



Mini Review

Review on CNTs nanocomposite sensors

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ABSTRACT

The one-dimensional hollow cylindrical carbon nanotube nanostructure has been crucial in advancing nanotechnology since its discovery. Carbon nanotubes have been utilized in technical fields both in their pristine form and as nanocomposites. They have been combined with various conductive and non-conductive matrices based on specific end goals. In sensing technology, remarkable progress has been made in the development of multifunctional carbon nanotube nanocomposites. Common matrices used in this context include conjugated polymers such as poly(3,4-ethylenedioxythiophene): polystyrene sulfonic acid, polyaniline, etc., along with thermoplastics like polyamide, polyurethane, etc. Within these matrices, carbon nanotubes can establish a percolation network for electron or charge transport and can also create interfacial interactions to enhance compatibility, stability, and durability. The sensing capabilities of the resulting carbon nanotube nanocomposites are influenced by their interactions with the analyte, whether it be gases/ions, biomolecules, or motion. As a result, nanocomposites have been employed in the creation of effective gas sensors, strain sensors, and biosensors. The performance of carbon nanotube sensors has been evaluated based on factors such as sensitivity, selectivity, detection limit, reproducibility, and responses to analytes.

Keywords: Carbon Nanotube, Nanocomposite, Sensors, Nanotechnology

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Introduction

The utilization of nanomaterials has led to significant advancements in the field of sensors [1]. Nanocomposite designs, in particular, have demonstrated high-performance sensing capabilities. In this regard, a variety of nanoparticles and matrices have been employed to create cutting-edge sensors. The resulting nanocomposite nanostructures play a crucial role in determining the sensing capabilities and features of these sensors. Polymer-based nanocomposites have been extensively studied in the sensor field. Both conjugated and non-conjugated matrices have been utilized in the design of these nanocomposites for sensor applications. Conjugated nanocomposites exhibit important properties such as percolation and electrical conductivity, which contribute to enhanced molecular sensing capabilities. Carbon nanotubes (CNTs) have garnered significant attention in research, particularly in the realm of nanocarbon nanoparticles [2]. Remarkable advancements involving carbon nanotubes have been witnessed in various technical domains through the development of nanocomposites. Incorporating carbon nanotubes into polymeric matrices has resulted in improvements in key physical characteristics such as electrical conductivity, dielectric properties, electrochemical behavior, thermal properties, mechanical strength, barrier properties, and electromagnetic properties [3]. The essential properties of polymeric nanocomposites have led to a wide range of beneficial applications. In the realm of supercapacitor electrode applications, polymer/carbon nanotube nanocomposites exhibit high surface area, desirable pore size and structure, excellent mechanical and thermal resistance, as well as an efficient electron-transporting percolating network formed by the nanotubes. As a result, the electrochemical, conductivity, and supercapacitance properties of electrodes have been extensively studied across various nanocomposite designs [4]. Another significant application of polymer/carbon nanotube nanocomposites has been noted in bulk heterojunction solar cells. This is attributed to the exceptional electron transportation and electron affinity properties of carbon nanotubes within light-harvesting polymer donor matrices [5]. Polymer/carbon nanotube nanocomposites have found advantageous applications in thermoelectric devices that require thermopower, electrical conductivity, and thermal conductivity. These nanocomposites offer superior and tunable electrical conductivity, thermal conductivity, and a tunable Seebeck coefficient. Moreover, in electromagnetic interference shielding systems, the high aspect ratio, electrical conductivity, magnetic properties, interfacial

