Fabrication of prototype flexible semi-conducting thin film with carbon nanomaterials
and carbon nanotubes using fish scale collagen

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\textbf{Abstract:} Carbon nanotubes (CNTs) exhibit extraordinary physical and electronic properties because of their intermolecular structure. In this proposed researched paper we introduced a novel technique for the preparation of Carbon nanotubes using \textit{Allium cepa} extract. Collagen thin film sheet is having a resistance of more than 10Mohms and it acts an insulator. Hence we want to prepare as a semiconducting collagen thin film, first, we incorporated a conducting ink to reduce the resistance to semiconducting range, less than 2M ohms. Therefore, a conducting ink was prepared by mixing carbon nanotubes, collagen and hydroxylethyl cellulose. Secondly, Collagen thin films were prepared using fish scales; it is an insulator thin film sheet which has flexibility and more physico-chemical strength.

\textbf{Keywords:} Thin film, Fish scales, Collagen, Semiconductor.

\textbf{I. INTRODUCTION}

Conductive thin film electrodes are widely used for resistance, current, voltage control based sensors, nano technology applied electronic devices and flexible switches. Among these applications in electronics the most commonly used materials are single walled carbon nanotubes mixed with suitable binders like agarose, ethylene, and gelatin etc. They are prone to variation of resistance; in addition, the binders and conductive adhesives are costly and require high temperature during thin film fabrication processes \cite{1-6}. However, the future nano tube based devices and other resistance based-electronic devices will require suitable methods such as ink-jet printing method for flexible electrodes to be produced at low cost and in a large scale. The search for such materials is mainly focused on conductive polymers and conductive nano-structures with precision, whereas the low conductivity of polymer thin film electrode (approximately 1 nanometer)\cite{7} restricts their applications. In recent years, nano-structures have been actively studied as future thin film electrode materials, including nanowires, nanotubes, and nanorods \cite{8-11}. Among these, carbon nanotubes are extensively explored in the past few years because of their theoretically high conductivity, good electromechanical properties, and chemical inertness \cite{12, 13}.
II. REVIEW OF LITERATURE

Sasirekha et al. extracted the collagen from Lates calcarifer, a species of catadromous fish in family latidae of order Perciformes and it is a sea based fish [16]. The fish scales were collected from fish market and washed with water. The scales were treated with acetic acid and then mixture of acetic acid and diethyl ether finally grounded with domestic mixture. The obtained paste is utilized for further studies by her. The prepared scaffold was assessed by various physiochemical and thermal studies [17].

Pati et al. extracted the collagen from scales of Labeo rohita (Rohu) is a species of fish and carp family Cyprinidae, found in rivers in South Asia [18] and Catla (Catla) is the only member of the genus Catla [19]. Their process starts with demineralization and extracted with acetic acid. The isolated protein was characterized by different physico-chemical techniques like FTIR, SDS-PAGE and CD spectroscopy. Thermal behaviour of isolated collagen was evaluated by thermogravimetric analysis [20].

Nagai et al. Extracted the fish scale collagen by means of decalcification using was decalcified with 0.05 m Tris–HCl (pH 7.5) containing 0.5 m EDTA- 4 Na for 2 days and then disaggregated with 0.1 m Tris–HCl (pH 8.0) containing 0.5 m NaCl, 0.05 m EDTA-2 Na and 0.2 m 2-mercaptoethanol (2-ME) for 3 days and then collagen was prepared by limited pepsin digestion. The amounts of collagen obtained from different scales were very high on a dry weight basis; sardine 50.9%, red sea bream 37.5% and Japanese sea bass 41.0%, respectively [21]. Bakers et al. Synthesized carbon deposits by means of nucleation, he decomposed the acetylene which were catalysed by nickel. After decomposition, it forms solids with filamentary, amorphous, or laminar form. The morphology was observed in SEM analysis were shown varies with reference to temperatures. 30–50 nm diameters at low temperature 870K and 300 nm in diameter at 1300 K [22].

