Designing of Carbon Nitride Supported ZnCo$_2$O$_4$ Hybrid Electrode for High-Performance Energy Storage Applications

Meenu Sharma & Anurag Gaur*

This study reports a unique graphitic-C$_3$N$_4$ supported ZnCo$_2$O$_4$ composite, synthesized through a facile hydrothermal method to enhance the electrochemical performance of the electrode. The g-C$_3$N$_4$@ZnCo$_2$O$_4$ hybrid composite based electrode exhibits a significant increase in specific surface area and maximum specific capacity of 157 mAh$^{-1}$ at 4 Ag$^{-1}$. Moreover, g-C$_3$N$_4$@ZnCo$_2$O$_4$ electrode maintained significant capacity retention of 90% up to 2500 cycles. Utilizing this composite in the development of the symmetric device, g-C$_3$N$_4$@ZnCo$_2$O$_4$/g-C$_3$N$_4$@ZnCo$_2$O$_4$ displays a specific capacity of 121 mAh$^{-1}$. The device exhibits an energy density of 39 Whkg$^{-1}$ with an equivalent power density of 1478 Wkg$^{-1}$. A good cycling stability performance with an energy efficiency of 75% and capacity retention of 71% was observed up to 10,000 cycles. The superior performance of g-C$_3$N$_4$@ZnCo$_2$O$_4$ is attributed to the support of the g-C$_3$N$_4$ which increases the surface area, electroactive sites and provides chemical stability for electrochemical performance. The outstanding performance of this exclusive device symbolizes remarkable progress in the direction of high-performance energy storage applications.

The need for advanced energy storage devices is in great demand because of numerous portable electronic devices and the emergence of hybrid electric vehicles in modern society. However, most of these new inventions require high-performance energy storage with high energy and power densities. Among different energy storage devices, electrochemical capacitors with high power density and batteries with high energy density have gained significant research attention to meet the needs of increasing demand for energy storage applications. Several materials like metal hydroxides/oxides, activated carbon and conducting polymers have been explored as electrodes material for energy storage applications, with an emphasis on exploring new composite to boost the electrochemical efficiency of the energy storage device. Lithium-ion batteries can store high energy up to 150–200 Whkg$^{-1}$, but confined to low power density and poor cycle life, whereas supercapacitors have high power energy, low cost and low maintenance for high-power delivery applications. Therefore, the fabrication of rationally designed hybrid electrode materials is in highest demand to enhance the electrochemical performance of energy storage applications.

Transition metal oxides with various nanostructures have been used widely for electrode material because of their high theoretical capacitance. In the past years, ZnCo$_2$O$_4$ has aroused one of the most capable electrode materials by researchers toward their applications for supercapacitors because of their high electrochemical activities and speedy faradic reactions. However, it suffers relatively poor electrical conductivity and a considerable reduction in capacitance during long cycling life and low surface area.

Among the various carbon-based nanostructures, graphitic carbon nitride (g-C$_3$N$_4$) is a soft polymer with porous nature and sheet-like crystallite has attracted considerable attention due to its highly active nitrogen sites, excellent physical and chemical strength, and low-cost feature. In the application of water splitting, waste-water detoxification, solar cells and supercapacitors, g-C$_3$N$_4$ carbon-based materials show superior performance because of its outstanding optical properties, high mechanical strength and thermal conductivity. The nitrogen presence in g-C$_3$N$_4$ provides more active sites and advances the capacitance while preserving the cyclability of the electrochemical device. Therefore, the composite of g-C$_3$N$_4$ and ZnCo$_2$O$_4$ could have great advancement.
in rate capability and specific capacitance. To date, only a few studies of g-C3N4 with Ni(OH)2, MnO2, and NiCo2O4 for energy storage application have been reported.

In this work, we synthesize g-C3N4 hybridized ZnCo2O4 composite for the electrode material in order to develop a high-performance symmetric supercapattery device. This hybrid g-C3N4@ZnCo2O4 composite exhibits excellent electrochemical performance through a specific capacity of 154 mAhg−1 at 4 Ag−1 with 90% of capacity retention up to 2500 cycles. Further g-C3N4@ZnCo2O4 based solid-state symmetric supercapattery device g-C3N4@g-C3N4@g-C3N4@g-C3N4@ZnCo2O4 has been assembled, which exhibits a 39 Whkg−1 of energy density with an equivalent power density of 1478 Wkg−1.

