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# One-step fabrication of poly(aniline-co-2,5 dimethoxyaniline) nanohybrid coated graphitic sheet electrode for efficient energy application

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## HIGHLIGHTS

- Facile preparation of copolymer of poly(aniline-2,5-dimethoxyaniline) nanocomposite.
- PANI-PDMA nanocomposite coated graphite sheet (GS) electrode was fabricated.
- A simple electrochemical deposition method was applied for electrode fabrication.
- GS@PANI-PDMA nanocomposite shows a significant specific capacitance 595 F/g.
- Energy density and power density were 52.8 W h kg<sup>-1</sup> and 399 W kg<sup>-1</sup>.

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## ABSTRACT

In this study, a facile one-step homogeneous electrochemical deposition method was utilized to fabricate poly(aniline-2,5-dimethoxyaniline)co-polymer (PANI-PDMA) nanocomposite coated on the surface of graphite sheet (GS) electrode for an effective high-performance supercapacitor application. Physio-chemical characterizations were examined using FT-IR, XRD, and energy-dispersive X-ray spectroscopy (EDX) techniques. The morphological view of as-synthesized copolymer nanocomposite was characterized using the FE-SEM technique. Electrochemical investigation of the as-fabricated modified electrode (GS/PANI-PDMA) was studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charging and discharging (GCD) studies.

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Polyaniline  
Poly 2,5-dimethoxyaniline  
Graphite sheet electrode  
Supercapacitor  
Green energy

Based on electrochemical studies, GS/PANI-PDMA modified co-polymer electrode shows a high specific capacitance of 595 F/g compared to GS@PANI and GS@PDMA. After 1000 cycles, it indicates 67% capacitance retention, which is indicated to be a potential alternative material for supercapacitor application.

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## Introduction

In recent years, electrochemical energy storage devices have been developed as a possible solution to the global problem of energy shortages and environmental concerns [1–3]. Because of their high-power delivery capabilities, fast charging-discharge rate, and low cost, Supercapacitors have played a significant role in energy storage for a long time. Electric double-layer capacitances (EDLC) are used to store electrochemical energy in carbon-based materials such as graphene, carbon nanotubes, and biocarbon. In contrast, pseudocapacitors are used to store energy in transition metal oxides, sulfides, and conducting polymers that rely on reversible surface Faradaic reactions [4–7].

Polyaniline, polydiphenylamine, poly(2,5-dimethoxyaniline), and polypyrrole are conducting polymers playing important roles in supercapacitors, fuel cells, and sensors, etc., electrocatalysts, and other applications that have sparked the scientific community's interest [8–14]. Conducting polymers including polyaniline, polypyrrole, polythiophene, and their derivatives, have been widely studied as pseudocapacitive materials [15,16] because they have higher theoretical capacitance than their inorganic counterparts of transition metal oxides and sulphides and can be processed more easily to fabricate flexible devices. As one of the most intriguing conducting polymers, Polyaniline has piqued the scientific community's interest due to its low cost, environmental stability, ease of chemical or electrochemical synthesis, and changeable mechanical, electric, and optical properties for several applications [17].

Copolymerization with other aniline derivatives is one method for increasing polyaniline's collective characteristics [18–20]. Furthermore, because it has different redox peaks (leucoemeraldine, emeraldine base, and pernigraniline) and high theoretical capacitive characteristics (2000 F/g), PANI plays a vital role in electrochemical capacitors (ECs) and provides pseudocapacitive behaviour [21]. Selecting appropriate side substituents on polyaniline could increase the polyaniline's solubility, processibility, and conductivity, as well as prolong the overall delocalized system to some extent. Liang et al., reported the chemically oxidizing aniline and pyrrole to form polyaniline/polypyrrole composite nanofibers with core-shell architectures and achieved maximum specific capacitances of up to 346 F g<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup>. Muthu et al., reported the synthesis of poly(aniline-co-m-anilic acid) by chemical oxidation polymerization method, and the specific capacitances reached up to 102 F g<sup>-1</sup> at a scan rate of 10 mV s<sup>-1</sup>, and Angélica et al., prepared Poly(diphenylamine-co-aniline) copolymers via oxidative polymerization in a

water/ethanol interfacial system, which showed a specific capacitance of 341.93 F g<sup>-1</sup> at 1 Ag<sup>-1</sup>. Based on the literature report conducting polymer, especially in the form of copolymer has better supercapacitive behaviour [22–24]. In current research, Poly(2,5-dimethoxyaniline) is a polyaniline derivative with an electron-donating methoxy group as a side substituent to boost the polymer's solubility [25–27]. According to the above studies, PANI and its derivatives serve as an excellent electrochemical performance towards supercapacitor applications.

A copolymer is a polymer made up of two or more distinct monomer units. When compared to their parent monomers, copolymers have synergistic qualities. Co-polymerization allows us to manage the chemical structure, composition, polarity, solubility, and hydrophobic/hydrophilic balance of monomers that can't be polymerized through homopolymerization because the optical and electrical properties of copolymers are intermediate between the monomers, they can be fine-tuned by changing their molar ratios. The relative abundance of individual units in copolymer chains is more important than their specific position in chains, keeping in mind that copolymer formation is unpredictable [28,29].

In this work, a simple electrodeposition approach was applied to fabricate a novel poly(aniline-2,5-dimethoxyaniline) (PANI-PDMA) copolymer nanocomposite coated on graphite sheet (GS) electrode for efficient supercapacitor application. The morphology and structural analyses of the manufactured PANI-PDMA copolymer nanocomposite are examined by field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) examinations, elemental mapping, X-ray diffraction pattern, and Fourier transforms infrared (FT-IR) analysis. The electrochemical behaviour of produced PANI-PDMA copolymer nanocomposite was investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD) experiments. The schematic diagram of GS@PANI-PDMA copolymer electrode for supercapacitor application (Fig. 1). The PANI-PDMA copolymer nanocomposite modified electrode demonstrated enhanced electrochemical performance for supercapacitor applications.

## Experimental section

### Materials

Graphite sheets (GS) were purchased from Graphite India Limited. Aniline (≥99.5%), 2,5 di-methoxyaniline (≥98%), and H<sub>2</sub>SO<sub>4</sub> (98.0%) were purchased from Merck Chemicals (India). Deionized water was used throughout the experiments.

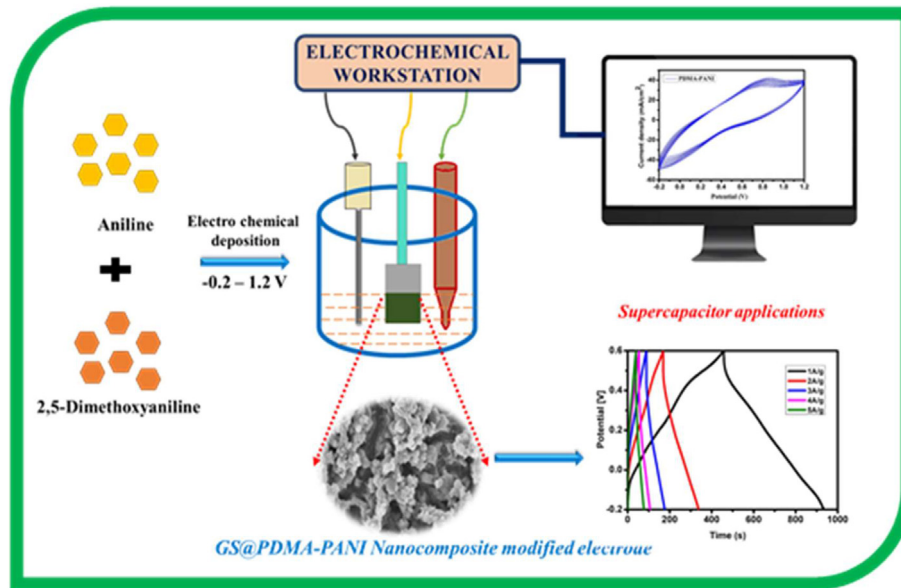


Fig. 1 – The schematic diagram of modified GS@PANI-PDMA copolymer nanocomposite electrode towards supercapacitor application.

