

13 Nanostructured Materials for Soft Robotics – Sensors and Actuators

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Abstract The advances in nanotechnology during the past two decades have led to several breakthroughs in material sciences. Ongoing and future tasks are related to the transfer of the unique properties of nanostructured materials to the macroscopic behaviour of composite structures and the system integration of novel materials for improved mechanical, electronic and optical devices. Nanostructured carbons, especially carbon nanotubes, are promising candidates as novel material for future applications in several fields. One of the big aims is the utilisation of the unique intrinsic mechanical and electronic properties of carbon nanotubes for sensing and actuation devices. The combination of excellent electrical conductivity and mechanical deformation makes carbon nanotubes ideal for applications in sensors and actuators and opens new possibilities in construction design of next generation robotic systems, which can be built with soft, bendable and stretchable materials. This chapter gives a brief overview on the properties of carbon nanotubes and their potential for actuators and sensors in soft robotics.

13.1 Introduction

Nanostructured carbon materials – first and foremost CNTs (Carbon Nanotubes) and graphene – are the fastest growing research domain in nanotechnology. Since their discovery in 1991 [1], CNTs have sparked huge interest as they exhibit outstanding mechanical and electronic properties [2, 3]. Formally, CNTs can be regarded as a rolled-up graphene sheet (Fig. 13.1). The roll-up vector C_h results from the vector addition $C_h = na_1 + ma_2$ of the graphene unit vectors a_1 and a_2 . The descriptors n and m are integers and define the nomenclature of the CNT (n,m) . As a result of the geometry and a model from solid state physics – the tight binding model – CNTs can be either metallic or semiconducting. Here we limit the description to the rule that CNTs are metallic if $(n-m)/3$ is an integer, e.g. $(7,4)$, $(5,5)$ or $(9,0)$. Other CNTs are semiconducting, e.g. $(6,5)$, $(7,3)$ or $(8,0)$. For further reading we refer to [2, 3] and the references therein. Besides single-wall carbon nanotubes (SWCNTs) there also exist multi-wall carbon nanotubes (MWCNTs), which consist of several rolled layers in a concentric alignment [2].

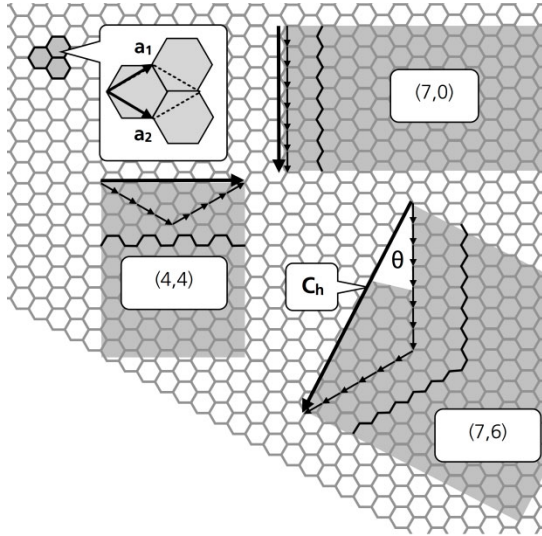


Fig. 13.1 Formal classification of three different carbon nanotubes based on the roll-up vector C_h

Hence, with regard to their electrical and optoelectrical properties, semiconducting CNTs and metallic CNTs offer different potential applications. Semiconducting CNTs are frequently discussed as single-electron transistors for future microelectronic components. In 1998, the IBM research division presented a single-electron transistor based on individual semiconducting CNTs [4]. By contrast, metallic CNTs are rather used as an ensemble in conductive films. In theory, CNTs can carry an electrical current density up to roughly $4 \cdot 10^9 \text{ Acm}^{-2}$, which is about a thousand times higher than for copper before breakdown due to electromigration [5]. The extraordinary high intrinsic conductivity occurs due to the strong chemical bonding of in the CNT walls.

The aforementioned potential benefits of carbon nanotubes have had a huge impact on the amount of work, which has been carried out and published in several fields for the past two decades. However, when it comes to the utilisation of these beneficial properties for macroscopic components, either as an ensemble consisting only of a CNT network or as a composite material such as CNT/polymer composites, things become challenging.

