# SYNTHESIS OF POLYANILINE/GRAPHITIC CARBON NITRIDE (PANI/gCN) NANOCOMPOSITES ELECTRODE FOR SUPERCAPACITOR

*Manohar D.Mehare[1], Abhay D.Deshmukh[2] and S.J.Dhoble[3]*

[1]Department of Physics, Shivaji Science College Nagpur-440012, India
[2]Energy Materials and Devices Laboratory, Department of Physics,R.T.M Nagpur University,Nagpur-440033, India
[3]Department of Physics,R.T.M Nagpur University, Nagpur-440033, India

***Abstract:*** Novel nanoflake polyaniline/graphitic carbon nitride (PANI/gCN) nanocomposite was successfully synthesized by simple electrodeposition method, and their performance is evaluated for supercapacitor application. PANI/gCN exhibits highest specific capacitance of 588.56 $Fg^{-1}$ at current density 1 $Ag^{-1}$ with the capacitance retention of 77.88% at even at current density 15 $Ag^{-1}$. The energy density obtained to be 20.43 $Whkg^{-1}$ within the potential window of 1.0V and a current density of 1$Ag^{-1}$. PANI/gCN present presented promising the candidate in future for potential application of supercapacitor

***Keywords-PANI, gCN, Electrodeposition, Nanocomposite, Supercapacitor***

## I. INTRODUCTION

Supercapacitor also called as electrochemical capacitor or ultracapacitor gain more and more attention for decades in the field of energy storage in comparison with other energy storage device like fuel cells and batteries, due to its unique characteristics such as high power density, fast charge-discharge rate, remarkable capacitance retention and operational security[1, 2]. In general depending upon the charge storage mechanism supercapacitor can be classified into two categories, electrical double layer capacitor (EDLCs) where capacitance is attributed due to physically adsorption of electrolyte ions on electrode-electrolyte interface having advantage of good electrical conductivity and long cyclic stability but revealing relatively low specific capacitance and Pseudocapacitors where capacitance is due to reversible redox of faradic charge transfer reaction of conducting polymer or transition metal oxide which escalate capacitance but having disavdavatage of poor stability which is prime parameter for the practical application of supercapacitor [3-5]. To overcome this flow, it is necessity to developed composite electrode materials having high power and energy density with good cyclic stability. Conductive polymer such as PANI is arising as good pseudocapacitive candidate due to its light weight, easy handle synthesis, low cost and eco-friendly [6], however low power density and poor stability limit its practical application single in field of energy storage [7]. There PANI/gCN composite electrode receive more attention to overcome above limitation.

Herein, we report facile method for synthesis of electrochemical Pseudocapacitor electrode by simple electrodeposition of PANI and gCN and evaluate its performance for potential application of Supercapacitor.

## 2. EXPERIMENTAL

### 2.1 Materials and reagents

Aniline monomer (99.5%), sulfuric acid (98%) was analytical grade obtained from Merck India limited and used as received without further purification. Melamine ($C_6H_6N_6$) was purchased from the Otto chemical company. Typically, Stainless Steel (SS-304) mesh (10 mm x 20 mm x 0.1 mm, 400ppi) was used as current collector. Doubly deionized water was used throughout the experiments.

### 2.2Synthesis of graphitic carbon nitride (gCN)

The graphitic carbon nitride (gCN) was prepared by simple condensation method using melamine as precursor reported previously [8]. In a typical preparation 5g of melamine was put in ceramic crucible with lid cover was heated up to 520°C for 2h and then extended to 540°C for 2h in muffle furnace. The heated sample was allowed to cool at room temperature. Finally, the product (light yellow color) grounded within a mortar and pestle and named as gCN.

### 2.3 Preparation of PANI/g-CN electrode

Typically, 3mg of g-CN was added successively in 2 ml of concentrated $H_2SO_4$ and heated at 80°C for few hours till to get clear transparent solution. 0.2 M of $H_2SO_4$ with gCN solution is added in 30 ml of distilled water and 0.1M aniline at room temperature followed by continuous stirring for 30min.Same process is repeated for 5, 7 mg g-CN. The PANI/g-CN electrode was prepared by simple single step electro-deposition method. Typically, Stainless steel (SS-304) mesh ( 10mm x 20mm x 0.1mm, 400 ppi) was clean by acetone followed by sonication for 10 min and then rinsed by double distilled water to remove all the impurities from the surface and dried at 80°C for 12 hour in vacuum oven. The three electrode cell was constructed at room temperature with clean SS directly adopted as working electrode, Ag/AgCl as reference electrode, Pt plate as counter electrode. The solution containing 0.1M aniline and 0.2M $H_2SO_4$ with g-CN was electropolymerized

on SS mesh by simple electro-deposition method for few second at a potential of 0.75 V versus reference electrode. The composite adsorbed substrate was washed with DI water and dried for further use. The as prepared electrode was denoted as PANI/gCN-X, X being the weight of gCN in mg.

