SYNTHESIS AND CHARACTERIZATION OF COF/C-DOT/CONDUCTING POLYMER COMPOSITE FOR SUPERCAPACITOR

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COLLEGE : MANIPAL INSTITUTE OF TECHNOLOGY, MANIPAL

GUIDE (S) : Dr. SUDHAKAR Y N

STUDENT (S) : Ms. ACHANIA CHANDRAN

Ms. RUTUJA RAJENDRA PATIL

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Introduction/Background

The population rise is a major factor contributing to the increasing demand for energy. As the population grows, so does the energy demand to power homes, businesses, and industries. Sustainable and renewable energy growth has resulted in decentralized energy producers.[1] Supercapacitors possess desirable characteristics such as high-power density, high specific capacitance, quick charging, environmental sustainability, and long-term durability, which make them a highly promising option for energy storage in the future.[2]

Covalent organic framework (COF) is a specific class of organic materials characterized by extended crystal structures, exceptional architectural properties, and high surface areas, with the added advantage of being able to adjust their pore size to suit specific applications. Modifiable redox-active groups within their structures, which make them highly promising materials for electrochemical capacitors.[3] COFs are primarily produced as bulk powders that cannot be dissolved or melted which attributes longer stability.[3]

Researchers are also exploring the use of various types of C-Dots in conductivity electrodes for supercapacitors.[2] The electrochemical characteristics of C-dots are crucial in the functioning of SCs. When C-Dots are added to the electrodes of supercapacitors, the resulting supercapacitor exhibit significantly higher capacitance compared to supercapacitor without C-dot electrodes.[2] Conductive polymers (CPs) offer several advantages, including high specific conductance, tunable electrical properties, high flexibility and easy fabrication which make them suitable for various applications, including energy storage devices, sensors, and electronic devices. Polyaniline (PANI) has been extensively researched as a conductive polymer due to its simple synthesis process, excellent environmental stability, and high conductivity when doped.[2] In present work, supercapacitor which includes high surface area COFs can increase storage capacity of ions, while C-Dots can improve the electrical conductivity of the composite material. PANI can also enhance the electrical conductivity and energy density of the composite material.

Table 1: Literature comparison studies

Reference	ELECTROLYTE	ELECTRODE	SPECIFIC CAPACITANCE	INFERENCE
4	0.5 M H_2SO_4	COF-C black mixture	22.4 Fg^{-1}	The insulating nature of pure COF results in a lack of charge-discharge capacity, leading to a significant deficiency in its electrochemical capacitance. The COF/rGO hybrids exhibit a partially deformed triangular shape, and their increased capacity is derived from two sources: the pseudocapacity induced by the redox-active anthraquinone and the additional electric double-layer capacity generated by the enhanced specific surface area.
		COF/rGO aerogel	269 Fg^{-1}	
6	1M Na_2SO_4	COF	190 Fg^{-1}	The exact cause of the higher specific capacitance observed in COFs/NH_2-rGO is not fully understood, but it is believed to be associated with two factors: the increased effective electrode surface area and the strong coupling between the surface COF and graphene.
		NH_2-r GO	226 Fg^{-1}	
		COF/NH_2-r GO	533 Fg^{-1}	

Objectives

- To synthesize and characterise covalent organic framework (COF). The COF/C-Dots were rarely used in energy application although it has potential energy storage abilities.
- To prepare carbon dot from biomass. The C-Dots development from biomass is economically feasible and eco-friendly. As the role of C-Dots in composite and energy applications is yet to be studied in detail.
- To characterize the composite using FTIR, XRD, SEM and electrochemical techniques.
- To fabricate supercapacitor using composite and evaluate its electrochemical properties.

