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Research Article

STUDIES OF HYBRID NANOCOMPOSITE CONTAINING rGO/Ni(OH)$_2$/PPy FOR SUPERCAPACITOR APPLICATION

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A B S T R A C T

Now-a-days with ever increasing demand of energy, developing of alternative power sources is an important issue all over the world. In this respect we have developed a hybrid material for electrochemical supercapacitor electrode, based on a conducting polymer like polypyrrole (PPy), graphene oxide (rGO) and Ni(OH)$_2$ for supercapacitor applications. The morphological characterisations were carried out by the Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). The electrochemical performance of the nanocomposite was characterized by three electrode method like cyclic voltametry (CV), impedance spectroscopy (EIS), galvanostatic charge-discharge (GCD). The nanocomposite rGO/Ni(OH)$_2$/PPy showed the highest specific capacitance of 512 F/g at 2mV/s scan rate and high cycle life of 98% capacitance retention over 1000 cycles.

INTRODUCTION

The utilization of sustainable clean energy in addition to efficient energy storage and conversion technology is the prime requirement. It is predicted that the world will require doubling its energy supply by 2050. For this purpose, advanced technology for both energy conversion and storage (supercapacitor and batteries) are being widely studied. Simultaneously, the draw backs of electrochemical supercapacitors including low energy density and high production cost have been recognized as major challenge for the advancement of electrochemical supercapacitor technologies. To overcome the barrier of low energy density, one of the most extensive approaches is the improvement of new materials for electrochemical supercapacitors electrodes. It has been proved that a hybrid composite conducting both electric double layer capacitor (EDLC) and pseudocapacitive materials, are more efficient in terms of both high energy density at a high power density and long cycle life. Conducting polymers, on the other hands, one well known for their redox-activity and can also act as pseudocapacitor. Low conductivity of metal hydroxides restricts the full utilization of electrode material and only in a very thin layer can give a close to theoretical specific capacitance value. [1]

In this present studies we have developed a hybrid material for electrochemical supercapacitor electrode, based on a conducting polymer like polypyrrole, graphene oxide (GO) and Ni(OH)$_2$ (nickel hydroxide) for supercapacitor applications. Preferred orientation of the polyperole nano rods was given on to the hybrid composite of graphene and Ni(OH)$_2$ to achieve for high capacitance values because of higher surface area accompanied by high cycles of charging and discharging.

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Experimental

Materials

A modified hydrothermal process was followed for the synthesis of rGO/Ni(OH)$_2$.GO was synthesized by a modified Hummer s method. 20 gm of GO was dispersed in a mixture of 15ml 0.1M Ni(NO$_3$)$_2$ and 15ml 0.5m urea by ultra-sonication for 30Min. Then the whole suspension was kept in an autoclave under 180^{0}c for 12h .Then the autoclave was cooled in air, then the precipitate was collected and washed with water ethanol for several times and dried under mild temp.

Synthesis of Polypyrrole

The ternary composite (PPy) was prepared using oxidative polymerization of pyrrol in presence of rGO/Ni(OH)$_2$. In this oxidative polymerization process $(NH_4)_2S_2O_8$ was used as an oxidant. The solution was then kept at around 5^{0}c for 10h for the polymerization composite. The composite was then filtered washed with water and rapped dried at around 80^{0}c for 12h to get ternary nanocomposite. [2]

Characterization

A Carl Zeiss-SUPRATM 40 field emission scanning electron microscopy (FESEM) with an accelerating voltage of 5 kV

was used to understand the morphology of the nanocomposites. The higher solution transmission electron microscopy (HRTEM) JEOL 2100 was used to check the coating of the doped PPy in rGO/Ni(OH)$_2$ surface. Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD) analysis of the materials were carried out on Biologic sp-150 VMP-3 instrument using a three electrode system. CV measurements were performed in the voltage range of 0.8 to -0.8 V vs. SCE. The specific capacitance of the nanocomposite was calculated by the help of following equation.

Specific Capacitance (C_{sp}) = ($I_+ - I_-$)/vm .....(1)

Where, I_+ and I_- signifies the maximum current in the positive and negative voltage scan, v is the scan rate and m is the mass of the nanocomposite. Electrochemical Impedance Spectroscopy (EIS) was cried out by using GAMRY ref.3000 using an ac voltage amplitude 5 mV between the frequency ranges 0.1 Hz to1 MHz. [3]

