

Advanced Materials for Energy Storage Applications

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ABSTRACT

Herein we have reported an easy and cost effective synthesis of rGO/Ni(OH)₂ hybrid nanocomposite for possible application as supercapacitor active material. The hybrid nanocomposite was able to show high capacitance of 189F/g and high cycle life of 95% capacitance retention over 500 cycles.

Keywords: Supercapacitor , Electrode, Graphene etc.

I. INTRODUCTION

Supercapacitor also known as electrochemical capacitor is the alternative source of energy that has been under immense interest recent days. Depending on the charge storage mechanism supercapacitor can be divided into two categories, electrical double layer capacitor and pseudocapacitor.¹ EDLC store charge via electrical double layer formation and Pseudocapacitor store electrical charge via some electron transfer faradaic reaction. Recently nanocarbon materials like CNT, graphene, and redox active materials like various metal oxides and hydroxides have shown promising behavior as active electrode materials.²⁻⁴ There is a recent trend to combine both of these EDLC and pseudocapacitive materials together to fabricate active electrode material. It is believed that in these type of hybrid nanocomposites the EDLC active materials will act as high power source whereas the redox active material as high energy source. Herein we have reported a hybrid nanocomposites of Ni(OH)₂ and graphene as active materials for supercapacitor application.

II. RESULT & DISCUSSION

A modified hydrothermal synthesis was followed for the synthesis of rGO/Ni(OH)₂. GO was synthesized by a modified Hummers method.⁵ 20 mg of GO was dispersed in a mixture of 15 ml 0.1 M Ni(NO₃)₂ and 15 ml 0.5M Urea by ultrasonication for 30 minutes. Then the whole suspension was kept in a 50 ml autoclave and under 180 °C for 12 h. Then the autoclave was cooled in air and the precipitation was collected and washed with water ethanol for several times and dried under mild temperature.

XRD pattern of the composite material confirms the formation of Ni(OH)₂ and reduction of GO in the reaction medium since the peak of GO is vanished in the composite material.

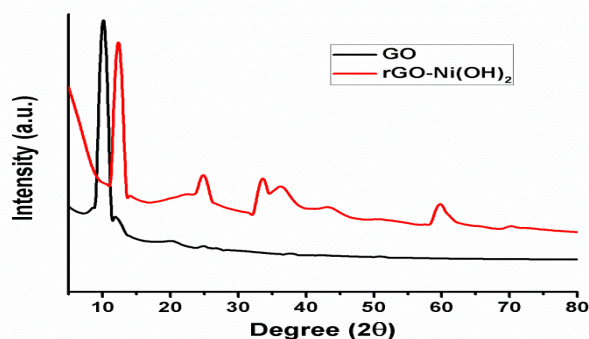


Fig.1. XRD pattern of GO and rGO-Ni(OH)₂ composite.

Fig. 2a and 2b indicate the FESEM analysis of the as prepared $\text{Ni}(\text{OH})_2$ and $\text{rGO-Ni}(\text{OH})_2$ hybrid composite. As can be seen from the FESEM images, $\text{Ni}(\text{OH})_2$ exhibit spherical flowery morphology and a well distribution of the rGO sheet over $\text{Ni}(\text{OH})_2$ flower within the composite material.

