5. A.1 Outline

The present work reported on the synthesis of CuO- Poly (acrylic) acid (PAA)/CNT hybrid thin films by a cost-effective spin coating technique for supercapacitor application. The functionalized CNTs with carboxylic group have been used to improve the electrical conductivity of the working electrode, in addition to its electrode characteristics. The PAA acts as a complexing agent for CuO–CNT. The coated films were annealed at 300, 400 and 500 °C to study its effect on the supercapacitor behavior. X-ray photoelectron spectroscopy (XPS) and Fourier Transform- Infrared spectroscopy (FT-IR) techniques are used for the phase identification and determination of the organic component in the hybrid films, respectively. SEM (scanning electron microscopy) micrographs revealed novel ring like structures and ring diameters changes from 500 nm to 1.2 µm with increase in annealing temperature from 300 to 500 °C. Cyclic voltammetry (CV) is employed to estimate the specific capacitance of the films in 1 M H₂SO₄ electrolyte. It is observed that the specific capacitance increases from 188 Fg⁻¹ to 258 Fg⁻¹ with increase in annealing temperature.
5. A.2 Introduction

One of the challenging issues in using them for high performance supercapacitor is the poor electronic conductivity of the electrode. Extensive research work has been focused on enhancing electronic conduction of electrode material by carbon coating that imparts high chemical stability, mechanical strength, active surface area and conductivity. Presently, integrating CNTs into functional architectures and composites is an active research field [6-7]. The functionalization of CNTs expected to play a vital role in improving the dispersion and therefore it was intensively studied in last decade in order to overcome their inherent insolubility [8-9]. The attachment of PAA on the surface of CNTs forms hydrophilic nanotubes, which improves the dispersion of CNTs in water [10]. Here a new approach has been attempted by making hybrid CuO-PAA/CNT thin films. CNTs improve electronic conductivity of the working electrode (CuO), in addition to providing double-layer capacitance.

5. A.3 Experimental section

The CNT powdered sample was purified and functionalized with COOH by acid treatments that involve refluxing them for 12 h in H$_2$SO$_4$/HNO$_3$ (3:1) solution and subsequent ultrasonication. The functionalized CNTs are subjected to further stirring for 24 h in doubly distilled water and then to centrifuge at 1200 rpm. The functionalized CNTs were then washed for several times with deionized water and dried in vacuum at 50 °C. 0.002 g of functionalized CNTs were added in the mixture of 1 M CuCl$_2$.2H$_2$O and 2 mM PAA solution. The Cu$^{2+}$ ions get covalently bonded to PAA by protonation reaction (according to Bjerrum model) and also to the functionalized CNTs via their carboxylic group [16], forming Cu-PAA/CNT in the solution. The solution was spin coated at 5000 rpm on to the steel and glass substrates. The films were annealed over 300 to 500 °C in an ambient air to oxidize ‘Cu’ and obtain CuO-PAA/CNT samples. Two types of samples were prepared to examine the effect of functionalized CNTs on the performance of CuO-PAA electrodes. The samples without CNTs are denoted as CP$_{500}$ and those containing functionalized CNTs as CPCNT$_{300}$, CPCNT$_{400}$ and CPCNT$_{500}$ respectively. Fig.5. A. 1 shows the schematic representation of the complex formation of
CuO-PAA/CNT. Two types of samples were prepared to examine the effect of functionalized CNTs on the performance of CuO-PAA electrodes. The samples without CNTs are denoted as CP$_{500}$ and those containing functionalized CNTs as CPCNT$_{500}$. The samples were subjected to the characterization by using a plethora of techniques.

Fig.5.A.1 Schematic representation of the complex formation of CuO-PAA/CNT.
5. A.4 Results and discussion

