



Full paper

Conductive silver nanowires-fenced carbon cloth fibers-supported layered double hydroxide nanosheets as a flexible and binder-free electrode for high-performance asymmetric supercapacitors



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ABSTRACT

Silver nanowires (Ag NWs) have attracted particular interest in the development of various electronic and energy storage devices due to their one-dimensional structure, good conductivity, fast charge transportation and direct contact to the current collector. Herein, we have successfully deposited the binder-free nickel-cobalt layered double hydroxide nanosheets on Ag NWs-fenced carbon cloth (NC LDH NSs@Ag@CC) by a facile electrochemical deposition method with a chronoamperometry voltage of -1.0 V for 120 s. The electrically conductive and superhydrophilic nature of the hybrid nanocomposite electrode led to relatively high areal capacitance (1133.3 mF cm $^{-2}$ at 1 mA cm $^{-2}$) and good cycling stability (80.47% after 2000 cycles) compared to the electrode prepared without Ag NWs. Using such hierarchical NC LDH NSs@Ag@CC as a positive electrode, we further fabricated a flexible asymmetric supercapacitor (ASC) with activated carbon coated CC as a negative electrode. The as-assembled ASC exhibited maximum operational potential window of 1.6 V, high areal capacitance of 230.2 mF cm $^{-2}$ and excellent cycling stability of 88.1% with remarkable energy densities at all the charge-discharge conditions (78.8 μ Wh cm $^{-2}$ at the power density of 785 μ W cm $^{-2}$ and 40 μ Wh cm $^{-2}$ at the high power density of 12.1 mW cm $^{-2}$, respectively)

1. Introduction

Recently, supercapacitors (SCs) have attracted appreciable attention as a new class of energy storage device owing to their inherent advantages of high power density, fast charge-discharge speed, long cycling lifetime and low cost [1–3]. Accordingly, SCs are utilized in various fields, including hybrid vehicles, back-up power systems, portable electronic devices, etc [4–6]. Although the SCs have many benefits over the batteries and fuel cells, they are still suffering from poor energy density problem [7–9]. Consequently, great attempts have been made for achieving the high energy density in SCs without affecting the power density. From the equation of $E = \frac{1}{2}CV^2$, it is evident that the energy density can be enhanced by maximizing the capacitance and working potential window of the device [10–12]. The construction of asymmetrical SCs (ASCs) is one of the promising approaches for achieving the superior energy density characteristics [13]. This ASC can be assembled by combining the two kinds of materials, namely, the battery-type electroactive material as an energy source and the electric-double layer capacitive electroactive material as a power source, respectively [14–16]. Thus, these two electroactive materials in the

device could utilize their entire well-separated potential windows, resulting in the higher operating voltage and delivering the remarkable capacitance and significantly enhanced energy density [17].

Up to now, several transition metal oxides/hydroxides such as Co $_3$ O $_4$, NiWO $_4$, Co(OH) $_2$, Ni(OH) $_2$, NiMoO $_4$, etc. have been widely explored as a battery-type or redox active material in ASCs, by virtue of their high charge storing capability and enhanced electrochemical activity [18–21]. Recently, several transition metallic layered double hydroxides (LDHs), usually represented by the formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively and A^{n-} could be mostly organic or inorganic anions (OH $^-$, CO $_3^{2-}$, NO $_3^-$, etc.), have been extensively investigated due to their high anion exchanging property and capability of intercalating anions [22–24]. In general, the metallic LDHs are composed of nanometer-thick layered structure, in which excessive positive charges corresponding to the trivalent or twice the tetravalent metal ions are compensated by the anions [25]. Such intrinsic properties of high surface area and tunable metal compositions of LDHs without varying their structure make them extensively used in the various fields, such as catalysis, anion exchanging, batteries,

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energy storage applications, etc [23,26]. Moreover, these materials comprising of transition metals have been extensively utilized as battery-type materials for SCs due to their enrich slabs, high electrochemical conductivity and versatile oxidation states within the transition metal atoms [24,27]. The anion exchange capacity in metallic LDH materials is greatly enhanced by the intercalating anions and water molecules into a large interlayer spacing of unique two-dimensional (2D) lamellar structures [28]. Due to the faradaic redox reactions with aqueous electrolytes, large electric charges may be collected on the surface of 2D thin layers and hence a high increment in the electrochemical performance can be observed [29]. Up to now, several combinations of LDH have been studied for supercapacitor applications, such as nickel-cobalt (NC), cobalt-aluminum, nickel-manganese, magnesium-aluminum LDHs, etc [24,30–32]. Among these LDHs, NC LDHs have received great interest because of their layered structures with large interlayer arrangement, high redox activity, multiple oxidation states and eco-friendly nature [33,34]. Particularly, NC LDHs with nanosheets/nanoflakes-like structures with high surface area and interconnected arrangement provide the effective paths for electrolyte diffusion, leading to the rapid redox reactions for enhanced electrochemical properties [35,36]. So far, these NC LDH nanosheets (NSs) have been prepared using several growth methods, in which the electrochemical deposition has attracted much attention owing to the low-temperature growth, short reaction time and safe apparatus [37]. Generally, conductive nickel foam, nano porous gold, metal foil, etc. based electrodes can be used as substrates for the binder-free growth of electroactive materials for SCs, but their rigidity and complicated manufacturing process imposes a limit on the development of flexible devices [38–41]. Therefore, carbon cloth (CC), graphene coated textiles and copper coated polyester fabrics based electrodes are gaining prominence as a current collector for the development of flexible/wearable SCs [19,42]. Among these substrates, the CC ensued the following advantages; high flexibility and excellent chemical/thermal stability compared to the other flexible fabrics [43]. Although CC has desirable flexible features, but it still suffers from relatively hydrophobicity and low conductive property compared to the conventional metal electrodes, which only offers a limited specific surface area platform and poor porosity for higher electroactive material loading [44,45]. To make use of CC as a promising substrate for high-performance energy storage devices, growth of conductive materials on CC could be expected to enhance the conductivity and hydrophilic property.