### 2.4 Characterization and Electrochemical Measurement

The surface morphology and microstructure of the as-prepared gCN sample were investigated by Field emission scanning electron microscope (JEOL JSM 7610F FEGSEM). The cyclic voltammetry (CV) curves,galvanostatic charge- discharge (GCD) curve, electrochemical impedance spectroscopy (EIS) were studied using Metrohm Autolab-128N (Netherlands, USA). The electrochemical performances of SS mesh with electrodeposited PANI/gCN-X use as working electrode were evaluated by using three electrode cell configurations in 1M $H_2SO_4$ aqueous electrolyte. Platinum foil was used as a counter electrode and Ag/AgCl was used as a reference electrode in 1M $H_2SO_4$ aqueous electrolyte. The CV and GCD measurement are carried out at different scan rate and different current density respectively in the potential window -0.2 to 0.8 V. The gravimetric capacitance ($Fg^{-1}$) was calculated from charge/discharge curve according to equations

$$C_g = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

m (g) is mass of active materials of electrode, I(A) is the applied current,$\Delta t(s)$is discharge time, $\Delta V(V)$ is potential window. The energy density ($Whkg^{-1}$) and power density ($Wkg^{-1}$) of the asymmetric supercapacitor ware calculated as the following equations

$$E = \frac{C_g \times \Delta V^2}{28.8} \quad (2)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (3)$$

Electrochemical impedance spectroscopy (EIS) measurement was carried out by applying an AC voltage with 10mV amplitude in a frequency range from 10 kHz to 10 mHz at open circuit potential.

## 3. RESULTS AND DISCUSSION

The morphology of obtained g-CN is as shown in figure 1a, which is completely temperature dependent [8]. At the calcination temperature of 540°C it reveals nanoflake, with the size located at the range of 0.5-0.8nm. At the high tempreture the process of thermal condensation occur which leads to grow the size of flake. In addition, SEM image shows, the most of g-CN particle located at the submicron, which exhibits the bright future in the field of energy storage.

