Fabrication and Patterning Methods of Flexible Sensors Using Carbon Nanomaterials on Polymers

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Flexible sensors composed of carbon nanostructures and elastic materials have been developed for healthcare monitoring, environmental monitoring, disposable biochemical or electrochemical sensors, and many other applications. Fabrication approaches for such sensors and their advantages and current issues related to patterning high-performance flexible sensors are reviewed. A focus is placed on patterning techniques for carbon-based flexible sensors including carbon nanotubes, graphene, and other carbon nanostructures. First, novel patterning techniques for nanomaterials are described, along with their current challenges. Next, emerging flexible sensors including humidity, temperature, strain, and pressure sensors are discussed. Finally, the challenges and perspectives for flexible sensors are addressed.

1. Introduction

Flexibility is one of the requirements for wearable sensors, allowing the sensor to conform to body movements. The ability to stretch is of importance for sensor-skin interaction. For example, bending of fingers generates simultaneous flexure and stretching. Along with the choice of materials, patterning techniques affect the performance parameters of the sensors. For flexible sensors measuring pressure and motion, two approaches are used to achieve high sensitivity: 1) choosing a substrate with a low Young’s modulus such as a polymer to provide higher deformations and 2) creating microstructures during fabrication which substantially improve the response of the sensor. The second approach includes microstructures such as pyramids,[1] domes,[2] and other rough surface morphologies.[3,4] It is through a rational choice of materials and fabrication techniques that sensors can be tailored for a specific application.

The ability of a process to fabricate 3D structures and form functional materials expands the list of available techniques beyond established silicon processes. Novel sensors require the integration of different functional materials such as structural elements, conductors, and biochemical components. Those materials are integrated in a variety of ways including deposition, coating, assembly, printing, etc., which exemplifies the diversity of processes used in sensor fabrication.

Flexible sensors are especially suited for novel applications in healthcare, which are represented by noninvasive, measurement and real-time monitoring of biophysical[3,4] and biochemical[6,7] signals from the human body, such as wrist pulse monitoring,[8] strain measurement,[9] humidity measurement,[10] vibration detection,[11] touch[12] and pressure[13] measurement, electrochemical detection,[14] body temperature measurement,[15] and many others. Table 1 shows the flexible sensors, materials used, their performance, and applications. Many of the sensors can be applied for diagnosing diseases, monitoring a person’s health, predicting cardiac events, and assisting in everyday tasks by providing signal feedback to actuators. It is evident that flexible sensors have promising applications in the next generation of healthcare technology. Representative applications are shown in Figure 1.

The focus of this Review is to describe the fabrication processes used in recently developed flexible sensors which use carbon nanomaterials. The patterning approaches, deposition methods, and ink formulation characteristics are reviewed with emphasis on film formation. Furthermore, different strategies are compared and analyzed with respect to patterning ability and sensor performance. Finally, the remaining challenges in flexible sensor fabrication are addressed.

2. Materials for Flexible Sensors

Largely due to advances in semiconductor processing technologies, deposition and patterning of metals have achieved considerable progress in rigid substrates. However, functional sensors that use large deformations present incompatibilities with surface-coated metal films. For example, microcracks and discontinuities are formed due to the difference in Young’s modulus of metal and substrate. In addition, the high cost and complexity...
of semiconductor processes pose a challenge in developing novel flexible sensors. Research efforts have been directed to leverage the properties of nanomaterials while preserving functionality and performance of the sensors, and the electrical conductivity of carbon nanomaterials makes them especially effective in the development of conductors, active layers, and transduction elements in flexible sensors. Among the emerging types of carbon nanomaterials are carbon nanotubes (CNTs), graphene and its derivatives, and carbon black. CNTs are carbon atoms arranged in a cylindrical configuration where the diameter reaches up to 100 nm, and the length is of the order of micrometers.\(^{16}\) CNTs are excellent electrical conductors, with intrinsic conductivities up to 106 S cm\(^{-1}\).\(^{17}\) This property is used in the fabrication of conductive films and electrodes. However, the conductivity of a printed CNT film greatly decreases from the intrinsic conductivity due to contact resistance, especially if the CNTs are not uniformly printed or form bundles.\(^{18}\) A nanotube formed by a single layer of arranged carbon atoms is regarded as a single-walled carbon nanotube (SWCNT), whereas for multiple layers, it is regarded as a multiwalled carbon nanotube (MWCNT). The Young’s modulus (E) of individual CNTs has been measured to be 1054 GPa for SWCNT and 1200 GPa for MWCNT.\(^{19}\) CNTs have been applied to a variety of sensors in microelectromechanical systems (MEMS),\(^{20}\) chemical sensors,\(^{21}\) and many others.\(^{22}\) Graphene is a single layer of carbon atoms which possesses outstanding mechanical, electrical, and chemical properties such as a Young’s modulus of 1.1 TPa, a high carrier mobility,\(^{23}\) and rich chemistry.\(^{24}\) Derivatives of graphene include graphene oxide (GO) and reduced graphene oxide (rGO), which are often preferred due to easier handling than pristine graphene and possessing more chemical interactions by attached functional groups. Due to the 1D and 2D nature of the described carbon nanomaterials, the majority of the carbon atoms are surface atoms, which are highly affected by conditions of the environment.\(^{25}\) This property is used in chemical, gas, and humidity sensors where a higher surface area endows a higher sensitivity to the sensor.

