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Enhanced Symmetric Supercapacitive Performance of $Co(OH)_2$ Nanorods Decorated Conducting Porous Graphene Foam Electrodes

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ABSTRACT

Hierarchical entangled $Co(OH)_2$ nanorods (NRs) are anchored on graphene foam (GF) electrodes by using a facile chemical bath deposition (CBD) method. The porous, conducting, and higher specific area access offered by the interconnected 3D graphene framework along with unique $Co(OH)_2$ NRs morphology of electrode displays ultrahigh specific capacitance, energy and power density. The $Co(OH)_2$/GF electrode reveals maximum specific capacitance about 1139 F g^{-1} at 10 A g^{-1} charge-discharge current density in 1 M KOH aqueous solution. Moreover, $Co(OH)_2$/GF electrode in the symmetric supercapacitor device, reveals a high energy (13.9 Wh kg^{-1}) with power (18 kW kg^{-1}) density. These results promote the potential applicability of $Co(OH)_2$/GF electrode in the supercapacitor field with effective boosting in charge transfer and storage mechanism.

1. Introduction

The ever-increasing energy and power demands in the applications such as cordless electric tools, hybrid electric vehicles, day/night storage, and industrial energy management [1–4]. Therefore, over the past few years, intense efforts have been made to develop high-energy and power electrochemical capacitors (ECs) due to their faster charge and discharge processes (seconds) compared to batteries. However, ECs are unable to achieve high energy density (normally <10 Wh kg^{-1}) as compare to batteries [5]. To address this problem, the innovation of new materials is essential to offer enhanced energy and power densities of energy storage devices [6,7]. On the other hand, fabricating symmetric/asymmetric devices is an effective approach to increase the supercapacitors the energy and power density [8–10].

Generally, despite of poor specific energy density, carbonaceous materials are used in the fabrication of symmetric and asymmetric supercapacitors devices due to exceptional cyclic stability and high interfacial capacitance [11–13]. The obstacle of low energy density can be overcome by employing pseudo-capacitive materials such as metal oxides/hydroxides and conducting polymers in supercapacitor devices [13]. To date, various materials such as transition metal oxides, metal hydroxides, and electronically conducting polymer materials have been extensively investigated for possible applications in supercapacitors such as NiO, CoOx, MnO_2, Mn_3O_4, CuO, $Ni(OH)_2$ and $Co(OH)_2$ [14–20]. The $Co(OH)_2$ is one of the most promising candidates for applications in high energy storage devices, especially in supercapacitors due to its high theoretical specific capacitance, low cost and well-defined electrochemical redox activity [21,22].

Up to now, different reports have been made by researchers on the performance evaluation of symmetric and asymmetric supercapacitors [8–10]. Recently, Jagadale et al. reported symmetric supercapacitive performance of electrodeposited $Co(OH)_2$ on stainless steel substrate with maximum energy density about 3.96 Wh kg^{-1} [9]. However, asymmetric type of supercapacitor formed with $Co(OH)_2$ and graphene has been proposed to be a power-oriented supercapacitive device by Hu et al. with lower value of specific energy 1.7 Wh kg^{-1} [13]. From past few years, to improve surface area and electrical conductivity, intensive studies have been focused on combining conductive carbon materials (e.g., Go, rGo, CNT) with $Co(OH)_2$ [22–24]. However, these materials have limitations in both energy and power density mainly due to their irregular pore sizes and relatively low electrical conductivity [17]. The $Co(OH)_2$-cabon composite based electrodes are commonly

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binder-enriched electrodes made by the traditional slurry-coating technique for electrochemical evaluation. The typical addition of a polymeric binder will not only hamper the charge transport rate, but also increase the total mass of the electrode.

Recently, light weight graphene foam (GF) (density ~10-20 mg cm^{-3}), a structure consisting of an ultrathin graphene skeleton with high electrical conductivity is used as an alternate to conventional current collectors such as nickel foam or carbon paper [25–27]. Advanced multifunctional structures of graphene is a strong contender as an electrode material due to many fascinating properties such as their enormous electron mobility, extremely high thermal conductivity, and extraordinary elasticity and stiffness [26,27]. X. Dong et al. reported specific capacitance about 1100 F g^{-1} for cobalt oxide on graphene foam by hydrothermal method [27].

Till date there is no report on the symmetric supercapacitor performance based on $Co(OH)_2$/GF electrodes. In the present work, direct synthesis of $Co(OH)_2$ nanorods (NRs) on graphene foam was successfully accomplished by using a facile chemical bath deposition (CBD) method. Furthermore, the supercapcitive performance of conventional symmetric devices fabricated by $Co(OH)_2$/SS and $Co(OH)_2$/GF electrodes were investigated and compared systematically.

2. Experimental Methods

2.1. Preparation of $Co(OH)_2$ nanorods on 3D graphene foam

The fabrication of self-supported $Co(OH)_2$ on 3D graphene foam consists of two stage procedure; preparation of the GF and fastening of $Co(OH)_2$ NRs on it. The graphene were grown on Ni foam by chemical vapour deposition (CVD) method, followed by etching of Ni foam through etchant, the details of process is described in ref. [26].