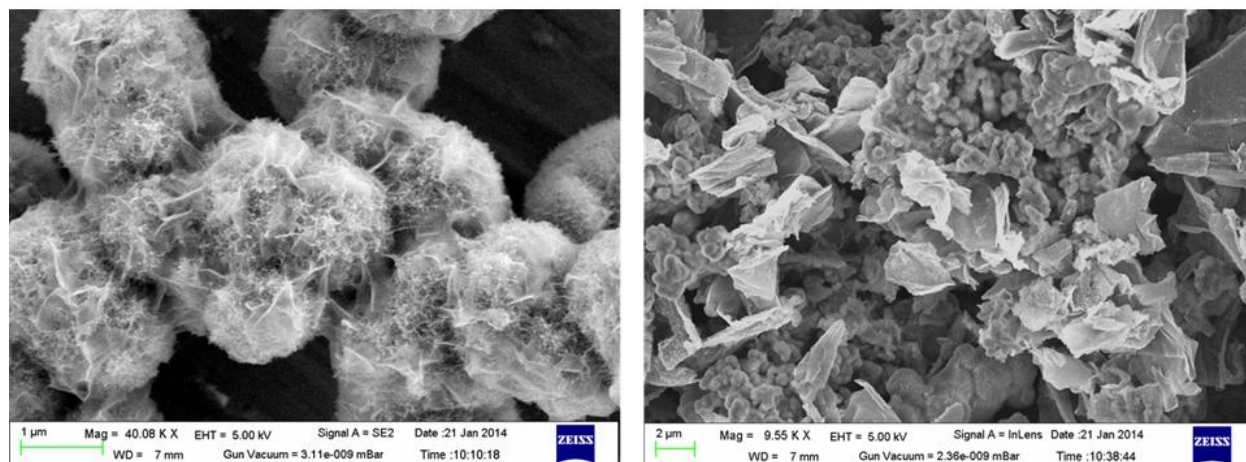


Fig.2. FESEM analysis of $\text{Ni}(\text{OH})_2$ and $\text{rGO-Ni}(\text{OH})_2$ hybrid composite.

The electrochemical characterization was carried out in a three electrode cell where the active materials were pasted over a Ni current collector and was used as working electrode, and Pt and saturated Calomel electrode was used as counter and reference electrode respectively. galvanostatic charge discharge, cyclic voltammetry and Electrochemical impedance spectroscopy analysis were carried out. Fig. 2a indicates the GCD plots of the as prepared $\text{Ni}(\text{OH})_2$ and $\text{rGO-Ni}(\text{OH})_2$ electrode within the potential range of 0-0.4V at current density of 3A/g.

The Maximum capacitance of 81 F/g was obtained from the pure $\text{Ni}(\text{OH})_2$. The GCD plot of the pure $\text{Ni}(\text{OH})_2$ electrode shows nonlinear behavior, indicating the pseudocapacitive behavior of the electrode. The pseudocapacitance within $\text{Ni}(\text{OH})_2$ in presence of KOH arises due to the $\text{Ni}(\text{II}) \leftrightarrow \text{Ni}(\text{III})$ redox reaction.⁶ As can be seen from the two consecutive GCD plots of the $\text{Ni}(\text{OH})_2$, the Coulombic efficiency of the first cycle increased in the second cycle, this indicates the increasing reversibility of the electrode materials with the cycle number. Also the capacitance obtained from the second cycle was higher (84 F/g) from the capacitance obtained from the first cycle. This increasing trend of capacitance was found upto certain consecutive cycles, during the cycle life testing of the electrode. The initial increase of the capacitance can be attributed to the slow wetting of the electrode by the electrolyte and the slow diffusion of the electrolyte ions. However, the specific capacitance obtained from the rGO based hybrid composite of $\text{Ni}(\text{OH})_2$ was higher compared to that of virgin $\text{Ni}(\text{OH})_2$. The maximum specific capacitance obtained was 189 F/g. The increased specific capacitance of the composite electrode compared to that of virgin metal hydroxide can be attributed to the use of reduced graphene oxide, that not only serve as the EDLC source but also increase the conductivity of the electrode. Thereby increase the efficiency of the electrode. The Coulombic efficiency obtained from the $\text{rGO-Ni}(\text{OH})_2$ electrode was close to 100%, which was consistent in the next cycle, demonstrating the reversibility of the electrode material. To understand the cycle life performance of the as prepared electrode materials the GCD test was continued upto 500 cycles at a higher current density of 5A/g and at the end specific capacitance retention of 92% was achieved. However, the $\text{rGO-Ni}(\text{OH})_2$ composite electrode showed higher specific capacitance retention of 95% at the end (Fig. 3d). The increased capacitance retention of the composite can be attributed to the presence of rGO. rGO provides flexible support to the $\text{Ni}(\text{OH})_2$ flowers and the volume change during the consecutive charge discharge cycling is somewhat minimized and thus cycle life performance is increased.

To further understand the reversible redox behavior of the composite electrode CV analysis was performed at a scan rate of 200 mV/s. The CV plot in Fig. 3b shows quite rectangular behavior. Moreover the current response during the positive and negative cycling is almost symmetrical. All these observation clearly indicates the reversibility of the electrode. To further understand the resistive behavior of the as prepared composite electrode, EIS analysis was carried out within the frequency range of 200 kHz to 0.1 Hz and the plot has been represented in terms of Nyquist plot in Fig.3c. The Nyquist plot starts with an initial semicircle followed by a straight line at an angle close to 45

degree with the real impedance axis. The starting semicircle indicates the presence of charge transfer resistance, and the post semicircle straightline indicates the Warburg behavior of the electrode. The solution and charge transfer resistance of the rGO-Ni(OH)₂ was calculated to be 3.9 and 1.8 Ohm respectively, which is low enough to cause the high current response of the electrode.

