recent works that the electrochemical properties of some complex oxides (such as $NiCo_2O_4$ and $MnCo_2O_4$) are superior to single oxides like NiO, MnO_2, and Co_3O_4 because of multiple oxidation states of different metal cations [10–12]. The $NiWO_4$ compound is an attractive material in the electrochemical field because of its high electrical conductivity of $\sim 10^{-7}$–10^{-3} S cm^{-1} [13–15], which is higher than NiO (10^{-13} S cm^{-1}), and $CoWO_4$ compounds [16]. It was reported that the incorporated W atoms had improved the electrical conductivity and electrochemical activity of the compound [17]. Recent reports on core-shell heterostructures with multi-component, such as $MnCo_2O_4/NiWO_4$, Ni.Co.Zn oxide/$NiWO_4$, and $NiWO_4/NiCO_2O_4$ grown on nickel foam showed enormous high electrochemical performance than the $NiWO_4$ lattice

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