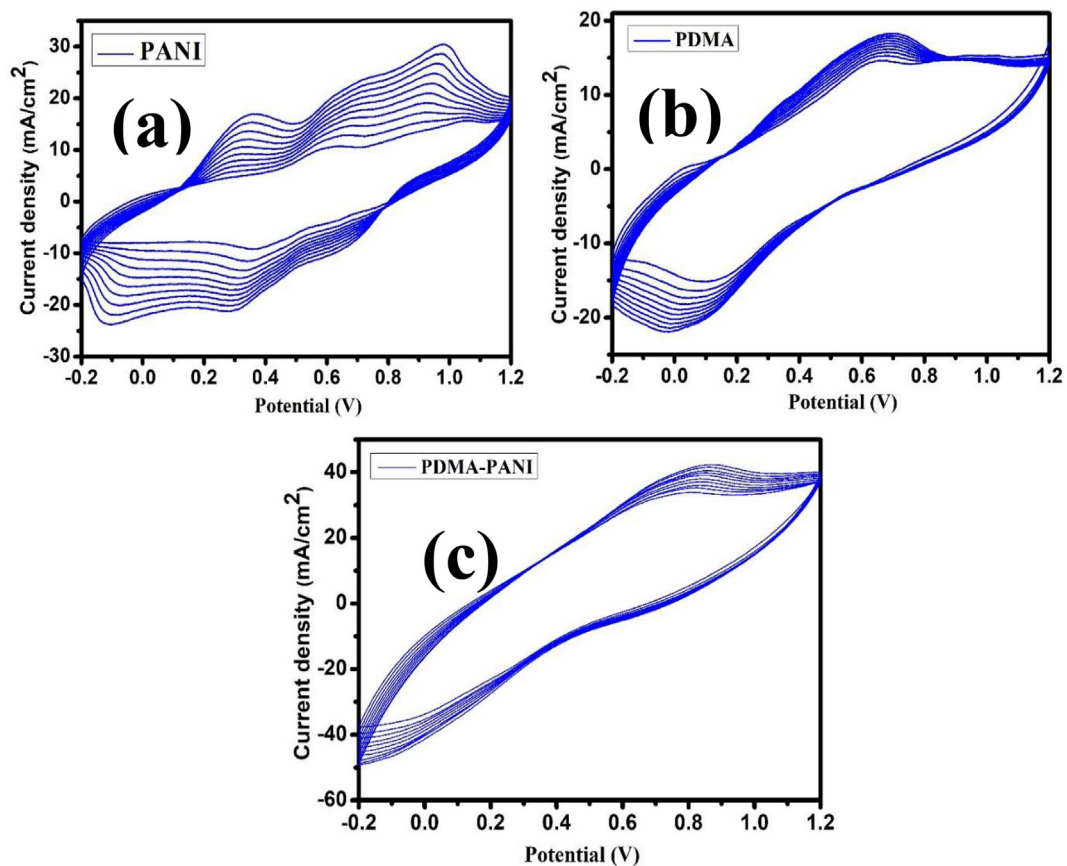
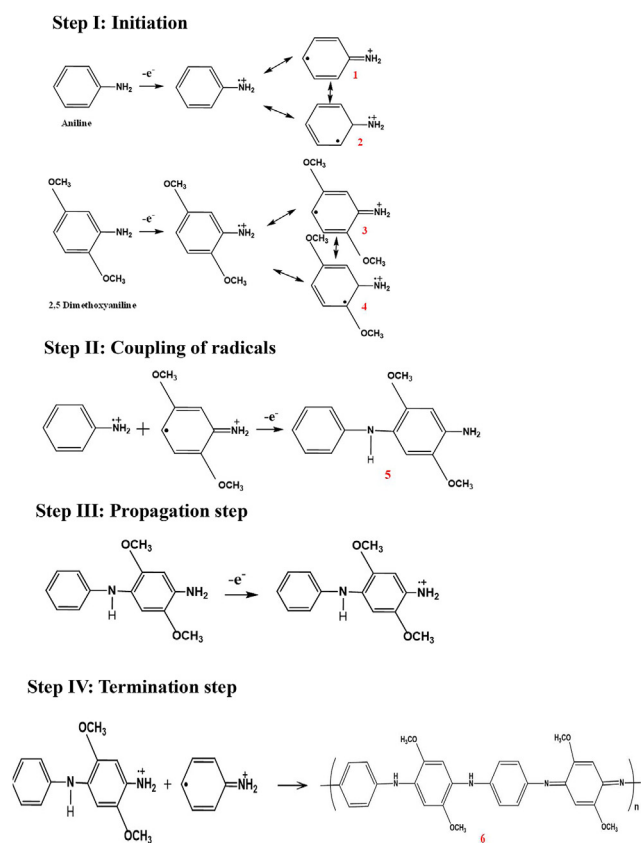


Fig. 2 – Electrochemical deposition of cyclic voltammety curve of (a) PANI (b) PDMA, and (c) (PANI-PDMA) nanocomposite synthesis.



**Fig. 3 – Mechanism of PANI-PDMA copolymer nanocomposite synthesis.**

### Physicochemical and electrochemical characterization

The structural characterization of GS@PANI-PDMA copolymer-modified electrode materials was analyzed using Siefert powder X-ray diffractometer (XRD, Richard Seifert, and Co., Ahrensburg, Germany) with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The molecular vibration spectra in the range of 4000 to 500  $\text{cm}^{-1}$  were recorded on the IR Affinity-1 Shimadzu spectrophotometer (Kyoto, Japan). The internal and surface morphology view of prepared copolymer electrode material was analyzed using a thermionic FESEM with 15.0 kv as an accelerated voltage. Electrochemical measurements were performed using OrigaLys-OFG500 electrochemical workstation (Made in France). Three electrode systems consisting of a working electrode GC@PANI-PDMA fabricated electrode, Ag/AgCl as a reference electrode, and platinum wire (OrigaLys) as a counter electrode were used in all electrochemical techniques experiments.

### Fabrication of GS@PANI-PDMA copolymer nanocomposite-modified electrode

A simple electrochemical co-deposition approach was used to fabricate a modified GS@PANI-PDMA electrode. Electrodeposition of GS@PANI-PDMA was carried out using aniline, and 2,5-dimethoxyaniline of 40 mM was dissolved in 0.5 M  $\text{H}_2\text{SO}_4$ . GS substrate was dipped into that solution. The potential window of  $-0.2$  V– $1.2$  V potential (vs Ag/AgCl as a reference electrode) was applied to the working electrode

with a scanning rate of  $100 \text{ mVs}^{-1}$  for 10 cycles. The resulting electrode of PANI-PDMA co-deposited onto the GS substrate (GS@PANI-PDMA) was obtained and allowed to dry at room temperature. The same procedure was followed for the GS@PANI and GS@PDMA as electrolyte solution in an acidic medium (Fig. 2).

