

**UTILISATION CERTIFICATE**  
**FOR THE FINANCIAL YEAR – (ENDING 31<sup>ST</sup> MARCH) (year) 2019-2020**  
*(To be given separately for each financial year ending on 31<sup>st</sup> March)*

U.C pertains to √ appropriate box	First Release	Second Release	Third Release	Fourth Release √	Final Release
--------------------------------------	------------------	-------------------	------------------	---------------------	------------------

- Is the UC provisional : YES
1. Title of the Project/Scheme : Development of graphene based conducting polymer nanocomposites for electrochemical energy storage applications
  2. Name of Principal Investigator : <sup>Lab</sup> Prof. Ashok Kumar
  3. Implementing Institution : Tezpur University
  4. SERB sanction order No & date : EMR/2015/000428 & 22/08/2016
  5. Amount brought forward from the previous financial year quoting SERB letter number and date in which the authority to carry forward the said amount was given : Amount : Rs. 2,39,119  
: Letter/Order No : SERB/F/1936/2019-2020  
: Date : 25/06/2019
  - 6a. Amount received during the financial year (Please give SERB letter/order no and date for the amount) : Amount : Rs. 6, 08,419  
: Letter/Order No: SERB/F/1936/2019-2020  
: Date : 25/06/2019
  - 6b. Interest earned, if any : Rs. 8138
  7. Total amount that was available for expenditure Rs. (excluding commitments) during the financial year (Sr. No. 5+6a+6b) : Rs. 8,55,676
  8. Actual Expenditure (Excluding commitments) : Rs. 2,01,571  
Incurred during the financial year (upto 31<sup>st</sup> March)
  9. Balance amount available at the end of the financial year (7-8):OR / Negative balance (If expenditure incurred is more than the funds released) : Rs. 6,54,105 (including interest)
  10. Unspent balance, if any, refunded to SERB (give details of cheque/DD No etc.) : Amount: None  
: Cheque/DD No.: None  
: Date
  11. Amount to be carried forward to the next financial year (if any) : Rs.

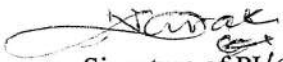
**UTILISATION CERTIFICATE**

Certified that out of Rs. 2,00,000/- of **Recurring** grants-in-aid sanctioned during the year 2019-2020 in favour of Tezpur University, Distt. Sonitpur, Napaam-784028, Tezpur under SERB letter No SERB/F/1936/2019-2020 dated 25/06/2019 and **Rs. 2,39,119/-** on account of unspent balance of the previous year and earned interest of **Rs. 8138/-**, a sum of **Rs. 2,01,571/-** has been utilized for the purpose for which it was sanctioned and that the balance of **Rs. 6,54,105/-** remaining unutilized at the end of the financial year will be returned back to DST-SERB.


Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Kinds of checks exercised:

- 1.
- 2.

  
Signature of PI/co-ef  
Date: 23/2/21

  
Signature of Finance Office  
Date: 23/2/21  
Finance Officer  
Tezpur University

  
Signature of Head of Institution  
Date: 23/2/21  
Registrar  
Tezpur University

**Science and Engineering Research Board**

UC accepted has been accepted by

Signature.....

Name of SERB Officer.....

Designation.....

**UTILISATION CERTIFICATE**  
**FOR THE FINANCIAL YEAR – (ENDING 31<sup>ST</sup> MARCH) (year) 2019-20**  
 (To be given separately for each financial year ending on 31<sup>st</sup> March)

U.C pertains to	First Release	Second Release	Third Release	Fourth Release <input checked="" type="checkbox"/>	Final Release
<input checked="" type="checkbox"/> appropriate box					

- Is the UC provisional : YES
1. Title of the Project/Scheme : Development of graphene based conducting polymer nanocomposites for electrochemical energy storage applications
  2. Name of Principal Investigator : <sup>Letter</sup> Prof. Ashok Kumar
  3. Implementing Institution : Tezpur University
  4. SERB sanction order No & date : EMR/2015/000428 & 22/08/2016
  5. Amount brought forward from the previous financial year quoting SERB letter number and date in which the authority to carry forward the said amount was given : Amount – Rs. 40,271  
: Letter/Order No.: SERB/F/1936/2019-2020  
: Date: 25/06/2019
  - 6a. Amount received during the financial year (Please give SERB letter/order no and date for the amount) : Amount: N/A  
: Letter/Order No  
: Date
  - 6b. Interest earned, if any : N/A
  7. Total amount that was available for expenditure Rs. (excluding commitments) during the financial year (Sr. No. 5+6a+6b) : Rs. 40,271
  8. Actual Expenditure (Excluding commitments) : Rs. 12,263.00  
Incurred during the financial year (upto 31<sup>st</sup> March)
  9. Balance amount available at the end of the financial year (7-8):OR / Negative balance (If expenditure incurred is more than the funds released) : Rs. 28,008 (including interest)
  10. Unspent balance, if any, refunded to SERB (give details of cheque/DD No etc.) : Amount : None  
: Cheque/DD No.: None, Date: None
  11. Amount to be carried forward to the next financial year (if any) : N/A


**UTILISATION CERTIFICATE**

It is certified that out of **Rs 27, 82,059/-** of **Non-Recurring** grants-in-aid sanctioned during the year **2016-17** in favour of **Tezpur University, Distt. Sonitpur Napaam-784164, Tezpur** under SERB letter No **EMR/2015/000428** dated **22.08.2016** and **Rs. 40,271/-** on account of unspent balance of the previous year sanctioned through SERB letter No **SERB/F/1936/2019-2020** dated **25/06/2019** with earned interest of **Rs 0** , a sum of **Rs 12,263/-** has been utilized for the purpose for which it was sanctioned and the remaining unutilized balance of **Rs. 28,008 /-** will be returned back to DST-SERB.


Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Kinds of checks exercised:

- 1.
- 2.

  
Signature of PI (COPI)  
Date: 23/12/21

  
Signature of Finance Officer  
Date: Finance Officer  
Tezpur University

  
Signature of Head of Institution  
Date: Registrar  
Tezpur University

**SCIENCE AND ENGINEERING RESEARCH BOARD**

UC accepted has been accepted by

Signature.....

Name of SERB Officer.....

Designation.....

REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

1. SERB Sanction Order No and date : EMR/2015/000428 & 22/08/2016  
2. Name of the PI : <sup>late</sup> Prof. Ashok Kumar  
3. Total Project Cost : Rs. 50,10,784/-  
4. Revised project cost (if applicable) : None  
5. Date of Commencement : 09/09/2016  
6. Statement of Expenditure : Month wise expenditure incurred during 01.04.2019-08.03.2020

Months (2018-19)	Grant	Expenditure
01.09.2019-30.09.2019	Equipment	12,263.00
	Travel	28,101.00
	Overhead	33,470.00
Total		73,834.00

1. Grant received in each year:


- a. 1<sup>st</sup> year : Rs. 35,24,966/-  
 b. 2<sup>nd</sup> year : Rs. 5,00,000/-  
 c. 3<sup>rd</sup> year : Rs. 6,00,000/-  
 d. 4<sup>th</sup> year : Rs. 2,00,000/-  
 e. Interest (if any) : Rs. 37,264/-  
 f. Total (a+b+c+d+e): Rs. 48,62,230/-

Annexure-II

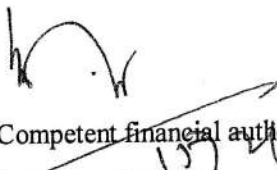
Statement of Expenditure from 09.09.2016 (Date of start) to 08.03.2020

Sr. No	Sanctioned Heads (II)	Total Funds Allocated (indicate sanctioned) (III)	Expenditure Incurred				Total Expenditure till 08.03.2020 (VIII = IV + V + VI + VII)	Available Balance on 08.03.2020	Remarks (if any)
			1 <sup>st</sup> Year 9.9.2016 (DOS) to 31.03.2017 (IV)	2 <sup>nd</sup> Year 1.04.2017 to 31.03.2018 (V)	3 <sup>rd</sup> Year & so on 1.04.2018 to 31.03.2019 (VI)	4 <sup>th</sup> Year 1.04.2019 to 31.03.2020 (VII)			
1.	Manpower costs	11,23,200	1,45,806	3,00,000	1,22,903	- 1,40,000	7,08,709	4,14,491+ 2,27,613* + 1,80,806**= 8,22,910	* Money refunded by Kashmiri Baruah ** Money refunded by Devalina Sarmah
2.	Consumables	3,50,000	1,25,230	1,25,148	99,619	0	3,49,997	3	
3.	Travel	1,50,000	41,460	37,524	39,570	28,101	1,46,655	3345	
4.	Contingencies	1,50,000	56,123	43,877	50,000	0	1,50,000	0	
5.	Others, (Interest)	-	-	-	-	-	-	37,264	Interest
6.	Equipment	27,82,059	2,17,788	19,08,943.75	6,42,339	12,263	27,81,334	726	
7.	Overhead expenses	4,55,525	3,05,525	17,945	94,901	33,470	4,51,841	0	

8.	Total	50,10,784	8,91,932	24,33,437.75	10,49,332	2,13,834	45,88,536	6,82,113***	Interest Added ***Obtained by subtracting total expenditure till 8/3/2020 from total released money i.e. 6,82,113= (48,62,230-45,88,536) +4,08,419 (refunded money)
----	-------	-----------	----------	--------------	-----------	----------	-----------	-------------	---

  
Name and Signature of Principal Investigator/

Date: 23/12/21 CO-PI

  
Signature of Competent financial authority (with seal)

Date: Finance Officer  
Jaspur University

**\* DOS – Date of Start of project**

---

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of SERB i.e Figures in Column (VII) should not exceed corresponding figures in Column (III).
2. Utilization Certificate (Annexure III) for each financial year ending 31<sup>st</sup> March has to be enclosed along with request for carry-forward permission to the next financial year.



**UTILISATION CERTIFICATE**  
**FOR THE FINANCIAL YEAR – (ENDING 31<sup>ST</sup> MARCH) (year) 2019-2020**  
*(To be given separately for each financial year ending on 31<sup>st</sup> March)*

U.C pertains to √ appropriate box	First Release	Second Release	Third Release	Fourth Release √	Final Release
--------------------------------------	------------------	-------------------	------------------	---------------------	------------------

- Is the UC provisional : YES
1. Title of the Project/Scheme : Development of graphene based conducting polymer nanocomposites for electrochemical energy storage applications
  2. Name of Principal Investigator : <sup>Late</sup> Prof. Ashok Kumar
  3. Implementing Institution : Tezpur University
  4. SERB sanction order No & date : EMR/2015/000428 & 22/08/2016
  5. Amount brought forward from the previous financial year quoting SERB letter number and date in which the authority to carry forward the said amount was given : Amount : Rs. 2,39,119  
: Letter/Order No : SERB/F/1936/2019-2020  
: Date : 25/06/2019
  - 6a. Amount received during the financial year (Please give SERB letter/order no and date for the amount) : Amount : Rs. 6, 08,419  
: Letter/Order No: SERB/F/1936/2019-2020  
: Date : 25/06/2019
  - 6b. Interest earned, if any : Rs. 8138
  7. Total amount that was available for expenditure Rs. (excluding commitments) during the financial year (Sr. No. 5+6a+6b) : Rs. 8,55,676
  8. Actual Expenditure (Excluding commitments) : Rs. 2,01,571  
Incurred during the financial year (upto 31<sup>st</sup> March)
  9. Balance amount available at the end of the financial year (7-8):OR / Negative balance (If expenditure incurred is more than the funds released) : Rs. 6,54,105 (including interest)
  10. Unspent balance, if any, refunded to SERB (give details of cheque/DD No etc.) : Amount: None  
: Cheque/DD No.: None  
: Date
  11. Amount to be carried forward to the next financial year (if any) : Rs.

