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Preparation and electrochemical analysis of graphene nanosheets/nickel hydroxide composite electrodes containing carbon nanotubes

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ABSTRACT

A set of graphene nanosheets (GNS)/nickel hydroxide ($Ni(OH)_2$) composites were successfully synthesized by adding single-walled carbon nanotubes (SWCNT) to the composites with various weight contents. The mixed composites were prepared by ultrasonication and chemical precipitation. It is postulated that the SWCNT act as additives in the composites, preventing the aggregation of the graphene sheets. The structural characterization indicated that the $Ni(OH)_2$ nanoparticles were deposited on the surface of GNS, and the SWCNT were dispersed between or onto the graphene sheets. The electrochemical performance of the composites was investigated by changing the contents of the added SWCNT. The prepared GNS/SWCNT/$Ni(OH)_2$ composites exhibited the superior electrochemical performance, indicated by the large specific capacitance over 1000 Fg^{-1} and excellent cycle performance over 2000 cycles. Among the prepared composites, the GNS/$Ni(OH)_2$ composite containing 20 wt.% SWCNT displayed the maximum specific capacitance with a value of 1149 Fg^{-1} at a in 6 M KOH electrolyte. Moreover, 92% of the initial specific capacitance of the composite was maintained after 2000-cycle test. Based on these results, the composite is thought to be suitable candidate for supercapacitor electrode materials.

Introduction

The increasing demand for portable electronics and power tools has brought the development of energy storage devices with high power density and high energy density in recent years. Among these devices, supercapacitors (also called electrochemical capacitors or ultracapacitors) are particularly attractive because of their high power density, long cycle life, and simple operational mechanism. Supercapacitors have large energy density compared to conventional capacitors, which has enabled their use in a wide range of applications such as memory backup systems, electrical vehicles, and industrial power supplies [1–4].

As electrode materials, carbon materials, transition metal oxides/hydroxides, and conducting polymers have been used for fabricating supercapacitors electrode [5]. Carbon materials that store a large amount of charge on the surface of electrodes are normally used for electrical double-layer capacitors. On the other hand, transition metal oxides/hydroxides and conducting polymers undergo fast and reversible Faradaic redox reactions. Generally, pseudocapacitors show significantly higher specific capacitance than electrical double-layer capacitors [6–8].

Nickel hydroxide ($Ni(OH)_2$) is one of the most promising candidates for supercapacitor electrodes owing to its low cost, high specific capacitance, and environment-friendly nature [9–11]. However, the use of $Ni(OH)_2$ electrode is severely limited by the poor electrical conductivity and the large volume expansion during the charge–discharge process, which degrades the electrochemical properties such as the rate capability and cycle stability. To resolve these issues, considerable efforts have been devoted to improving the performance of $Ni(OH)_2$ by combining it with highly conductive carbon materials [12–15].

On the other hand, graphene nanosheets (GNS), which are two-dimensional carbon materials with atomic thickness, have received much attention because of their chemical stability, high

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surface area, good mechanical flexibility, and high electrical conductivity [16–20]. Based on these characteristics, GNS are considered as a matrix for enhancing the electrochemical activity of transition metal oxides/hydroxides. Recently, researchers have reported on synthesizing graphene-based materials such as graphene/$Ni(OH)_2$ composites [21,22]. However, GNS actually undergo irreversible aggregation during the fabrication process because of van der Waals interactions. Owing to this reason, the available surface area of graphene could be reduced, resulting in lower specific capacitance than theoretical value. Therefore, preventing GNS agglomeration is an important task for enhancing the electrochemical performance of graphene-based materials [23,24].

Combination with other carbon materials such as carbon blacks, carbon nanotubes, and fullerene has been exploited to prevent the aggregation of graphene sheets and improve their unique features. Among these additives, single-walled carbon nanotubes (SWCNT) have been regarded as particularly promising because they could enhance the ion accessibility by giving some space or vacancy between the graphene sheets. Furthermore, their high electrical conductivity gives a positive effect on improved electrical performance [25–29].

The main objective of this paper is the synthesis and electrochemical characterization of the GNS/$Ni(OH)_2$ composites containing SWCNT as an additive via a facile method. An addition of SWCNT into the graphene sheets was proposed to promote ion accessibility by sterically preventing the aggregation of the graphene sheets and improves the electrical conduction of the electrode, resulting the enhanced supercapacitive performance of the composites. The effect of the SWCNT on the composites was evaluated by analyzing the structural and electrochemical properties of the GNS/SWCNT/$Ni(OH)_2$ composites. The optimum weight content of SWCNT for the composites was also determined for the best performance of electrodes.