### Mechanism

The electrochemical synthesis, i.e., the electro-polymerization of PANI-PDMA, follows a four-step process such as initiation, coupling of radicals, propagation, and termination steps [30–33]. Step I is the initial step of the electrochemical copolymerization in which cationic radicals were formed. In the initiation step, the aniline radical and dimethoxy aniline radical were produced with their respective resonant structures (para (1) and ortho (2) position of ANI and para (3) and ortho (4) position of DMA) in the initial initiation reaction with aniline and dimethoxy aniline. The generated aniline and dimethoxy aniline radicals were then involved in a coupling process to create the appropriate dimer structure (4-amino-2,5-dimethoxydiphenylamine) in the second stage (5). After which, the dimer structure underwent additional interaction with another para position radical cation, and the reaction was advanced to the next phase propagation to form a dimer radical. Finally, the generated radicals were polymerized to form a copolymer of polyaniline-2,5-dimethoxyaniline (6). The possible mechanism of PANI-PDMA synthesis is shown in Fig. 3.

## Result and discussions

### Morphology and elemental analysis

The PANI, PDMA, and PANI-PDMA copolymer nanocomposites were synthesized by the electrochemical deposition method. The morphology of homopolymers and copolymers were shown in Fig. 4(a–c). Fig. 4 (a) PANI shows nanotube network-like morphology with an average diameter of 100 nm and (b) PDMA shows the morphology of agglomerated network of nanoparticles with an average diameter of 250 nm, and (c) PANI-PDMA copolymer nanocomposite depicts the interconnection of the nanotube network structure of PANI with the agglomerated network of PDPA nanoparticles.

The copolymer of PANI and PDMA is interconnected by  $\pi$ - $\pi$  interactions, electrostatic interactions, and hydrogen bonding. The self-assembly characteristic of the PANI and PDPA accounts for this morphology of the PANI-PDPA copolymer.

The elemental composition of (a) PANI, (b) PDMA, and (c) PANI-PDMA copolymer nanocomposite was confirmed using the FESEM's energy dispersive X-ray (EDX) spectroscope with mapping, as shown in Fig. 5. Fig. 5 (i-iii) shows the elements (Carbon, nitrogen, oxygen) and the atomic percentage of the PANI, PDMA, and PANI-PDPA copolymer nanocomposite. Fig. 5 (i) displays that PANI contains carbon (C- 50.35%), nitrogen (N- 32.50%), oxygen (O – 17.15%), and its mapping (a-d) images, respectively. Fig. 5 (ii) illustrates PDMA containing carbon (C – 53.26%), nitrogen (N – 35.11%), oxygen (O – 11.62%), and its mapping (e-h) images, respectively, and Fig. 5 (iii) depicts



PANI-PDMA copolymer nanocomposite contains carbon (C – 58.57%), nitrogen (N – 30.52%), oxygen (O – 10.90%), and its mapping (i-l) images, respectively.

#### FT-IR and XRD studies

FT-IR spectroscopy was used to investigate the vibrational studies of the chemical compound. The infrared spectra of (a) PANI, (b) PDMA, and (c) PANI-PDMA copolymer nanocomposite in the range of 500–4000  $\text{cm}^{-1}$  are shown in Fig. 6. In the FT-IR spectra, Fig. 6 (a) PANI has a peak at 3693  $\text{cm}^{-1}$ , which is ascribed to the N–H bond stretching vibration mode. The C=C and C=N stretching in benzenoid and quinoid rings of PANI are shown by the high characteristic peaks at 1574 and 1494  $\text{cm}^{-1}$ , respectively. The peak at 1230  $\text{cm}^{-1}$  is assigned to the C–N modes of secondary aromatic amines, whereas the peak at 800  $\text{cm}^{-1}$  is related to aromatic C–H out-of-plane bending [34,35]. Fig. 6 (b) PDMA exhibits a peak at 3790  $\text{cm}^{-1}$  which is assigned to the N–H bond stretching vibration mode. The high characteristic peaks at 1572 and 1510  $\text{cm}^{-1}$  represent the C=C and C=N stretching in benzenoid phenyl rings and quinoid phenyl rings of PDMA, respectively. The C–N modes of the secondary aromatic amine are attributed to the peak at 1221  $\text{cm}^{-1}$ , the band at 1065  $\text{cm}^{-1}$  indicates the presence of the O–methoxy groups in PDMA, and a band related to aromatic C–H out-of-plane bending of aromatic C–H is ascribed to the peak at 800  $\text{cm}^{-1}$ , respectively [36,37]. Fig. 6

(c) depicts the PANI-PDMA copolymer nanocomposite containing all of the PDPA and PANI characteristic peaks, but owing to the synergistic interactions generated by the hybrid synthesis of PDPA, PANI, some of the bands are slightly shifted. The PDMA, PANI, and PANI-PDMA copolymer nanocomposites were successfully synthesized based on these findings.

XRD studies are used to investigate the crystalline nature of the synthesized materials. Fig. 7 depicts the XRD pattern of (a) GS@PANI, (b) GS@PDMA, and (c) GS@PANI-PDMA copolymer nanocomposite in the range of 10–80°. Fig. 7 (a) GS@PANI represents the pair of sharp peaks at 26.3° and 54.4°, corresponding to the miller indices of (200) and (002). Fig. 7 (b) GS@PDMA shows a couple of sharp peaks at 26.4° and 54.4° corresponding to the miller indices of (122) and (002), which designates the crystalline structure of PDMA with graphite sheet, which indicates the crystalline structure of PDMA, and Fig. 7 (c) GS@PANI-PDMA copolymer nanocomposite reveals a dual sharp peak at 26.4° and 54.4°, which represents the combined peaks of homopolymers of GS@PDMA and GS@PANI [33,36,38–40]. These observations confirm that synthesized GS@PDMA, GS@PANI, and GS@PANI-PDMA copolymer nanocomposites are crystalline in nature.

#### Electrochemical characterization of the modified electrodes

The electrochemical behaviour of PDMA, PANI, and PANI-PDMA copolymer nanocomposites CV, GCD, and EIS were