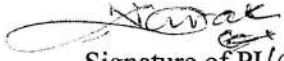
**UTILISATION CERTIFICATE**


Certified that out of Rs. **2,00,000/-** of **Recurring** grants-in-aid sanctioned during the year **2019-2020** in favour of **Tezpur University, Distt. Sonitpur, Napaam-784028, Tezpur** under SERB letter No **SERB/F/1936/2019-2020** dated **25/06/2019** and **Rs. 2,39,119/-** on account of unspent balance of the previous year and earned interest of **Rs. 8138/-**, a sum of **Rs. 2,01,571/-** has been utilized for the purpose for which it was sanctioned and that the balance of **Rs. 6,54,105/-** remaining unutilized at the end of the financial year will be returned back to DST-SERB.

Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Kinds of checks exercised:

- 1.
- 2.

  
Signature of PI/co-ef  
Date: 23/2/21

  
Signature of Finance office  
Date: 23/2/21  
Finance Officer  
Tezpur University

  
Signature of Head of Institution  
Date: 23/2/21  
Registrar  
Tezpur University

**Science and Engineering Research Board**

UC accepted has been accepted by

Signature.....

Name of SERB Officer.....

Designation.....

**UTILISATION CERTIFICATE**  
**FOR THE FINANCIAL YEAR – (ENDING 31<sup>ST</sup> MARCH) (year) 2019-20**  
 (To be given separately for each financial year ending on 31<sup>st</sup> March)

U.C pertains to	First Release	Second Release	Third Release	Fourth Release	Final Release
√ appropriate box				√	

- Is the UC provisional : YES
1. Title of the Project/Scheme : Development of graphene based conducting polymer nanocomposites for electrochemical energy storage applications
  2. Name of Principal Investigator : <sup>lectr</sup> Prof. Ashok Kumar
  3. Implementing Institution : Tezpur University
  4. SERB sanction order No & date : EMR/2015/000428 & 22/08/2016
  5. Amount brought forward from the previous financial year quoting SERB letter number and date in which the authority to carry forward the said amount was given : Amount – Rs. 40,271  
: Letter/Order No.: SERB/F/1936/2019-2020  
: Date: 25/06/2019
  - 6a. Amount received during the financial year (Please give SERB letter/order no and date for the amount) : Amount: N/A  
: Letter/Order No  
: Date
  - 6b. Interest earned, if any : N/A
  7. Total amount that was available for expenditure Rs. (excluding commitments) during the financial year (Sr. No. 5+6a+6b) : Rs. 40,271
  8. Actual Expenditure (Excluding commitments) : Rs. 12,263.00  
Incurred during the financial year (upto 31<sup>st</sup> March)
  9. Balance amount available at the end of the financial year (7-8):OR / Negative balance (If expenditure incurred is more than the funds released) : Rs. 28,008 (including interest)
  10. Unspent balance, if any, refunded to SERB (give details of cheque/DD No etc.) : Amount : None  
: Cheque/DD No.: None, Date: None
  11. Amount to be carried forward to the next financial year (if any) : N/A


**UTILISATION CERTIFICATE**

It is certified that out of **Rs 27, 82,059/-** of **Non-Recurring** grants-in-aid sanctioned during the year **2016-17** in favour of **Tezpur University, Distt. Sonitpur Napaam-784164, Tezpur** under SERB letter No **EMR/2015/000428** dated **22.08.2016** and **Rs. 40,271/-** on account of unspent balance of the previous year sanctioned through SERB letter No **SERB/F/1936/2019-2020** dated **25/06/2019** with earned interest of **Rs 0** , a sum of **Rs 12,263/-** has been utilized for the purpose for which it was sanctioned and the remaining unutilized balance of **Rs. 28,008 /-** will be returned back to DST-SERB.

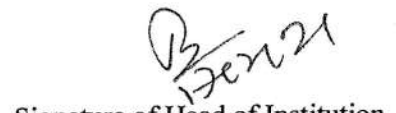
Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Kinds of checks exercised:

- 1.
- 2.

  
Signature of PI/COPI  
Date: 23/12/21

  
Signature of Finance Officer  
Date: Finance Officer  
Tezpur University

  
Signature of Head of Institution  
Date: Registrar  
Tezpur University

**SCIENCE AND ENGINEERING RESEARCH BOARD**

UC accepted has been accepted by

Signature.....

Name of SERB Officer.....

Designation.....

**REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE**

1. SERB Sanction Order No and date : EMR/2015/000428 & 22/08/2016
2. Name of the PI : <sup>Late</sup> Prof. Ashok Kumar
3. Total Project Cost : Rs. 50,10,784/-
4. Revised project cost (if applicable) : None
5. Date of Commencement : 09/09/2016
6. Statement of Expenditure : Month wise expenditure incurred during 01.04.2019-08.03.2020

Months (2018-19)	Grant	Expenditure
01.09.2019-30.09.2019	Equipment	12,263.00
	Travel	28,101.00
	Overhead	33,470.00
Total		73,834.00

1. Grant received in each year:


- a. 1<sup>st</sup> year : Rs. 35,24,966/-  
 b. 2<sup>nd</sup> year : Rs. 5,00,000/-  
 c. 3<sup>rd</sup> year : Rs. 6,00,000/-  
 d. 4<sup>th</sup> year : Rs. 2,00,000/-  
 e. Interest (if any) : Rs. 37,264/-  
 f. Total (a+b+c+d+e): Rs. 48,62,230/-

Annexure-II

Statement of Expenditure from 09.09.2016 (Date of start) to 08.03.2020


Sr. No	Sanctioned Heads	Total Funds Allocated (indicate sanctioned)	Expenditure Incurred				Total Expenditure till 08.03.2020	Available Balance on 08.03.2020	Remarks (if any)
			1 <sup>st</sup> Year 9.9.2016 (DOS) to 31.03.2017 (IV)	2 <sup>nd</sup> Year 1.04.2017 to 31.03.2018 (V)	3 <sup>rd</sup> Year & so on 1.04.2018 to 31.03.2019 (VI)	4 <sup>th</sup> Year 1.04.2019 to 31.03.2020 (VII)			
1.	Manpower costs	11,23,200	1,45,806	3,00,000	1,22,903	1,40,000	7,08,709	4,14,491+ 2,27,613* + 1,80,806**= 8,22,910	* Money refunded by Kashmiri Baruah ** Money refunded by Devalina Sarmah
2.	Consumables	3,50,000	1,25,230	1,25,148	99,619	0	3,49,997	3	
3.	Travel	1,50,000	41,460	37,524	39,570	28,101	1,46,655	3345	
4.	Contingencies	1,50,000	56,123	43,877	50,000	0	1,50,000	0	
5.	Others, (Interest)	-	-	-	-	-	-	37,264	Interest
6.	Equipment	27,82,059	2,17,788	19,08,943.75	6,42,339	12,263	27,81,334	726	
7.	Overhead expenses	4,55,525	3,05,525	17,945	94,901	33,470	4,51,841	0	

8.	Total	50,10,784	8,91,932	24,33,437.75	10,49,332	2,13,834	45,88,536	6,82,113***	Interest Added  **Obtained by subtracting total expenditure till 8/3/2020 from total released money i.e. 6,82,113= (48,62,230-45,88,536) +4,08,419 (refunded money)
----	-------	-----------	----------	--------------	-----------	----------	-----------	-------------	--

  
Name and Signature of Principal Investigator/

Date: 23/11/21

CO-PI

  
Signature of Competent financial authority (with seal)

Date: 15/11/21  
Finance Officer  
Jaspur University

**\* DOS – Date of Start of project**

---

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of SERB i.e Figures in Column (VII) should not exceed corresponding figures in Column (III).
2. Utilization Certificate (Annexure III) for each financial year ending 31<sup>st</sup> March has to be enclosed along with request for carry-forward permission to the next financial year.



## Progress Report

## Annexure-V

1. Project Title: "Development of graphene based conducting polymer nanocomposites for electrochemical energy storage applications"	DST No: SERB/F/3239/2016-17
2. PI(Name &Address): Prof. Ashok Kumar Department of Physics, Tezpur University, Napaam-784028, Assam, Telephone: (03712) 267007,8,9/Ex.5553 Fax: (03712) 267006; Email: ask@tezu.ernet.in	Date of Birth: 01/02/1964
3. Co-PI(Name & Address): Prof. Niranjana Karak Department of Chemical Sciences, Tezpur University, Napaam-784028, Assam, Telephone: (03712) 267007, 8, 9/ Ext.5056 (O) Fax: (03712) 267006; Email: nkarak@tezu.ernet.in	Date of Birth: 21/02/1968
<b>4. Broad area of Research: Physical Sciences</b> <b>4.1 Sub Area: Condensed Matter Physics and Materials Science</b> <b>5. Approved Objectives of the Proposal:</b> The objective of the proposed project is to develop graphene based conducting polymer nanocomposites via nanoscale structural manipulation that generate large specific capacitance and improved cyclic stability for electrochemical energy storage and conversion applications. In order to realize these objectives, the following goals are set: 1. Preparation of graphene and graphene oxide sheets of enhanced specific surface area and improved conductivity by modified Hummers method. 2. Synthesis of graphene based conducting polymer nanocomposites by in situ polymerization of different conducting polymer nanostructures dispersed with exfoliated graphene or graphene oxide sheets. 3. Synthesized graphene-conducting polymer nanocomposites will be characterized by TEM, SEM, XRD, TGA, Raman, XPS and FTIR spectroscopy for analysis of their physico-chemical properties. 4. Electrochemical performance of the synthesized nanocomposites will be investigated by cyclic voltammetry, electrochemical impedance spectrometry, galvanostatic charge-discharge and I-V characteristics for their application as electrode material in electrochemical devices.	
Date of Start: <b>09/09/2016</b>	Total cost of Project: <b>Rs. 50,10,784.00</b>
Date of completion: <b>08/03/2020</b>	Expenditure as on: <b>08/03/2020</b> Capital – Rs. 27,81,334 /- General – Rs. 13,98,783/- (Excluding the refunded money of Rs. 4,08,419/- by Devalina Sarmah and Kashmiri Baruah from fellowship grant)
<b>6. Methodology:</b> 1. Procurement of chemicals and consumables as well as installation of the remaining sanctioned equipments. 2. Bulk graphitic carbon nitride (g-C <sub>3</sub> N <sub>4</sub> ) was prepared by template-free method at Tezpur University. 3. Protonated graphitic carbon nitride (pg-CN) was prepared by treating g-C <sub>3</sub> N <sub>4</sub> with acid and ultrasonicated and then stirred overnight at Tezpur University. 4. Synthesis of Polypyrrole nanotubes (PPyNTs) were done by reactive self-degraded template method using ferric chloride, methyl orange and pyrrole monomer as precursors at Tezpur University. 5. Graphene oxide (GO) was synthesized by improved hummers' method using sulphuric acid, phosphoric acid, graphite flake and Potassium permanganate as oxidant at Tezpur University. 6. Exfoliated Graphene Oxide was reduced to reduced graphene oxide (rGO) with hydrazine hydrate followed by hydrothermal treatment at Tezpur University. 7. rGO-modified pg-CN (rGO-pg-CN) hybrid was prepared by adding 1 g of the as-prepared pg-CN added to GO suspension and ultrasound-treated for an hour. After that, the mixture was vigorously stirred for 1h to achieve homogeneous suspension. To reduce GO in the synthesis mixture, hydrazine hydrate was subsequently added. The resulting mixture was stirred at 80° C for 3h, after which the reaction mixture was cooled to room temperature and washed several times with ethanol and DI water to remove excess hydrazine hydrate. Finally, the as- obtained precipitate was obtained by self- assembly method for 12 h at Tezpur University. 8. The ternary nanocomposite rGO-pg-CN/PPyNTs was prepared by polymerizing pyrrole using self-degradation template method. 9. Protonated graphitic carbon nitride (pg-CN), rGO-modified pg-CN (rGO-pCN), rGO-modified rGO-pg-CN/PPyNTs	

ternary nanocomposite were characterized with Scanning electron microscope (SEM), X-Ray Diffraction (XRD), Raman and FTIR at Tezpur University.