FT-IR studies

The FT-IR spectra were recorded for the analysis and confirmation of bonding between CuO-PAA and CNTs. Fig. 5.A.2 (a) shows spectrum of the pristine CNTs without any bonding. Four characteristic peaks; at 2939, 2845, 1614 and 1450 cm\(^{-1}\) corresponding to SP\(^3\) C-H, SP\(^2\) C-H stretching vibrations and C=C bonds are observed [10]. In addition to the aforementioned peaks of the pristine CNTs, a peak at 1745 cm\(^{-1}\) is observed for the functionalized CNTs (Fig. 5.A.2 (b and d)). The existence of this peak indicates the attachment of –COOH functional group to the CNTs. Fig. 5.A.3 (a) shows the spectrum for CP\(_{500}\) sample. The high frequency modes at 532 and 592 cm\(^{-1}\) correspond to Cu-O stretching along \([10\bar{1}]\) and \([\bar{1}0\bar{1}]\) directions respectively are observed [20]. Further, the existence of three more peaks (1624, 1456 and 1732 cm\(^{-1}\)) ascertain the presence of C=C bond and COOH group that stem from the PAA component of the samples. This information helps confirm formation of CuO-PAA. Figs. 5.A.3(b-d) show the spectra for CPCNT\(_{300}\), CPCNT\(_{400}\) and CPCNT\(_{500}\) films respectively. The effect of addition of CNTs to the CuO-PAA complex is revealed in the spectrum as (i) blue shift in the Cu-O twin peak, (ii) increment in the intensity of peak correspond to Cu-O stretching, and (iii) blue shift of the peak corresponding to –COOH group. The modifications in the spectrum revealed the covalent bonding between CuO-PAA and CNTs. Thus the CuO-PAA/CNT formation is confirmed.
Fig. 5.A.2  FT-IR spectrum of (a) pristine CNTs without any bonding, (b) functionalized CNT

Fig. 5.A.3  FT-IR spectrum of (a) CP500 (b) CPCNT300, (c) CPCNT400 and (d) CPCNT500 films.
X-ray photoelectron spectroscopy

A high resolution Cu2p and O1s XPS spectra are used for the qualitative investigation of CP_{500} and CPCNT_{500} samples. Fig. 5.A.4 (a) shows the core level spectrum for the Cu2p peak over 930-970 eV corresponding to the CPCNT_{500}. The peaks observed at (i) 934.68 eV and (ii) 954.90 eV, are assigned to Cu2p_{1/2} and Cu2p_{3/2} respectively. Additionally, two satellite peaks are observed at 944.61 and 963.16 eV that are positioned at higher binding energies as compared to the main peaks and the difference between them is found to be about 9 eV. These results indicate the formation of the CuO phase [17]. Fig. 5.A.4 (b) shows the core level spectrum for the Cu2p peak corresponding to the CP_{500} sample. Similar to the CPCNT_{500} sample, two main and two satellite peak are observed, albeit with less intensity, confirming the formation of CuO phase. However, there is a red shift of about 0.5 to 1.0 eV in their binding energies. This shift indicates chemical bonding between CuO-PAA and CNT [18]. C.C. Chusuei et al. have reported the synthesis of CuO thin films by spin coating on Si wafer and XPS results are reported. Our results are in good agreement with this report [19].

![Fig. 5.A.4. The core level spectra of Cu2p peaks for (a) CPCNT_{500} and (b) CP_{500} thin films.](image-url)
Fig. 5.A.5 (a) shows O1s core level spectrum for CPCNT$_{500}$ sample deconvoluted with three components at 532.1, 533 and 530.6 eV, which were assigned to the carbonyl groups, hydroxyl groups and O$^{2-}$ respectively, of CuO. The spectrum also indicates that Cu$_2$O phase doesn’t exists in the sample. A slight shift in the O1s spectrum of CPCNT$_{500}$ is observed, due to the presence of CNTs in the sample.

![O1s core level spectra for CPCNT$_{500}$ and CP500 films.](image)

**UV-Vis spectroscopy**

The optical properties of CP$_{500}$ and CPCNT$_{500}$ samples were studied on the basis of transmission and absorption spectra. Fig. 5.A.6 (a) shows the variation of $(\alpha h\nu)^2$ vs. $h\nu$ for the CP$_{500}$ sample. The band gap energy was estimated to be 1.2 eV by extrapolating the linear portion of the curve to the energy axis (shown by a dotted line). The sample was highly absorbance. Upon addition of CNTs in CuO-PAA film (Fig. 5.A.6 (b)); two distinct regions, corresponding to CuO (1.2 eV) and CNT (3.5eV) components are observed. The excitonic peak of CNTs is also seen in the curve, which revealed CNTs
without change in its electronic structure [21]. Fig. 5.A.7 shows the transmittance vs. wavelength variation of CP$_{500}$ and CPCNT$_{500}$ samples. This plot reveals that the CPCNT$_{500}$ sample exhibits higher transmittance than that of the CP$_{500}$. The addition of CNTs render these samples 75% transparent. This is an interesting result to be used further for the fabrication of the transparent supercapacitors.