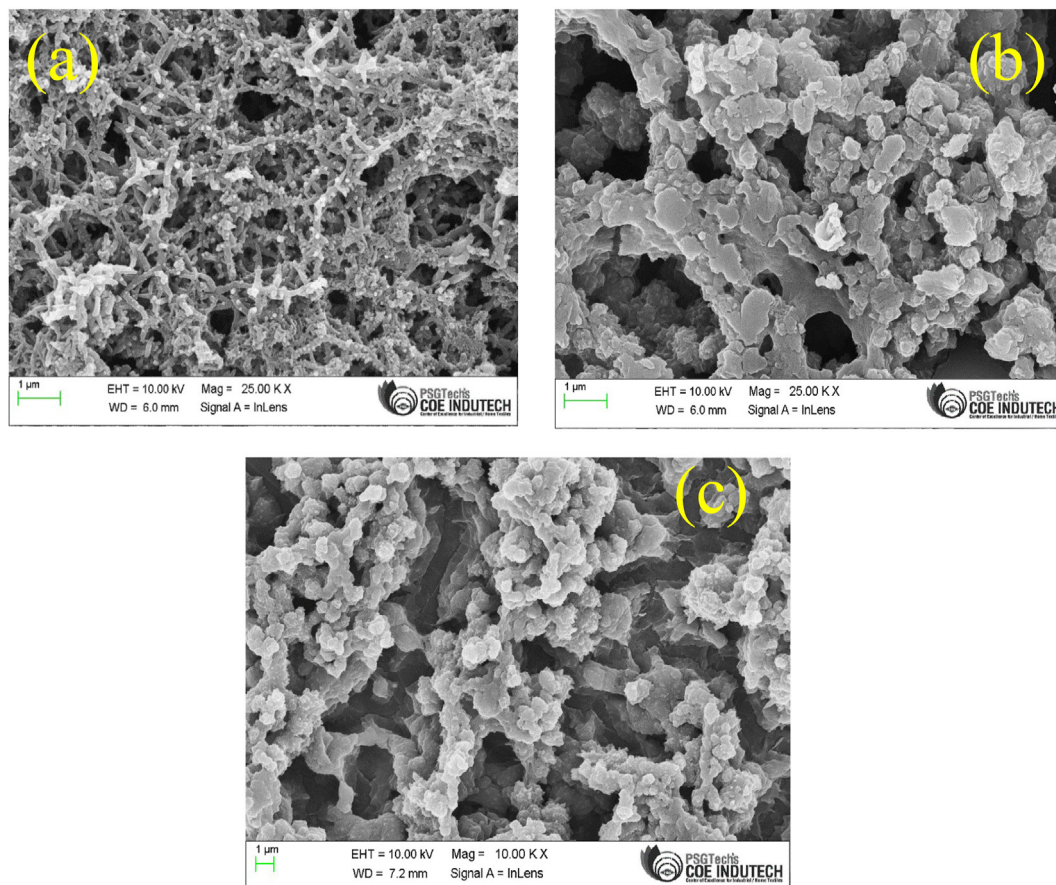
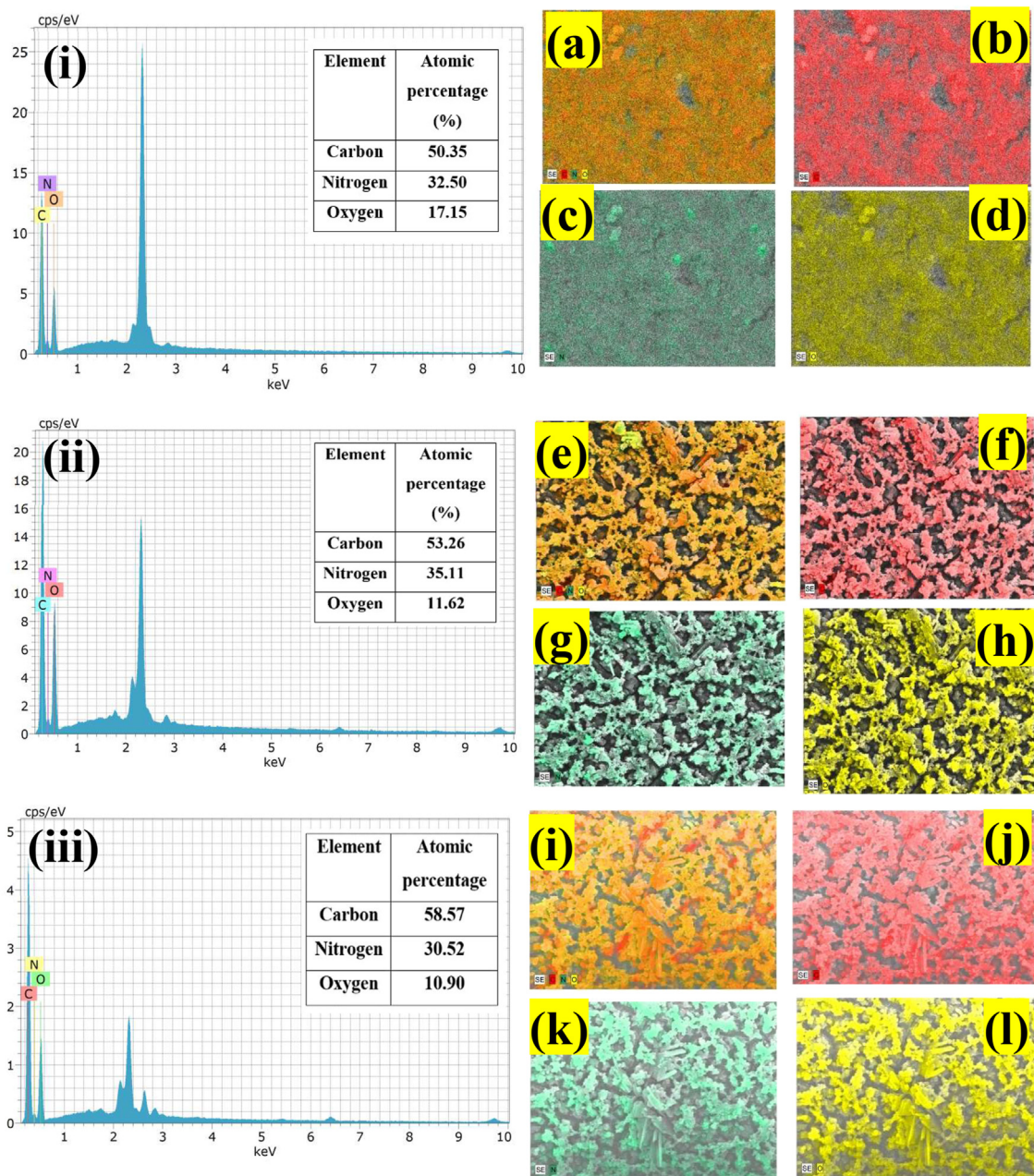


Fig. 4 – FESEM image of (a) PANI, (b) PDMA, and (c) PANI-PDMA nanocomposite.



**Fig. 5 – EDX studies of (i) PANI, (ii) PDMA, and (iii) PANI-PDMA with Mapping images of (a–d) PANI, (e–h) PDMA, and (i–l) PANI-PDMA.**

performed using three-electrode schemes in a 0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte background.

#### Cyclic voltammetry analysis

The cyclic voltammetry studies of modified electrodes of GS@PDMA, GS@PANI, GS@PANI-PDMA copolymer nanocomposites are shown in Fig. 8 (i) with the potential range from  $-0.2$  to  $1.2$  V for  $100 \text{ mVs}^{-1}$  in 0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte solution. Fig. 8 (i) (a) Bare GS shows the typical rectangular box-like profile of EDLC with a little pseudocapacitance behaviour, (b) GS@PDMA depicts a pair of redox peaks at  $0.37/-0.06$  V and  $0.6/0.24$  V, which represents the shift from

wholly reduced leucoemeraldine to emeraldine (polaron cation radical) is represented by the first redox peak, whereas the transition from emeraldine to fully oxidized pernigraniline (bipolaron) is shown by the second redox peak [31,37]. Fig. 8 (i) (c) GS@PANI shows three redox peaks at  $-0.021/0.130$  V,  $0.36/0.35$  V, and  $0.68/0.57$  V, which indicates that the first shift represents the oxidation of leucoemeraldine to emeraldine, the second shift attributed to the transition from emeraldine to pernigraniline, and the third shift reveals the pernigraniline to emeraldine form [39–42].