10. Brunauer-Emmett-Teller (BET) was performed in quantachrome (model) instrument using nova software to determine the surface area and pore diameter at Tezpur University.
11. X-Ray Photoelectron Spectroscopy (XPS) was performed by X-Ray Photoelectron Spectrometer Thermo Fisher Scientific model ESCALAB Xi+.
12. All the electrochemical measurements were evaluated at room temperature in three electrode system (AUTOLAB 302N Modular Potentiostat Galvanostat, FRA32M Module/ Kanaalweg 29/G, 3526 KM Utrecht, Netherlands) installed at Material Research Laboratory (MRL) of Tezpur University.
13. 3M KCl containing Ag/AgCl was employed as reference electrode, platinum as counter electrode and ITO loaded with active material was used as working electrode. The working electrodes were prepared by incorporating the prepared active material with carbon black and nafion in the mass ratio of 85:10:5 in DD water followed by ultrasonication for 20 min. The obtained slurry was dropped casted on ITO coated glass and leave for drying in desiccator.
14. Cyclic Voltammetry (CV) was performed to observe the current response of the composites within a potential window of -0.3 V to 1 V and at different scan rates i.e. 10, 30, 60, 90 and 100 mV for rGO-pg-CN/PPyNTs/ITO, binary pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes in 1 M KCl electrolyte.
15. Galvanostatic charge-discharge (GCD) has been done to measure the change in potential of the electrodes with respect to time with cut off voltage -0.3 to 1 V and current densities 0.5, 1, 3, 5, 7 A/g as well as to calculate the specific capacitance.
16. Electrochemical Impedance Spectroscopy (EIS) was performed in AUTO FRA modular in 1M KCl solution within a frequency range 0.1 Hz to  $10^6$  Hz to study the charge transport behaviour of the electrode.
17. Preparation of Final Technical Report for submission to DST-SERB.

## 7. Salient Research Achievements:

### 7.1 Summary of Progress:

#### 7.1.1. Procurement and installation of equipment:

All the equipment sanctioned in the project have been installed in the Materials Research Laboratory, Department of Physics, Tezpur University.

#### 7.1.2. Experimental works done:

Bulk  $g\text{-C}_3\text{N}_4$  was prepared by template free method. 12 g of urea powder was put into an alumina crucible with a lid and then heated to  $550^\circ\text{C}$  in a muffle furnace for two hours. The resulting yellowish powder is the required  $g\text{-C}_3\text{N}_4$  which is then collected and ground into powder for further use.

Protonated graphitic carbon nitride (pCN) was prepared by adding 1g of the as-obtained bulk  $g\text{-C}_3\text{N}_4$  into 200mL of HCl aqueous solution (0.5mol/L) and ultrasonicated for around 1 hour. After that, the exfoliated  $g\text{-C}_3\text{N}_4$  in the acid suspension was vigorously stirred overnight at room temperature for its further protonation. The mixture was then filtered and repeatedly washed with distilled water to remove excess HCl until the pH of the filtrate water became neutral. Finally, the pCN product was dried and then ground into powder.

rGO-pCN was synthesized by self-assembly of rGO nanosheets pCN nanosheets. rGO was synthesized from graphite using the improved Hummers' method. 1 g of the as-prepared pCN was added to GO suspension and ultrasound-treated for an hour. After that, the mixture was vigorously stirred for 1h to achieve homogeneous suspension. To reduce GO in the synthesis mixture, hydrazine hydrate was subsequently added. The resulting mixture was stirred at  $80^\circ\text{C}$  for 3h, after which the reaction mixture was cooled to room temperature and washed several times with ethanol and DI water to remove excess hydrazine hydrate. Finally, the as-obtained precipitate was dried at  $70^\circ\text{C}$  in an oven for 12 h.

Ternary rGO-pg-CN/PPyNTs nanocomposites were synthesized by in-situ polymerization of pyrrole monomer using self-degradation template method. 1 g of rGO-pg-CN hybrids were dispersed in 30 mL of DD water using ultrasound for 20 min. Then 5 mM methyl orange were added into the dispersion followed by the addition of 1.5 mM of ferric chloride. The mixture was stirred vigorous for 1 h. 1.5 mM of pyrrole monomer was added drop wise into the solution and the solution was stirred for 24 h at room temperature. The precipitate was washed several times with DD water and ethanol followed by drying at  $60^\circ\text{C}$ .

Scanning Electron Microscopy was conducted by JEOL microscope model JSM 6390LV. X-ray diffraction of the samples

were performed using diffractometer of model D8 Focus and make Bruker Axs, Germany. Fourier transform infrared spectroscopy (FTIR) was performed by preparing pellets of KBr in the ration of 1:20 by mass, using spectrometer PerkinElmer of model Frontier MIR FIR. Specific surface area and pore size were studied by Brunauer-Emmett Teller (BET) measurements (Quantachrome, Nova 1000E). Raman spectroscopy was done by spectrometer RENISHAW, UK of model RENISHAW BASIS SERIES WITH 514 LASERS using software Wire 3.4. XPS was performed by X-Ray Photoelectron Spectrometer Thermo Fisher Scientific model ESCALAB Xi+.

Electrochemical measurements were carried out using AUTOLAB 302N Modular, Netherlands, in three electrode system at room temperature. In the three electrode system, 3 M KCl containing Ag/AgCl employed as reference electrode, platinum as counter electrode and ITO loaded with active material was used as working electrode. All the ITO coated glass pieces were cut in 1x2 cm<sup>2</sup> dimension followed by dually washed with DD water and ethanol. The synthesized nanocomposites were mixed with carbon black and binder (nafion) in the mass ratio of 85:10:5 in DD water followed by ultrasonication for 20 min. The obtained slurry was dropped casted on ITO coated glass and leave for drying in desiccator.

### 7.1.3. Results and discussion:

#### 7.1.3.1 Microstructure

##### Scanning electron microscopy (SEM)

The SEM images of pg-CN, binary pg-CN/PPyNTs and ternary rGO-pg-CN/PPyNTs nanocomposites are depicted in figure 1. The nanosheets of pg-CN as shown in figure 1 (i) get segregated and granular structures are formed which may be due to agglomeration of the pg-CN nanosheets. Figure 1 (ii) confirms the formation of PPyNTs over the surface of pg-CN in the binary pg-CN/PPyNTs nanocomposite. On making composite with PPyNTs, the agglomeration of pg-CN decreases but granular structures are still found. The nanosheets of rGO and pg-CN are prevented from agglomeration and no granular structures are observed in the SEM micrographs of rGO-pg-CN/PPyNTs ternary nanocomposites in figure 1(iii). Layer-by-layer heterostructures of rGO-pg-CN minimize the agglomeration of the nanosheets increasing the electrochemically active surface area. The layered heterostructures of rGO-pg-CN are also shown in figure 1(iv).

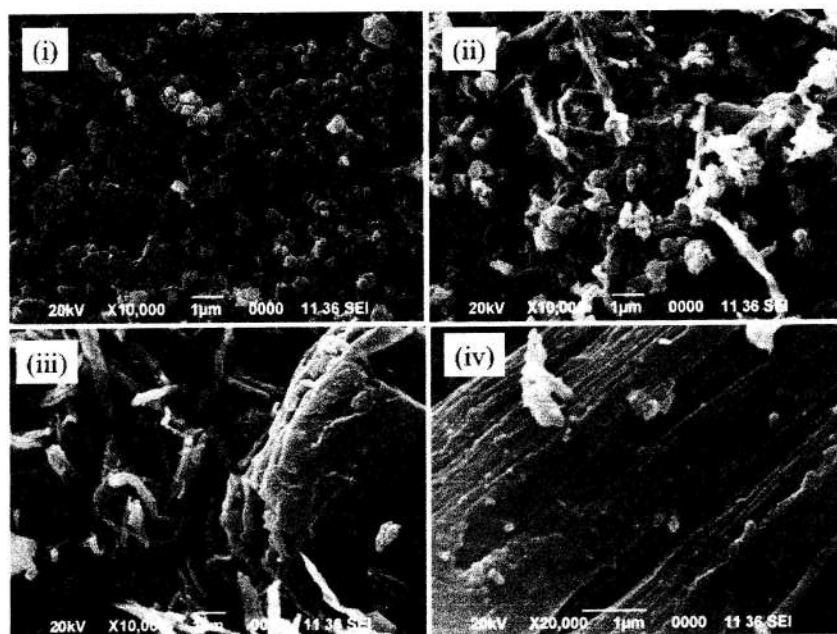


Figure 1: SEM images of (i) pg-CN, (ii) pg-CN/PPyNT, (iii)-(iv) rGO-pg-CN/PPyNT at 10,000 and 20,000 magnification respectively

##### Field Emission Scanning Electron Microscopy (FESEM)

The layer-by-layer heterostructure of rGO-pg-CN is prominent from the FESEM images in fig. 2 (i), (ii), and (iii), suggesting the fact that the self-assembled structure do not get disturbed or damaged by thermal reduction of GO and elimination of functional groups. The PPyNTs are clearly visible in the FESEM images in fig. 2 (iv), (v), and (vi). In the FESEM images of ternary nanocomposite, the rGO-pg-CN heterostructures are covered by PPyNTs (shown by yellow circle in fig. 2 (vi)). Thus,

from the FESEM images, we can confirm the formation of PPyNTs in the ternary hybrid nanocomposite rGO-pg-CN/PPyNTs.

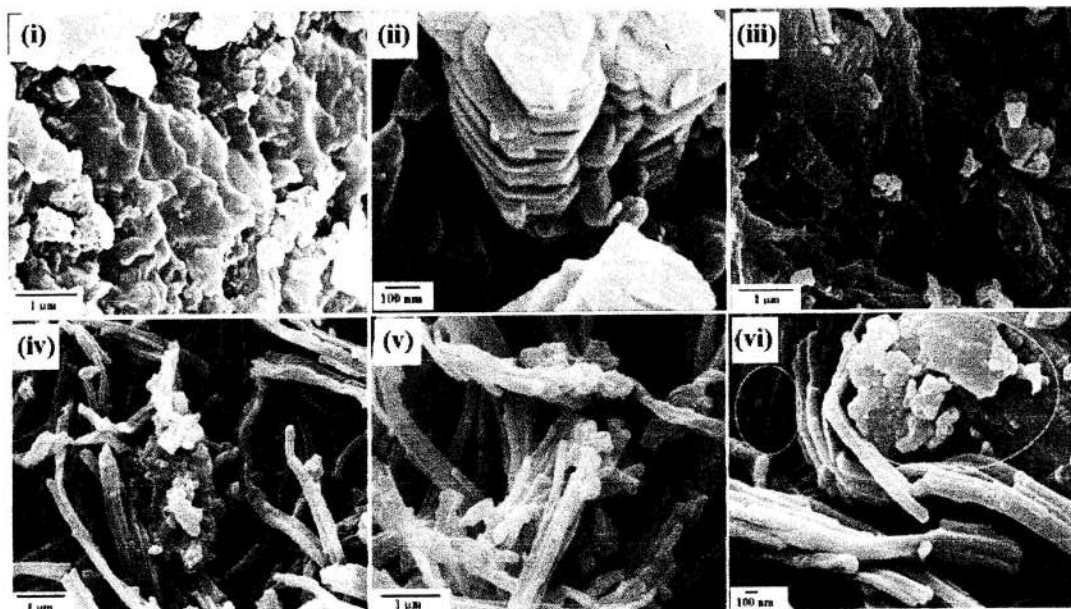


Figure 2: FESEM images of (i), (ii), (iii) rGO-pg-CN, and (iv), (v), (vi) ternary rGO-pg-CN/PPyNT nanocomposite

#### X-ray diffraction (XRD) analysis

The crystal structure formation of the nanocomposites was investigated by powder X-Ray diffraction and shown in figure 3(a). The peaks at  $13^\circ$  and  $27.4^\circ$  confirms the successful formation of pg-CN. Peak at  $27.40^\circ$  indicate the plane (002) and it corresponds to interlayer stacking of aromatic segments, and the peak at  $13^\circ$  indicate the plane (100) and it corresponds to in-plane structural packing of repeating units of tri-s-triazine. PPy shows a broad low angle plateau at  $20.16^\circ$  corresponding to the repetition of pyrrole ring units, which is characteristic of amorphous nature of polypyrrole. The shifting of diffraction peak of pg-CN in the binary nanocomposite pg-CN/PPyNT to lower diffracting angle, is due to the increase in the interlayer spacing which suggests the fact that polypyrrole nanotubes are well inserted inside the pg-CN nanosheets. The diffraction peak at  $25.8^\circ$  in the binary composite pg-CN/rGO corresponds to the (002) plane which confirms the formation of rGO nanosheets as it resembles quite well with the diffraction peak of graphite. From reported literature, a diffraction peak at  $26.7^\circ$  corresponds to the hexagonal graphitic structure of graphite corresponding to the (002) plane. In our work the diffraction angle slightly shifts to a lower angle due to the formation of nanosheets of rGO and also the presence of oxygen containing groups is not totally reduced by hydrazine hydrate. The ternary nanocomposite electrode is constituted of rGO-pg-CN/PPyNT which is also confirmed by observing the XRD peaks occurring at  $12.3^\circ$ ,  $20.17^\circ$ ,  $23.3^\circ$  and a broad hump centered around  $26.2^\circ$ . The broad hump is due to the presence of polypyrrole nanotubes and the peak at  $20.17^\circ$  is due to rGO. All the angles shift to a lower value implying the formation of the nanocomposite.