**Table 1.** Flexible sensors, materials used, their performance, and applications.

| Type of sensor\(^a\) | Sensitivity | LOD | Response/ recovery time | Durability | Range | Materials used | Applications | Ref. |
|----------------------|-------------|-----|-------------------------|------------|-------|----------------|--------------|------|
| Pressure | 34.47 kPa\(^{-1}\) | 0.8 Pa | 16.7 ms | 10 000 cycles | NA | Silk nanofiber from silkworm cocoons | Pressure distribution mapping, pulse wave, respiration monitoring | [8] |
| Pressure | 1.1 kPa\(^{-1}\) | 4 Pa | 60 ms | 11 000 cycles | 10 kPa | Carbon conductive paste/PDMS composite | Arterial pulse wave and breath measuring | [87] |
| Strain | GF 112% | NA | 45 ms | 15 000 cycles | up to 91% | Carbon black/PDMS composite | Finger, foot motions | [82] |
| Humidity | 0.75%/%RH | NA | 330 s/377 s | NA | 11–95% RH | Cellulose Nanofibers and CNTs | Humidity sensing | [96] |
| Humidity | 0.15%/%RH | 4% RH | 1.9 s/1.5 s | NA | 4–95% RH | Carbon nanocoils and liquid crystal polymer | Respiration, speaking, blowing, and noncontact fingertip sensation | [72] |
| Humidity | 0.048%/RH | NA | 20 s/35 s | NA | 20–80% RH | SWCNT/ hydroxyethyl cellulose composite | Humidity sensing | [97] |
| Temperature | 0.008 °C\(^{-1}\) | NA | 3.91 s/4.58 s | 100 cycles | NA | Graphene/PDMS composite | Skin temperature measurement | [94] |
| Temperature | 0.8% °C\(^{-1}\) | NA | 10 000 cycles | 30–80 °C | rGO/polyurethane fibers | Skin temperature measurement | [15] |

\(^{a}\)NA: not available, LOD: limit of detection, PDMS: poly(dimethylsiloxane), RH: relative humidity, GF: gauge factor.
to achieve functional physical and chemical sensors: it is necessary to deposit additional materials on PDMS to act as transduction elements. Therefore, the methods reviewed in the next section have been developed with the aim of printing and embedding CNTs in PDMS.

3. Processing of Carbon Nanomaterials for Flexible Sensors

Due to the electrical properties of carbon nanomaterials and the need to fabricate functional composites which are responsive to strain, several methods have been developed to embed CNTs in PDMS, such as in situ polymerization, mixing PDMS prepolymer and curing agent for CNT dispersion through solvents, mixing and grinding, screen printing, vacuum filtration, etc. In this section, each method is reviewed and analyzed with regard to its advantages and drawbacks. Table 2 shows material deposition methods on PDMS for the fabrication of flexible sensors.

3.1. Filtration

Filtration of carbon nanomaterials can be used for the formation of highly uniform films. A porous membrane is used to filter the carbon material while a positive or negative pressure is applied to control the flow of solvent through the membrane.
Table 2. Methods for material deposition on PDMS.

| Name of the method               | Short description                                                                 | Materials  | Sheet resistance/ resistivity | Ref. |
|----------------------------------|------------------------------------------------------------------------------------|------------|-----------------------------|------|
| Vacuum filtration                | Vacuum filtration followed by PDMS casting and peeling.                            | MWCNT on PDMS | NA                          | [35] |
| Transfer printing                | Transfer CVD-grown SWCNT from a silicon wafer to a flexible substrate such as PET. | SWCNT on PET, PDMS stamp | 265 Ω sq⁻¹ | [37] |
| µCP                              | Vertically aligned MWCNT on PDMS.                                                 | CNTs, PDMS | NA                          | [44] |
| µCP and cast molding             | MWCNT and PDMS were separately dissolved in toluene and later mixed.              | CNTs, PDMS  | 16.6 Ω cm                  | [43] |
| Spray coating                    | Spray coating SWCNT onto PDMS.                                                    | SWCNT, PDMS | 328 Ω sq⁻¹                  | [46] |
| Direct mixing                    | Carbon black nanopowder was mixed in PDMS and cast onto a patterned glass mold. CNTs were mixed with PDMS in a planetary mixer and cast onto an acrylic mold. | MWCNT on PDMS | 1 Ω cm                      | [48,102] |
| Indirect mixing                  | Graphite was microwave exfoliated, dispersed into hexane, mixed with PDMS base, and then mixed with PDMS resin. | Exfoliated graphite on PDMS | 2.5 Ω cm                    | [103] |
| Screen printing                  | Screen printing SWCNT on PDMS.                                                    | SWCNT, PDMS | 100 Ω cm                   | [30] |
| Inkjet printing                  | Inkjet print aqueous solution of CNTs on PET film and transfer the printed material to PDMS after spin coating PDMS. | CNTs, PDMS | 1.2 kΩ sq⁻¹                 | [57] |
| EPD and transfer micromolding    | Carboxylated CNTs were dispersed in solution, and a gold-coated silicon was immersed and energized. | CNTs, PDMS | NA                         | [41] |
| Drop casting                     | Drop casting carbon nanocoils on polymer substrate and gold electrodes.            | Carbon nanocoils, liquid crystal polymer | NA                          | [72] |

a) NA: Not available.