RESULT AND DISCUSSION

FESEM Analysis

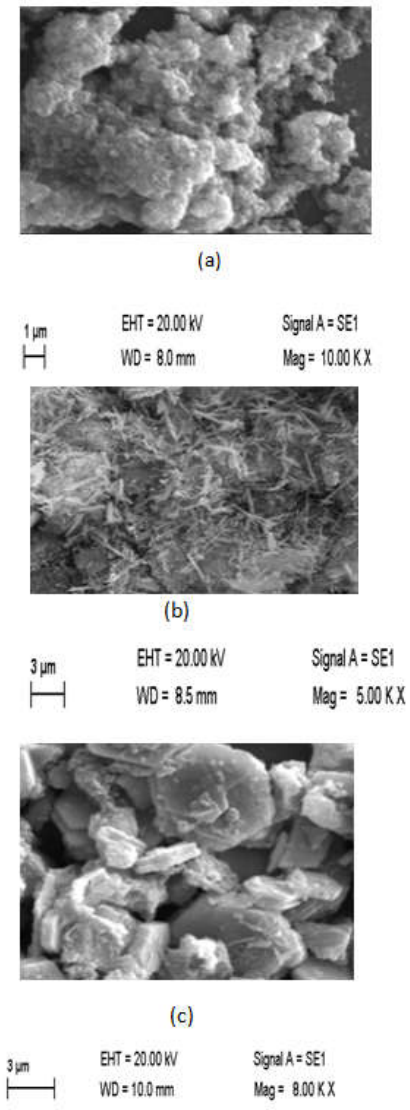


Figure 1 FESEM images of (a) Ni (OH)$_2$,(b)rGO/Ni(OH)$_2$ and(c) rGO/Ni(OH)$_2$/PPy nanocomposites

The surface morphologies of the prepared nanocomposites were analysed by FESEM. Figures 1(a), (b) and (c) represent the FESEM images of Ni(OH)$_2$, rGO/Ni(OH)$_2$,and rGO/Ni(OH)$_2$/PPy. The FESEM image gives the evidence of smooth surface of the Ni(OH)$_2$. The FESEM images of the rGO/NiOH$_2$/PPy nanocomposites are shown in Figures 1(c) which show a uniform coating of the PPy over the as prepared modified nanocomposites rGO/Ni(OH)$_2$ surface. However the rGO/Ni(OH)$_2$ surface shows needle shaped texture, which probably augment the PPy coating on the surface. [4]

TEM Analysis

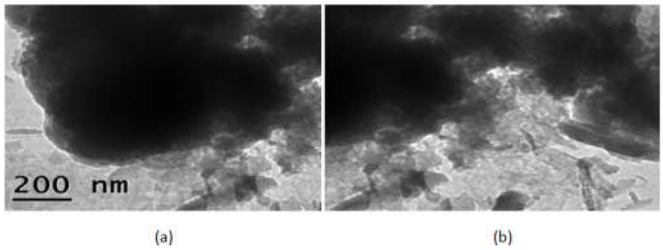


Figure 2 TEM images of (a)rGO/Ni(OH)$_2$ (b)rGO/Ni(OH)$_2$/PPy composites.

Figure-2(a) represents the TEM photograph of rGO/Ni(OH)$_2$ nanocomposites, where it is clear that Ni(OH)$_2$ is strongly anchored with rGO sheets. However PPy was not vertically aligned on the binary composite system rGO/Ni(OH)$_2$ (exception of PPy composite). In figure-2(b) presence of PPy the composites are more uniform in nature. [5]

Electrochemical Characterization

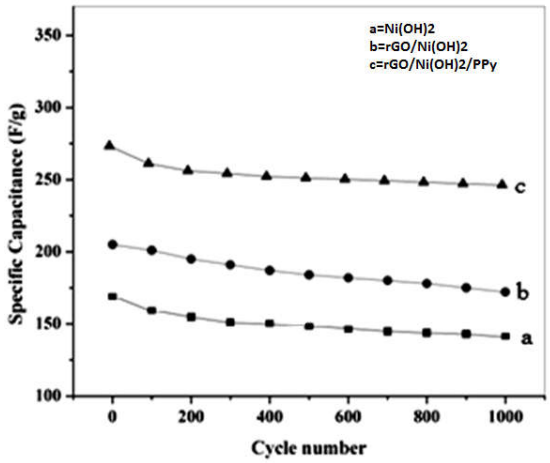


Figure 3 Plot of specific capacitance vs. Cycle number of Ni(OH)$_2$,rGO/Ni(OH)$_2$ and rGO/Ni(OH)$_2$/PPy

Table 1 Calculated energy density (Wh kg^{-1}) and power density (W kg^{-1}) from charge-discharge measurements.

	Energy density (Wh/kg)		Power density (W/kg)	
scan rate	2mV/s	10mV/s	2mV/s	10mV/s
Ni(OH)$_2$	16.02	9.6	650	1720
rGO/Ni(OH)$_2$	24.10	19.02	650	1720
rGO/Ni(OH)$_2$/PPy	50.50	44.10	800	2110

The energy density of the Ni(OH)$_2$, rGO/Ni(OH)$_2$ nanocomposite and rGO/Ni(OH)$_2$/PPy were calculated by the help of following equation

Energy Density (E) = ½ (CV^2) ..... (2)

Where, C denotes the specific capacitance and V is the operating voltage.