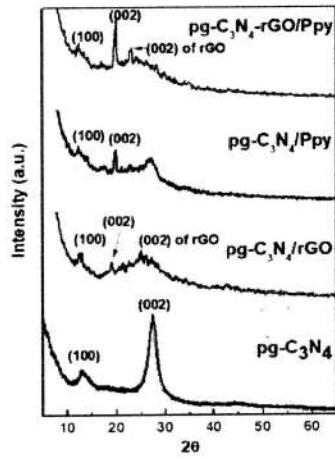


Fig. 3: XRD spectra (from bottom): pg-C<sub>3</sub>N<sub>4</sub>, pg-C<sub>3</sub>N<sub>4</sub>-rGO, pg-C<sub>3</sub>N<sub>4</sub>/PPyNTs and pg-C<sub>3</sub>N<sub>4</sub>-rGO/PPyNTs

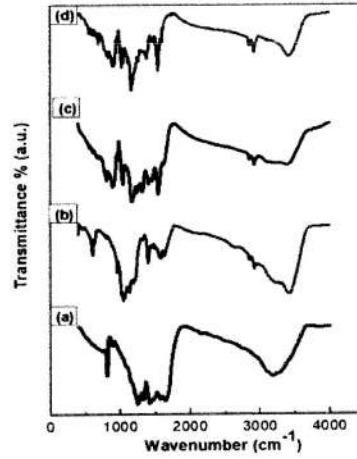


Fig. 4: FTIR spectra: (a) pg-C<sub>3</sub>N<sub>4</sub> (b) pg-C<sub>3</sub>N<sub>4</sub>-rGO, (c) pg-C<sub>3</sub>N<sub>4</sub>/PPyNTs and (d) pg-C<sub>3</sub>N<sub>4</sub>-rGO/PPyNTs

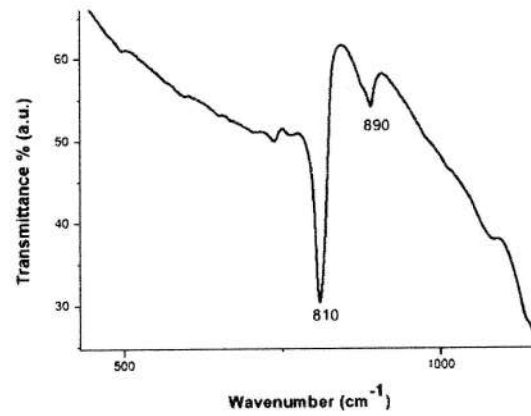
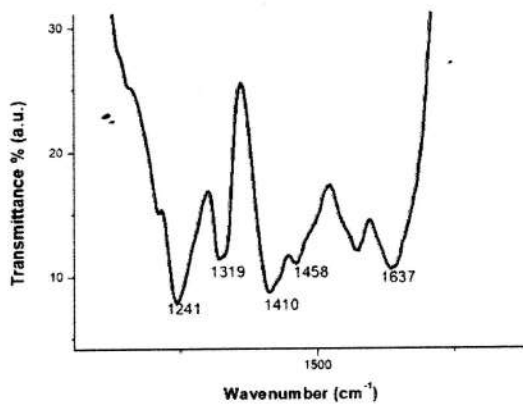


Figure 5: FTIR of pg-CN (zoomed view)

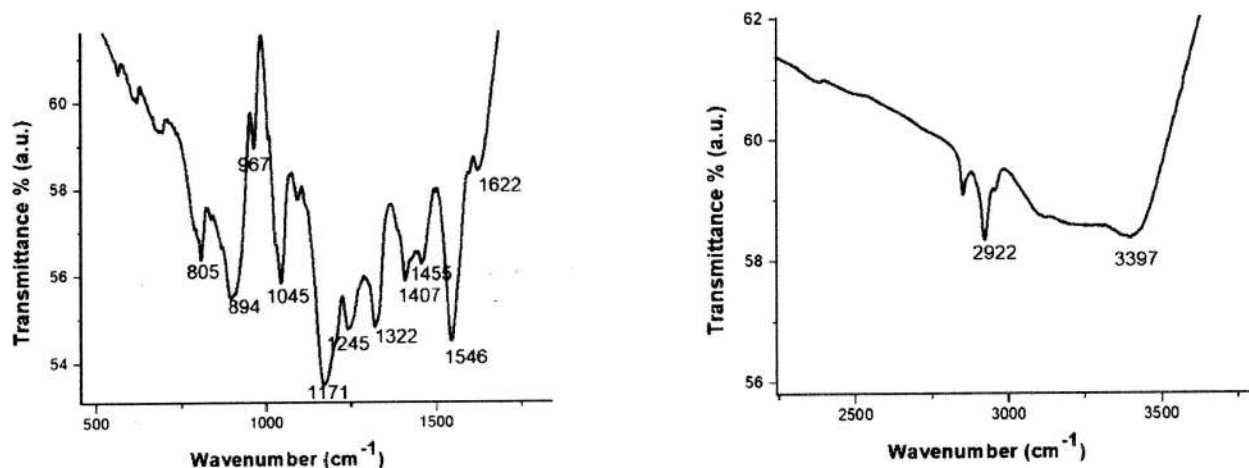


Figure 6: FTIR of binary pg-CN/PPyNT (zoomed view)

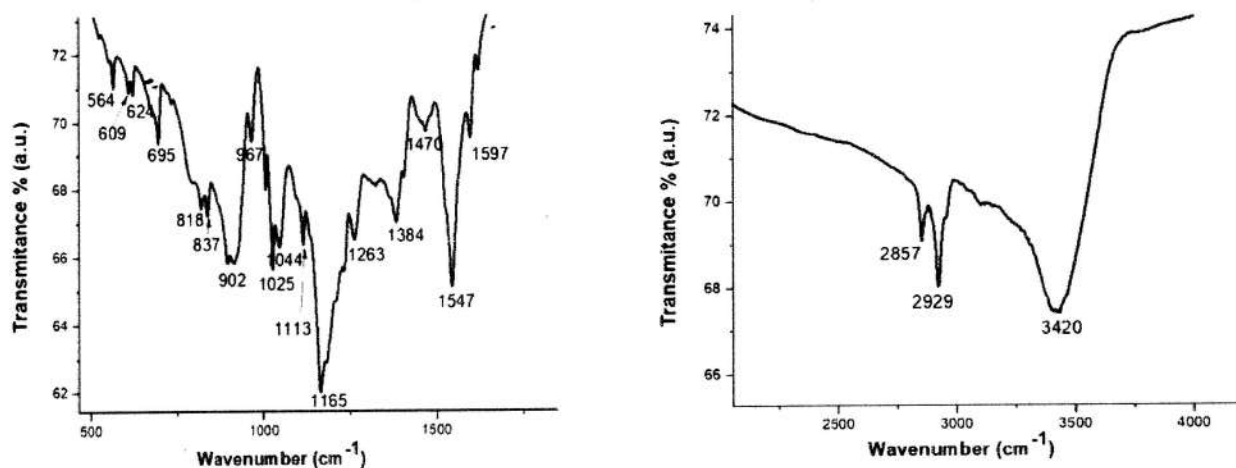


Figure 7: FTIR of ternary nanocomposite rGO-pg-CN/PPyNT

#### Fourier transforms infrared (FTIR) spectroscopy

FTIR spectroscopy has been carried out to investigate the chemical interactions in the prepared nanocomposites. Figure 4 depicts the FTIR spectra of the synthesized nanocomposites. In the FTIR spectra of pg-CN (figure 5), the peak at  $810\text{ cm}^{-1}$  is due to out-of-plane bending vibration of the heptazine units and the peak at  $890\text{ cm}^{-1}$  is attributed to the bending modes of N-containing heterocycles. The absorption bands observed at  $1241$ ,  $1319$ ,  $1458$ ,  $1571$ ,  $1637\text{ cm}^{-1}$  indicate the vibrations of the heptazine skeletal ring units. The absorption peaks at  $1458$ ,  $1571$  and  $1637\text{ cm}^{-1}$  are attributed to C=N stretching, while bands at  $1319$  and  $1241\text{ cm}^{-1}$  are due to stretching vibration of C-N(-C)-C and C-NH-C, respectively. The broad peak at  $3215\text{ cm}^{-1}$  is due to the N-H stretching which confirms the hydrogenation of N. The peak at  $1410\text{ cm}^{-1}$  confirms the stretching vibrations of the s-triazine ring units. The zoomed view of FTIR band of pg-CN/PPyNTs and rGO-pg-CN/PPyNTs is shown in figure 6,7 respectively. In figure 6 several absorption bands of PPyNTs are observed. The peak at  $1171\text{ cm}^{-1}$  arises due to C-N stretching vibrations of polypyrrole ring, absorption peak of N-H symmetric stretching vibration of the polypyrrole ring

appears at  $3397\text{ cm}^{-1}$ . The absorption peak of C=C stretching of polypyrrole appears at  $1546\text{ cm}^{-1}$ . The peak at  $1322\text{ cm}^{-1}$  is attributed to the in-plane C-H vibration polypyrrole. The peak at  $1407\text{ cm}^{-1}$  is due to the C-N deformation bond and  $1245\text{ cm}^{-1}$  is attributed to the = C-H in plane vibration. Absorption bands at  $1546$  and  $1407\text{ cm}^{-1}$  are ascribed to the fundamental vibrations of polypyrrole ring. The peak at  $1045\text{ cm}^{-1}$  arises due to the C-N stretching vibration and  $967\text{ cm}^{-1}$  is associated with out of plane bending of C-H of PPy. The corresponding vibrations at  $805, 894, 1245, 1322, 1455, 1622$  and  $3397\text{ cm}^{-1}$  of pg-CN vibrations are also observed for the binary electrode pg-CN/PPy nanocomposite suggesting the formation of binary nanocomposite. In figure 6, the peaks at  $2857$  and  $2929\text{ cm}^{-1}$  are due to the  $sp^2$  hybridized carbon of graphene, which is not fully restored by hydrazine hydrate. The broad absorption peak at  $3420\text{ cm}^{-1}$  is due to the overlapping of two absorption peaks, namely N-H stretching of pg-CN at  $3215\text{ cm}^{-1}$  and C-OH stretching vibrations of rGO at  $3430\text{ cm}^{-1}$ . Small peak at  $1597\text{ cm}^{-1}$  is due to vibration of the hexagonal carbon ring of graphene. Also, less intense FTIR peaks are observed at  $1627$  and  $1745\text{ cm}^{-1}$ , arising due to stretching vibrations of C=O and C=C bonds, respectively.