**Results and Discussion**

The synthesis of g-C3N4@ZnCo2O4 hybrid composite with high surface area is performed through a simple hydrothermal process. The schematic illustration of g-C3N4@ZnCo2O4 formation mechanism along with the testing of the fabricated electrode is shown in Fig. 1. The obtained g-C3N4@ZnCo2O4 based electrode is incorporated into a solid-state symmetric Supercapattery device, which possesses a favourable energy density and power density.
Figure 3. SEM images: (a) ZnCo$_2$O$_4$, (b,c) g-$\text{C}_3\text{N}_4$@ZnCo$_2$O$_4$ composite.

Figure 4. EDX of (a) ZnCo$_2$O$_4$ (b) g-$\text{C}_3\text{N}_4$@ZnCo$_2$O$_4$ composite.

Figure 5. N$_2$ adsorption/desorption isotherms with corresponding pore size distributions: (a) pure ZnCo$_2$O$_4$ and (b) g-$\text{C}_3\text{N}_4$@ZnCo$_2$O$_4$ composite.
XRD pattern of g-C₃N₄, ZnCo₂O₄, and g-C₃N₄@ZnCo₂O₄ is displayed in Fig. 2. For ZnCo₂O₄ sample, all the peaks of the XRD patterns are well matched to the (JCPDS No. 14-0117) whereas XRD pattern of g-C₃N₄@ZnCo₂O₄ shows the diffraction peaks corresponding to ZnCo₂O₄ and g-C₃N₄, implying the good formation of g-C₃N₄@ZnCo₂O₄ composites. Figure 3(a) shows the SEM micrographs of pristine ZnCo₂O₄ and Fig. 3(b,c) shows the SEM micrographs of g-C₃N₄@ZnCo₂O₄ composites at different magnifications. The SEM images of pristine ZnCo₂O₄ shows the agglomerate clusters, whereas g-C₃N₄@ZnCo₂O₄ composites show clusters with fibres distribution. The visible spaces between clusters could provide a channel for the movement of electrolyte ions and achieve a high specific surface area. Figure 4(a) represents the EDX pattern of ZnCo₂O₄ and Co, Zn, and Ag fibres distribution. The visible spaces between clusters could provide a channel for the movement of electrolyte ions and achieve a high specific surface area. The SEM images of pristine ZnCo₂O₄ shows the agglomerate clusters, whereas g-C₃N₄@ZnCo₂O₄ composites show clusters with fibres distribution. The visible spaces between clusters could provide a channel for the movement of electrolyte ions and achieve a high specific surface area.

The electrochemical analysis of fabricated electrodes in a three-electrode configuration is schematically illustrated in Fig. 6. The CV curves of pristine ZnCo₂O₄ and g-C₃N₄@ZnCo₂O₄ electrodes at a constant scan rate of 20 mVs⁻¹ in the potential range of 0.0 to 0.5 V is shown in Fig. 7(a). The CV curve for g-C₃N₄@ZnCo₂O₄ shows a very high amplitude of current as compared to ZnCo₂O₄ electrode, resulting in an enhancement in the specific capacity. A pair of redox peaks is primarily raised from faradic redox reactions linked to M-O/M-O-OH (M = Zn or Co)19,20. Figure 7(b) demonstrates the CV curves of g-C₃N₄@ZnCo₂O₄ at different scan rates from 2–100 mVs⁻¹. The amplification and shift in the position of the anodic and cathodic peak are appeared with the increase of scan rates, indicating the quick and reversible redox responses happening at the electro/electrolyte interface21,22. The GCD curves of ZnCo₂O₄ and g-C₃N₄@ZnCo₂O₄ electrodes at a constant specific current of 4 Ag⁻¹ is shown in Fig. S1. Figure 7(c) displays the GCD curves of g-C₃N₄@ZnCo₂O₄ at a various specific current of 4, 6, 7 and 8 Ag⁻¹. Figure 7(d) represents the specific discharge capacity of the g-C₃N₄@ZnCo₂O₄ electrode evaluated from GCD curves. The maximum specific capacity obtained for the hybrid g-C₃N₄@ZnCo₂O₄ electrode is 157 mAhg⁻¹ at 4 Ag⁻¹. The superior capacity retention of 90% up to 2500 constant GCD cycles at 10 A g⁻¹ is demonstrated by the g-C₃N₄@ZnCo₂O₄ based single electrode.