Fig. 5.A.6 shows the variation of $(\alpha h \nu)^2$ Vs $h \nu$ for (a) CP500 and (b) CPCNT$_{500}$ samples.

Fig. 5.A.7 Plot of transmission (%) Vs wavelength (nm) for CP500 and CPCNT$_{500}$ films
Scanning electron microscopy

Fig. 5.A.8 shows the SEM micrograph of the CP\textsubscript{500} sample. The CuO crystallites located inside the ring are surrounded by PAA grafted ring. Loosely bound PAA starts decomposing during annealing process at 500 °C and have formed CuO crystallites surrounded by PAA grafted ring with 15µm diameter (shown in the inset). Fig. 5.A.9 (a) shows the SEM micrograph of the CP\textsubscript{300} sample. Overgrowth having spherical shaped crystals is observed. Fig. 5.A.9 (b) shows the FE-SEM of CPCNT\textsubscript{300} sample. From this image it reveals that CNTs do not change the shape of the rings. However, it is observed that CNTs shrink the size of the rings to 500 nm diameter. Fig. 5.A.10 shows the SEM micrograph of the CPCNT\textsubscript{400}. The image clearly showed the well formed and uniformly distributed rings. Similar to CPCNT\textsubscript{300} sample, the shape of the ring is not changed but the size of the rings is changed to 600 nm diameter. Fig. 5.A.11 shows the SEM micrograph of the CPCNT\textsubscript{500}. Similar to the CPCNT\textsubscript{300} and CPCNT\textsubscript{400} films the change in size of the rings (1.2 µm) without change in shape is observed. Hence, additions of the CNTs affect the size ring like structure.

Fig. 5.A.8 SEM micrograph of the CP\textsubscript{500} film
Fig. 5.A.9 (a) SEM micrograph and (b) FE-SEM micrograph of the CP$_{300}$ sample.
Fig. 5.A.10 SEM micrograph of the CPCNT\textsubscript{400}.

Fig. 5.A.11 SEM micrograph of the CPCNT\textsubscript{500}.

Fig. 5.A.12 (a-c) shows the photographs of contact angle of water on the film surface of CPCNT\textsubscript{300}, CPCNT\textsubscript{400} and CPCNT\textsubscript{500} samples respectively. The contact angles 120°, 90° and 65° are observed for CPCNT\textsubscript{300}, CPCNT\textsubscript{400} and CPCNT\textsubscript{500} respectively. It is clear that the contact angle decreased making a change from a hydrophobic to a hydrophilic surface. As the annealing temperature increased, tuning of the wettability of CNT added CuO-PAA samples is a matter of considerable importance for the supercapacitor as
hydrophilic surface facilitates ionic diffusion processes and reduces resistance of the electrolyte into the electrode.

Fig. 5.A.12 Photographs of contact angle of water on the film surface of CPCNT\textsubscript{300}, CPCNT\textsubscript{400} and CPCNT\textsubscript{500} films

**Cyclic Voltammetry Study**

Fig. 5.A.13 shows CV curves of CP\textsubscript{500} and CPCNT\textsubscript{500} samples in 1M H\textsubscript{2}SO\textsubscript{4}. The CP\textsubscript{500} sample was swept between ±0.5V where as CPCNT\textsubscript{500} was swept between +0.8 to -0.6 V with respect to SCE. The higher current density over large potential window in the CV of CPCNT\textsubscript{500} indicates the higher specific capacitance (252 Fg\textsuperscript{-1}) and power density as compared to CP\textsubscript{500} (136 Fg\textsuperscript{-1}) at 20 mVs\textsuperscript{-1}. The enhancement in the specific capacitance of the CPCNT\textsubscript{500} was due to the increased conductivity of the electrode and the electrical double layer capacitance of the CNTs. A. T. Chidembo et al. have reported the improvement in specific capacitance (981 Fg\textsuperscript{-1}) of nickel (II) tetraaminophthalocyanine (NiTAPc) by forming the composite with functionalized MWCNT with respect to pure NiTAPc sample (198 Fg\textsuperscript{-1}) [22].
The differences between the anodic and cathodic peak potentials define the reversibility of the film. The CV of CPCNT\textsubscript{300} shows cathodic peak at -0.34 V and anodic peak at 0.041 V with potential difference ($\Delta V$) of 0.29 V. This difference is relatively large, hence CPCNT\textsubscript{300} film is relatively irreversible. This may be due to relatively low conductivity and wettability of the film. Similar to this CV, CNCNT\textsubscript{400} shows the cathodic and anodic peaks at -0.21 and 0.041 V respectively causing $\Delta V$ to be 0.16 V. Therefore CPCNT\textsubscript{400} film is more reversible than the CPCNT\textsubscript{300} film. The CPCNT\textsubscript{500} film exhibits peaks in the close proximity to reduce $\Delta V$ to 0.043 V indicating an improvement of its reversibility. Improvements in the specific
capacitance and the reversibility over larger potential window for CPCNT$_{500}$ film are due to an apparent increase in the electronic conductivity and wettability of films.