polarization, as well as real and imaginary permittivity characteristics of polymer/carbon nanotube nanocomposites have led to an effective shielding against radiation. These nanocomposite shields offer advantages such as low density, cost-effectiveness, and resourceful properties compared to metal shields [6]. In the realm of water purification membranes, polymer/carbon nanotube nanocomposite membranes have been significantly utilized. This is attributed to their tunable surface chemistry, structural features, as well as manageable pore sizes and porosity characteristics, which are crucial for effective water purification processes. As a result, these membranes have been employed for the elimination of salts, toxic ions, organic substances, dyes, and biological impurities from water. The sensing capabilities of carbon nanotubes have been enhanced due to their high surface area, nanoscale dimensions, cylindrical one-dimensional nanostructure, and conductivity characteristics [7]. Sensitivity of the carbon nanotube nanocomposite sensors has been perceived towards various gaseous, biomolecules, and other species. In addition to nanomaterial design, carbon nanotube interactions and amounts in the matrices led to high conducting and sensing features. The adoption of appropriate processing techniques significantly influences the homogeneity of nanocomposites and their final properties. As a result, the field of sensors has attracted significant research interest in the detection of gases, bio/chemical substances, and strain effects [8]. Comparatively, metal oxide sensors are known for their high costs, complex fabrication processes, and requirement for high operating temperatures. As a result, sensor designs based on polymer/carbon nanocomposites have been created, incorporating a synergistic blend of electrical and mechanical characteristics along with tunable electroactive properties. This integration forms an excellent sensing platform for efficient gas and chemical detection. Both conjugated and non-conductive polymers, along with carbon nanotube-based systems, have been documented to exhibit high-specific surface area, physicochemical adsorption capabilities, efficient charge transportation, porosity, and specific interactions with analytes. These properties contribute to high selectivity, sensitivity, and responses in sensing applications [9]. In this context, the functionalization of carbon nanotubes and nanocomposite formation has significantly boosted the affinity towards specific analyte species. As a consequence, gas/chemical/bio sensors derived from polymer/carbon nanotube combinations exhibit superior sensitivity, rapid response times, excellent reproducibility, and low detection limits. Furthermore, high-performance strain sensors have been successfully developed utilizing carbon nanotube nanocomposites. In carbon nanotube dispersed polymer

matrices, the tunneling effect has been noted within the nanotube network. This combination of tunneling and percolation properties has led to the discovery of high piezoresistive sensitivity, enhancing strain sensing capabilities [10]. Due to the observed literature so far, recently vast research has been reported regarding the efficient and gas, chemical, or strain sensors. In this way, novel and significant contributions of polymer/carbon nanotube nanocomposite sensors have been observed. In this context, high-performance nanocomposites have been industrialized by incorporating functional carbon nanotubes into both conducting and non-conducting matrices. As a result, multifunctional carbon nanotube nanocomposite designs, processing techniques, properties, and sensing capabilities have been explored. Significant applications have been identified in the fields of gas sensors, strain sensors, and biosensors [11]. This review appears to be groundbreaking in the realm of carbon nanotube nanocomposite sensors, offering a comprehensive outline, coverage of relevant literature, and detailed sensor designs for efficient investigations. According to the literature, there have been notable reports on carbon nanotube nanocomposites specifically related to sensor applications. It seems that comprehensive review articles detailing the current state, advancements, and future prospects in the field of carbon nanotube nanocomposites have not been widely available. Therefore, this review aims to provide a valuable summary for researchers in the field, offering insights into designs and processing methods to address challenges and enhance the development of multifunctional sensors.

1. Carbon nanotube and nanocomposites

Since the groundbreaking discovery of carbon nanotubes in 1991 [12], nanocarbon nanoparticles have garnered significant attention in various technological fields. A carbon nanotube is a carbon nano-allotrope, composed of sp^2 hybridized carbon atoms arranged in a hexagonal configuration to create a hollow tubular nanostructure. Carbon nanotubes exist in various forms, including single-walled, double-walled, and multi-walled structures. Single-walled carbon nanotubes can have a diameter as small as 1 nm and lengths of up to 100 nm, resulting in unique dimensions, morphological characteristics, and chirality features [13]. The optical, electronic, mechanical, and physical properties of carbon nanotubes have been extensively studied and explored. As a result, the unique carbon nanostructure of carbon nanotubes exhibits high surface area and