Diener et al. synthesised the single-walled carbon nanotubes (SWNTs) in soothing, Iron and nickel act as catalyst for flame generation by subliming their bis (cyclopentadienyl) derivatives into an inert gas feed line that mixes with the hydrocarbon fuel and oxygen at the burner surface. This method is cost effective for large-scale synthesis, which is lacking in arc- and laser-based SWNT synthetic techniques [23].

Maruyama et al. used alcohol as the carbon source; a new simple catalytic chemical vapour deposition technique to synthesize high purity single-walled carbon nanotubes at low temperature is demonstrated. Because of the etching effect of decomposed OH radical attacking carbon atoms with a dangling bond, impurities such as amorphous carbon, multi-walled carbon nanotubes, metal particles and carbon nanoparticles are completely suppressed even at relatively low reaction temperature such as 700–800° C. By using methanol, generation of SWNTs even at 550° C were demonstrated. The high-purity synthesis at low temperature promises large scale production at low cost and the direct growth of SWNTs on conventional semiconductor devices already patterned with aluminium [24].

Sinani et al. prepared nanostructured thin films using semiconductor nanoparticles (NPs) are of great interest for biomedical applications, but NP materials based on heavy metals can be cytotoxic. Her preparation of semiconductor NPs followed the protocol of layer-by-layer (LBL) assembly, which alleviates this problem. Collagen/poly(acrylic acid) bilayers were added to CdTe/polycation LBL films to produce porous collagen bilayers. Such stratified multilayer systems showed successful cell attachment and survival while native NP films were strongly cytotoxic.

III. MATERIALS AND METHODS

Collagen was isolated from the fish scales (Lates calcarifer) collected from the local fish market (Royapuram, Chennai, India). Hydroxyl ethyl cellulose and ethanol were purchased from SD fine chemicals Pvt. Ltd., Chennai, Tamilnadu, India.

Preparation of fish scale collagen (FSC): Fish scales were washed with 10% sodium chloride solution to remove proteins attached on the surface followed by the demineralization of the scales using 0.5M EDTA solution (pH 7.4) for 48 hours, later they were washed three times with distilled water. Collagen extraction was done following the slight modification of the method explained by Pati et al. [15]. The demineralize scales were treated with 0.5M acetic acid
(pH 2.5) for 48 hours under stirring in cold room (4°C), later the insoluble scales were filtered out. Acetic acid soluble collagen was extracted by salting out using 0.9 M NaCl and kept undisturbed for 24 hours at 4°C, then the suspension was centrifuged and the precipitate was resolublized in 0.5 M acetic acid and dialyzed against 0.1 M acetic acid followed by distilled water for 24 hours and freeze dried.

**Preparation of Carbon nano particle (CNP) and Carbon nano tube (CNT):** Onions (Allium cepa) were collected and ground in domestic mixer and the juice was filtered using a cotton cloth. Cotton wick was dipped in this onion extract and dried at room temperature (30°C) and the process was repeated for four times. Thus treated wicks were put in a earthenware pot (capacity 50ml) containing 40 ml of gingelly (sesamum Indicum) oil. The wick was lit and the soot emanating from smoke was collected on the bottom surface of a spherical surface of earthenware vessel with a diameter of 10cm (Figure.1). The soot was collected from the bottom of the earthenware using stainless steel scalpel and stored separately. In the native Indian medicine this carbon soot along with the ghee is mixed well and used as an eye liner. Control experiments were performed wherein wick as such was dipped in gingelly oil and lit and the soot was collected. The carbon tube soot prepared using control wick is denoted as (CNP) where as the soot prepared using onion extract dipped wick is denoted as CNT.

![Figure 1 Synthesis of CNP and CNT](image)

**Preparation of CNP and CNT impregnated FC sheet:** 50mg of the CNP and CNT were taken separately and dispersed in 2ml of ethanol and sonicated. Various amounts of CNP and CNT were added separately to the 10% FC solution by stirring. In a typical experiment 25ml of FC (60% solid weight) were taken and the sonicated CNP, CNT were mixed separately by using Ultra Turrax (T-25 basic, 1KA werke) at a 17,500 rpm/min for 3 min at 1 min interval. The air bubbles were removed my using vacuum pump and were poured in to a plastic tray measuring 7.5 x 5cm, air dried at room temperature at 30-35°C and stored.