Fig. 8 (i) (d) GS@PANI-PDMA copolymer nanocomposites show three oxidation and reduction peaks at  $-0.023/-0.067$  V,



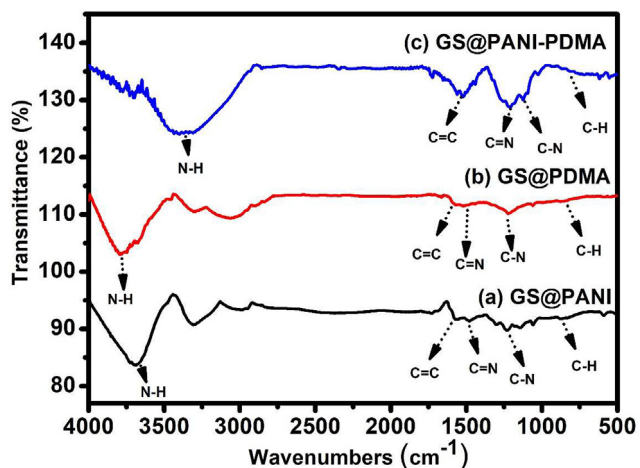


Fig. 6 – FT-IR spectrum of (a) PANI (b) PDMA (c) PANI-PDMA

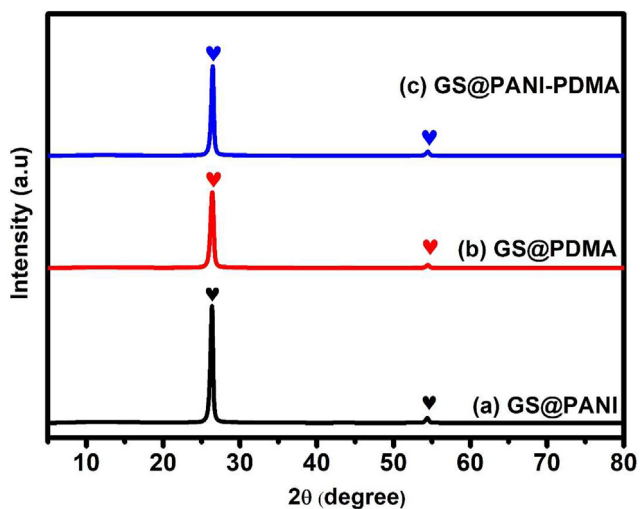


Fig. 7 – XRD studies of (a) PANI, (b) PDMA, and (c) PANI-PDMA.

0.40/0.175 V, 0.79/0.76 V, respectively, which represents the combination of PDMA and PANI peaks. The current density of PANI-PDMA copolymer nanocomposites was higher compared to the homopolymer of PDMA and PANI because of the synergistic interactions of PDMA and PANI. Fig. 8 (ii) GS@PANI-PDMA copolymer nanocomposite shows the rate capability of the final modified electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> acidic solution at various scan speeds ranging from 5 to 100 mV s<sup>-1</sup>. With increasing scan rate, the potential peak of the current density of anodic and cathodic grew linearly. All of these indicate that the GS@PANI-PDMA copolymer nanocomposite has excellent rate capability.

#### Electrochemical impedance studies

The electrochemical performance of modified electrodes of GS@PDMA, GS@PANI, GS@PANI-PDMA copolymer nanocomposites in an electrode-electrolyte system was studied using an electrochemical impedance spectrum. In EIS studies, the Nyquist plot shows Imag Z versus Real Z. Fig. 9 shows the

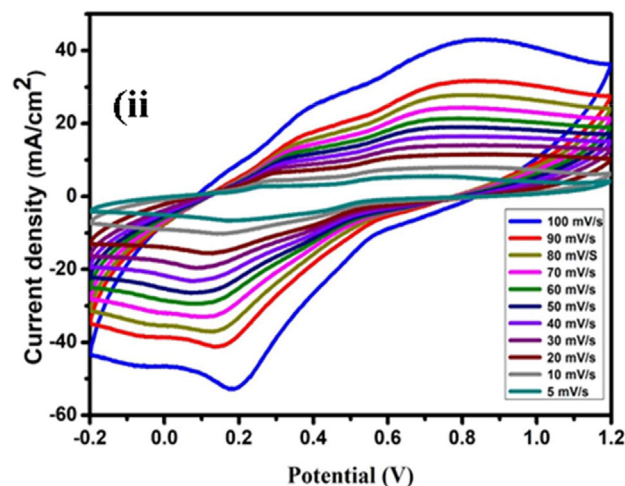
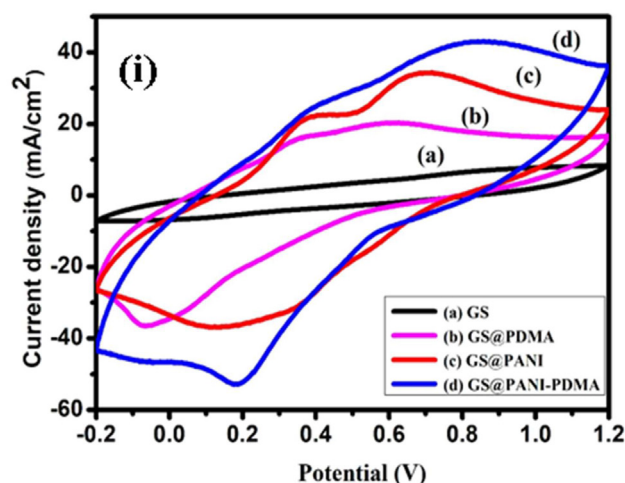


Fig. 8 – CV studies of (i) (a) bare GS (b) GS@PDMA (c) GS@PANI (d) GS@PANI-PDMA nanocomposite electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> (ii) various scan rate (5–100 mV s<sup>-1</sup>) of GS@PANI-PDMA nanocomposite electrode 0.5 M H<sub>2</sub>SO<sub>4</sub>.

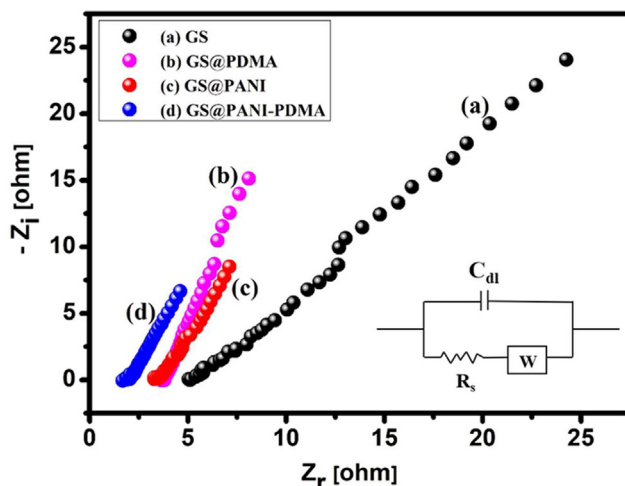


Fig. 9 – Nyquist plot of (a) Bare GS, (b) GS@PDMA, (c) GS@PANI and (d) GS@PANI-PDMA in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Inset: Equivalent circuit of the electrodes.

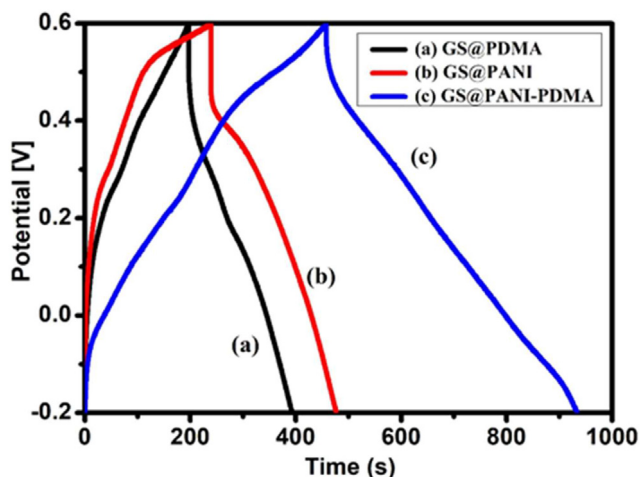


Fig. 10 – GCD curves of (a) GS@PDMA (b) GS@PANI (c) GS@PANI-PDMA in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 1 A/g current density.