Figure 7(c) demonstrates the CV curves of g-C₃N₄@ZnCo₂O₄ at different scan rates from 2–100 mVs⁻¹, respectively. The similarity in CV curves of the device with increasing scan rates indicates the excellent rate capability of the device28,29. The GCD measurements at a specific current of 4.6, 5.9, 7.2 and 8.5 Ag⁻¹ is shown in Fig. 9(c) within the potential window of 0 to 1.5 V. By using these GCD curves, the specific discharge capacity (Qₛ) is calculated and plotted as a function of specific current in Fig. 9(d). The Qₛ values calculated from GCD curves of the symmetric device are 121, 100, 96 and 89 mAhg⁻¹ for 4.6, 5.9, 7.2 and 8.5 Ag⁻¹, respectively. To estimate the overall efficiency of the assembled symmetric device, energy and power density were calculated and illustrated as a Ragone plot in Fig. 10(a). This device achieved a maximum energy density of 39 Whkg⁻¹ at a power density of 1478 Wkg⁻¹. The g-C₃N₄@ZnCo₂O₄/gel electrolyte/g-C₃N₄@ZnCo₂O₄ symmetric device...
maintained an energy efficiency of 75% in addition to a capacity retention of 71% up to 10000 continuous cycles at 15 $\text{Ag}^{-1}$ as shown in Fig. 10(b). This demonstrates long-term electrochemical stability of the symmetric device. To further assess the electrochemical properties of the device, the EIS analysis in Fig. 10(c) shows the solution resistance ($R_s$) before and after 10000 cycles of GCD. In the high-frequency region, $R_s$ is the intercept on the $Z'$-axis, which is a combination of resistance in the electrolyte and the material electrode. The calculated value of $R_s$ before and after 10000 cycles is estimated to be 1.1 and 1.5 $\Omega$, respectively, representing the stability of the synthesized material for the fabricated supercapattery device. Moreover, the Nyquist plot for the g-C$_3$N$_4$@ZnCo$_2$O$_4$/gel electrolyte/g-C$_3$N$_4$@ZnCo$_2$O$_4$ symmetric device was fitted as shown in Fig. 10(d) with its corresponding equivalent circuit displayed in the inset.

**Experimental**

**Synthesis of the g-C$_3$N$_4$@ZnCo$_2$O$_4$ composite.** All the reagents were of analytical quality and used without additional refinement. The g-C$_3$N$_4$ was prepared through simple pyrolysis of urea under ambient atmosphere. Initially, urea was dried at 80 °C for 24 hours and it was placed in a crucible for heat treatment in an oven. After heating the precursor at 550 °C for 3 hours, g-C$_3$N$_4$ of yellow-coloured was obtained. Then, 1 mM of Zinc Nitrate, 2 mM of Cobalt Nitrate and 5 mM of urea was dissolved properly in 40 mL deionized (DI) water by stirred for 30 min. The prepared 10 mg of the obtained g-C$_3$N$_4$ was then mixed with the prepared solution and stirred
firmly for an additional 1 h. Then the entire solution was moved to a 70 mL Teflon-lined autoclave box and heated to 180 °C for 12 h. After the autoclave box was cooled to room temperature, the precursor was collected, rinsed consecutively with DI wand ethanol. Afterwards, the final product was calcinated at 450 °C for 2 h.

Electrochemical analysis of electrode and symmetric device. To fabricate the working electrodes, 80 wt% of as-synthesized g-C₃N₄@ZnCo₂O₄, 10 wt%) of carbon black and a polymer binder (polyvinylidene fluoride; PVDF, 10 wt%) was mixed using few drops of N-Methyl-2-pyrrolidone (NMP). The resulting slurry was applied on a flexible nickel mesh substrate (current collector) using the drop-casting method, followed by drying it at 120 °C for 12 h in an oven. The electrochemical measurements of electrodes were carried out on Biologic potentiostat workstation in a 6 M KOH electrolyte using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements. In three electrodes configurations, the as-prepared electrode was used as a working electrode, Ag/AgCl and platinum were used as reference electrode and counter electrode, respectively.