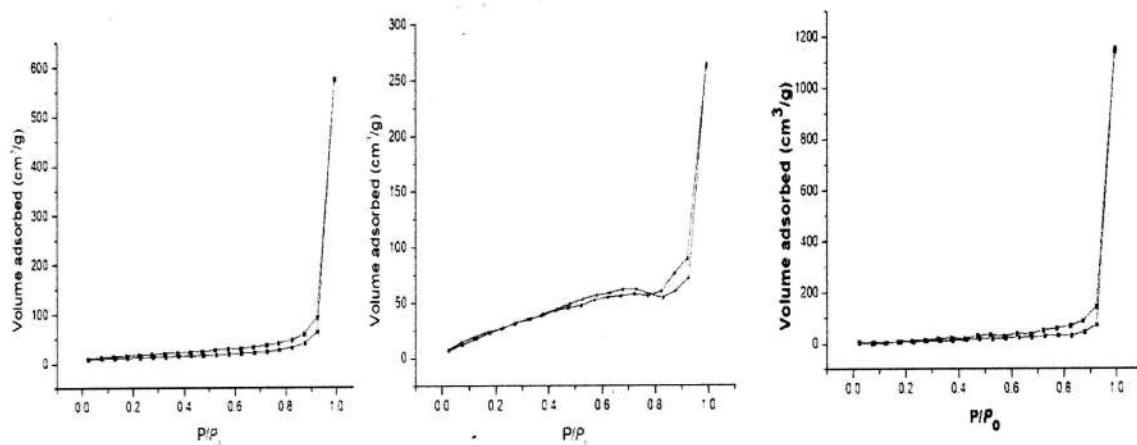


Fig. 8: Nitrogen adsorption-desorption isotherms of (a) pg-C<sub>3</sub>N<sub>4</sub>, (b) pg-C<sub>3</sub>N<sub>4</sub>/PPyNTs, (c) pg-C<sub>3</sub>N<sub>4</sub>-rGO/PPyNTs

#### Brunauer–Emmett–Teller (BET) measurements

The BET isotherms of pg-CN, binary pg-CN/PPyNTs and ternary rGO-pg-CN/PPyNTs nanocomposites are displayed in figure 8 and pore size distribution of the three electrodes are shown in figure 9, respectively. Protonated graphitic carbon nitride (pg-CN), binary (pg-CN/PPyNTs) and ternary (rGO-pg-CN/PPyNTs) electrodes exhibit combination of type III and IV isotherms and H3 hysteresis loop. We can conclude that the electrodes are composed of both mesoporous and macroporous materials since type III isotherm is exhibited by macroporous materials and type IV isotherm occurs due to capillary condensation taking place in mesoporous materials. H3 hysteresis loop confirms the presence of plate-like particles forming slit-like pores. BET surface area of pg-CN is about  $62\text{ m}^2/\text{g}$  and average pore diameter of  $3.6\text{ nm}$  is obtained. On addition of polypyrrole nanotubes over the surface of pg-CN, surface area increases from  $62$  to  $138\text{ m}^2/\text{g}$  and average pore size becomes  $4\text{ nm}$ . After incorporation of rGO to the binary nanocomposite, surface area further increases due to formation of heterostructures on self-assembly of positively charged g-C<sub>3</sub>N<sub>4</sub> with negatively charged rGO. The agglomeration of both rGO and pg-CN nanosheets decreases due to the formation of heterostructure, resulting in an increase in surface area of the ternary nanocomposite to  $158\text{ m}^2/\text{g}$  and the average pore size becomes  $3.22\text{ nm}$ . The mesoporous nature and high surface area of the ternary nanocomposite enhance the rate of redox reactions in a supercapacitor electrode.

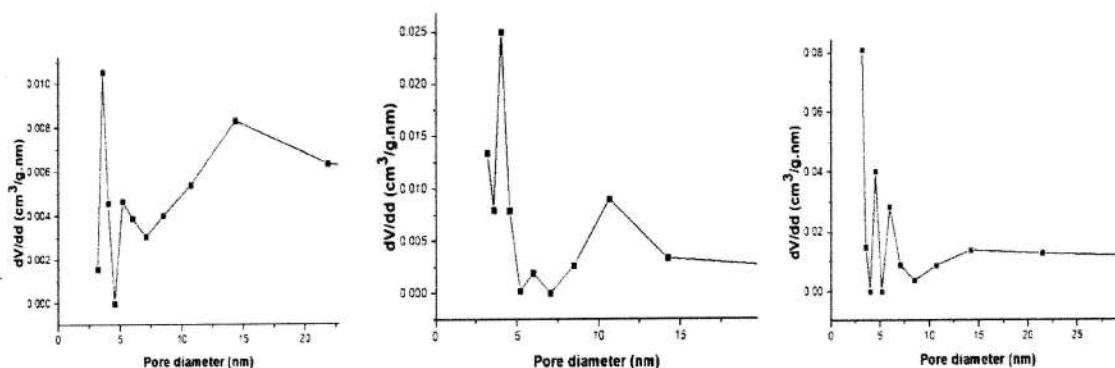


Figure 9: (a) pg-C<sub>3</sub>N<sub>4</sub>, (b) pg-C<sub>3</sub>N<sub>4</sub>/PPy, (c) pg-C<sub>3</sub>N<sub>4</sub>-rGO/PPy

#### Raman spectroscopy

At this wavelength, the Raman peaks are observed at 703, 760, 988, 1357, 1570 cm<sup>-1</sup> for pg-CN. The peaks at 703 and 988 cm<sup>-1</sup> are due to breathing mode 2 and breathing mode 1, respectively of s-triazazine ring present in the g-C<sub>3</sub>N<sub>4</sub> structure. The band at 768 cm<sup>-1</sup> is assigned to the A<sub>1</sub>' vibrational modes of tri-s-triazazine rings. Vibrational peak at 1357 cm<sup>-1</sup> corresponds to the D band of disordered carbon and the peak at 1570 cm<sup>-1</sup> corresponds to in-plane C-C stretching vibrations of the sp<sup>2</sup> C at the Brillouin zone centre and is known as G band. Raman peaks of Polypyrrole are observed at 968, 990, 1048, 1293, 1311, 1373, 1560 and 1594 cm<sup>-1</sup>. The vibrational mode at 1594 cm<sup>-1</sup> corresponds to C=C symmetry stretching. The peak at 1560 cm<sup>-1</sup> is observed due to C=C stretching mode. Vibrational bands at 1311 and 1373 cm<sup>-1</sup> are attributed to the inter-ring C-C stretching and the vibration at 1293 cm<sup>-1</sup> is due to N-H in plane deformation. The peak at 1048 cm<sup>-1</sup> corresponds to the C-H in-plane bending vibration of PPy. The vibrational bands at 968 and 990 cm<sup>-1</sup> corresponds to ring deformation associated with dication and radical cation, respectively. For the ternary electrode, additional Raman 2D peak is observed at 2685 cm<sup>-1</sup> which is due to the graphene second order zone-boundary phonons. Thus, the above Raman results confirms the formation of pg-CN, pg-CN/PPyNTs and rGO-pg-CN/PPyNTs which is further confirmed by XRD and FTIR results.

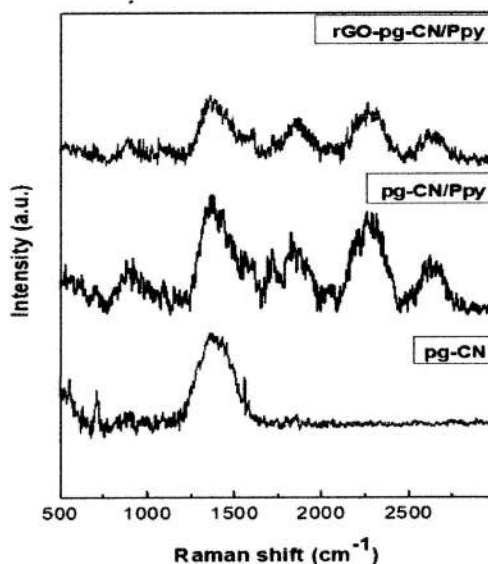


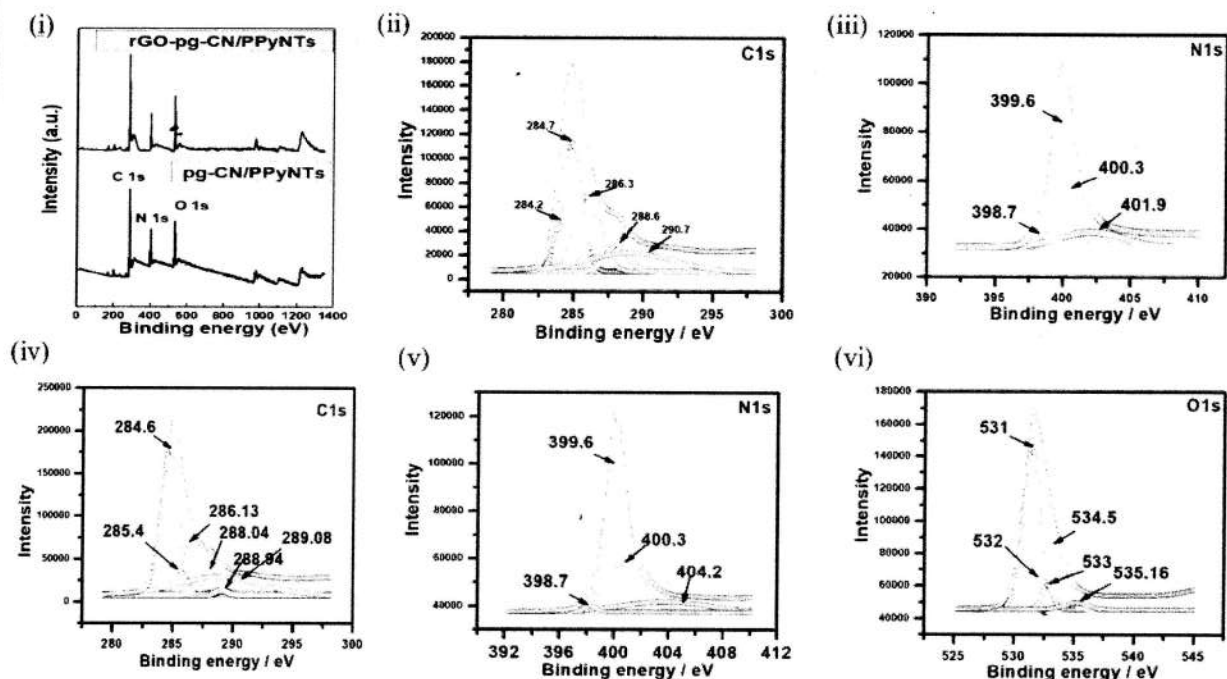
Fig.10: Raman spectra at 785 nm excitation wavelength