(Figure 2a). CNTs that are dispersed in aqueous solution can be filtrated to produce a highly conductive film. A potentially large-area film can be fabricated (>cm²) if the membrane is left in its pristine form. Alternatively, selective areas can be patterned on the membrane using photolithography, such that CNTs preferentially deposit on the patterned areas (Figure 2b). Furthermore, the thickness of the film is controlled by nanotube concentration and volume of ink used during filtration. Transfer of the film to a receiving substrate is required, along with postpatterning of the film. Transfer of the film can be accomplished either by dissolving the membrane, directly pouring PDMS on the film with subsequent curing, or using a PDMS stamp to transfer CNTs from the membrane to a final substrate. Filtration has shown potential for large-area, high-conductivity patterns of CNTs, but the use of photolithography hinders the low-cost fabrication of devices.

3.2. Transfer Printing Techniques

Transfer printing techniques comprise printing materials on a source substrate and transferring them with the use of a polymeric stamp. A molded stamp transfers only selected areas of the printed patterns, thereby serving as a patterning template. Alternatively, photolithography steps may be used for patterning the required areas. The method can be used to pattern CNTs on a variety of substrates, such as polyethylene terephthalate (PET), poly(methyl methacrylate) (PMMA), glass, and silicon. It relies on the adhesion of CNTs to the surface of the receiving material. Materials with a higher surface energy can receive CNTs just by contact. Transfer printing is used for transferring CNTs grown by chemical vapor deposition (CVD) on a silicon wafer (SiO₂/Si) to a flexible substrate. To this end, Cao et al. transfer printed SWCNTs from the silicon substrate to a PET film with help of an elastomeric stamp of PDMS. Highly uniform SWCNT films were obtained with a low sheet resistance of 265 Ω sq⁻¹. Several photolithography steps were required to pattern SWCNT films onto the flexible substrate. In addition to transferring CNTs which are directly grown from CVD, transfer printing can be used to transfer CNTs which are solution processed. Hu et al. filtrated SWCNTs and used a PDMS stamp to transfer the patterns to a PET film. They were able to achieve 50 μm of resolution using PDMS stamps and sheet resistance of 150 Ω sq⁻¹. In a modified transfer method by Lee et al., a patterned film of SWCNT was embedded in PDMS. First, a porous membrane of anodic aluminum oxide (AAO) was used to filtrate SWCNT, then the membrane was dissolved in sodium hydroxide, whereas the SWCNT film remained floating in water. Subsequently, SWCNTs were transferred to a gold-coated silicon wafer by direct contact, and various patterns were defined with photolithography techniques. To embed SWCNTs in PDMS, the PDMS prepolymer was poured onto the patterns, cured, and peeled off from the silicon substrate. Finally, the gold layer was etched away, exposing the SWCNT film. In this modified method, the patterned film of SWCNTs embedded in PDMS was used as a piezoresistor in the fabrication of pressure sensors. Other methods of depositing solution-processed CNTs with subsequent transfer have been developed, such as streaming a CNT solution onto a substrate and electrophoretic deposition (EPD) of CNTs. Meitl et al. used a method that consisted of streaming a solution of SWCNTs with sodium dodecyl sulfate (SDS) and another solution of methanol onto a rotating substrate.
The methanol removes SDS from the solution, and CNTs spread over the rotating substrate without agglomerating. A PDMS stamp was contacted afterward to transfer CNTs to a final substrate. Good uniformity was achieved on the first substrate; however, the films transferred to the final substrate presented poor uniformity. Moreover, the thickness of the film was not controllable. Xu et al.\cite{41} obtained micropatterned CNTs on PDMS using EPD and subsequent transfer to PDMS. CNTs were carboxylated in acid to improve water dispersibility. Silicon containing the desired microstructures and gold seed layer was immersed into CNT solution and electrically energized. The negatively charged CNTs preferentially migrated and precipitated onto the gold seeds. The thickness of the CNT layer was determined by the duration of the experiment. PDMS was poured onto the sample and peeled off with CNTs attached to it. Although micropatterning was achieved, fabrication of the mold and deposition of gold layer still required the use of standard lithographic methods, which would add cost and complexity. In addition, control over the deposition of CNTs was only achieved where gold was deposited.

Therefore, the transfer printing technique requires either pre- or post-photolithography steps to obtain patterned films of CNTs.
In addition, due to the contact between the stamp and CNTs, only the surface nanotubes can be transferred, limiting control of the final thickness of the film.

### 3.3. Microcontact Printing

Microcontact printing (μCP) is a special case of transfer printing. In μCP, a PDMS stamp selectively contacts a composite ink and transfers the patterns to the desired substrate,\(^{[42]}\) whereas transfer printing is the general term that applies for a variety of processes, having the characteristics of additive transfer, subtractive transfer, or deterministic assembly of materials.\(^{[26]}\) Patterning CNT/PDMS composites in which the CNT film is embedded into PDMS has been developed through μCP. Liu and Choi\(^{[43]}\) mixed MWCNTs with PDMS to form a composite ink, which was then spun on a silicon wafer. A micromachined PMMA stamp was used to selectively contact the ink and transfer the patterns to a final PDMS substrate (Figure 3). Curing and subsequent coating with a PDMS layer formed an all-elastomer strain sensor.\(^{[43]}\) This method produced patterns of randomly oriented CNTs embedded in PDMS. To produce vertically aligned CNTs on PDMS, Kim et al.\(^{[44]}\) used CVD to grow vertically aligned CNTs on a silicon wafer. With nanoimprint equipment, they transferred CNTs to a cured layer of PDMS by simply contacting the vertically aligned CNTs to the PDMS substrate. Although CNTs were successfully transferred, the height of CNTs shrunk from 400 to 60 μm due to the necessary pressure applied during contact. Although their objective was to obtain vertically aligned CNTs, it was not possible to pattern CNTs with this method.