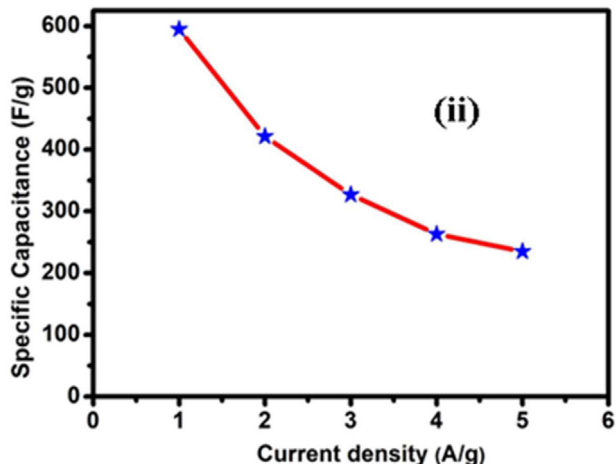
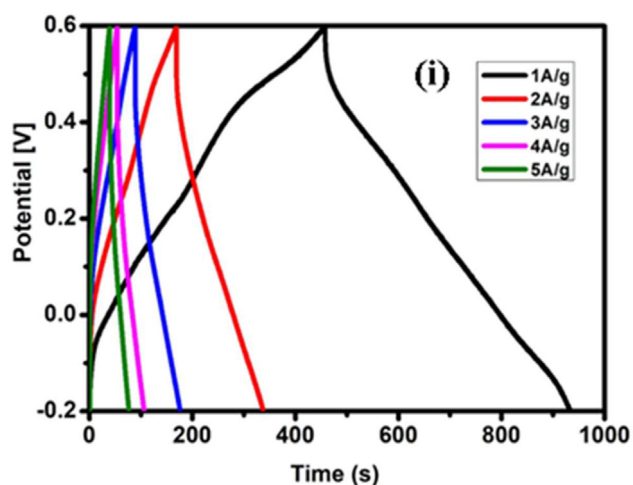


Fig. 11 – GCD curves of (i) GS@PANI-PDMA in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different current densities (1–5 A/g) (ii) GCD curves of GS@PANI-PDMA specific capacitance as a function of current density.

Nyquist plot of (a) GS, (b) GS@PDMA, (c) GS@PANI, (d) GS@PANI-PDMA copolymer nanocomposites in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. As observed in the graph in Fig. 9, the impedance spectroscopy

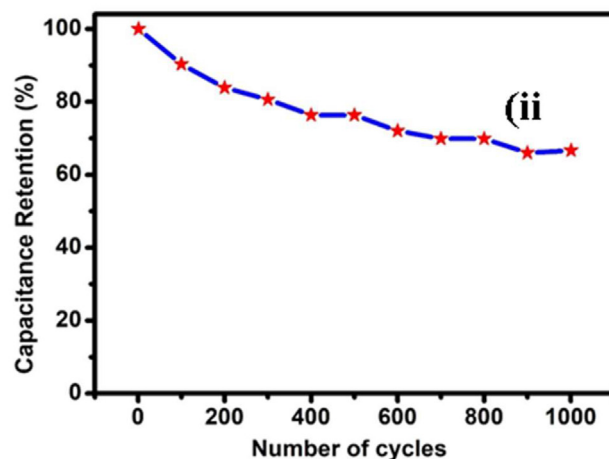
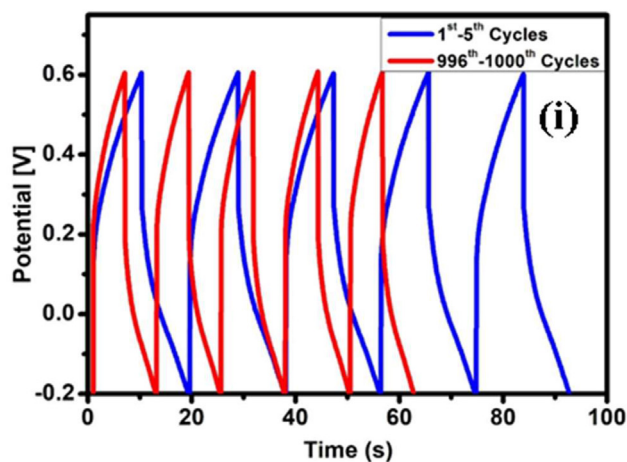


Fig. 12 – GCD curves of (i) GS@PANI-PDMA 1<sup>st</sup> - 5<sup>th</sup>, 999<sup>th</sup> - 1000<sup>th</sup> cycle at 10 A/g and (ii) cycling stability of GCD curves at 10 A/g (ii) Capacity retention of (i) GS@PANI-PDMA as a function of cycle number.

observation was plotted in the frequency range of 1 kHz to 1 MHz for pure and composite electrodes. This indicates that the composite electrode has a lower resistance than the individual electrodes. All the electrodes show a straight line when the frequency was low. In this medium, the Warburg impedance is a reflection of ion diffusion into the material functioning as electrode and diffusion resistance. The solution resistance ( $R_s$ ) is a measure of ionic conductivity through the electrolyte, observed for a) GS, (b) GS@PDMA, (c) GS@PANI, and (d) GS@PANI-PDMA copolymer nanocomposites was 5.1  $\Omega$ , 3.7  $\Omega$ , 3.2  $\Omega$ , and 1.85  $\Omega$ , respectively. The lower solution resistance of GS@PANI-PDMA copolymer nanocomposites shows higher conductivity than other modified electrodes.

#### Galvanostatic charge- discharge studies

The galvanostatic charge/discharge (GCD) is a general approach for achieving supercapacitance electrochemical performance. Fig. 10 shows the GCD curves for the different modified electrodes of a) GS, (b) GS@PDMA, (c) GS@PANI, and (d) GS@PANI-PDMA copolymer nanocomposites at 1 A/g current density within a potential window amid -0.2 V–0.6 V. The specific capacitance of the modified electrode is calculated by GCD curves using equation (1).



$$C_{sp} = \frac{It}{m\Delta V} \quad (1)$$

Where  $C_{sp}$  denotes the specific capacitance in F/g,  $I$  the current (A),  $t$  the discharge duration (s),  $m$  the active material mass (g), and  $V$  the potential window (V) [15]. The specific capacitance of (a) GS@PDMA, (b) GS@PANI, and (c) GS@PANI-PDMA copolymer nanocomposites is 246 F/g, 299 F/g, and 595 F/g at 1 A/g current density, respectively.

The energy density  $E$  (Wh kg<sup>-1</sup>) and power density  $P$  (W kg<sup>-1</sup>) can be derived from the Galvanostatic charge-discharge data according to Equations (2) and (3):

$$\text{Energy Density (E)} = \frac{1}{2} \times C \times v^2 \quad (2)$$

$$\text{Power Density (P)} = \frac{E}{\Delta t} \quad (3)$$

$V$  ( $\Delta V$ ) is the discharge potential window, and the  $\Delta t$  (s) is the discharge time. It is observed that a maximum power density of 399 W kg<sup>-1</sup> was observed at the energy density range of 52.8 W h kg<sup>-1</sup> for GS@PANI-PDMA copolymer nanocomposite-modified electrode.

The specific capacitance of GS@PANI-PDMA copolymer nanocomposites is higher compared to GS@PDMA, and GS@PANI modified electrodes due to the synergistic interactions of PDMA and PANI. Fig. 11 (i) reveals the modified electrodes of GS@PANI-PDMA copolymer nanocomposites at different current densities (1–5 A/g) and Fig. 11 (ii) depicts the various current densities of 1,2,3,4 and 5 A/g of calculated specific capacitance using equation (2) from GCD to get 595, 421, 327, 263, and 235 F/g, respectively. Specific capacitance diminishes as current density increases due to reduced ion transports compared to electron mobility. The charge/discharge cycle tests were also used to assess the modified electrode of GS@PANI-PDMA copolymer nanocomposites' stability. The electrochemical stability of the modified GS@PANI-PDMA copolymer nanocomposites electrode is demonstrated in Fig. 12 (i) by a 1000-cycle charge-discharge procedure between -0.2 and 0.6 V at a current density of 10 A/g. The capacitance retention studies of the modified electrode of GS@PANI-PDMA copolymer nanocomposites after 1000 cycles is 67%, as shown in Fig. 12 (ii). These findings demonstrate that GS@PANI-PDMA copolymer nanocomposites electrode has significant storage capability, and its long-life cycle suggests that it might be used in practical supercapacitor applications.