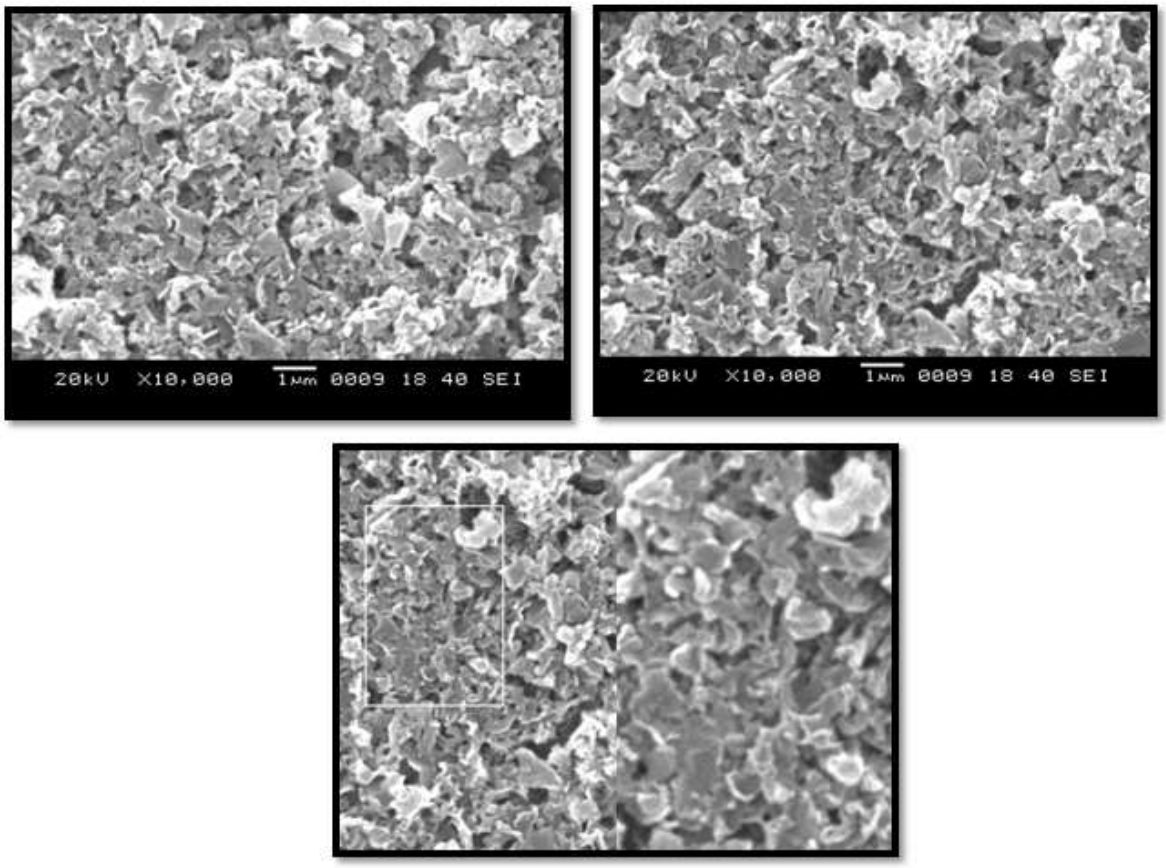

**Figure1.SEM image of gCN thermally condensed at 540ºC for 4hr**

The electrochemical performance of PANI/gCN-X electrode was evaluated in three electrode system with 1M $H_2SO_4$ as electrolyte. Figure 1a shows the CV curve of PANI/gCN-3, PANI/gCN-5, and PANI/gCN-7 electrode at the scan rate 10 $mVs^{-1}$ within the potential range of -0.2V – 0.8V versus Ag/AgCl. The CV curve represents typical characteristics of PANI with two redox peak which attributed to the leucoemeraldine/ emeraldine and emeraldine/ pernigraniline transition of PANI revealing the pseudocapacitive behavior of the conducting polymer [9, 10]. It was observed that the area under the CV profile of PANI/gCN-5 electrode was larger than PANI/gCN-3 and PANI/gCN-7 electrodes at the same scan rate elucidate its high specific capacitance. Figure 2b shows CV profile comparison of PANI/gCN-5 electrode at different sweep rate varies from $10mVs^{-1}$ to $100mVs^{-1}$.It was noted that anode peaks shifted toward positive and peak shifted toward negative with increase in sweep rate symbolize that high scan rate prevent the accessibility of ions to the surface of electrode [11]. Figure 1c shows the comparative study of GCD curve of PANI/gCN-3, PANI/gCN-5 and PANI/gCN-7 electrodes at the current density $1Ag^{-1}$. PANI/gCN-5 electrode exhibits excellent capacitive behaviour compare to other two electrodes support the results depicted in figure 1a. The GCD curve of PANI/gCN-5 electrode at different current densities varies from $1Ag^{-1}$ to 15 $Ag^{-1}$ shown in figure 2d. All the CGD curve revealing almost rectangular shape even at high scan rate as a indicative of the reversible behaviour of the ideal capacitor. The specific capacitance calculated from CGD curve using equation $C_s = \frac{I \times \Delta t}{m \times \Delta V}$[12]. The highest specific capacitance obtained to be 588.56 $Fg^{-1}$ at the current density $1Ag^{-1}$. It was observed that with increase in current density from $1Ag^{-1}$ to $15Ag^{-1}$ there is progressive depletion in specific capacitance shown in figure 2e due to internal resistance and polarization effect [13]. With the increase in current density from $1Ag^{-1}$ to $15Ag^{-1}$ PANI/gCN-5 electrode shows the capacitance retention of 72.88 % which remarkable as compare to PANI/gCN-3 (66.90%) and PANI/gCN-7 (64.9%) electrodes. The cyclic stability curve of PANI/gCN-3, PANI/gCN-5 and PANI/gCN-7 electrodes were compare at the current density $3Ag^{-1}$ as illustrate in figure 2f which exhibits PANI/gCN-5 shows the capacitance retention of 55.75% of its initial capacitance where as PANI/gCN-3 and PANI/gCN-7 shows the capacitance retention of 50% and 49% of its initial values over 1000 continuous charge discharge cycles. Low specific capacitance may be due to ineffective contact between PANI and gCN which results deterioration of electron transfer and ion diffusion [14].