### 3.4. Spray Coating

Spray coating of CNT dispersions has been developed to form large-area, low-resistivity CNT films. A solution of dispersed nanomaterials is loaded into a spray gun and directly sprayed onto the receiving substrate. Both organic and aqueous solutions have been used as the solvent, but due to the slow evaporation rate of aqueous solutions, nonuniform areas may occur. Moreover, spray coating of MWCNTs on PDMS obtained lower resistivity than graphene and rGO sprayed with similar conditions.\(^{[45]}\) Lipomi et al.\(^{[46]}\) directly sprayed an organic solution of SWCNTs onto PDMS, which was used to fabricate capacitive pressure sensors. Kim and Yun\(^{[47]}\) patterned CNTs on PDMS with the assistance of spray coating and transfer printing. First, a photoresist layer was spun on a silicon substrate and selectively cured using photolithography methods. CNT was then sprayed on the photoresist layer. When the photoresist was developed, patterns of CNT remained on top of the exposed photoresist. A semicured PDMS layer was attached to the CNT film and then fully cured. Finally, the PDMS layer was peeled off. This method provided the sheet resistance of 96 Ω sq\(^{-1}\) for PDMS and 45 Ω sq\(^{-1}\) on photoresist when coated seven times, which was comparable with that of indium tin oxide (ITO) films (60–90 Ω sq\(^{-1}\)). Figure 4 shows the process of spray coating and transfer printing. Spray coating can be used when the nanomaterials are in the form of an ink (organic or aqueous), it allows the formation of films with a large area and low resistivity but relies heavily on photolithography for patterning the carbon nanomaterials, which adds complexity to the process.

![Figure 3. μCP and cast molding used for transferring conductive patterns of MWCNTs from the substrate to PDMS. Reproduced with permission.](www.advintellsyst.com)
3.5. Bulk Mixing

Mixing CNTs and PDMS has been performed directly and indirectly. In the direct method, a planetary centrifugal mixer was used to mix MWCNT with PDMS. A planetary centrifugal mixer rotates the viscous mixture in both directions, thus enabling mixing, deaeration, and dispersion simultaneously. Although no dispersion quality was provided, the MWCNT–PDMS composite with 7 wt% of MWCNT achieved a resistivity of $10^{-1} \Omega \text{cm}$. The viscous composite was cast onto acrylic grooves formed by micromilling and then partially cured. Then, another PDMS layer was cast on top of the MWCNT–PDMS composite, and the layers were fully cured. Finally, the cured PDMS having conductive tracks was peeled off from acrylic to form tactile sensors.

In the indirect method, CNTs and PDMS are separately dispersed in a common solvent and subsequently mixed into a uniform dispersion. The dispersion of CNTs in a suitable solvent entails the use of mild sonication to debundle agglomerated nanotubes. During and after mixing, the solvent is allowed to evaporate, leaving CNTs in the PDMS matrix. Through dispersion of MWCNTs in different organic solvents for 30 min, it was found that after 70 h, reaggregation of CNTs occurred in the order of toluene $> \text{chloroform} > \text{tetrahydrofuran (THF)} > \text{dimethylformamide (DMF)}$. However, due to incompatibility of THF and DMF with PDMS base, chloroform was best suited as the common solvent for CNTs and PDMS.[49] Noimark et al.[50] prepared a MWCNT–PDMS composite by mixing MWCNT in xylene, which is a solvent for both materials (MWCNT and PDMS). The dispersion was then mixed with PDMS to form a light-absorbing composite. The coatings were applied to the ends of optical fibers for the fabrication of ultrasound transmitters. Lee et al.[51] fabricated graphene and CNT nanocomposite strain sensors. MWCNT was added to PDMS base, along with isopropyl alcohol (IPA) and Stoddard solvent, and sonicated for complete mixing. The crosslinker was then mixed, and the resulting nanocomposite was patterned onto a pure PDMS layer previously cured. The highest conductivity of the MWCNT–PDMS composite was $10^{-1} \text{S cm}^{-1} \times 12\%$ of filler material. Bulk mixing therefore can be used when the filler has to be embedded into the base, creating a conductive polymer matrix, instead of being patterned on the surface. Low resistivities can be achieved, but the compatibility and slow evaporation of the solvents are the main issues of this method.

3.6. Screen Printing

Screen printing has been developed to pattern carbon nanomaterials on flexible substrates. Differently from inkjet printing, the formulated paste contains a conductive carbon material which is mixed with binders and solvents. The highly viscous nature of the paste allows patterning with a stencil and subsequent evaporation of the solvent. Screen printing was used by Sekitani et al.[30] to coat SWCNT on PDMS. First, a SWCNT gel was formed by stirring SWCNT, ionic liquid, and 4-methyl-2-pentanone for 16 h, followed by processing the gel.
in a jet milling, which untangled or exfoliated the SWCNT. In the next step, 4-methyl-2-pentanone and a fluorinated copolymer were added and stirred for another 16 h and dried in air for 6 h to produce a SWCNT paste. The paste was then screen printed onto PDMS. A conductivity of 100 S cm⁻¹ was achieved for SWCNT loading of 15.8 wt%.