**Preparation of collagen sheet (FC):** 25 ml of freeze dried FC (60% solid weight) were taken and they were mixed with water and poured into a plastic tray measuring 7.5 x 5cm, air dried at room temperature at 30-35°C and the dried sheets were stored.

**Preparation of semiconducting thin film using CNP, CNT and mixture of CNP and CNT**

The thin film of collagen with carbon nanoparticles (CNP) and carbon nanotubes (CNT) are made as shown in figure 2. (c) and 2.(d) for different concentration of nanoparticles to make the variable resistances required for different applications.

Also the mixture of CNP and CNT can be added to make a different concentration using both for studying it characteristics.
Current resistors in use for various applications:

The current resistors in use are bulky and also power handling capacities, working voltage, temperature or heat dissipation when in operation are more when compared to the thin film collagen based resistors. Figure 3 (a-d).
Graphical Abstract

Figure 4. Shows the complete steps from raw material to the end product CNP and CNT based collagen thin film in application

The expected life of this product is more than 10 years. The maximum temperature it can withstand is 80º C. [A] Indian onion purchased from local market for preparing nanotubes. [B] Cotton thread dipped in onion extract used as wick in the lamp to form carbon nanotubes on the bottom surface of the china cub as shown in the experimental set up. [C] Carbon nano particle is made using the wick. [D] Carbon nanotubes is made using the cotton wick dipped in onion juice. [E] SEM picture of CNP and CNT. [F] Collagen of fish scale mixed with CNP and CNT separately and remote pad button conductor is made to use as switch, which is flexible and strong in physico mechanical strength. [G] The remote control of a TV. [H] The remote control is in on condition using the collagen as switch.

IV. RESULTS AND DISCUSSION

TEM analysis: TEM images of CNP and CNT are shown in Figure 5. CNP has shown spherical nanoparticle with the size in the range of 40 to 50nm (Figure.5a). The TEM picture of CNT has exhibited tubular structures along with spherical nanoparticles, the diameter of the CNT was found to be in the range of 150-200 nm (Figure. 5b) the reasons for the formation of nanotubes in the case of CNT is not known. The diameter of CNT is more compared to CNP this may be due to layer by layer coating of Allium cepa extract on to the CNTs.

Fig. 5 TEM images of (a) CNP having - 41.14 nm diameter (b) CNT having 157.37 nm diameter and (c) FTIR spectra of CNP and CNT
FTIR analysis: The FTIR spectra of CNP and CNT exhibited a broad band around 3400 cm\(^{-1}\) which may be attributed to -OH group present on the surface of the samples. Sharp peaks at 1513 cm\(^{-1}\) (CNP) and 1505 cm\(^{-1}\) (CNT) are due to C = C stretching mode, the absorption peaks at 1720 cm\(^{-1}\) for both the samples correspond to C = O stretching mode. Absorption bands at around 1457, 1243 and 1037 cm\(^{-1}\) are attributed to -C–H- and -C–C- bending mode in CNP, all these bands are slightly shifted in the IR spectrum of CNT (Figure. 5c). The FTIR spectrum of these CNT’s is comparable with that of earlier studied \(^{15}\).

Thermo-gravimetric analysis: In thermo-gravimetric analysis loss of weight due to the increase in temperature of the materials is plotted. Biomaterials lose their weight due to the decomposition of CO\(_2\), CO, NO\(_X\), and water. In the present study the thermo gram of FC, FC-CNP and FC-CNT are shown in the Figure 6. In the case of FSC a two step weight loss was occurred i.e., between 295\(^{\circ}\)C and 242\(^{\circ}\)C with the weight loss of 48% and between 432\(^{\circ}\)C and 646\(^{\circ}\)C with the weight loss of 13%, at 800\(^{\circ}\)C 4% residue was observed, however in the case of FC-CNP and FC-CNT a single step weight loss was observed between 272\(^{\circ}\)C to 514\(^{\circ}\)C and 241\(^{\circ}\)C to 498\(^{\circ}\)C respectively. More amounts of residues were observed in FC-CNP and FC-CNT samples. These results indicate thermal stability of FC-CNP and FC-CNT.