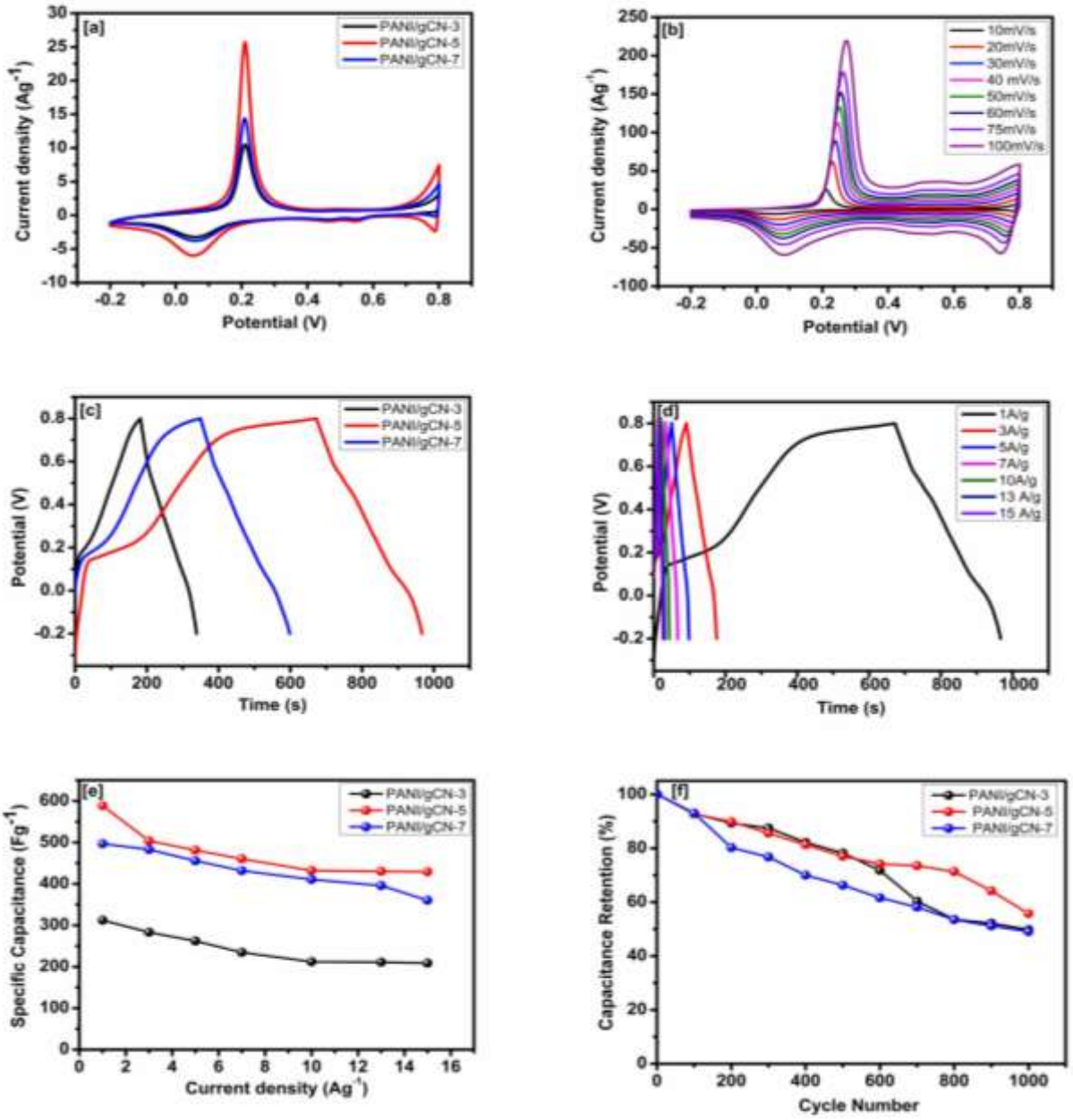

**Figure 2. (a) CV comparison of PANI/gCN-X electrode at scan rate 10mVs$^{-1}$ (b) CV profile of PANI/gCN-5 at different scan rate (c) GCD comparison of PANI/gCN-X electrode at current density 1Ag$^{-1}$ (d) GCD profile of PANI/gCN-5 at different current densities. (e) Specific capacitance as function of current density for PANI/gCN-X electrode (f) Capacitance retention vs cycle number for PANI/gCN-X electrode**