The conductivity of carbon materials has been utilized in several applications, ranging from flexible electronics, displays, sensors, supercapacitors, and batteries. Lowering the resistivity of carbon-based inks has been a challenge in these applications. Carbon materials diluted in water usually agglomerate, such that a dispersion agent is required. In conductive paste development, a binder is necessary, which increases the resistivity of the final paste. Recently, Phillips et al. found that a mixture of graphite and carbon black (ratio of 6 to 1) produced an optimal conductivity of 0.029 Ω cm with good rheology properties for screen printing. The much smaller carbon black fills graphite gaps, resulting in a more conductive composite.

Liao et al. reduced the resistivity further by adding dihydroxyphenyl-functionalized MWCNTs (MWCNT-f-OH) to the carbon black and graphite mixture, along with using acrylic resin as binder. The resistivity achieved was 29 Ω sq⁻¹ when the mass fraction of the components was 10.2%, 3.0%, and 4.1% for graphite, carbon black, and MWCNT-f-OH, respectively. Screen printing is suitable for the mass production of devices, achieving low resistivities, with a range of paste formulations available. However, the resolution of the features is relatively low (>75 μm).

### 3.7. Inkjet Printing

Classically used for printing text and images, inkjet printing has recently found applications in many branches. Its advantages include the ability to print solutions of various materials, the extremely low waste, and fine control of deposition parameters such as droplet location and number of printed droplets. Inkjet printing has been used to print thin-film transistors on plastic substrates, fabricate tactile sensors, 2D force sensors, biosensors, and in a variety of other applications.

Inkjet printing can be classified into the solution processing category which also includes spraying, aerosol-based, layer-by-layer, simple solution-evaporation, and dip coating.

In one of the earliest developments in inkjet printing applied to flexible electronics, MWCNTs were inkjet printed onto transparent foil and paper. In that study, CNTs were functionalized with nitric acid treatment so that they could be dispersed in water. The achieved sheet resistivity was 40 kΩ sq⁻¹ with multiple prints (minimum 30 prints to become conductive).

Kim et al. inkjet printed SWCNTs directly onto the PDMS substrate. The aqueous ink was developed with SWCNT and sodium dodecyl benzene sulfonate (SDBS), a surfactant that disperses nanomaterials in aqueous solutions. The ink was filtrated and inkjet printed one to five times on previously cured PDMS. A treatment with water and nitric acid was performed to improve the sheet resistance. The minimum line width achieved was 80 μm, and the sheet resistance for five prints was 19.08 Ω sq⁻¹ (with post-treatment). Cracks appeared on the CNT film upon stretching, which were attributed to the low adhesion of the PDMS surface to CNTs, as the CNTs were not completely embedded into the PDMS matrix.

Ding et al. used a dual method for achieving CNTs on PDMS. CNTs were vertically grown on a silicon wafer, followed by PDMS pouring and subsequent curing. Using inkjet printing, GO was deposited on top of the CNTs. The final step was to reduce the GO. By printing both materials, they achieved a sheet resistance of 386 Ω sq⁻¹.

Kumar et al. inkjet printed SWCNTs modified with carboxylic groups on agarose gel and transferred the patterns to silicon oxide substrate by contact. Agarose gel is a porous hydrophilic polymer that readily absorbs water. The lowest sheet resistance achieved was 0.5 kΩ sq⁻¹ for 40 prints.

Inkjet printing has been used in the fabrication of flexible electrochemical and chemiresistive sensors. Due to the electrocatalytic activity of CNTs, electrodes composed uniquely of CNTs have been developed to measure analyte concentrations. Furthermore, selectivity is attained by the addition of metal nanoparticles which catalyze the reaction of specific analytes. Tortorich et al. inkjet printed SWCNT on the PET film, obtaining sheet resistance of 132 Ω sq⁻¹. The fabricated sensors were low cost, flexible, and disposable, capable measuring iron concentration through cyclic voltammetry. da Costa et al. inkjet printed CNTs directly on paper for the fabrication of low-cost and disposable dopamine sensors, whereas Song et al. fabricated flexible chemiresistive sensors on the PET film for glucose quantification. The CNTs were inkjet printed as electrodes, and polyaniline nanowires were deposited between electrodes as resistive transduction elements.

In spite of the versatility of inkjet printing, some drawbacks still remain for inkjet printing of CNTs onto PDMS. Due to the hydrophobicity of PDMS, water droplets do not wet its surface. Even when the surface is chemically treated to become hydrophilic, water droplets form rings during the drying process. In addition, if the previous droplet has not completely dried, the coalescence of droplets occurs, in which case nonuniformities appear. It can be minimized by heating the substrate to enhance evaporation. Finally, nanomaterials formed on the surface of PDMS do not adhere well and form cracks if the PDMS is stretched. In addition, nanoparticles usually require sintering to become highly conductive, in which case cracks become evident upon stretching.

### 3.8. Drop Casting

Drop casting has been used to deposit ink on a variety of substrates. A formulated ink is simply dropped on the substrate to dry through evaporation of the solvent. Chemical, biological, and electrochemical sensors are usually fabricated with this method. The stability of the deposited material is highly dependent on the interaction between ink and substrate. In addition, evaporation, the deposited material may not form a uniform layer.

With the drop-casting method, carbon nanocoils were deposited on a liquid crystal polymer substrate to fabricate a humidity sensor that achieved a record response and recovery times of 1.9 and 1.5 s, respectively. The hydrophobic nature of the liquid
crystal polymer caused a weak adsorption of water molecules on the sensor, which resulted in fast recovery upon desorption of water molecules.\textsuperscript{[72]} Drop casting was also used to deposit GO onto water-transfer paper to fabricate a strain sensor/actuator for detecting throat motion and emitting the respective sounds. First, GO dispersion was drop cast onto water-transfer paper and dried, followed by laser scribing a defined region to reduce the GO (rGO). Then, the paper was immersed in deionized water to wash off unreduced graphene, leaving only rGO supported on a poly(vinyl alcohol) (PVA) film, which was used as a sensor to detect skin motion\textsuperscript{[11]} (Figure 5).