On the other hand, the power density of the $Ni(OH)_2$, $rGO/Ni(OH)_2$ and $rGO/Ni(OH)_2/PPy$ nanocomposites were determined by the following equation:

Power Density (P) = E/t ..... (3)

Where, t is the time in sec for complete the cycle.

The $rGO/Ni(OH)_2/PPy$ nanocomposite showed the highest energy density 50.50 Wh/kg with power density of 800W/kg at 2 mV/s scan rate. On the other hand $rGO/Ni(OH)_2$ and $Ni(OH)_2$ showed the energy density 24.10 Wh/kg and 16.02 Wh/kg with power density of 650W/kg and 650W/kg respectively at the same scan rate .Whereas, the energy density 44.10Wh/kg, 19.02Wh/kg, 9.6Wh/kg with power density of 2110 W/kg, 1720W/kg, 1720W/kg was obtained for the $rGO/Ni(OH)_2/PPy$, $rGO/Ni(OH)_2$, $Ni(OH)_2$ nanocomposites respectively at 10 mV/s scan rate in Table-1. The very high energy density without significant loss of power density is a key to consider them as smart supercapacitor.[10]

GCD Analysis

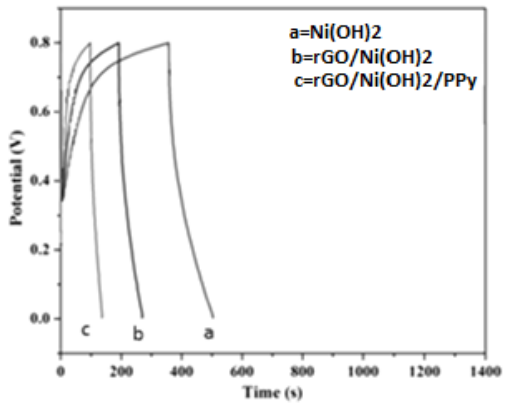


Figure 4 The galvanostatic charge-discharge of $Ni(OH)_2$, $rGO/Ni(OH)_2$ and $rGO/Ni(OH)_2/PPy$

Table 2 Specifi c capacitance (F/g) calculated from charge-discharge measurements.

	Specific Capacitance	Coulombic Efficiency
Ni(OH)2	246F/g	95%
rGO/Ni(OH)2	355F/g	97%
rGO/Ni(OH)2/PPy	510F/g	98%

The cyclic stability of the $rGO/Ni(OH)_2/PPy$ nanocomposite along with $rGO/Ni(OH)_2$ and $Ni(OH)_2$ were carried out in 1 M KCl solution and at a current density of 2 A/g and shown in Figure-4. The $rGO/Ni(OH)_2/PPy$ nanocomposite show specific capacitance retention of 98% after 1000 cycles. However, $rGO/Ni(OH)_2$ and $Ni(OH)_2$ show specific capacitance retention of 97 %, 95% after 1000 cycles show in Table-2. The highest cyclic stability of the nanocomposite is due to the doping effect. [11]

Cyclic Voltametry

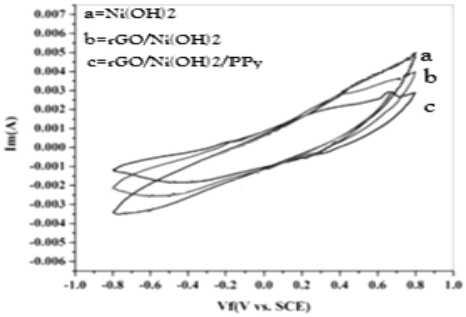


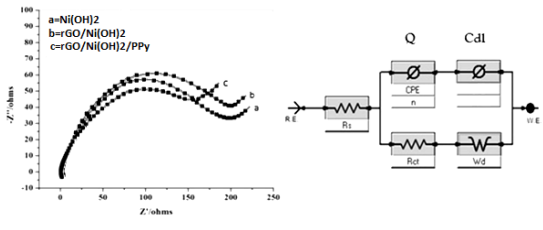
Figure 5 Cyclic voltammogram of $Ni(OH)_2$, $rGO/Ni(OH)_2$ and $rGO/Ni(OH)_2/PPy$

Table 3 Calculated specific capacitance by integrating the area of the curve at 2mV/s scan rate.