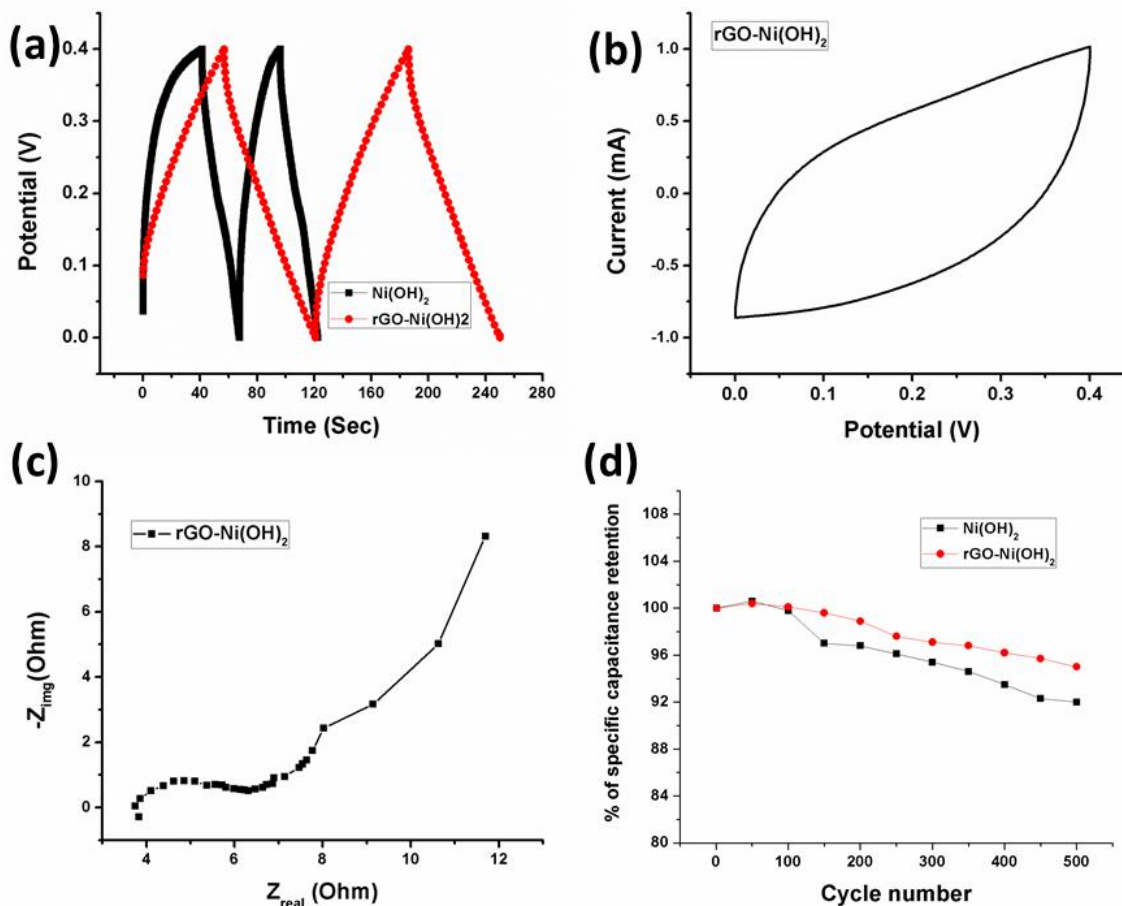


Fig.3. GCD plot of Ni(OH)₂ and rGo-Ni(OH)₂ composite electrode (a), CV plot of rGo-Ni(OH)₂ composite electrode (b), Nyquist plot of rGo-Ni(OH)₂ composite electrode (c). Cycle life plot of Ni(OH)₂ and rGO-Ni(OH)₂ (d).

III. CONCLUSION

This manuscript demonstrates the formation of insitu reduced graphene oxide based hybrid composite of pseudocapacitive Ni(OH)₂. The composite materials showed superior electrochemical behavior over the virgin Ni(OH)₂. The maximum capacitance of 289 F/g was achieved at a current density of 3A/g, which leads to high energy density of 6.42 Wh/kg. The high energy density accompanied by the high cycle life indicates the high efficiency of the rGo-Ni(OH)₂ composite as supercapacitor electrode.

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