Methodology

Cyanuric chloride and urea were used to synthesize COF. C-Dots were synthesized using coffee silver skin and hydrazine. Aniline after distillation is electrochemically polymerized into PANI, conducting polymer. COF was synthesized from known literature. C-dots were synthesized hydrothermally from coffee silver skin. C-dots were incorporated into COF by sonication, soaking, and coated into a stainless-steel electrode of dimension 1*1 by grinding and making a paste using a binder and solvent. The stainless-steel surface was prepared for coating using emery sheets. PANI was electrochemically deposited using a surfactant, SDS. 0.1M Na_2SO_4 is used as the electrolyte. COF/C-Dot/PANI electrodes, separated by a separator are used as the symmetric electrodes for supercapacitor. Cyclic Voltammetry, AC impedance, and Galvanic Charge-Discharge were performed for the fabricated supercapacitor. 1M Na_2SO_4 was used as the electrolyte.

Results and discussions

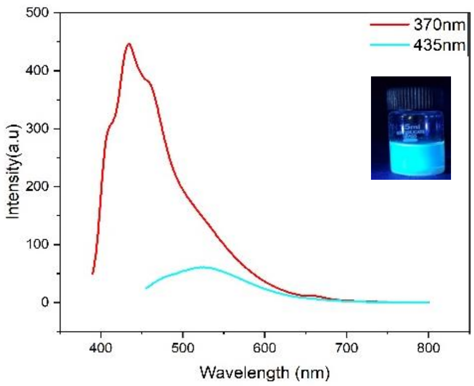


Figure 1:Photoluminescence of C-dot

The photoluminescence (PL) of carbon dots arises from a combination of a quantum effect and the presence of various emissive traps on the surface of the C-dots. [7] When the excitation wavelength is increased, the emission peaks were shifted, and intensity was decreased. (Figure 1) The FT-IR data (Figure 2) of COF showed a broader band around 3329-3061 cm^{-1} which indicates the presence of NH stretching in the group NHCONH and NH_2 free terminal group. The absence of C-Cl groups is confirmed by