#### X-ray Photoelectron Spectroscopy (XPS)

The XPS full scan spectra of binary pg-CN/PPyNTs and ternary rGO-pg-CN/PPyNTs are depicted in figure 11 (i). In the full scan survey of binary nanocomposite pg-CN/PPyNTs, the peaks at 284.4 and 402.3 eV correspond to binding energy of C 1s and N 1s, respectively. The third peak at 531.1 eV arises due to the surface adsorbed CO<sub>2</sub> and H<sub>2</sub>O molecules. C 1s XPS peak of binary (figure 11 ii) is deconvoluted into five peaks obtained at 284.20, 284.7, 286.3, 288.6 and 290.7 eV. The peaks at 284.20 and 284.7 eV are linked to  $\beta$  and  $\alpha$  carbon atoms in the polypyrrole ring i.e. C-C, C-H or C=C. The component



centered at 286.3 eV is due to the =C-N<sup>+</sup> bond of polypyrrole polarons and the fourth component appearing at 288.6 eV is due to C=O species. The fifth component of the binary C1s at binding energy of 290.7 eV corresponds to carbonate group of graphitic carbon nitride. It is reported that for pure pg-CN, three components of C1s are observed at 284.8, 286.4, 288.2 eV corresponding to C-C coordination of surface carbon, C-O from CO<sub>2</sub> adsorbed on the surface and N=C-N<sub>2</sub>, respectively. As the peak positions of C 1s components of pg-CN and PPy are situated at almost same binding energies, the C 1s spectra of the binary composite shows only five prominent peaks due to overlapping of peaks. The XPS spectra of N 1s spectra of binary pg-CN/PPyNTs (figure 11 iii), after deconvolution consists of four components at 398.7, 399.6, 400.3 and 401.9 eV, which may be ascribed to both the graphitic N 1s and PPy N 1s as a result of merging of four component each of pg-CN and PPy. The N 1s peaks of pg-CN arises at these binding energies corresponding to C=N-C, pyridine N group on pyrrole, N-(C)<sub>3</sub> and C-NH, respectively. Again, these peaks also correspond to imine (=N-) structure, neutral nitrogen in the PPy ring i.e. -N-H structures, positively charged nitrogen of polaron (-N-H<sup>+</sup>) and bipolaron (=N-H<sup>+</sup>) species, respectively of PPyNTs. In the ternary nanocomposite rGO-pg-CN/PPyNTs, full scan XPS spectra shows three peaks for C 1s, N 1s and O 1s. Upon deconvolution of C 1s spectra of the ternary nanocomposite, we obtain four peak components at binding energies of 284.6, 285.4, 286.13 and 289.04 eV corresponding to rGO nanosheets. The peak at 284 eV arises due to sp<sup>2</sup> hybridized carbon of rGO and that at 285.4 eV corresponds to sp<sup>3</sup> C atom, whereas the peaks at 286.13 and 289.04 eV are due to C-OH bond and C-OOH of rGO, respectively. XPS spectra of O 1s (figure 11 vi), present in rGO, display the peaks at binding energies of 531, 532.1, 533, 534.5 and 535.16 eV corresponding to different chemical environment of O in C=O, C-OH, C-O-C, C-O bonds and adsorbed water molecules, respectively. N 1s XPS spectra of the ternary nanocomposite rGO-pg-CN/PPyNTs (shown in figure 11 v) show an increase in binding energy of 2.3 eV which implies the stronger attractive interaction between pg-CN and PPyNTs. After compositing with rGO, the 284.2 is shifted to 284.6 eV (figure 11 iv), which may be attributed to increasing interaction between the C 1s environment present in rGO and pg-CN nanosheets or to the increasing interaction between PPyNTs and pg-CN at the β carbon position. The interaction between C environment in rGO and pg-CN nanosheets suggests the formation of rGO-pg-CN heterostructures.



**Figure 11:** XPS spectra of pg-CN/PPyNTs and rGO-pg-CN/PPyNTs nanocomposites. (i) Survey spectra of pg-CN/PPyNTs and rGO-pg-CN/PPyNTs, (ii) C1s spectrum of pg-CN/PPyNTs, (iii) N1s spectrum of pg-CN/PPyNTs, (iv) C1s spectrum of rGO-pg-CN/PPyNTs, (v) N1s spectrum of rGO-pg-CN/PPyNTs, and (vi) O1s spectrum of rGO-pg-CN/PPyNTs

## 7.2 New Observations:

### 7.2.1 Cyclic Voltammetry (CV) studies

The current vs. voltage responses of rGO-pg-CN/PPyNTs/ITO, pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes have been studied with CV measurement and the curves are displayed in Fig. 12 (a - c). The CV patterns of rGO-pg-CN/PPyNTs/ITO,

pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes at the scan rate of 30 mV s<sup>-1</sup> are shown in Fig. 12 (a). It is observed that the capacitive response of pure pg-CN/ITO electrode is very less compared to the binary and ternary electrodes. The integrated area of the CV curve increases for the binary pg-CN/PPyNTs/ITO electrode than that of pure pg-CN/ITO electrodes after incorporation of PPyNTs in pg-CN, which is attributed to the higher storage capacity of the pseudocapacitive material. Moreover, Polypyrrole provides a homogeneous matrix to pg-CN leading to the better dispersion of pg-CN in the binary nanocomposite. Capacitive response has further enhanced for ternary rGO-pg-CN/PPyNTs/ITO electrode after addition of rGO. rGO nanosheets built a conductive network in ternary nanocomposite by lowering the intrinsic resistance of the electrode and hence the current vs. voltage response increases. The CV patterns of pure pg-CN/ITO electrode exhibit nearly rectangular geometry as shown in Fig. 12 (b). The rectangular geometry suggests the presence of EDLC charge storage mechanism in the synthesized proton functionalized pg-CN electrode and therefore possesses lower capacitive behaviour. pg-CN/PPyNTs/ITO electrode possesses quasi-rectangle shaped CV patterns, attributes to both the charge storage mechanisms i.e. EDLC from pg-CN and pseudocapacitive from polypyrrole nanotubes. The CV curves of ternary rGO-pg-CN/PPyNTs/ITO electrode at the scan rate range of 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup> are shown in the Fig. 12 (c). The ternary electrodes also possess quasi-rectangular geometry at smaller as well as high scan rates, suggesting the presence of good reversibility in the electrode material.

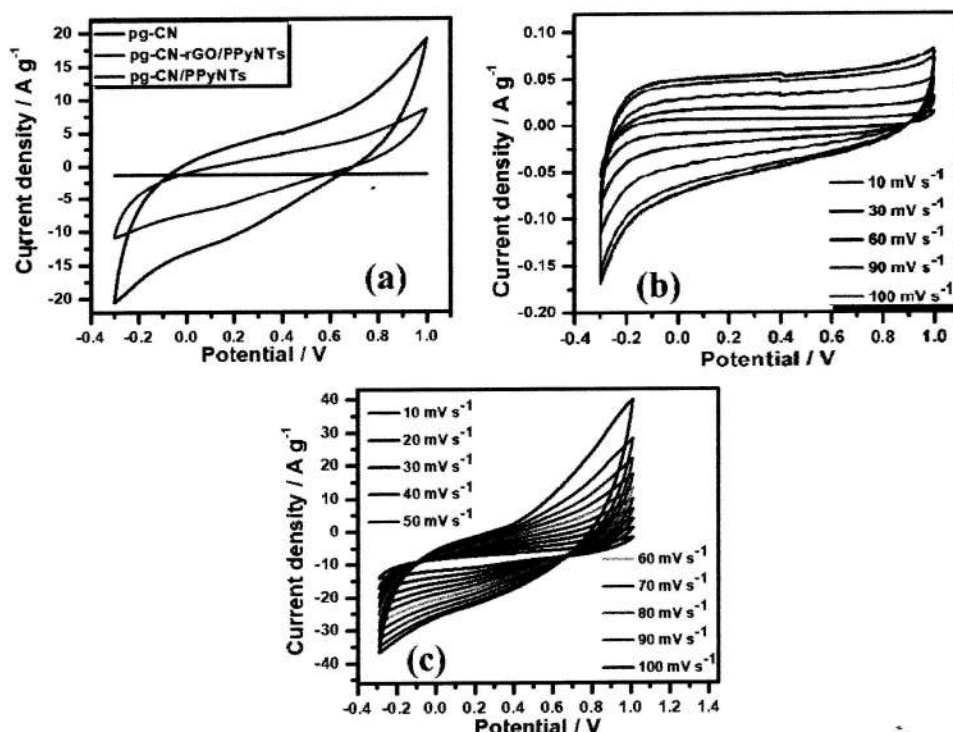


Fig. 12: Cyclic voltammetry measurements in 1 M KCl electrolyte (a) rGO-pg-CN/PPyNTs/ITO, binary pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes at scan rate of 30 mV s<sup>-1</sup>, (b) pure pg-CN/ITO electrode at different scan rates, and (c) rGO-pg-CN/PPyNTs/ITO electrode at scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV s<sup>-1</sup>.

### 7.2.2 Galvanostatic charge-discharge (GCD) measurements

The GCD graphs of the synthesized electrodes are depicted in Fig. 13. Figure 13 (i) illustrates the GCD patterns of rGO-pg-CN/PPyNTs/ITO, pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes at specific current of 0.5 A/g in 1 M potassium chloride. pg-CN/ITO electrode exhibits an almost triangular shaped GCD pattern by maintaining linearity both in charging and discharging curves. Linearity in the GCD pattern confirms the presence of EDLC charge storage mechanism in pure g-C<sub>3</sub>N<sub>4</sub>,

which supports the results obtained from CV measurements. The GCD curve of pg-CN/PPyNTs/ITO electrode is linear in the beginning for both charging and discharging, followed by deviation from linearity. This kind of behaviour is usually observed due to the presence of both EDLC and pseudocapacitance charge storage mechanisms. The discharge duration increases for the binary electrode than that of pristine g-C<sub>3</sub>N<sub>4</sub> after incorporation of the pseudocapacitive component PPyNTs. pg-CN nanosheets disperse uniformly in the PPyNTs matrix, resulting in enhanced discharge duration due to increased number of electroactive sites in the binary electrode. Appearance of quasi-equilateral triangular geometry in the GCD pattern of rGO-pg-CN/PPyNTs/ITO electrode after incorporation of rGO suggests the increasing contribution of EDLC mechanism in the ternary electrode in comparison to the binary one. The discharge period is further enhanced for ternary rGO-pg-CN/PPyNTs/ITO electrode after incorporation of rGO. rGO-pg-CN heterostructures prevent the agglomeration of both the nanosheets and provide larger surface area leading to enhanced electroactive sites in the ternary nanocomposite. The increasing galvanostatic discharge duration for the ternary electrode is because of the increasing S<sub>BET</sub> and mesoporous nature of ternary nanocomposite, as observed from BET measurements, which leads to the enhanced specific capacitance, C<sub>sp</sub>. The C<sub>sp</sub> of the synthesized electrodes have been calculated using the following relation:

$$C_{sp} = \frac{I \times \Delta T_d}{m \times \Delta V} \quad (1)$$

where,  $I$ ,  $\Delta T_d$ ,  $m$ , and  $\Delta V$  are discharging current, discharge duration, mass loaded on the electrode and potential window of discharging. Pure pg-CN/ITO delivers capacitance of 14.6 F g<sup>-1</sup>, as only EDLC mechanism is operative. The calculated specific capacitances for binary pg-CN/PPyNTs/ITO and ternary rGO-pg-CN/PPyNTs/ITO electrodes are 480 and 803 F/g, respectively. Increase in the capacitance value for the nanocomposites is due to: (i) larger surface area of the nanocomposites provide higher concentration of electroactive sites for redox reaction at the surface of the electrode and the presence of mesopores help in the easy penetration of electrolyte ions into the electrode surface, (ii) uniform dispersion of pg-CN in the PPy matrix provide a homogeneous distribution of electroactive sites, (iii) rGO-pg-CN heterostructures prevent the agglomeration of both the nanosheets in the ternary nanocomposites, leading to maximum usage of electrode surface area.