remarkable structural and physical characteristics. These exceptional nanostructures are synthesized using a variety of techniques such as chemical vapor deposition, laser ablation, arc discharge, catalytic growth, and organic routes. Carbon nanotubes find applications in various practical sectors including energy devices, sensors, electronics, membranes, engineering structures, aerospace/automobile industries, and biomedical fields [14]. The remarkable nanostructure of carbon nanotubes has resulted in a wide range of properties observed in high-performance polymer/carbon nanotube nanocomposites. These nanocomposites exhibit valuable electrical, dielectric, thermal, mechanical, rheological, and other characteristics due to the reinforcement by carbon nanotubes. Increasing the amount of carbon nanotubes has been found to enhance the physical properties of these nanocomposites. Moreover, factors such as functionalization of the carbon nanotube surface, processing methods, interactions with matrices, and interface formation significantly influence the properties of these nanocomposites. The electrical properties of carbon nanotubes are dependent on their aspect ratio and intrinsic conductivity features [15]. By integrating carbon nanotubes into matrices, the electrical conductivity within polymer matrices is initiated, leading to the creation of three-dimensional conducting networks for electron conduction. Electrical conduction occurs as electrons hop or tunnel through the dispersed carbon nanotubes in the matrices. At a specific minimum loading of carbon nanotubes, a percolation threshold is reached as a continuous network forms. Due to their electrical conductivity properties, polymer/carbon nanotube nanocomposites find applications in various fields such as conducting coatings, electrostatic coatings, electrostatic dissipation, electromagnetic interference shielding, anti-static packaging, electronic devices, automotive, aerospace industries, and many other areas [16].

2. Carbon nanotube nanocomposites for sensing

The sensing performance of various nanostructures towards gases, ions, and chemical species has been extensively studied in the literature [17]. In addition to their advantageous structural and physical characteristics, carbon nanotubes possess inert and environmentally friendly properties that make them suitable for practical applications. Key sensing properties of carbon nanotubes include electron and charge transportation mechanisms. Carbon nanotubes have been utilized in sensing applications due to their fine sensitivity, selectivity, and rapid response properties.

Polymer/carbon nanotube nanocomposites have been manufactured using various processing methods [18]. The choice of processing technique depends on the type of polymer matrix selected for processing. Regardless of the method used, the primary focus is on achieving uniform dispersion of carbon nanotubes in the matrices. Various techniques such as in situ fabrication, solution processing, interfacial methods, electropolymerization, coating processes, and related approaches have been employed to create conjugated polymer/carbon nanotube nanocomposites for sensor applications. Solution processing involves mixing carbon nanotubes in a matrix solution through mechanical stirring, shaking, shear mixing, or sonication. For successful formation of solution nanomaterials, the polymer should be soluble in a readily processable solvent. Mixing forces are utilized to improve the de-bundling of nanotubes, aiming for their fine dispersion within the matrices [19]. This method is straightforward and cost-effective. Interfacial polymerization has also been employed to create nanomaterials for sensors. This technique involves the reaction of the polymer and nanoparticles at the interface of two immiscible liquid phases to generate a film at the interface. In situ polymerization enables the polymerization of monomers in the presence of a dispersed carbon nanotube for the production of well-dispersed nanocomposites [20]. This method is commonly used for forming conjugated polymer/carbon nanotube nanocomposites. The electropolymerization method involves the direct deposition of the polymer or nanocomposite onto the electrode surface by oxidizing the monomer in an electrochemical cell. Melt processing has been a preferred method for the commercial-scale production of carbon nanotube nanocomposites. This technique involves the use of molten polymer flow and high shear forces to de-agglomerate and uniformly mix the polymer/carbon nanotube nanomaterials. While each method has its limitations, these drawbacks can be addressed by employing combination techniques that incorporate aspects of in situ, solution, and melt processing [21]. Additionally, more advanced coating and fabrication techniques have been utilized for creating sensor designs, such as doctor blading, spin coating, and freeze-drying methods. In doctor blading, the polymer/carbon nanotube nanocomposite solution is applied onto a substrate [22]. In the doctor blading method, the solution is spread by maintaining a constant relative movement between the blade and substrate to create a thin layer, which is then dried to form a film. This method allows for operation at various speeds, resulting in films of different thicknesses. In spin coating, the solution is placed on a substrate and rotated at high speed under specific conditions to generate centrifugal force. This process ensures the

even spreading of the solution on the substrate, producing ultrafine and homogeneous films. Freeze drying involves placing the polymer nanocomposite solution in a mold. Initially, water is introduced into the organic solution, followed by rapid freezing with liquid nitrogen. Subsequently, the pressure is reduced to a few millibars to facilitate the sublimation of the mixture. These techniques provide efficient and straightforward methods for sensor fabrication [23].

