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# Electrically conducting nanobiocomposites using carbon nanotubes and collagen waste fibers

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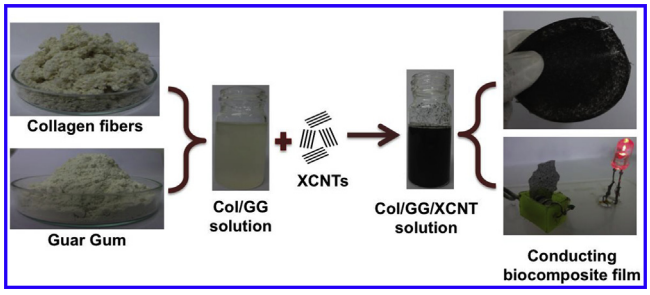
## HIGHLIGHTS

- Hybrid nanobiocomposite films prepared using collagen, guar gum and CNTs.
- Examined the effect of CNT doping on the properties of hybrid biocomposite films.
- Higher CNT loading improved the conductivity radically, especially for BCNT.
- The ability of developed hybrid films to lit up a LED lamp was demonstrated.
- The results suggest a new way to transform biowaste into advanced materials.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Electrically conducting hybrid biocomposite films were prepared using a simple and cost-effective method by incorporating different types of carbon nanotubes (XCNTs) viz., few walled carbon nanotube (FWCNT) and boron doped carbon nanotube (BCNT) into biopolymers. Collagen extracted from animal skin wastes was blended with guar gum and XCNTs in varying proportions to form flexible and electrically conducting hybrid films. We found that the electrical conductivity of both types of hybrid films increases radically as the XCNT loading increases. BCNT incorporated hybrid films show better electrical conductivity ($3.0 \times 10^{-1}$ S/cm) than their FWCNT loaded counter parts ($4.8 \times 10^{-4}$ S/cm) at a dosage of 2 wt.%. On the other hand, mechanical and other physical properties such as transparency, flexibility and surface smoothness of the developed hybrid films were affected as a function of XCNT concentration. We also demonstrated that the developed hybrid films lit up a LED lamp when inserted between batteries and the brightness of the emitted light depended on the XCNT loading. These results suggest a new way to transform an industrial biowaste into innovative advanced materials for applications in fields related to biomedicine, biosensors and electronics.



## 1. Introduction

Carbon nanomaterials in various forms have exceptional mechanical, thermal and electronic properties, which resulted in their

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usage in various fields such as composites, capacitors, sensors, energy storage devices, etc [1–3]. Doping of CNTs is carried out commonly since their discovery for enhancing their functional (i.e., electronic, thermal and mechanical flexibility) properties. For example, doping of CNT with boron was found to enhance the emission current density by 35% [4]. Such CNTs have been incorporated into the polymeric matrix to form polymer nanocomposites for various applications. For instance, single walled CNTs (SWNTs) were functionalized and incorporated with polypyrrole to form composites for energy storage applications [5,6]. Addition of small amount of CNT in polymer nanocomposites exhibits remarkable increase in their electrical conductivity due to large length to diameter ratio [7–9]. Few-walled carbon nanotubes (FWCNTs) with 2–6 walls, diameter ranging from 3 to 8 nm, were used as the structural reinforcing fillers in the formation of polymeric composites and found to enhance the mechanical properties markedly [10]. However, the use of synthetic polymers in the preparation of nanocomposites is expected to affect environmental sustainability. In this scenario, biocomposites based on renewable biopolymers are of great interest due to their biocompatibility and biodegradability. Type I collagen (Col), one such biopolymer, is the most important structural protein found in connective tissues such as tendon, bone and skins of animals. It possesses a triple helical structure stabilized by inter and intramolecular hydrogen bonding [11]. It is approximately 300 nm long and 1.5 nm in diameter. It has high tensile strength and low extensibility [12,13]. It is widely utilized as a biomaterial for tissue engineering applications in the form of hydrogels, sponges [14], scaffolds [15], films, sheets etc [16]. Guar gum (GG), another natural biopolymer derived from the seeds of guar plant (*Cyamoposis tetragonoloba*), attracted several researchers due to its low cost, non-toxicity, biocompatibility, biodegradation and physico-chemical properties [17]. GG and their derivatives have been used as thickening agent, thickener in cosmetics, dispersing agent, superabsorbent, etc [18]. GG is also used as a template to synthesize novel hybrid nanocomposites [19].