The $Co(OH)_2$ NRs were prepared by mixing $Co(NO_3)_2.6H_2O$ (Sigma-Aldrich USA) as Co source and urea as an oxidant (Sigma-Aldrich USA) in 50 ml of DI water. The aqueous bath was prepared from 0.1 M $Co(NO_3)_2.6H_2O$ and 0.1 M urea ($CO(NH_2)_2$). The 3D skeleton of graphene foam was dipped in a prepared bath with the support of glass micro slides. Then, the prepared bath was heated at 90 °C for 4 hours. After cooling to room temperature, the graphene foams with $Co(OH)_2$ deposits were washed with deionized (DI) water and dried at room temperature. Further, the prepared pink colour $Co(OH)_2$/GF was used as an electrode in a supercapacitor cell. For comparison, $Co(OH)_2$ NRs from the same bath were deposited on a commercial stainless steel (SS) substrate and used in the fabrication of a conventional supercapacitor device.

2.2. Characterization

The electrode materials were structurally characterized by XRD, XPS and FESEM measurements. The X-ray diffraction (XRD) was carried out on a Rigaku Ultima diffractometer using Cu-Kαradiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a thermo scientific ESCALAB 250 (Thermo Fisher Scientific, UK). The morphology of the composite was examined by field-emission scanning electron microscopy (FESEM, JSM-7001F, JEOL).

2.3. Electrochemical Measurements

2.3.1. Half-test cell testing of $Co(OH)_2$/SS and $Co(OH)_2$/GF electrodes

The individual electrochemical performances of $Co(OH)_2$/GF and $Co(OH)_2$/SS electrodes were measured by half-test cell testing. A conventional half-test cell contains three-electrode system comprises with $Co(OH)_2$/SS or $Co(OH)_2$/GF as working electrode, Ag/AgCl as reference electrode and platinum (Pt) as counter electrode in a 1 M KOH aqueous electrolyte.

2.3.2. Symmetric $Co(OH)_2$/1 M KOH/$Co(OH)_2$ test cell fabrication

The symmetric supercapacitor test cells were fabricated with a two-electrode configuration. The symmetric cells were made of both identical $Co(OH)_2$/SS and $Co(OH)_2$/GF electrodes. Fig. 1 shows the schematic of the supercapacitive test cells which consists of two $Co(OH)_2$ electrodes separated by a thin polypropylene separator in 1 M KOH aqueous electrolyte solution. Actual photographs of $Co(OH)_2$, pink in color, coated GF substrates (having an area of 2×4 cm^2) shown in Fig. 1. Cyclic Voltammetry (CV), galvanostatic charge/discharge tests and EIS measurements were performed using ZIVE SP2 LAB analytical equipment (South Korea).

3. Results and Discussion

3.1. Fabrication of $Co(OH)_2$/SS and $Co(OH)_2$/GF electrodes

For the fabrication of GF, graphene networks were grown by methane using CVD on Ni foam. The graphene foam maintains a 3D porous structure with a smooth and thin graphene skeleton after the exclusion of Ni (figure S1 (a, b, c)) (see ESI). The thickness of the graphene foam is ~1.4 mm and the width of an individual graphene sheet is around ~25 μm, as shown in figure S1 (d) (see ESI). The recorded Raman spectra of 3D graphene at different places on the foam exhibited two distinct peaks at ~1,559 cm^{-1} (G-band) and ~2,699 cm^{-1} (2D-band), as shown in figure S2 (see ESI) [28,29]. The integral ratio of the 2D and G band indicates few layered domains

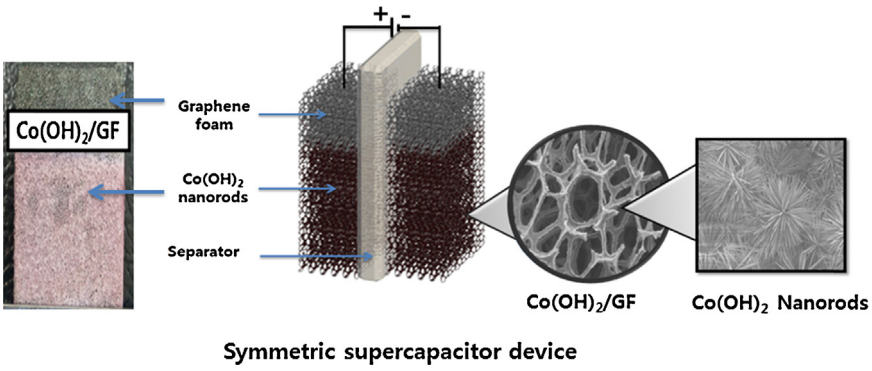

Fig. 1. The actual photograph of $Co(OH)_2$/GF electrode and schematic of symmetric device based on $Co(OH)_2$/GF electrodes.