The fundamental properties of supercapacitor electrode can also be evaluated by electrochemical impedance spectra (EIS) analysis [15]. Nyquist plot of PANI/gCN-3, PANI/gCN-5 and PANI/gCN-7 electrodes in 1M $H_2SO_4$ aqueous electrolyte in the frequency range from 10 kHz to 10 mHz display in figure 3a inset figure shows magnified high frequency regions of PANI/gCN-5 electrode. The Nyquist plot normally compose of three characteristics regions (a) intercept at Z' axis represent equivalent series resistance (Rs) (b) The diameter of partial semicircle in the high frequency region represent charge transfer resistance (Rct) (c) Vertical line parallel to (Z") in the low frequency region represent capacitive behaviour [16, 17]. The comparision of series resistance (Rs), charge transfer resistance (Rct) for PANI/gCN-X electrode is depicted in tabular form.

| Component | PANI/gCN-3 | PANI/gCN-5 | PANI/gCN-7 |
|---|---|---|---|
| $R_s(\Omega)$ | 1.04 | 0.98 | 1.54 |
| $R_{ct}$ ($\Omega$) | 2.49 | 0.58 | 2.01 |

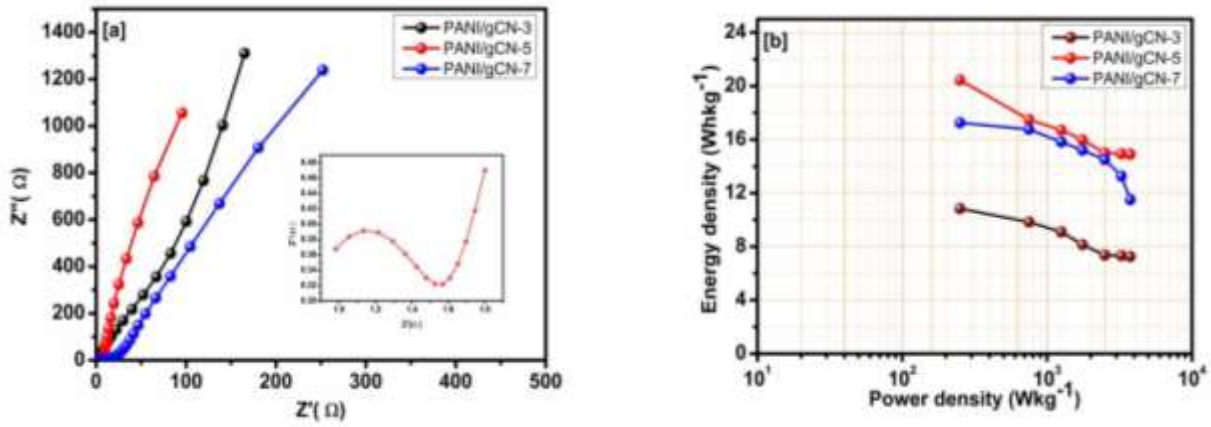


**Figure 3. (a) Nyquist plot (b) Regone plot of PANI/gCN-X electrode in 1M $H_2SO_4$ aqueous electrolyte**

Which signifies that PANI/gCN-5 electrode exhibits good electrical interconnectivity. Regone plot of PANI/gCN-3, PANI/gCN-5 and PANI/gCN-7 electrodes display in figure3b. PANI/gCN-5 electrode exhibits high energy density of 20.45 Whkg$^{-1}$ and power density of 250 Wkg$^{-1}$ at current density 1Ag$^{-1}$, moreover it can still deliver an energy density of 14.89 Whkg$^{-1}$ even at current density increase to 15Ag$^{-1}$ indicating good potential electrode for supercapacitor application.

## 4. CONCLUSION

In summary, novel nanoflake like PANI/g-CN composite was successfully synthesized by simple thermal condensation and electrodeposition method. The PANI/gCN-5 nanocomposite electrode exhibits excellent capacitive performance with highest capacitance obtained to be 588.56 Fg$^{-1}$ at current density 1Ag$^{-1}$ and revealing remarkable capacitance retention of 72.88% even at current density 15 Ag$^{-1}$. The highest energy density obtained to be 20.43 Whkg$^{-1}$ which still retained to be 14.89 Whkg$^{-1}$ with increase in current density from 1Ag$^{-1}$ to 15Ag$^{-1}$. This study suggested that PANI/gCN-5 is a promising candidate electrode material for potential application of supercapacitor.

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