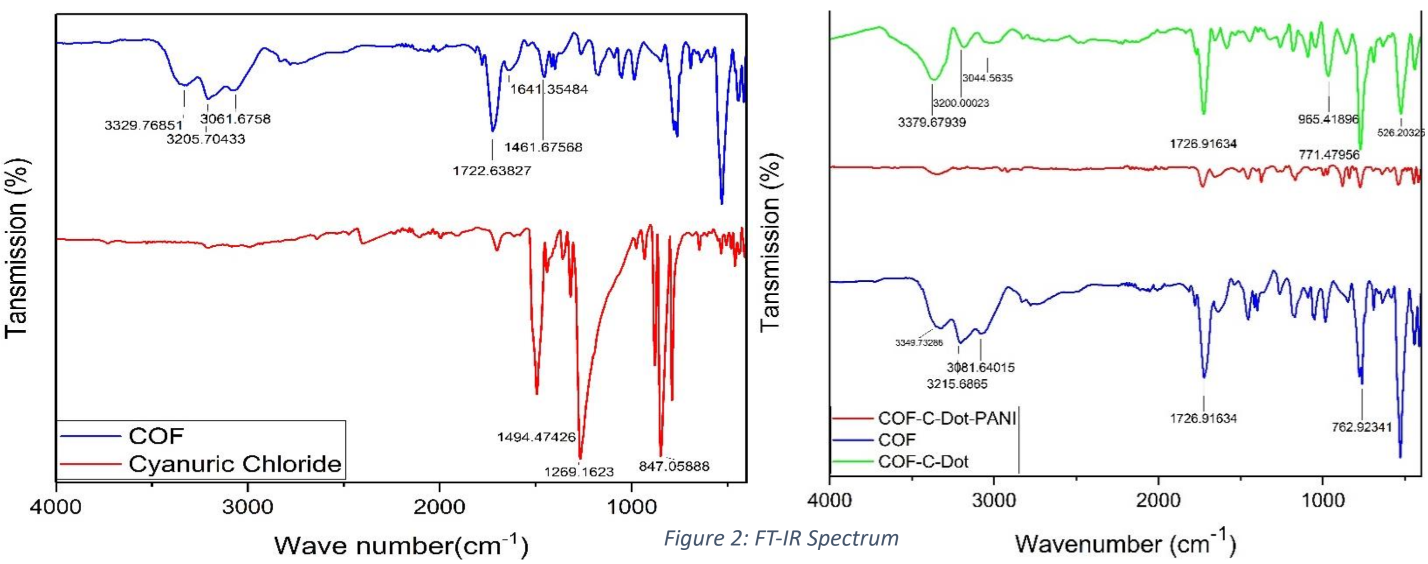


Figure 2: FT-IR Spectrum

the absence of a peak at 850 cm^{-1} indicating the replacement of chlorine atom by NH_2 of urea. C=N medium bond stretching is indicated by the peak observed at 1641 cm^{-1}, this is further confirmed by the peaks in the range 1200-1655cm^{-1} that indicates the CN heterocycles. There is a strong peak at 1722 cm^{-1} that indicates the presence of carbonyl group in the urea.[8] The FT-IR spectra of COF-C-Dot shows the retention of few peaks from COF and C-Dot. The FT-IR spectra of the composite, COF-C-Dot-PANI shows that the peaks COF- C-Dot peaks are masked by the deposition of the PANI.

The X-Ray diffraction (Figure 3) was done 3˚/minute in the range 2-45˚. The new peaks with low intensity were formed in the region lower region[8] which shows the formation of COF indicating the low crystalline nature of COF. When C-dots is incorporated to the COF the intensity of the peaks were reduced, and some peaks disappeared on depositing PANI.