The efficiency of an electrode is presented as coulombic efficiency ( $\eta$ ) according to the following equation:

$$\eta = \frac{\Delta T_d}{\Delta T_c} \times 100 \quad (2)$$

where,  $\Delta T_c$ ,  $\Delta T_d$  are charging and discharging period in the GCD curves. Pure pg-CN/ITO electrode exhibit almost 100% coulombic efficiency, which is attributed to the presence of EDLC charge storage with almost ideal CV and GCD curves. rGO-pg-CN/PPyNTs/ITO and pg-CN/PPyNTs/ITO electrodes exhibit coulombic efficiency of 98% and 99%, respectively. Irreversible or quasi-reversible faradic processes in the polymer chain are the cause of lower coulombic efficiency in the binary and ternary electrodes. Energy density and power density are two important supercapacitor performance parameters and calculated as below:

$$\text{Energy density, } E = \frac{1}{2} C_{sp} (\Delta V)^2 \quad (3)$$

$$\text{Specific power, } P = \frac{E \times 3600}{T_{dis}} \quad (4)$$

where,  $C_{sp}$  is the specific capacitance,  $\Delta V$  is potential window during discharge and  $T_{dis}$  is the discharge duration. Pure pg-CN/ITO electrode exhibits specific energy of 3.43 Wh/kg and specific power of 324.4 W/kg at 0.5 A/g current density. pg-CN/PPyNTs/ITO electrode possesses specific energy and power of 112.67 Wh/kg and 324.5 W/kg, respectively at 0.5 A/g

density of current. Ternary rGO-pg-CN/PPyNTs/ITO electrode offers specific energy of 188.49 Wh/kg and specific power of 324.83 W/kg at 0.5 A/g density of current. Rate capabilities of the synthesized samples have been evaluated in order to understand the capacitive retention at higher current densities. GCD curves of pg-CN/ITO, pg-CN/PPyNTs/ITO and rGO-pg-CN/PPyNTs/ITO electrodes at different current densities are depicted in the Fig. 13 (ii-iv). GCD patterns of binary and ternary electrodes exhibit both linear and non-linear components attributed to the EDLC contribution from rGO and pg-CN and faradic reactions at the polymer backbones, respectively. It is observed that the discharge duration decreases with the increase in current density and accordingly the specific capacitance decreases. The plot of specific capacitance vs. current densities is displayed in Fig. 13 (v). The lower value of specific capacitance at higher current density is attributed to the low ion penetration to the electrode surface as compared to that of low current density, which is a typical supercapacitor behaviour. Transport of ions to the active sites is completed within a short time due to high rate of polarization at higher current density which minimizes the faradic processes at the interface of electrode-electrolyte. pg-CN/ITO, pg-CN/PPyNTs/ITO and rGO-pg-CN/PPyNTs/ITO electrodes exhibit rate capability of 37%, 59% and 61%, respectively at 7-fold of current density. It is observed that pure pg-CN electrode with EDLC charge storage mechanism exhibits higher rate capability than that of binary pg-CN/PPyNTs electrode. Ternary rGO-pg-CN/PPyNTs electrode shows rate capability of 61%, which is favored by (i) presence of rGO greatly improves the electrode conductivity and (ii) interfaces between the rGO - pg-CN heterostructures and the mesopores present in the ternary nanocomposite which reduces the electrolyte dynamic resistance within the pores. To demonstrate the overall performances of the synthesized electrodes, Ragone plot is shown in Fig. 13 (vi). It is observed that pg-CN/ITO electrode possesses typical supercapacitor behaviour with high power density of 4543.1 W kg<sup>-1</sup> and low energy density of 1.28 Wh kg<sup>-1</sup> at 7-fold of current density. Increased energy density of 66.9 Wh kg<sup>-1</sup> for the binary and of 115.02 Wh kg<sup>-1</sup> for the ternary electrodes are obtained while retaining high power density of ~ 4,550 W kg<sup>-1</sup> at 7 A g<sup>-1</sup> current density.

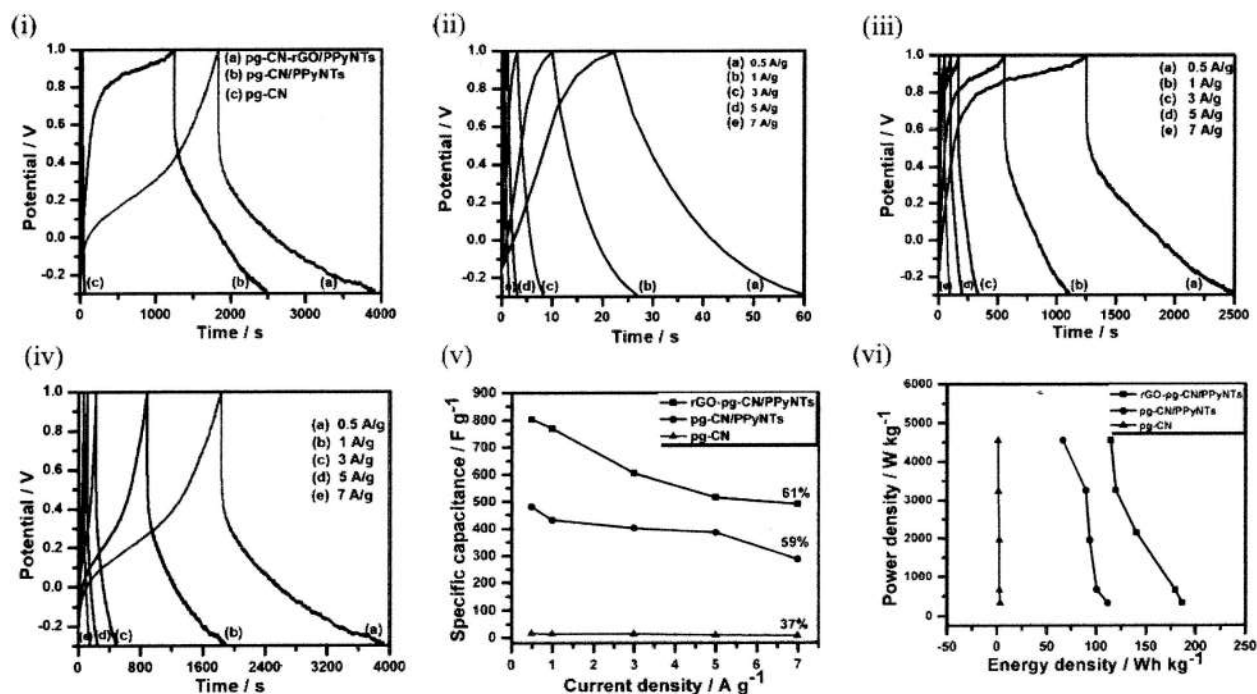


Fig. 13: GCD measurements of (i) rGO-pg-CN/PPyNTs/ITO, binary pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes at current density of 0.5 A/g, (ii) pg-CN/ITO at current densities of 0.5, 1, 3, 5, and 7 A/g, (iii) pg-CN/PPyNTs/ITO at current densities of 0.5, 1, 3, 5, and 7 A/g, (iv) rGO-pg-CN/PPyNTs/ITO electrode at current densities of 0.5, 1, 3, 5, and 7 A/g, (v) Specific capacitance vs. current densities and (vi) Ragone plot of rGO-pg-CN/PPyNTs/ITO, binary pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes.

### 7.2.3 Cycling Stability Analysis:

Longer cycle life is required for electrochemical supercapacitors. Cycling stability of rGO-pg-CN/PPyNTs/ITO, pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes has been evaluated for 5000 repeated GCD cycles in 1 M potassium chloride electrolyte within the potential window of -0.3 V to 1 V at 7 fold of current density. Retention of specific capacitance vs. cycle number is displayed in Fig. 14. pg-CN/ITO electrodes show 94.6%, 94% and 92 % of cycling stability after 2000, 4000 and 5000 GCD cycles, respectively, which is attributed to the presence of EDLC charge storage mechanism without the involvement of any chemical reactions. 86.9%, 73.2%, and 69.5% cycling stability of binary pg-CN/PPyNTs/ITO electrodes correspond to 2000, 4000 and 5000 repeated GCD cycles. Faster degradation of cycling stability of the binary electrode after 2000 cycles is attributed to the swelling and shrinkage in the polymer due to continuous insertion and desorption of electrolyte ions, which weakens the mechanical strength of the supercapacitor electrode. Ternary rGO-pg-CN/PPyNTs/ITO electrode possesses cycling stability of 96.4%, 94.1%, 88%, and 82.8% after 1000, 2000, 4000, and 5000 repeated GCD cycles. The obtained cycling stability of the ternary electrode is due to: (i) porous nature of the nanocomposite can accommodate volumetric changes occurring in the polymer chain which helps in mitigating the mechanical strength of the supercapacitor electrode, (ii) increasing the EDLC components i.e. both the presence of rGO and pg-CN as well as EDLC charge storage contribution to the overall specific capacitance at higher current density (7 A/g) improves cycling stability of the ternary electrode than that of the binary one, (iii) minimum dissolution of electrode material due to the usage of neutral electrolyte (1 M KCl) as the solution used in electrochemical cell remains transparent after 5000 GCD cycles also.

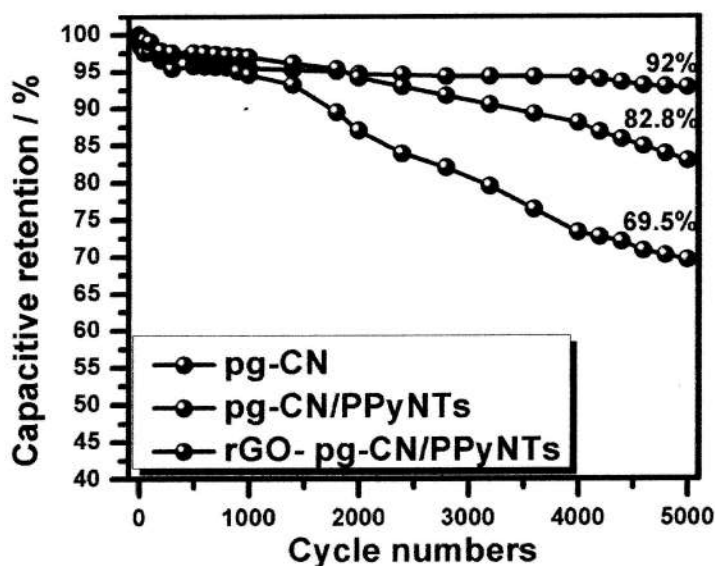


Figure 14: Capacitive retention vs. cycling stability for rGO-pg-CN/PPyNTs/ITO, binary pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes at 7 fold current density in 1 M KCl electrolyte.

### 7.2.4: Electrochemical impedance spectroscopy (EIS) studies:

EIS is an important analytical method to study the supercapacitor parameters. The Nyquist plots of rGO-pg-CN/PPyNTs/ITO, pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes are shown in Fig. 15. Frequency range used for EIS study is 0.1 Hz to  $10^6$  Hz. Nyquist plots of all electrodes exhibit a semi-circular arc towards the higher frequency side followed by a straight line towards the lower frequency. The intercept of the semicircle in the real axis at high frequency region known as equivalent series resistance (ESR), is an important supercapacitor characteristic. Lower value of ESR indicates high conductivity of the electrode. Pure pg-CN/ITO electrode exhibits ESR of 29  $\Omega$  in 1 M KCl electrolyte. pg-CN/PPyNTs/ITO electrode exhibits

lower ESR of  $14.6 \Omega$ , which is attributed to the homogeneous dispersion of pg-CN in polypyrrole matrix. ESR further decreases to  $9.8 \Omega$  for ternary rGO-pg-CN/PPyNTs/ITO electrode due to incorporation of rGO which reduces the electrode resistance. Moreover, the layer-by-layer structure of rGO-pg-CN provides higher number of electro-active sites by preventing the agglomeration of pg-CN and rGO nanosheets. The diameter of the semicircle gives charge transfer resistance ( $R_{ct}$ ), which appears due to electric double layer capacitance and redox processes at the electrode/electrolyte interfaces. Charge transfer resistance is found to be  $147 \Omega$  for pure pg-CN electrode and decreases for the binary ( $51 \Omega$ ) and ternary ( $34 \Omega$ ) electrode. Lower value of  $R_{ct}$  may be attributed to the shorter diffusion paths of the electrolyte ions and increased number of interfaces in the rGO-pg-CN heterostructures. The semi-circular arc is followed by  $45^\circ$  spike, called Warburg impedance appears for pure pg-CN/ITO electrode, suggesting frequency dependent ions transportation processes from the electrode to the electrolyte. For binary and ternary electrodes, slope of the complex spectra appears after the semicircle at lower frequency is close to  $90^\circ$ , which is responsible for the ideal capacitive behaviour of the electrodes.