	Specific capacitance
$Ni(OH)_2$	252F/g
$rGO/Ni(OH)_2$	360F/g
$rGO/Ni(OH)_2/PPy$	512F/g

The electrochemical characterization of the $Ni(OH)_2$,$rGO/Ni(OH)_2$, and $rGO/Ni(OH)_2/PPy$ nanocomposite was examined by cyclic voltammetry (CV). The electrochemical characterizations were carried out by three electrode system. 1 M KCl solution was used for all the electrochemical tests. The CV was taken in the voltage range between -0.8 V – 0.8 V. The cyclic voltammogram of $Ni(OH)_2$,$rGO/Ni(OH)_2$, and $rGO/Ni(OH)_2/PPy$ nanocomposite at a scan rate of 2 mV/s are shown in Figure-5. The $rGO/Ni(OH)_2/PPy$ nanocomposite showed the highest specific capacitance value of 512 F/g at 2 mV/s scan rate. On the other hand $Ni(OH)_2$,$rGO/Ni(OH)_2$ showed the specific capacitance of 360 F/g and 252 F/g at the same scan rate in Table-3. The highest specific capacitance of the nanocomposite is increased due to the presence of PPy. Transition metal doping also enhances the specific capacitance of the nanocomposite.[12-13]

Electrochemical Impedance Spectroscopy



(a) **(b)**

Figure 6 (a)Nyquist plot of $Ni(OH)_2$, $rGO/Ni(OH)_2$ and $rGO/Ni(OH)_2/PPy$, (b) Equivalent circuit model to which the EIS data fitted.

Table 4 The EIS fitted data by a suitable equivalent circuit fitting.

Circuit parameter	$Ni(OH)_2$	$rGO/Ni(OH)_2$	$rGO/Ni(OH)_2/PPy$
Frequency power($0<n\leq1$)	0.69	0.72	0.81
Solution resistance(R_s) (ohm)	3.9	3.1	2.8
Charge transfer resistance(R_{ct}) (ohm)	91.09	24.0	11.2
C_{dl} (F)	1.2_x10^{-6}	0.9_x10^{-6}	1.1_x10^{-6}
Warburg(W) resistance($S_xs^{1/2}$) (ohm)	29.2_x10^{-3}	679_x10^{-6}	769_x10^{-6}
CPE (Q)(S_xs^n)	1.0_x10^{-3}	22_x10^{-3}	32_x10^{-3}

The electrodes were also analyzed by electrochemical spectroscopy with the frequency range of 1MHz to 10 MHz, and have been represented in terms of nyquist plot figure-6(a) after fitting with an equivalent electrical circuit figure-6(b). All the nyquist plots exhibited similar nature of a flattened semicircle at initial high frequency followed by a straight line at an angle close to 45^0. The high frequency semicircle indicates the presence of charge resistance (R_{ct}), the diameter of which determines the magnitude of R_{ct} and the intercept with real impedance axis indicates the solution resistance (R_s). Although the electrolyte resistance are comparable for all three electrode methods, they differ in the R_{ct} with maximum of 91.9(ohm) for $Ni(OH)_2$ and a gradual decreased R_{ct} of 24.0(ohm) and 11.2(ohm) for the composites $rGO/Ni(OH)_2$ and $rGO/Ni(OH)_2$/PPy respectively. The decreased R_{ct} can be attributed to the presence of highly conducting rGO which increases the overall conductivity of the composite material. In case of ternary composite PPy, forms several conducting tunnel within the composite material through which the charge can effectively pass ensuring the lowest R_{ct}. The deviation of the post semicircle straight line from becoming parallel to the imaginary impendence axis indicates the non-ideality of the electrode materials and can be represented in terms of constant phase element CPE. CPE (Q) exclude the real world capacitor and generates due to different defects in the electrode materials i.e. the edge effect, different coating thickness of electrode material on current collector, distribution of reaction sites, etc. CPE constant (n) determines the ideality of the electrode material and a value close to 1 indicates nearer ideal behaviour. For the $Ni(OH)_2$, $rGO/Ni(OH)_2$, and $rGO/Ni(OH)_2$/PPy the CPE constant n was found to be 0.69, 0.72, and 0.81, respectively. The post semicircle straight line inclined at an angle close to 45^0 indicates diffusion behaviour of the electrode. A straight line with higher slope indicates lower diffusion resistance, hence high surface availability and higher ion accessibility. The presence of rGO is the main source of double large capacitance of 0.9F in the $rGO/Ni(OH)_2$ and 1.1F in the $rGO/Ni(OH)_2$/PPy composite. [14-17]

CONCLUSION

The ternary composites $rGO/Ni(OH)_2$/PPy by in situ polymerization method showed the highest specific capacitance value of 512 F/g at 2 mV/s scan rate and highest energy density of 50.50 Wh/kg at the same scan rate. The retention specific capacitance of 98% was obtained for the ternary nanocomposite $rGO/Ni(OH)_2$/PPy at around 1000 cycle. This hybrid material $rGO/Ni(OH)_2$/PPy developed, proves to be an improved electro chemical electrode for supercapacitor electrode application.

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