Experimental

Synthesis of graphene nanosheets (GNS)

Graphite oxide (GO) was synthesized from natural graphite powder (SP-1 graphite, Bay Carbon, Inc., Michigan, USA) using a modified Hummer's method [30]. Typically, 1 g of graphite powder and 1 g of $NaNO_3$ were added to 46 mL of H_2SO_4 (98%) in a 300 mL flask. The mixture was then placed in an ice bath for 30 min. Under vigorous stirring, 5 g of $KMnO_4$ was added to the above mixture and the temperature of the mixture was kept below 20 °C. The mixture was then removed from the ice bath and the solution was maintained at 35 °C for 2 h. To the solution, 80 mL of deionized (DI) water and 7 mL of 30% H_2O_2 were slowly added. The oxidized solution was filtered and washed with HCl (10%) and DI water several times to obtain solid GO. The bright yellow solid GO was dispersed in DI water and centrifuged (3600 rpm, 5 min) several times with DI water and ethanol. GO powders were obtained after freeze-drying.

GNS was synthesized by the following procedure. 0.1 g of GO was dispersed in 100 mL of DI water. The GO suspension was then sonicated for 1 h. The mixture was reduced with sodium borohydride ($NaBH_4$) as described elsewhere and stirred at 90 °C for 4 h [31]. After filtered and washed several times with ethanol and DI water, the final black powers were obtained by drying in a vacuum-oven at 60 °C for 12 h.

Synthesis of GNS/SWCNT/Ni(OH)$_2$ composites

The GNS/SWCNT/$Ni(OH)_2$ composites were synthesized by a facile chemical precipitation method. First, 0.1 g of GNS and prescribed amounts of SWCNT were dispersed in 100 mL of DI water. The added amounts of SWCNT were 10, 20, and 30 weight percent per weight of GNS; the samples were hereafter denoted as GNS/$Ni(OH)_2$ composites (x wt.% SWCNT, x = 10, 20, and 30). The mixture was sonicated for 1 h to produce a homogeneously dispersed solution. 3 g of nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) was then added to the above solution. Subsequently, ammonium hydroxide was added into the solution to maintain the pH at 10, and the solution was vigorously stirred for 3 h. Finally, the precipitate was filtered and washed with DI water and ethanol several times and dried in an oven at 100 °C for 12 h. For comparison, the GNS/$Ni(OH)_2$ composites were also synthesized using the same procedure as described above in the absence of SWCNT.

Characterization methods

The crystalline structure of the composites was analyzed using an X-ray diffractometer (XRD, Philips X'Pert-MPD system) with Kα radiation in the 2θ range from 10° to 80°. Fourier transform infrared (FT-IR) spectra were acquired in the wavelength range of 400–4000 cm^{-1} using a KBr pellet. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Theta Probe AR-XPS system with a monochromated Al Kα radiation ($h\nu$ = 1486.6 eV). The surface structures of the prepared samples were evaluated using a field emission scanning electron microscopy system (FE-SEM, SUPRA25 and Raith Quantum Elphy), and the morphology of the samples was investigated by using a transmission electron microscope (TEM, JEOL JEM-2010). Surface area and pore measurements were conducted by the physical adsorption and desorption of N_2 at 77 K (Micromeritics ASAP 2010) and obtained by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method.

Electrochemical characterization

All electrochemical measurements were carried out using an Iviumstat (Ivium Technologies, Netherlands) in a three electrode system at room temperature. Working electrodes were prepared according to the following method. The prepared composites, carbon black (Super-P, Alfa-Aesar), and polyvinylidone fluoride (PVDF) were mixed in a mass ratio of 85:10:5 in an agate mortar. *N*-methyl-2-pyrrolidene (NMP) was used as a solvent. The homogeneously mixed slurry was coated on a nickel foam substrate (1 cm × 1 cm). The resulting electrodes were then dried in a vacuum oven at 100 °C for 12 h. Each electrode contained ca. 3–4 mg of electro-active materials. A saturated calomel electrode (SCE) and Pt wire were used as the reference electrode and counter electrode, respectively. The measurements were performed in 6 M aqueous KOH electrolyte. The cyclic voltammograms (CV) were acquired between −0.1 and 0.5 V at different scan rates of 5, 10, 20, 50, 100 and 200 mV s^{-1}. Galvanostatic charge–discharge curves were acquired in the potential range of −0.1 to 0.45 V at a current density of 1 Ag^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 0.01 Hz–100 kHz at open circuit potential with an alternating current (AC) perturbation of 5 mV. The specific capacitance of the composites was calculated from the CV curves using the following equation:

$$C = \frac{\int I dV}{\nu m \Delta V} \quad (1)$$

where I is the response current density (A cm^{-2}), ν is the potential scan rate (V s^{-1}), m is the mass of the composite in the electrodes (g cm^{-2}), and ΔV is the difference between the highest and lowest potential (V) [32].