3.9. Patterning Methods

In addition to the deposition of nanomaterials onto substrates and bulk mixing to form nanocomposites, many applications require patterning of the nanomaterials. Inkjet printing has the ability to deposit and pattern nanomaterials in a single step, but other methods require a combination of pre- or post-patterning. Laser ablation is a technique used to define patterns onto a flexible substrate such as PET. A focused laser delivers high optical energy to the substrate, thereby breaking up the molecular bonds and evaporating the molecules in gaseous form.\textsuperscript{[73]} A conductive CNT/PDMS nanocomposite is then poured into the grooves, and the extra amount is removed by a blade. Another plain PDMS layer is coated on top of the patterns and finally cured. Upon debonding, relief structures of conductive CNT/PDMS were formed onto a bulk PDMS (Figure 6a). The laser ablation method forms extruding features without any masks, stamps, or lithography steps, while achieving feature sizes as low as 20 \( \mu \)m on the PET substrate (shown in Figure 6b). Similarly, micromilling can be used to define features on a plastic substrate such as acrylic, with a minimum feature size of 30 \( \mu \)m.\textsuperscript{[48]} Micromilling uses milling bits (endmills) which are capable of cutting the substrate both axially and laterally. A variety of flexible materials can be used as substrates and it is most suited to fabricating molds.\textsuperscript{[74]}

3.10. Discussion of Processing Methods

In summary, several methods have reported depositing and patterning CNTs on PDMS. Spray coating takes advantage of the solution processability of CNTs in aqueous solutions. It deposits over a large area but requires additional patterning. Transfer techniques usually require some form of photolithography or micromachining prior to CNT transfer. Filtration methods also require a postpatterning step. The highest conductivities were achieved with the use of SWCNTs and with minimum impurities.

High-quality dispersion of carbon nanostructures in water is important for several reasons, for example, to avoid the use of toxic organic solvents, obtain low cost and low complexity formulations, attain compatibility with biomolecules, etc. However, due to the hydrophobic interactions in water, graphene and CNTs agglomerate, which hinders the direct dissolution of those materials in water. Therefore, alternative aqueous dispersions are being developed. Georgakilas et al.\textsuperscript{[75]} developed a carbon-based ink in which no surfactants or hydrophilic polymers were necessary for dispersion. The CNTs were made hydrophilic by functionalization with dihydroxy phenyl groups and subsequently added to the exfoliated graphene. The stabilization of graphene by CNTs in aqueous solution occurred by preferential trapping of CNTs between graphene sheets or modification of graphene edges. The solution was stable and achieved a minimum sheet resistance of 25 \( \Omega \) sq\(^{-1}\).

Most commercial CNTs are available in the form of powder or dispersed into solvents. For powder-based CNTs, dispersion in water requires the use of a surfactant or chemical

![Figure 5. Drop-cast method to deposit GO onto water-transfer paper: a) drop cast GO on paper, followed by laser scribing to reduce GO, followed by immersion in water to wash off unreduced graphene, forming a sensor on PVA film; b) sensor used to detect motion of the throat and emit corresponding sounds; and c) the working mechanism of the sensor, in which throat movements generate strain on the sensor, and sound is emitted through thermoacoustic effect. Reproduced with permission.\textsuperscript{[11]} Copyright 2019, American Chemical Society.](image-url)
modification. But due to the low electrical conductivity of surfactants, the final conductivity of the printed film is impaired, so the remaining surfactant molecules are regarded as undesired impurities. Therefore, patterning inks of carbon nanomaterials still presents challenges, especially for low-cost and low-complexity fabrication of sensors.

4. Other Fabrication Techniques

4.1. Coating of Carbon-Based Materials on Foams

Sensors that monitor human body motions have attracted significant interest. Specifically, strain and tactile sensors are most often researched for applications in real-time monitoring of movements and assistive devices. Due to the large movements experienced by the limbs, it is important that the sensors achieve not only flexibility but also large elongation ability. Sensors composed of a foam substrate present an advantageous approach to fabricate strain and motion sensors with large elongation linearity. Strain sensors have been fabricated on polyurethane[76–81] and PDMS[82] substrates with a large strain range up to 150%.

Polyurethane fibers with a large surface area can be fabricated by mixing reagents in solvent and electrospinning the dispersion into a foam or as standalone fibers. As conductive fillers, several nanomaterials have been assembled onto polyurethane fibers, such as carbon black,[78] MWCNTs,[80] 2D transition metal carbide/carbonitride (MXene),[81] graphene/PEDOT:poly(4-styrenesulfonic acid) (PSS),[83] and silver nanowires (AgNWs).[84]

4.2. Microstructure Engineering

A low Young’s modulus is desirable to improve the sensitivity of sensors that rely on physical changes such as strain to acquire a signal. Several strategies have been successfully implemented in this regard through the use of foams and nanofibers, in addition to modifying the microstructure of polymer substrates with the introduction of pyramids.[11] Furthermore, by directly curing PDMS on micromolds, microstructures can be created in the shape of textile[85] and natural leaves.[4,86]

Sodium chloride (NaCl) salt microcrystals have been dispersed in PDMS to create foamy substrates[12,87] NaCl microcrystals were mixed with PDMS and carbon conductive paste, followed by curing. The composite was then immersed in water so that the salt microcrystals could dissolve, leaving a porous microstructure with pore sizes between 100 and 300 μm. The porous structure reduced the compression modulus of the composite, allowing a larger compression at the same applied pressure[87] PDMS foams have been fabricated with the assistance of sacrificial sugar crystals.[82] Sugar was vigorously mixed with the PDMS prepolymer, curing agent, and carbon black powder, with subsequent curing and dissolution of sugar in water.