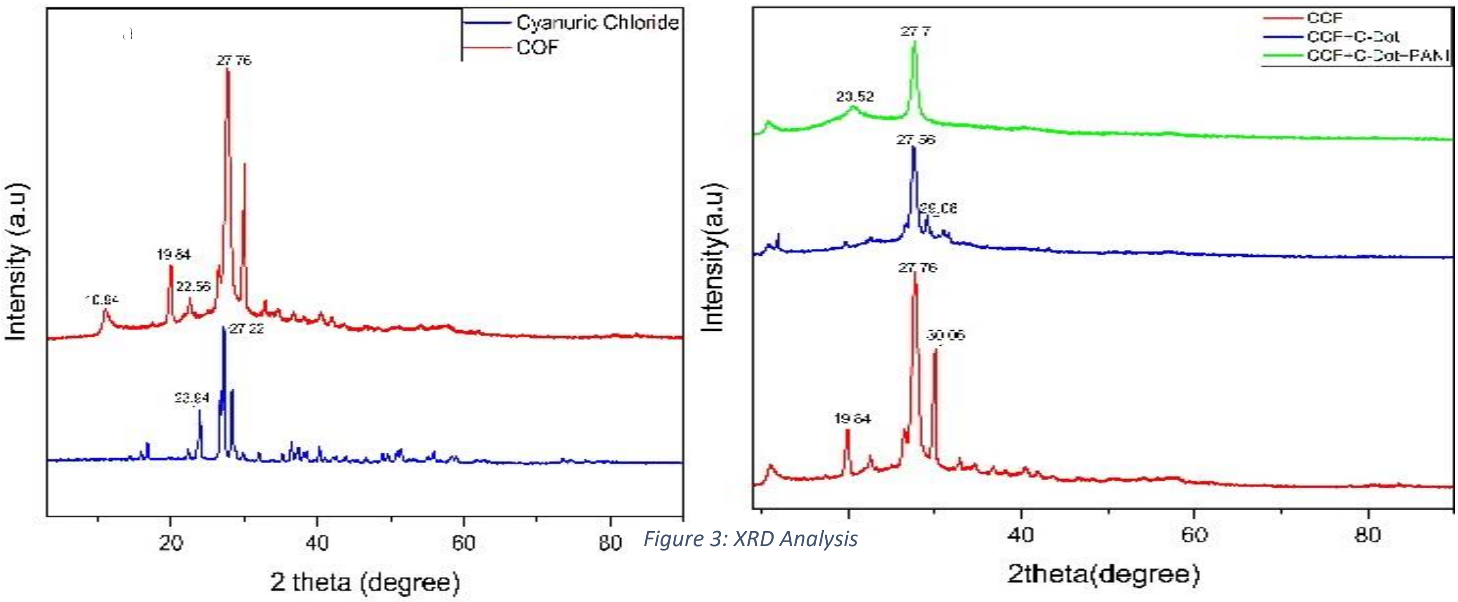
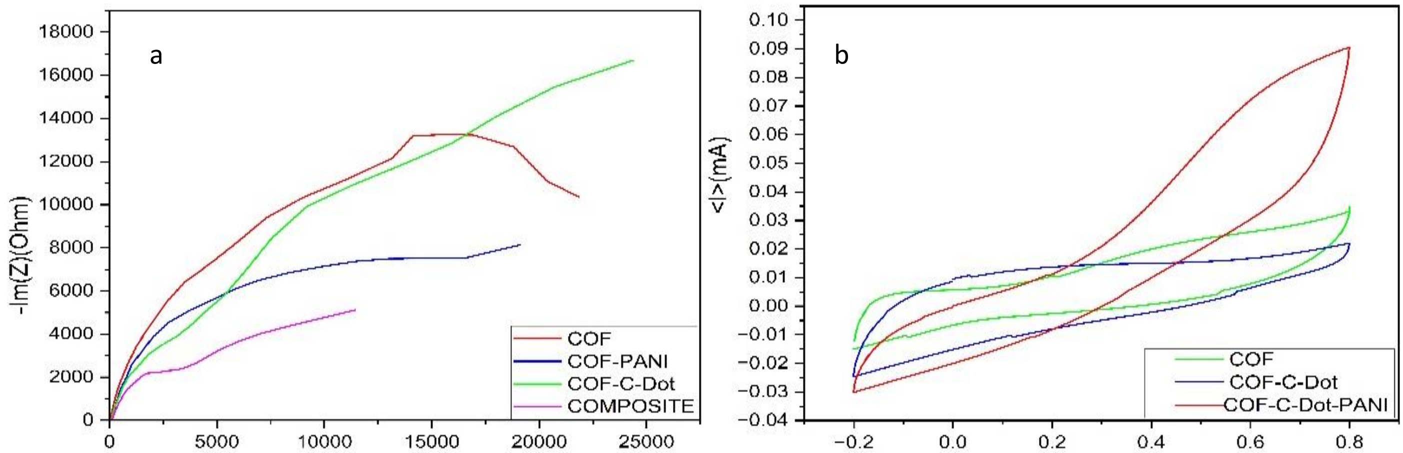


Figure 3: XRD Analysis

SEM Fig 4a shows the pristine COF having porous structures. The pores are uniform throughout the COF powder which provides space for nucleation of PANI. In Fig 4b the pore size decreased due to PANI deposition which is visible as small globules on the surface. Therefore, the COF along with PANI provides a channel for movement of ions and provides enhanced retention property. The C-dot are not visible because of sub nanometre size.