## Conclusion

In this work, the nanocomposite of polydimethoxy aniline and polyaniline copolymer modified electrode (GS@PANI-PDMA) was fabricated using a simple electrochemical deposition method. In the current research, a polyaniline derivative containing an electron-donor methoxy group is known as Poly(2,5-dimethoxyaniline) which enhances the electrochemical behaviour as well stability. As a result, the modified electrode of GS@PANI-PDMA nanocomposite exhibits excellent specific capacitances of 595 F/g at 1 A/g current density and 67% capacity

retention after 1000 cycles in an acidic medium. Also, the energy density and power density of GS@PANI-PDMA copolymer nanocomposite-modified electrodes is 52.8 W h kg<sup>-1</sup> and 399 W kg<sup>-1</sup> was observed. Such fascinating electrochemical performance was attributed to the unique morphology and the synergistic effect between the capacitive contributions of the PDMA and PANI. As a result, a copolymer of polydimethoxyaniline and polyaniline nanocomposite, which was made using a simple and profitable approach, offers a lot of potential for supercapacitor applications.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## REFERENCES

- [1] Eftekhari A, Li L, Yang Y. Polyaniline supercapacitors. *J Power Sources* 2017;347:86–107. <https://doi.org/10.1016/j.jpowsour.2017.02.054>.
- [2] Bramhaiah K, Alex C, Singh VN, John NS. Hybrid films of Ni(OH)<sub>2</sub> nanowall networks on reduced graphene oxide prepared at a liquid/liquid interface for oxygen evolution and supercapacitor applications. *ChemistrySelect* 2019;4:2519–28. <https://doi.org/10.1002/slct.201803340>.
- [3] Alex C, Sathiskumar C, John NS. Role of metal ion sites in bivalent cobalt phosphorus oxygen systems toward efficient oxygen evolution reaction. *J Phys Chem* 2021;125:24777–86. <https://doi.org/10.1021/acs.jpcc.1c05614>.
- [4] Nasrin K, Gokulnath S, Karnan M, Subramani K, Sathish M. Redox-additives in aqueous, non-aqueous, and all-solid-state electrolytes for carbon-based supercapacitor: a mini-review. *Energy Fuels* 2021;35:6465–82. <https://doi.org/10.1021/acs.energyfuels.1c00341>.
- [5] Karnan M, Subramani K, Sudhan N, Ilayaraja N, Sathish M. Aloe vera derived activated high-surface-area carbon for flexible and high-energy supercapacitors. *ACS Appl Mater Interfaces* 2016;8:35191–202. <https://doi.org/10.1021/acsami.6b10704>.
- [6] Kumar R, Thangappan R. Electrode material based on reduced graphene oxide (rGO)/transition metal oxide composites for supercapacitor applications: a review.