Electrical properties of FC sheets impregnated with CNP and CNT: The electrical properties of the samples are shown in Table 1. In the case of FC-CNP the electrical resistance decreases with the increase in the amount of CNP. Similar properties was also observed in the case of FC-CNT, however the electrical resistances were much lower in the case of FC-CNT. (>25 times).

![Thermo grams of FC, FC-CNP and FC-CNT](image)

**Table 1. Electrical property of FC sheets impregnated with CNP and CNT**

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<thead>
<tr>
<th>S.No</th>
<th>Voltage(V)</th>
<th>Current(mA)</th>
<th>Resistance(KΩ)</th>
<th>Power Dissipation(Watts)</th>
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<tr>
<td></td>
<td>CNP</td>
<td>CNT</td>
<td>CNP</td>
<td>CNT</td>
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<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>1.4</td>
<td>48.8</td>
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<tr>
<td>2</td>
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<td>150</td>
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<td>200</td>
<td>8.3</td>
<td>158.7</td>
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<tr>
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<td>250</td>
<td>250</td>
<td>12.9</td>
<td>198.4</td>
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Power dissipation in CNT impregnated samples was found to be better than the case of FC-CNP.
Details are given in Table 1. By regulating the amount of CNT in the composite electronic devices with required resistance can be fabricated. The reduction in the resistance facilitates more current and power dissipation and this property will be useful for the preparation of electronic sensors/noses.

**Testing of FC-CNP and FC-CNT in an electronic device (Television remote control):** FC-CNP and FC-CNT sheets were cut in to a size of remote controller switch button size which was used in television remote control and they were sandwiched between the key and printed circuit of the TV remote controller. It was practically operated to find the conductivity between the switch and the printed circuit of remote control; the samples were separately sandwiched in between them. The TV remote panel button switch was found to be operating well (on and off). It was found to be having perfect continuity and conduction which facilitates on and off function of the TV remote control as shown in the Figure 7. as switch.

![Figure 7. Testing of FC-CNP and FC-CNT in a Television (TV) remote control](image)

**V. CONCLUSION**

The FC-CNT’s prepared in this study seem to have interesting electrical properties which can be applied in the fabrication of devices like electron sensors/noses. From our experiment results it has been shown that the prepared FC-CNT’s possessing novel electrical, conducting properties. It can be used as a switch for controlling remote control field emission source for TV displays, remote control applications in electrical appliances such as remote AC, remote motor control and remote switch for car switch etc. It is well understood that the collagen from different sources can be used for wound healing, bio medical applications, for wastewater cleaning, lenses in human eye, collagen drink for arthritis problem and electronics applications, such as thin film resistors, thin film PCB, thin film transistors, thin film switches etc.

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**REFERENCES**

Dr. Inbasekaran Sundaramurthy is a Senior Technical/ Research Officer, working in Bioproducts Lab., CLRI since 1994. He has Published 8 papers in National and international journals and filed 1 patent and authored 1 book in IT. He has presented 6 papers and posters in international conferences, guided more than 25 projects at PG level on Nanoparticle Impregnated, Bioproducts and conducting materials. Development of Nano materials. His area of interest is Nano particle Impregnated, Bio-products and conducting materials. Development of Nano materials.

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<th>Dr. G. Ramamurthy</th>
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<td>is a Senior Principal Technical officer, Bioproducts Laboratory, CSIR-CLRI. He has Published 18 papers in National and international journals and filed 11 patents. He has presented 25 papers and posters in national and international conferences. Successfully guided M.Sc., M.Phil., B.Tech., and M.Tech., more than 30 Students. His area of interest is Preparation, Characterization and application of keratin proteins in leather and allied industries.</td>
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