Recently, development of multifunctional biocomposites is on escalation due to their applicability in several fields. Significant efforts have been employed by researchers to produce conducting biopolymer based composites and electrolytes with improved dielectric property and AC conductivity [20–23]. Incorporation of carboxylated SWNTs with the collagen matrix does not affect the cell viability and proliferation of the formed composites [24]. Attempts were also made to prepare conducting nanobiocomposites from collagen/chitosan sources utilizing graphitic nanocarbons as well as copper nanoparticles [25,26]. Herein, we fabricated flexible and conducting collagen-guar gum (Col-GG) hybrid nanobiocomposite films by incorporating FWCNTs and boron doped carbon nanotubes (BCNTs) as fillers. Here, the matrix biopolymer, collagen is derived from protein waste generated from animal skins of leather industry while guar gum is a co-matrix renewable biopolymer obtained from plant sources. Two types of CNTs were chosen as filler, namely undoped (FWCNT) and doped (BCNT), in order to understand the effect of doping of CNTs on the multifunctional properties of the nanobiocomposites. The difference in the properties of the developed hybrid nanobiocomposite films are compared and analyzed. Their ability to glow a light emitting diode lamp when inserted between batteries is also investigated.

## 2. Materials and methods

### 2.1. Preparation of hide powder

The animal skin trimming wastes collected from a local tannery at Chennai, India were purified using conventional method as described elsewhere [27]. In brief, skin trimming waste were soaked, limed, dehaired, relimed, fleshed and delimed completely. The delimed skin pieces were soaked in 35 and 70% acetone, followed by 100% methanol for complete removal of moisture. Finally, the skin pieces were squeezed, vacuum dried and grounded thoroughly using Wiley mill into powder of mesh size 2 mm.

### 2.2. Preparation of nanobiocomposite films

About 1 L stock solution of collagen (10 mg/ml) was prepared by soaking collagen powder in 0.5 N acetic acid followed by blending to form a homogenous viscous solution. The formed viscous stock solution was stored in refrigerator for further studies. FWCNT and BCNT were received from Prof. Ajayan's group and their diameters were reported to be around 40–150 nm for BCNT [28] and 8–12 nm for FWCNT [29]. Both the nanotubes (XCNTs) were purified by adding concentrated nitric acid followed by stirring and heating at 65 ± 5 °C at 300 rpm for 2 h. The XCNTs were finally washed with distilled water until the pH reaches 7 and dried under hot air oven at 100 ± 2 °C for 5 h.

The XCNT incorporated nanobiocomposite films were prepared by blending collagen with guar gum. The amount of GG was fixed at 10 wt.% (percentage based on the weight of collagen). GG was added directly to 20 ml of collagen (10 mg/ml) solution. The Col-GG blends were stirred for 1 h at 45±3 °C to obtain viscous homogeneous solutions. To this solution, purified nanotubes (BCNT and FWCNT) were added in different proportions such as 0.25, 1 and 2 wt.% (percentage based on the weight of collagen) and probe sonicated (Sonic-150W, Lark Innovative Fine Teknowledge, India) intermittently for a total of 3 h with regular intervals. The samples were sonicated for 15 min followed by 10 min interval between each sonication in order to reduce the heat formation. The sonicated mixtures were further stirred at 40±5 °C for 12 h. The blends were poured into Petri plates (9 cm dia.) and dried at 35±5 °C to obtain hybrid biocomposite (Col/GG/XCNT) films with a thickness of 80 ± 10 μm.

### 2.3. Characterization of the developed nanobiocomposite films

The mechanical properties such as load (N), stress (MPa) and strain (%) of the developed nanobiocomposite films were analyzed using Instron-4501 universal testing machine. Three films from each composition were cut perpendicular to each other into dumbbell shaped specimen of 40 × 5 mm (length:width) and analyzed using ASTM D882 standard and their average values were calculated [30]. The load cell used was 100 N and the crosshead speed was set at 50 mm/min. Fourier transformed infrared (FTIR) spectra were recorded for all the samples (MB3000; ABB Bomem Inc.) in the range of 400–4000 $cm^{-1}$ using an attenuated total reflection (ATR) placed on a diamond ATR crystal. An average of 30 scans and 4 $cm^{-1}$ resolution were used for all the samples. Thermogravimetric analysis (TGA) of developed nanobiocomposite films was carried out using TGA Q50 (V20.6 Build 31, TA Instruments). About 10 mg of the specimen was heated under nitrogen atmosphere at a heating rate of 20 °C/min. The analysis was carried out from 30 to 700 °C. The surface morphology of the nanobiocomposite films were analyzed using Field emission scanning electron microscopy (FESEM; SU6600, Hitachi) operated at 10 kV. The specimens were coated with gold using a sputter coater (E–1010, Hitachi) for 20 s before analysis. Electrical resistance of the developed nanobiocomposite films was measured using a two probe 4.5 digit micro-ohm meter. The samples were cut into 1 × 1 $cm^2$ area and used for the analysis. Thickness of the nanobiocomposite films was measured using a bench type thickness gauge (S.No. 2201.2.4, Baker, India) to the nearest 0.01 mm at 3 random positions and their average values were calculated [31].