- Emergent Materials 2022;1–7. <https://doi.org/10.1007/s42247-021-00339-7>.
- [7] Sathishkumar S, Karthik M, Boopathiraja R, Parthibavarman M, Nirmaladevi S, Sathishkumar S. Effect of conducting polymer incorporated heterostructure morphology of  $\text{MgCo}_2\text{O}_4$ @PPy nanosheets: a promising cathode material for asymmetric supercapacitor applications. Researchsquare.com; 2022. <https://doi.org/10.21203/rs.3.rs-1276547/v1>.
- [8] Madaswamy SL, Keertheeswari NV, Dhanusuraman R. **Conducting polymers: fundamentals, synthesis, properties, and applications.** In: *Conducting Polymers*; 2022. p. 29–48.
- [9] Ragupathy D, Gomathi P, Lee SC, Al-Deyab SS, Lee SH, Do Ghim H. One-step synthesis of electrically conductive polyaniline nanostructures by oxidative polymerization method. *J Ind Eng Chem* 2012;18:1213–5. <https://doi.org/10.1016/j.aiepr.2021.08.001>.
- [10] Madaswamy SL, Wabaidur SM, Khan MR, Lee SC, Dhanusuraman R. Polyaniline-graphitic carbon nitride based nano-electrocatalyst for fuel cell application: a green approach with synergistic enhanced behaviour. *Macromol Res* 2021;29:411–7. <https://doi.org/10.1007/s13233-021-9044-1>.
- [11] Ragupathy D, Gopalan AI, Lee KP, Manesh KM. Electro-assisted fabrication of layer-by-layer assembled poly (2, 5-dimethoxyaniline)/phosphotungstic acid modified electrode and electrocatalytic oxidation of ascorbic acid. *Electrochem Commun* 2008;10:527–30. <https://doi.org/10.1016/j.elecom.2008.01.025>.
- [12] Madaswamy SL, Keertheeswari NV, Alothman AA, mana AL-Anazy M, Alqahtani KN, Wabaidur SM, Dhanusuraman R. Fabrication of nanocomposite networks using Pd nanoparticles/Polydiphenylamine anchored on the surface of reduced graphene oxide: an efficient anode electrocatalyst for oxidation of methanol. *Adv Industrial Eng Polymer Res* 2022;5:18–25. <https://doi.org/10.1016/j.aiepr.2021.08.001>.
- [13] Lakshmi MS, Wabaidur SM, Alothman ZA, Ragupathy D. Novel 1D polyaniline nanorods for efficient electrochemical supercapacitors: a facile and green approach. *Synth Met* 2020;270:116591. <https://doi.org/10.1016/j.synthmet.2020.116591>.
- [14] Magu T, Agobi A, Hitler L, Dass P. A review on conducting polymers-based composites for energy storage application. *J Chem Rev* 2019;1:19–34. <https://doi.org/10.33945/SAMI/JCR.2019.1.1934>.
- [15] Boeva ZA, Sergeev VG. Polyaniline: synthesis, properties, and application. *Polym Sci C* 2014;56:144–53. <https://doi.org/10.1134/S1811238214010032>.
- [16] Madaswamy SL, Alfakeer M, Bahajjaj AAA, Ouladsmane M, Wabaidur SM, Chen CX, Dhanusuraman R. Remarkable electrocatalytic activity of Pd nanoparticles dispersed on polyaniline-polydiphenylamine copolymer nanocomposite for methanol and ethanol oxidation reaction. *Synth Met* 2021;281:116925. <https://doi.org/10.1016/j.synthmet.2021.116925>.
- [17] Tkachenko LI, Ozkan SZ, Efimov ON, Karpacheva GP, Nikolaeva GV, Kostev AI, Dremova NN, Kabachkov EN. Electrochemical behavior of polydiphenylamine-2-carboxylic acid and its hybrid nanocomposites with single-walled carbon nanotubes on anodized graphite foil in lithium aprotic electrolyte. *React Funct Polym* 2022;173:105225. <https://doi.org/10.1007/s10854-018-8834-5>.
- [18] Palaniappan SP, Richard Prabhu Gnanakan S, Lee YS, Manisankar P. Mechanochemical synthesis of poly (2, 5-dimethoxy aniline) nanobelts and its electrochemical performance in hybrid supercapacitors. *Ionics* 2011;17:603–6. <https://doi.org/10.1007/s11581-011-0612-9>.
- [19] Li H, Wang J, Chu Q, Wang Z, Zhang F, Wang S. Theoretical and experimental specific capacitance of polyaniline in sulfuric acid. *J Power Sources* 2009;190:578–86. <https://doi.org/10.1016/j.jpowsour.2009.01.052>.
- [20] Lakshmi MS, Wabaidur SM, Alothman ZA, Johan MR, Ponnusamy VK, Dhanusuraman R. Phosphotungstic acid-Titania loaded polyaniline nanocomposite as efficient methanol electro-oxidation catalyst in fuel cells. *Int J Energy Res* 2021;45:8243–54. <https://doi.org/10.1002/er.5950>.
- [21] Keertheeswari NV, Madaswamy SL, Wabaidur SM, Habila MA, Al-Anazy MM, Dhanusuraman R, Ponnusamy VK. Platinum nanoparticles/phosphotungstic acid nanorods anchored poly (diphenylamine) nanohybrid coated electrode as a superior electro-catalyst for oxidation of methanol. *Prog Org Coating* 2021;161:106470. <https://doi.org/10.1016/j.porgcoat.2021.106470>.
- [22] Liang Banglei, Qin Zongyi, Zhao Jianyun, Zhang Yu, Zhou Zhe, Lu Yaqing. Controlled synthesis, core-shell structures and electrochemical properties of polyaniline/polypyrrole composite nanofibers. *J Mater Chem* 2014;2(7):2129–35. <https://doi.org/10.1039/C3TA14460G>.
- [23] Selvakumar Muthu, Pitchumani Sethuraman. Hybrid supercapacitor based on poly (aniline-co-m-anilic acid) and activated carbon in non-aqueous electrolyte. *Kor J Chem Eng* 2010;27(3):977–82. <https://doi.org/10.1007/s11814-010-0120-z>.
- [24] Domínguez-Aragón Angélica, Hernández-Escobar Claudia A, Vega-Rios Alejandro, Armando Zaragoza-Contreras E. Poly (diphenylamine-co-aniline) copolymers for supercapacitor electrodes. *J Mater Sci Mater Electron* 2018;29(18):15329–38. <https://doi.org/10.1007/s10854-018-8834-5>.
- [25] Ragupathy D, Park JJ, Lee SC, Kim JC, Gomathi P, Kim MK, Lee SM, Ghim HD, Rajendran A, Lee SH, Jeon KM. Electrochemical grafting of poly (2, 5-dimethoxy aniline) onto multiwalled carbon nanotubes nanocomposite modified electrode and electrocatalytic oxidation of ascorbic acid. *Macromol Res* 2011;19:764–9. <https://doi.org/10.1007/s13233-011-0802-3>.
- [26] Ragupathy D, Lee SC, Al-Deyab SS, Rajendran A. Electrochemical synthesis of a novel poly (2, 5-dimethoxy aniline) nanorod for ultrasensitive glucose biosensor application. *J Ind Eng Chem* 2014;20:930–6. <https://doi.org/10.1016/j.jiec.2013.06.025>.
- [27] Yuan C, Zhang L, Hou L, Lin J, Pang G. Green interfacial synthesis of two-dimensional poly (2, 5-dimethoxyaniline) nanosheets as a promising electrode for high performance electrochemical capacitors. *RSC Adv* 2014;4:24773–6. <https://doi.org/10.1016/j.colsurfa.2021.127125>.
- [28] Xiong S, Shi Y, Chen S, Li J, Wang X, Chu J, Gong M, Wu B. Interfacial polymerization of poly (2, 5-dimethoxyaniline) and its enhanced capacitive performances. *J Appl Polym Sci* 2014;131. <https://doi.org/10.1002/app.40666>.
- [29] Mungkalodom P, Paradee N, Sirivat A, Hormnirun P. Synthesis of poly (2, 5-dimethoxyaniline) and electrochromic properties. *Mater Res* 2015;18:669–76. <https://doi.org/10.1590/1516-1439.235513>.
- [30] Khalid M, Honorato AMB, Varela H. **Polyaniline: synthesis methods, doping and conduction mechanism.** 2018.
- [31] Han WJ, Lee JH, Choi HJ. Poly (diphenylamine)/polyaniline core/shell composite nanospheres synthesized using a reactive surfactant and their electrochromology. *Polymer* 2020;188:122161. <https://doi.org/10.1016/j.polymer.2020.122161>.
- [32] Singu BS, Srinivasan P, Pabba S. Benzoyl peroxide oxidation route to nano form polyaniline salt containing dual dopants for pseudocapacitor. *J Electrochem Soc* 2011;159:A6. <https://doi.org/10.1149/2.036201jes>.
- [33] Srinivasan P, Gottam R. Infrared Spectra: useful technique to identify the conductivity level of emeraldine form of polyaniline and indication of conductivity measurement

- either two or four probe technique. *Mater Sci Res India* 2018;15:209–17. <https://doi.org/10.13005/msri/150302>.
- [34] Masikini M, Williams AR, Sunday CE, Waryo TT, Nxusani E, Wilson L, Qakala S, Bilibana M, Douman S, Jonnas A, Baker PG. Label free poly (2, 5-dimethoxyaniline)-multi-walled carbon nanotubes impedimetric immunosensor for fumonisin B1 detection. *Materials* 2016;9:273. <https://doi.org/10.3390/ma9040273>.
- [35] Dey Sadhu S, Meena PL, Kumar J, Gupta J, Choudhary S, Gupta A. Preparation and characterization of polyaniline- and polythiophene-based copolymer and its nanocomposite suitable for electro-optical devices. *Polym Compos* 2020;41:4619–30. <https://doi.org/10.1002/pc.25738>.
- [36] Roy BC, Gupta MD, Bhowmik L, Ray JK. Synthesis and characterization of poly (2, 5-dimethoxyaniline) and poly (aniline-Co-2, 5-dimethoxyaniline): the processable conducting polymers. *Bull Mater Sci* 2001;24:389–96. <https://doi.org/10.1007/BF02708636>.
- [37] Cevik E, Karaman B, Gunday ST, Bozkurt A. Graft copolymer electrolytes for electrochemical double layer electrochemical capacitor applications. *Synth Met* 2021;278:116814. <https://doi.org/10.1016/j.synthmet.2021.116814>.
- [38] Dhivya C, Vandarkuzhali SAA, Radha N. Antimicrobial activities of nanostructured polyanilines doped with aromatic nitro compounds. *Arab J Chem* 2019;12:3785. <https://doi.org/10.1016/j.arabjch.2015.12.005>.
- [39] Patil D, Seo YK, Hwang YK, Chang JS, Patil P. Humidity sensitive poly (2, 5-dimethoxyaniline)/WO<sub>3</sub> composites. *Sensor Actuator B Chem* 2008;132:116.
- [40] Qu K, Dai W, Bai Y, Chen Y, Chen Z, Deng M. One electron oxidation of ascorbic acid facilitated by ionic liquid-doped poly (3, 4-ethylenedioxythiophene) as artificial enzyme. *J Electroanal Chem* 2020;878:114702. <https://doi.org/10.1016/j.jelectrochem.2020.116346>.
- [41] Liu B, Sun H, Peng T, Zhi X. 3D core-shell poly (aniline-co-pyrrole)/reduced graphene oxide composite for supercapacitor performance. *Diam Relat Mater* 2021;118:108498. <https://doi.org/10.1016/j.diamond.2021.108498>.
- [42] Shah SS, Alfasane MA, Bakare IA, Aziz MA, Yamani ZH. Polyaniline and heteroatoms-enriched carbon derived from Pithophora polymorpha composite for high performance supercapacitor. *J Energy Storage* 2020;30:101562. <https://doi.org/10.1016/j.est.2020.101562>.