The specific discharge capacity, \( Q_s \) (mAhg\(^{-1}\)) and energy efficiency, \( \eta \) (%) of electrodes was calculated from galvanostatic charge-discharge measurements by using the following equation

\[
Q_s = \frac{I \Delta t}{3.6 m}
\]

\[
\eta = \frac{E_d \times 100}{E_c}
\]

where \( I \) represent discharge current, \( \Delta t \) is the discharge time taken to complete the discharge cycle, \( m \) is the active mass of the electrode, \( \eta \) is energy efficiency, \( E_d \) and \( E_c \) represents the charge and discharges energy\(^{31}\).

The assembling of the symmetric device has been done using gel electrolyte (PVA/KOH), which works both as an electrolyte and a separator. To prepare the gel polymer electrolyte, 6g of PVA was added to 6 M solution of...
KOH and then heating at 95 °C followed by firmly stirring for 2 h. To assemble a solid-state symmetric device, the gel electrolyte membrane was sandwiched between the two as-fabricated g-C3N4@ZnCo2O4 electrodes. The specific discharge capacity ($Q_s$) of symmetric device calculated from the GCD curves according to Eq. 1, where $m$ is the total mass of active materials on both electrodes of the assembled device. The energy density ($E_d$) and power density ($P_d$) of the symmetric device is calculated using the following equations

$$E_d = \frac{I}{3.6m} \int Vdt$$

(3)

$$P_d = \frac{E_d \times 3600}{\Delta t}$$

(4)

where $I$ describe the discharge current, $m$ represents the mass of active material, the integral term is the area under the CD curve and $\Delta t$ is the discharge time (seconds).

Characterization techniques. The phase and structure of the samples were investigated by X-ray powder diffraction (XRD) diffractometer with radiation of Cu Kα ($\lambda = 0.15405$ nm). The surface morphology of samples was characterized by scanning electron microscope (SEM, JEOL JSM-6390LV, 20 kV). To study the elemental composition of synthesized samples X-ray energy dispersive analyzer was used. The Brunauer-Emmett-Teller (BET) measurements were used to calculate the specific surface area and pore size distributions, performed on a Belsorp Max system using nitrogen gas adsorption/desorption isotherms.

Conclusions

We have developed a g-C3N4 supported ZnCo2O4 composite electrode using a simple hydrothermal method for improving the electrochemical performance of the electrode. The synergistic effect of g-C3N4 and ZnCo2O4 in g-C3N4@ZnCo2O4 hybrid composite shows a significant increase in a specific surface area along with a specific discharge capacity of 157 mAhg$^{-1}$. Accordingly, g-C3N4@ZnCo2O4/gel electrolyte/g-C3N4@ZnCo2O4 symmetric supercapattery device is fabricated, which displays a high specific discharge capacity of 121 mAhg$^{-1}$ at 4.6

Figure 10. (a) Ragone plot for g-C3N4@ZnCo2O4//gel electrolyte//g-C3N4@ZnCo2O4 symmetric device. (b) Capacity retention and energy efficiency of g-C3N4@ZnCo2O4//gel electrolyte//g-C3N4@ZnCo2O4 symmetric device for 10000 cycles at 15 Ag$^{-1}$. (c) Nyquist impedance plot of g-C3N4@ZnCo2O4//gel electrolyte//g-C3N4@ZnCo2O4 symmetric device before and after cycling. (d) Fitted Nyquist plot of g-C3N4@ZnCo2O4//gel electrolyte//g-C3N4@ZnCo2O4 symmetric device and the equivalent circuit (insert).
Ag\(^{-1}\). The device exhibits the highest energy density of 39 Whkg\(^{-1}\) at a power density of 1478 Wkg\(^{-1}\). A good cycling stability performance with an energy efficiency of 75% is observed up to 10,000 cycles. This novel strategy establishes a stage towards the construction of a hybrid electrode with prominent performance, which is the present demand for energy storage devices.

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Author contributions
M. Sharma is the Ph.D student, who performed the experimental measurements. Dr. Anurag Gaur is the Ph.D advisor, who contributed in the data analysis and writing the manuscript.

Competing interests
The authors declare no competing interests.

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