2.1 Gas sensors

Carbon nanotubes have been effectively employed in gas sensor designs because of their ability to adsorb, link, and bond with gas molecules. When utilized in the form of nanocomposites, carbon nanotube-based nanomaterials exhibit superior electrical conductivity and durability, making them ideal for gas sensing applications [24]. Lapointe et al. [25] developed nylon 69/carbon nanotube nanocomposites for gas sensing applications, utilizing them as field-effect transistors for gas sensing purposes. Carbon nanotubes have been dispersed on the surface of the field-effect transistor. The high surface area of solid interfaces allows for enhanced interaction with the surrounding environment. Nanocomposites of conjugated polymers such as polyaniline, polypyrrole, and polythiophene have been commonly fabricated and studied for sensing applications. These designs have been utilized to create sensors for detecting NO_x. Furthermore, conducting polymer/carbon nanotube nanocomposites have demonstrated sensing capabilities towards gases such as methane, halogens, and oxides of carbon, sulfur, and nitrogen [26].

2.2. Strain sensors

In addition to gas sensing applications, nanocomposites have found significant use in the field of strain sensing, offering competent electrical and optical responses. Polymeric nanocomposites filled with conductive nanofillers exhibit excellent stability and sensitivity for target analytes in diverse sensing applications, including strain sensing. For strain sensing purposes, thermoplastics in combination with conjugated polymer nanocomposites have been utilized. Thermoplastics such as polyurethane, when combined with conjugated matrices filled with conducting carbon nanoparticles, have been employed for the development of strain sensors. Thermoplastic polymers have been effectively utilized in the fabrication of strain sensors [27]. Ding and

colleagues [28] have industrialized carbon nanotube-reinforced nanocomposites based on a thermoplastic polyurethane matrix and hydroxyethyl cotton cellulose nanofibers for strain sensing applications.

2.3. Biosensors

Nanocomposite sensors have also demonstrated potential for detecting biological and chemical species. In the realm of biosensing, designs based on metal nanoparticle nanocomposites have been highlighted. These sensors are utilized to study the chemical processes within biological systems and have shown high biosensitivity and selectivity [29]. However, inorganic nanocomposites containing metal nanoparticles can potentially have toxic effects on living systems. As a result, polymer/nanocarbon composites, particularly polymer/carbon nanotube nanocomposites, have emerged as efficient options for biosensing applications [30]. Numerous biosensor designs based on carbon nanotubes boast features such as high surface-to-volume ratio, conductivity, electrocatalytic activity, reproducibility, sensitivity, and rapid responses for biomolecules. Yamada et al. [31] devised a sensor utilizing a polyethylenimine/carbon nanotube nanocomposite coated on gold tungsten wires to detect a bacterial strain, *Escherichia K-12A*. Khan and colleagues [32] developed a biosensor utilizing a printable ink based on carbon nanotube-DNA fragments to detect lysozymes. This biosensor exhibited a detection range of 0–1 $\mu\text{g/mL}$ with a detection limit of 90 ng/mL. Shao et al. [33] documented a single-walled carbon nanotube-based field-effect transistor biosensor designed to detect the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). Carbon nanotube-based biosensors have been miniaturized to offer high stability, minimal toxicity, rapid responses, and low detection limits. Despite their advantages, some drawbacks have been noted for these biosensors, such as challenges in selectively removing nanotubes while ensuring sensor stability. High performance carbon nanotube nanocomposites have been reported having the gas sensing, strain sensing, and biosensing potential [34]. The polymer/carbon nanotube nanocomposite sensors revealed fine sensing performance due to fine nanotube alignment, dispersion, and interfacial effects to better sense the gaseous or biomolecules.

Conclusion

This overview discusses efficient carbon nanotube nanocomposite designs for gas sensing, strain sensing, and biosensing applications. It covers fabrication, physical characteristics, and sensing performance. The sensors use carbon nanotubes reinforced in thermoplastic and conjugated matrices. Research indicates that specific polymer matrices and fabrication techniques have improved selectivity, sensitivity, linear resistance responses, and reproducibility of these advanced sensing designs. By combining conjugated polymers with carbon nanotube nanofillers, a more effective percolation network is formed in the matrices for electron transfer, enhancing the sensing capabilities of the nanomaterials. As a result, these designs have shown improved detection of gaseous molecules, motion changes, and biological species. Indeed, this innovative article effectively highlights the progress in the field of polymer/carbon nanotube nanocomposite-based sensors. It can serve as a valuable resource for scientists and researchers in the field, guiding them to explore further developments and opportunities in this area.

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