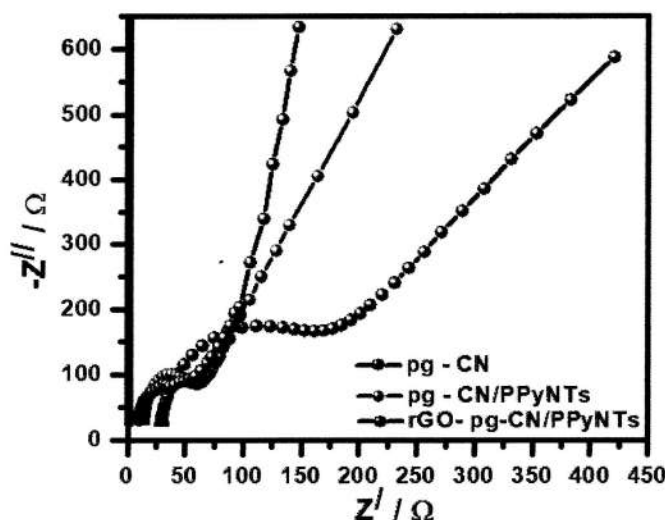


Figure 15: Nyquist plot for rGO-pg-CN/PPyNTs/ITO, binary pg-CN/PPyNTs/ITO and pg-CN/ITO electrodes in 1 M KCl electrolyte

#### 7.2.5: Assembly of symmetric supercapacitor (SC) device:

To have an idea about the practical implementation of rGO-pg-CN/PPyNTs as a supercapacitor electrode, we assembled a symmetric supercapacitor by using rGO-pg-CN/PPyNTs as the positive and negative electrodes with 1 M KCl solution as the electrolyte. Cyclic voltammetry of rGO-pg-CN/PPyNTs SC device has been performed to optimize the potential window (fig. 16 (i)). Among different potential windows (0-0.9), (0-1.0), (0-1.1), and (0-1.2); it is observed that the area under the curve remains the same for the windows 0.9 and 1 V with quasi-rectangular shape, implying pseudocapacitive behavior. However, when the window increased from 1 V, the area under the CV curve decreased, suggesting reduced capacitive response, may be due to the degradation of the polymer chain at higher potential. As shown in fig. 16 (ii), the shape of CV curve does not change much with scan rate, implying redox ability of the SC device. The optimized potential window of the assembled device is around 1 V, as the capacitive response degrades beyond that, which is mainly because of the degradation of the PPyNTs. The GCD curves of rGO-pg-CN/PPyNTs SC device (depicted in fig. 16 (iii)), are nearly linear in both charging and

discharging processes, due to the presence of EDLC contributing pg-CN and rGO nanosheets. The discharging time of the SC device decreases with increase in current density, leading to reduction of specific capacitance. A specific capacitance of 232.21 F/g is obtained at 0.5 A/g current density. The retention of specific capacitance value of SC device to 71.52 F/g even at higher current density (4 A/g) suggests rGO-pg-CN/PPyNTs to be an excellent and stable SC electrode. The Ragone plot reflects the SC device performance in terms of energy density and power density. As depicted in fig. 16 (iv), rGO-pg-CN/PPyNTs SC device delivers an energy density of 8.063 Wh/kg and power density of 125.002 W/kg at 0.5 A/g current density. However, at higher current density of 4 A/g, the energy density gets reduced to 2.483 Wh/kg at a power density of 999.89 W/kg.

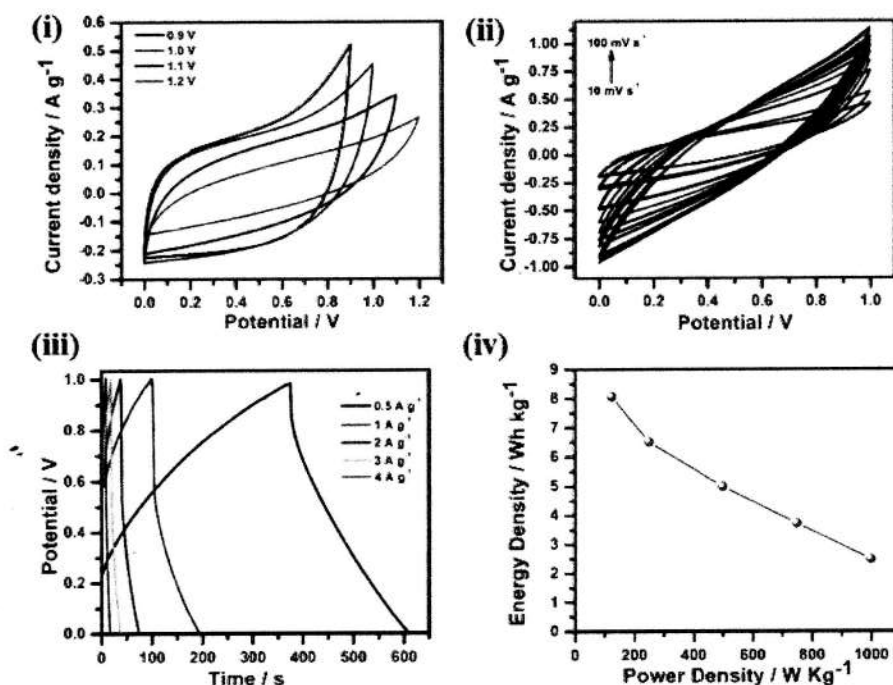


Figure 16: Cyclic voltammetry measurement of rGO- pg-CN/PPyNTs SC device in 1Molar potassium chloride electrolyte at (i) potential window of 0.9, 1.0, 1.1 and 1.2 V, (ii) different scan rate, (iii) GCD curves of rGO- pg-CN/PPyNTs SC device at different current densities, (iv) Ragone plot of the rGO- pg-CN/PPyNTs symmetric SC device.

### 7.3 Application Potential:

Conducting polymer, graphitic carbon nitride and rGO based ternary nanocomposite have also been found to be an excellent candidate for photocatalytic reduction of carbon dioxide to methane, catalyst for Oxygen Electrode of High Rate Rechargeable Li-O<sub>2</sub> Cells, decomposition of organic pollutants like phenol, MB, MO, RhB under visible light, etc.

Ph.D.s Produced no.	Technical Personnel trained	Research Publications arising out of the present project
<b>01 (Registered for Ph.D.)</b>	<b>02</b>	<b>03</b>

List of Publications from this Project (including title, author(s), journals & year(s))

(A) Papers published only in cited Journals (SCI):

1. Devalina Sarmah, Ashok Kumar, "Layer-by-layer self-assembly of ternary MoS<sub>2</sub>-rGO@PPyNTs nanocomposites for high performance supercapacitor electrode", Synthetic Metals 243 (2018) 75–89.

DOI:10.1016/j.synthmet.2018.06.001. (I.F. 2.52)

2. Devalina Sarmah, and Ashok Kumar, "Ion beam modified molybdenum disulfide-reduced graphene oxide/polypyrrole nanotubes ternary nanocomposite for hybrid supercapacitor electrode." *Electrochimica Acta*, 312 (2019) 392 - 410. DOI: 10.1016/j.electacta.2019.04.174. (I. F. 5.38)
3. Aditi Saikia, Devalina Sarmah, Ashok Kumar, and Niranjana Karak, "Bio-based epoxy/polyaniline nanofiber-carbon dot nanocomposites as advanced anticorrosive materials." *Journal of Applied Polymer Science* (2019): 47744. DOI: 10.1002/app.47744. (I. F. 1.86).
4. Kashmiri Baruah, Devalina Sarmah, and Ashok Kumar, "Ternary Hybrid Nanocomposites of Polypyrrole Nanotubes with 2D Self-assembled Heterostructures of Protonated g-C<sub>3</sub>N<sub>4</sub>-rGO as Supercapacitor Electrodes", *Journal of Ionics* (under review).

(B) (i) Papers published in Conference Proceedings, Popular Journals etc.:

1. Devalina Sarmah, Ashok Kumar, "Electrochemical Behaviour of Ternary MoS<sub>2</sub>/rGO Heterostructure and PPyNTs Nanocomposites for Supercapacitor Electrode", XI Biennial National Conference of Physics Academy of North East (PANE), In *Journal of Physics: Conference Series* (In press).

(ii) Papers presented in Conference:

1. Devalina Sarmah, Arati Sharma and A. Kumar, "Studies of Structural and Dielectric properties of IL functionalized Polypyrrole", National Conference on Hard and Soft Condensed Matter Physics, 2-4 March, 2017.
2. Devalina Sarmah, Ashok Kumar, "Development of MoS<sub>2</sub>-rGO@PPyNTs nanocomposites for Supercapacitor application", International conference on emerging trends in chemical sciences, Dibrugarh University, Assam, India, February 26-28, 2018.
3. Devalina Sarmah, Ashok Kumar, O<sup>7+</sup> Swift-heavy ions irradiation effects on MoS<sub>2</sub>-rGO@PPyNTs nanocomposite for Supercapacitor Applications, International conference on Renewable and Alternate Energy (ICREA), Assam Science and technology University, Guwahati, India, December 4 - 6, 2018.
4. Devalina Sarmah, Ashok Kumar, Layered Molybdenum Disulfide (MoS<sub>2</sub>) - reduced graphene oxide (rGO) / Polypyrrole nanotubes (PPyNTs) based ternary nanocomposites for hybrid supercapacitor electrode, Second National Conference on Hard and Soft Condensed Matter Physics (NCHSCMP), Tezpur University, Assam, India, March 4 - 6, 2019.
5. Kashmiri Baruah, Devalina Sarmah, Ashok Kumar, "Self-assembly of rGO-pgC<sub>3</sub>N<sub>4</sub> nanosheets decorated by polypyrrole nanotubes (PPyNTs) for supercapacitor application", International conference on advanced nanomaterials and nanotechnology (ICANN2019), Centre for nanotechnology, IIT Guwahati, India, December 18-21, 2019.

Patents filed/to be filed: Nil

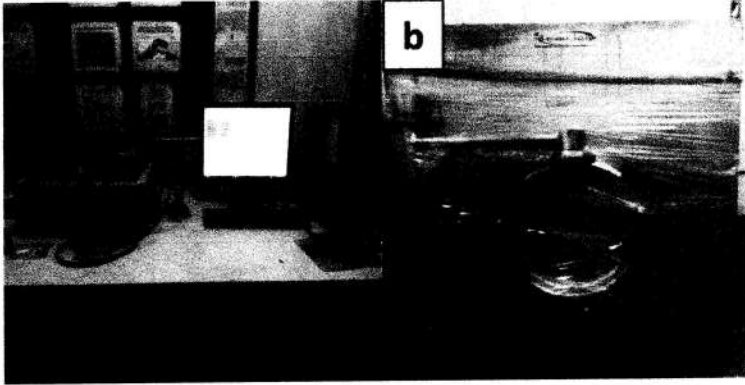
**Major Equipments (Model and Make)**

Sl. No	Sanctioned List	Procured (Yes/No) Model & make	Cost (Rs in lakhs)	Working (Yes/No)	Utilization Rate (%)
1	Electrochemical Workstation AUTO-LAB 302N Modular Potentiostat/ Galvanostat	FRA32M Module/ Kanaalweg 29/G, 3526 KM Utrecht.	24,84,829.50 INR (Foreign component)	Yes	80%
2	High Temperature Vacuum Furnace	Furnace Tech	2,00,000.00 INR	Yes	60%
3	Minor equipments (Magnetic Stirrer, Autoclave, Ice-bath)	Lakshmi Engineering Industries, Antech, Zenith India	88,680.00INR	yes	90%



Upload Images of equipment's:

Major Equipment:



Minor Equipment:

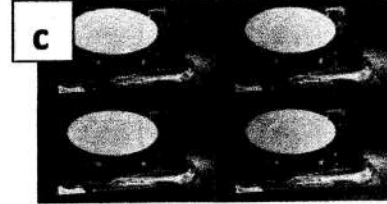


Fig 17: photographs of equipments installed in Material Research Laboratory (MRL), Tezpur University. (a)Electrochemical Workstation (Metrohm India Limited), (b)High Temperature Vacuum Furnace (Furnace Tech Pvt. Ltd.), (c) Magnetic Stirrer (Antech Pvt. Ltd) and (d) Autoclave (Lakshmi Engineering Pvt. Ltd.)