4.3. CNTs/Fiber Composites

Cellulose nanofibers recently emerged as a material for wearable textiles. It has the advantages of being weavable with conventional textiles and having good mechanical resilience to harsh conditions. However, due to their low electrical conductivity, the final conductivity of the printed film is impaired, so the remaining surfactant molecules are regarded as undesired impurities. Therefore, patterning inks of carbon nanomaterials still presents challenges, especially for low-cost and low-complexity fabrication of sensors.

Figure 6. Laser ablation for patterning CNT/PDMS nanocomposite: a) a focused laser beam ablates PET regions (features as low as 20 μm), then CNT/PDMS nanocomposite is poured and the extra amount removed by a blade. A plain PDMS is then coated on top of the patterns. After curing the device is debonded, having conductive CNT/PDMS structures exposed, and b) relief structures on PDMS after debonding, showing a minimum width of 19 μm. Reproduced with permission.[73] Copyright 2012, IOP Publishing Ltd.
conditions such as deformation, stretching, and twisting. Nanofibers can be fabricated with a variety of processes, including wet,\textsuperscript{88} dry,\textsuperscript{89} and electrospinning processes.\textsuperscript{88} A wet-spinning process was used to form cellulose/CNT nanofibers. Cellulose nanofibers extracted from tunicate were mixed with SWCNTs/double-walled CNTs and injected into a syringe, which allowed alignment of the fibers upon extrusion. The syringe was dipped into a coagulation bath containing acetone for fiber precipitation, which was subsequently rolled into a fiber thread (Figure 7). The obtained fibers were electrically conductive, with good mechanical durability even after several deformations. Nanocellulose/CNTs fabricated in this way possessed a high surface area and good distribution of mesopores, which benefitted the application as a textile-based wearable gas sensor.

4.4. CNTs/Polymer Composites

In addition to PDMS, CNTs have been integrated in a variety of other polymer matrices. For example, MWCNTs were dispersed in poly(acrylic acid) (PAA) with the help of PSS for the fabrication of flexible humidity sensors.\textsuperscript{90} Interestingly, a high MWCNT loading was achieved (33 wt%) while retaining flexibility of the composite. In addition, the sheet resistance was low (30 $\Omega$ sq$^{-1}$). An MWCNT–polyimide composite has also been developed. The mixing of MWCNT powder in polyimide solution and subsequent sonication yielded a stable dispersion, which was subsequently spin coated onto the substrate and finally patterned.\textsuperscript{91} CNT paste mixed with silver nanoparticles was screen printed on flexible substrates of silicone rubber, PET, and polyethylene (PE).

Figure 7. Wet spinning process for fabrication of nanocellulose/CNT fibers: a) nanocellulose fibers mixed with CNTs are injected in a syringe and precipitated in a coagulation bath, forming a conductive fiber, b) The meter-scale fiber, c) the response of the sensor to increasing NO$_2$ concentration, d) test showing strength of the fibers, e) scanning electron microscopy (SEM) image depicting TCNF/CNT fiber, and f) surface area measurement of the fibers. Reproduced with permission.\textsuperscript{88} Copyright 2019, American Chemical Society.
Subsequent steps involved laser cutting the substrate to form cantilevers which worked as temperature and strain sensors. The sheet resistance of the composite with 40 wt% silver nanoparticles was 120 mΩ sq⁻¹. A composite structure of CNTs/silver nanowires was applied to Ecoflex substrate (silicone). First, a CNT solution was filtered through a membrane, then silver nanowire solution was filtered to form a transparent, conductive composite. Finally, a silicone film was gently put on the membrane, and the composite transferred to the substrate through vacuum. The many choices of hardness make Ecoflex a versatile substrate for flexible sensors.

4.5. 3D Printing of Graphene/PDMS Composites

3D printing has emerged as a versatile technique to print polymers in the form of thermoplastic filaments, which become hard at room temperature. However, PDMS is more challenging to print as the base and curing agent have to be mixed and heated to cure. In addition, uncured PDMS wets the substrate surface due to the low surface tension of uncured PDMS. Therefore, ink rheology has to allow flow inside the printing device, while preserving the geometry on the substrate. Graphene/PDMS composites were 3D printed to fabricate stretchable temperature sensors with low interference from strain on the resistance change. To be 3D printable, a nonflowable graphene/PDMS nanoplatelet ink was formulated and used in a 3D direct ink writing printer. With this setup, a temperature sensor was fabricated by printing a grid structure of the composite ink directly on a silicon wafer. The temperature sensor was used to measure skin temperature on curved surfaces. This shows novel technologies such as 3D printing being used for the fabrication of flexible and stretchable temperature sensors, which have applications in monitoring skin temperature.