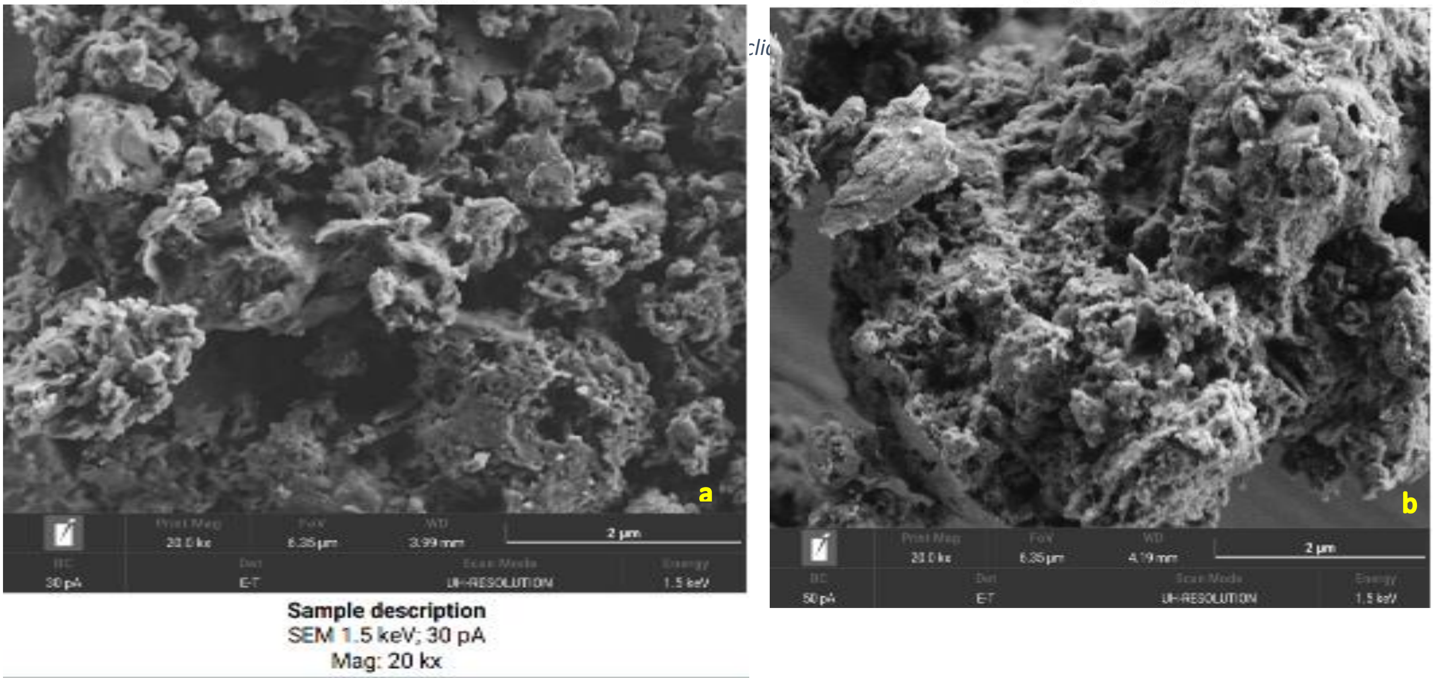


Figure 4:SEM Analysis a) Pristine COF b) Composite(COF-C-Dot-PANI)

From the plot (Figure 5a) it is evident that impedance of the composite has drastically reduced thus decreasing the resistance. The semicircle shows the combined effect of capacitance and impedance. As observed in Fig 13, the resistance (R_{ct}) has decreased from COF to COF/C-Dot/PANI (composite) respectively. Therefore, the composite showed lower impedance at higher frequency region, it is chosen for supercapacitor fabrication. The CV technique can supply insights about various processes such as redox reactions, electron transfer between different phases, and adsorption of species. CV was performed for the potential window -0.2 to 0.8 V at 100 mV/s. The current window increased with addition of C-dot and PANI indicating the easy access of ions through the pores of composite (Figure 5b).

What is the innovation in the project?

Use of COF in energy device is promising but due to poor conducting it has limited application. In the present work COF is modified with C-dot and PANI which enhanced the electric and ionic conductivity thereby improvising the specific capacitance of supercapacitor. Hence, modified COF composite can be used as electrode material for energy device.

Scope for future work

The COF/C-dot can be further explored as synthesis of C-dot from various other biomass materials as a green source. COF can be doped with metal or metal oxide like ZnO etc., to develop redox active sites and increase the conductance property of COF. Furthermore, conducting polymer can be varied to optimize the synergic effect with COF. The ternary blends can be prepared mainly containing COF/C-dot/Conducting polymer and used in application in battery. The supercapacitor fabricated can be further connected in series to provide required application based on the stability of the electrode material.

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