As is well known, silver (Ag) has the highest electrical conductivity (6.3×10^7 S/m) among the miscellaneous metals, which facilitates the direct electronic conduction [46,47]. Accordingly, the Ag based nanostructures (particularly, Ag nanowires (NWs)) were investigated as the effective collector for improving the electrical conductivity as well as the electrochemical performance in SCs [48,49]. For example, Yu et al. reported that an electrode with sandwich-like Ag NW/PEDOT: PSS-nanopillar/MnO₂ composite exhibited much higher specific capacitance owing to larger electrochemical conductivity of the nanocomposite [50]. Yuksel et al. integrated the coaxial Ag NW@Ni(OH)₂ core-shell structure, in which the conductive Ag NW core helps to increase the conductivity to obtain the larger electrochemical capacitance [51]. Furthermore, Wu et al. synthesized Ag NW coupled Ni-Al LDH NSs composite material and their pseudocapacitance was comparatively higher than that of bare Ni-Al LDH NSs [52]. Besides, Qiao et al. also prepared the hierarchical network of MnO₂@Ag NWs composite with much larger specific capacitance compared to the pristine MnO₂ without Ag NWs [53]. The high conductive nature of Ag NW promotes the rapid reaction kinetics during the energy storage measurements.

Considering their thin diameter, high aspect ratio and superior conductivity, in this work, we synthesized Ag NWs on CC (Ag@CC) using a simple dip-coating approach, eventually improving its hydrophilic nature and conductivity. The 3D network of Ag NWs on CC (Ag@CC) could be also expected to increase the mass loading of electroactive

material. Moreover, the high conductive nature of Ag NWs provides the effective pathways for electron transportation during the energy storage process [51,52]. Using a facile electrochemical deposition (ECD) technique, we further deposited NC LDH NSs on Ag@CC substrate (i.e. NC LDH NSs@Ag@CC) as a battery-type electrode. The electrochemical properties of the binder-free NC LDH NSs@Ag@CC showed high areal capacitance with good rate capability and long cycling lifetime in 1 M KOH electrolyte solution. Furthermore, the ASC was also fabricated for practical applications using NC LDH NSs@Ag@CC as a battery-type electrode and the activated carbon (AC) as an electric-double layer capacitive electrode, respectively. The energy storage properties of the ASCs device were characterized in detail.

2. Experimental section

2.1. Chemicals

Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and nitric acid (HNO₃) were received from Daejung Chemicals Ltd., South Korea. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) and potassium hydroxide (KOH) were obtained from Sigma-Aldrich Co., South Korea. Ag NWs suspension in isopropanol was purchased from PlasmaChem GmbH Co. The CC was purchased from Nara Cell-Tech Corp., South Korea. All the chemicals were of analytical grade and used directly without any further purification after purchasing.

2.2. Synthesis of NC LDH NSs@Ag@CC

The hierarchical NC LDH NSs were uniformly deposited on Ag@CC substrate by a simple and one-step ECD method at room temperature (RT). Initially, the bare CC was sonicated in concentrated HNO₃ solution for 10 min and dried in an oven for one hour after cleaning thoroughly with de-ionized (DI) water for several times. Then, the well-cleaned CC was cut into the rectangular pieces with sizes of 1×2.5 cm², dipped directly into Ag NWs solution two times and thermally annealed at 200 °C under argon atmosphere to improve the adhesion and conductivity. The as-prepared Ag@CC substrate was attached to the polyethylene terephthalate (PET) film for restricting the deposition of NC LDH NSs on the back side of the substrate. After that, the ECD process was carried out in a conventional beaker-type three-electrode cell, which consists of Ag@CC as a working, saturated calomel electrode (SCE) as a reference, and platinum (Pt) wire as a counter electrode, respectively. Here, the total area of Ag@CC (1×2.5 cm²) is divided into two parts using a plastic tape, in such a way that the 1×2 cm² active area is utilized for the deposition of NC LDH and the remaining part (1×0.5 cm²) is assigned for electrode contact, respectively. Meanwhile, the growth solution was prepared by mixing appropriate amounts of Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O (0.067 and 0.033 M, respectively) in a glass beaker containing 40 mL of DI water under constant magnetic stirring at RT. Then, the ECD process was performed after carefully immersing the three-electrode system into growth solution with an applied cathodic voltage of -1.0 V for 120 s (chronoamperometry technique) using an IviumStat electrochemical workstation (The Netherlands). After ECD process, the NC LDH NSs@Ag@CC was removed from experimental set-up and washed gently with DI water to remove the partly adhered NC LDH NSs on substrate. Then, the sample was dried under the flow of pure nitrogen gas and kept in a vacuum oven at 80 °C for 2 h. The mass loading of NC LDH NSs on Ag@CC was obtained to be ~ 0.7 mg/cm². For comparison, the NC LDH NSs were also deposited on bare CC using the same ECD process under similar conditions and it was designated as NC LDH NSs@CC (~ 0.3 mg/cm²).

2.3. Characterization

The surface morphologies and nanostructures of the prepared

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