5. Applications

Carbon nanomaterials find applications in many sensor areas due to their electrical, optical, and chemical properties. Human physical signals are important indicators of a person’s health and well-being. Pressure and strain sensors that respond to different physical stimuli are ideal for wearable integrated monitoring tools. Strain sensors of carbonized silk nanofiber membranes incorporated into PDMS films can be used to monitor wrist pulse signals through resistance change due to conformal attachment of the sensor to the skin. Interestingly, the characteristic peaks of the pulse waveform were clearly identified, and the resistance change had a higher amplitude after exercise (Figure 1a). In addition, strain sensors are well suited for measuring a variety of human motor movements such as bending of fingers (as shown in Figure 1b), arms, and legs.

A great deal of research has been devoted to wearable sensors capable of detecting humidity changes. rGO fibers have been developed as highly sensitive humidity sensors. To increase the electrical properties of the rGO film, nitrogen reduction was performed to dope the rGO film as n-type. Leveraging the property of platinum nanoparticles (PtNPs) as a water dissociation catalyst, PtNPs were deposited and sintered on the surface of the film to enhance sensitivity toward humidity changes. As a demonstration, breath humidity was monitored by a flexible sensor which contained a wireless data transmission unit (Figure 1c).

Assistive devices are especially important for rehabilitative purposes. Wearable sensors that provide transduction of physical parameters can be integrated with actuators that provide assistance. In this regard, skin vibration can be detected (Figure 1d) and translated to a predefined sound. Throat movements stretch and contract a graphene-based strain sensor, whereas an integrated graphene-based sound emitter generates sound through the thermoacoustic effect. Another example of assistive device is the robotic arm that contains force and pressure sensors on the tip of the fingers (Figure 1e). The sensors measure the amount of force applied to them, whereas the actuator sends a signal to grasp an object. Similarly, highly sensitive pressure sensors allow measurement of the contact pressure developed across a specific area containing the sensor, such as palm or fingers. This is accomplished with tactile sensing arrays of individually addressable electrodes (Figure 1f).

The high surface area of nanotubes and graphene coupled with their high catalytic activity enables their use in electrochemical sensors, supercapacitors, and biochemical sensors. In electrochemical sensors, MWCNTs are used to enhance the sensitivity of the sensor’s response to analytes. Modified working electrodes can be constructed by simply drop casting an MWCNT dispersion on a gold-coated PET substrate, as shown in Figure 1g. In addition, platinum or silver nanoparticles can be deposited or electrochemically formed on the modified electrode to facilitate charge transfer. Finally, flexible temperature sensors allow the monitoring of skin temperature. They can be sewn into regular fabrics to measure the temperature in different parts of the body or attached to a bandage (Figure 1h). Through geometric engineering, it is possible to minimize the interference of strain on the temperature response.

6. Conclusions and Outlook

We have reviewed the recent developments in patterning carbon nanomaterials on PDMS for the fabrication flexible sensors. Carbon nanomaterials such as graphene and CNTs possess interesting electrical properties, making them the preferred nanomaterial for a variety of sensors, including force/pressure, strain/motion, temperature, humidity, and biochemical sensors. Flexibility and stretchability are essential in novel sensors specifically designed to monitor health-related signals. Several coating techniques provide large-area conductive films but lack patterning ability. In contrast, inkjet printing enables patterning of carbon nanomaterials through aqueous solutions. Furthermore, conductive nanocomposites have been fabricated through a variety of mixing processes, chemical modifications, filtration, and transfer printing techniques. Through the choice of materials and microstructures, it is possible to develop sensors with higher sensitivities, which directly improves the quality of the measured signal. In addition, patterning ability gives the possibility of printing multiple materials onto a relatively small area, which reduces the overall size of sensors. Overall, real-time monitoring of physiological signals, assistive technologies, and many
other applications will benefit from the advances of novel fabrication techniques.

Fabrication and patterning methods have achieved considerable developments in the past few years. Future challenges for patterning methods will include the development of simple and inexpensive techniques to mass produce functional sensors which can be used in the personal monitoring of health-related signals. In addition, printing multiple functional materials on different layers has proved to be a challenge of current methods. Novel sensors will require integration of several functional materials, which ideally should be deposited through a single- or few-deposition methods.

There has been tremendous growth in the development and demonstration of flexible sensors. Some of the immediate applications of these novel technologies include personal health monitoring, detection of disease and monitoring of its progression, prosthetic devices, and assistive sensors and actuators. But for applications focused on monitoring body signals, it is necessary that the sensors consume low power or be self-sufficient, issues that have not been fully addressed up to now. Moreover, communication and interfacing with external receivers will be a requirement for the successful implementation of such sensors. Issues that the recent literature addresses very well are the stability and mechanical durability of the proposed sensors. However, long-term signal stability as measured by drift still requires more careful attention. In addition, signal interference is still the major concern in currently demonstrated sensors. It is, therefore, with careful design and engineering of novel flexible sensors that great advancements in healthcare will be achieved, thus projecting them to truly disruptive technologies.

The excellent properties of carbon nanomaterials represent an advantage in transduction mechanisms for flexible sensors. For example, a crystalline film of aligned SWCNTs has been shown to present strong anisotropic optical properties and nanotube plasmon resonance, which could be used in highly sensitive optical biosensors. In addition, high-quality films of SWCNTs were used as highly sensitivity electrochemical sensors. Due to the versatility of carbon nanomaterials, they are likely to replace other materials in diverse applications. Thus, research efforts may be directed toward fabricating high-quality patterned films of carbon nanomaterials onto flexible and more accessible sensors that perform on-site measurements.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
carbon nanomaterials, flexible sensors, patterning techniques

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