Fig. 5.A.14 CVs of the CPCNT$_{300}$, CPCNT$_{400}$ and CPCNT$_{500}$ films were swept between 0.9 to -0.5 V Vs SCE in 1 M H$_2$SO$_4$.

To evaluate the rate capability of the CuO-PAA/CNT films, CVs at different scan rates were recorded in 1 M H$_2$SO$_4$ electrolyte. Fig. 5.A.15 (a-c) shows the variation of the specific capacitance Vs scan rate in 1 M H$_2$SO$_4$ of CPCNT$_{300}$, CPCNT$_{400}$ and CPCNT$_{500}$ films respectively. For all films, it is observed that the specific capacitance decreases with increase in scan rate. Because, in the present study, the redox processes is mainly governed by the insertion/desertion of the H$^+$ from the electrolyte into/out of the CPCNT$_{500}$ samples. An increase in the scan rate has a direct impact on the diffusion of the H$^+$ into the host matrix, since at higher scan rates H$^+$ ions only approach the outer surface of the electrode material.
Fig. 5.A.15 (a-c) CVs at different scan rate for films (a) CPCNT\textsubscript{300} (b) CPCNT\textsubscript{400} and (c) CPCNT\textsubscript{500}

The stability of an electrode material is important for its use in supercapacitor. Fig. 5.A.16 (a-c) Show CVs of CPCNT\textsubscript{300}, CPCNT\textsubscript{400} and CPCNT\textsubscript{500} up to the 2000 cycle in the voltage range of +0.7 to -0.4 Vs SCE at 20 mV/s in 1 M H\textsubscript{2}SO\textsubscript{4} respectively. The inset figures of Fig. 5.A.16 (a-c) show the variation of the specific capacitance of CPCNT\textsubscript{300}, CPCNT\textsubscript{400} and CPCNT\textsubscript{500} films as a function of CV cycle number. Fig. 5.A.16 (a) shows the CVs of CPCNT\textsubscript{300} film. Inset figure of Fig. 5.A.16 (a) shows the large decrease in specific capacitance (58 %) 110 Fg\textsuperscript{-1} up to 100 cycles with respect to specific capacitance (188 Fg\textsuperscript{-1}) of first cycle. Further there is no decrease in specific capacitance from 1000 to 2000 cycles. Fig. 5.A.16 (b) shows CVs of CPCNT\textsubscript{400}. Inset figure of Fig. 5.A.16 (b) also shows the large decrease in specific capacitance (56 %) 125 Fg\textsuperscript{-1} up to 100 cycles with respect to specific capacitance (220 Fg\textsuperscript{-1}) of the first cycle. There is no decrease in specific capacitance from 1000 to 2000 cycles. Fig. 5.A.16 (c) shows the CVs of CPCNT\textsubscript{500}. Inset figure of Fig. 5.A.16 (c) also shows relatively less reduction in the specific capacitance (45 %) 117 Fg\textsuperscript{-1} up to 100 cycles. There is no further
decrease in specific capacitance above 100 cycles and up to 2000 cycle. From this study it is concluded that the stability of the CuO-PAA/CNT films increases with increase in the annealed temperature up to 500 °C. The CPCNT\textsubscript{500} film is stable as compared to the CPCNT\textsubscript{300} and the CPCNT\textsubscript{400} respectively.
Conclusions

A synthetic strategy to deposit CuO-PAA/CNT films and detailed study of the effect of annealing temperature (300 to 500 °C) on the performance of supercapacitor is presented. The phase pure CuO–PAA/CNT films are confirmed from two complimentary techniques: XPS and FT-IR. The novel ring like morphology is observed for all the films and its diameter increases (from 500 nm to 1.2 µm) with increase in the annealing temperature. The specific capacitance, reversibility and stability of the films increased substantially with increase in annealing temperature. The highest specific capacitance (258 Fg⁻¹) is observed for film annealed at 500 °C.