Basically there are two major problems. At first, today's production techniques for CNTs deliver soot that contains CNTs of various diameters and consequently a mixture of metallic and semiconducting CNTs [6]. For high purity CNT samples – either metallic- or semiconductive-enriched – further purification methods such as ultracentrifugation [7, 8] or chromatography [9] have to be applied. These methods are the bottleneck in the development of components as they are only scalable to some extent. The second challenge concerns the integration of the CNTs into a

polymer matrix or onto a substrate. As an example, despite the aforementioned high electrical conductivity of metallic CNTs, a transparent network of metallic carbon nanotubes still does not reach the low sheet resistance of indium tin oxide or silver nanowires within the same transparency range [10]. This is due to the high resistances of the junction points in the CNT network. However, during the past years the performance of these films could be improved and the sheet resistances of films containing carbon nanotubes have reached values, which come closer to the industrial demands in display industry [11, 12]. Furthermore the films are bendable and stretchable. This property is a significant advance over conventional materials such as brittle indium tin oxide when it comes to the usage in mechanically flexible components for soft robotic devices. Here we will report on the potential of CNTs for actuators followed by a section on CNT-based sensors for applications in soft robotics.

13.2 Actuators

Actuators are mechanical devices, which can be used for the purpose of inducing strain into a system in order to generate a movement or a change of shape. Conventional actuators function based on pneumatic, electric or hydraulic principles. With regard to applications in soft robotics, these actuator types are not always suitable as weight, size, restrictive shapes and stiff materials limit the freedom of component design. Stretchable and bendable polymers can overcome these problems. Electroactive polymers (EAPs) are a relatively new class of actuator materials. They can change their shape or size as a response to electric stimuli [13]. Besides the mechanical flexibility, EAPs offer several other major benefits such as light weight, structural versatility, easy material processing and usually low costs.

Various classes of EAPs can be used as actuators to be integrated into robotic systems. More importantly the soft nature of the polymer based actuator is intrinsically suited for the next generation of robotics: soft robotics. EAPs are commonly classified in two major classes (Fig. 13.2). Ionic EAPs are activated by an electrically-induced transport of ions and/or molecules. The intercalation of ions into a host material such as a CNT network induces a change of the electric structure of the chemical bonding [13].

The changing of the electronic structure generates a deformation of the bonds and consequently expansion or shrinking. In dielectric EAPs the actuation is induced by electrostatic interactions between two electrodes, which encircle the polymer. Electronic EAPs can generate large strain at reasonable rates while demonstrating large displacements (strain %). However the use of high voltages makes them not particularly well suited for mobile applications such as soft robotics and is thus not discussed in much detail within this chapter.

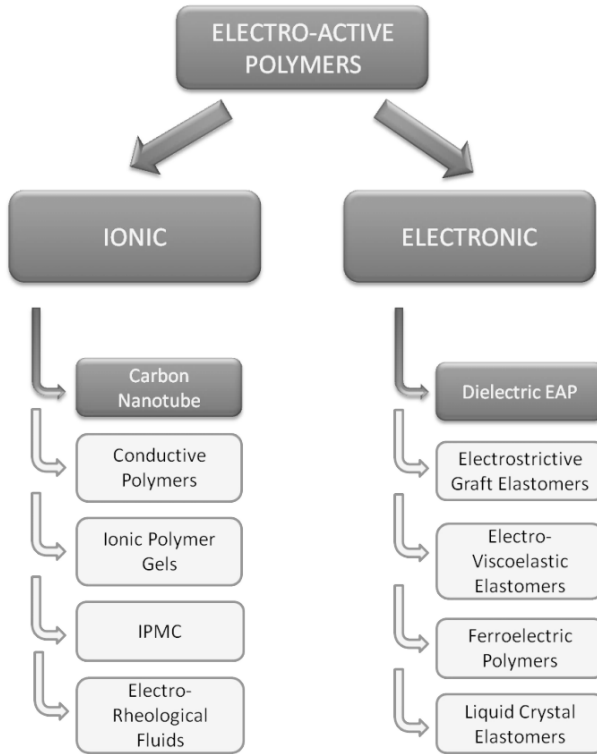


Fig. 13.2 Classification of materials for actuators based on electroactive polymers

When contemplating the use of EAP materials for soft robotics, one major consideration arises, which is the relation between the applied electrical stimuli and the resulting displacement, force and reaction rate. This is one of the fundamental question in which the answer will govern the possible application. From this, both ionic EAPs and electronic EAPs have their advantages and disadvantages. In the case of ionic EAPs, their low voltage operation could make them ideal candidate for soft robotic applications if it was not for the fact that – in most cases [14] – they need to be hydrated at all times. Ionic/polymer/metal-composites, being one example of ionic EAPs, show promising properties with respect to biomimetic uses. Ionic polymer/metal composites consist of a thin ionomeric membrane with noble metal electrodes plated on its surface. It also has cations to balance the charge of the anions fixed to the polymer backbone [15]. However, the force generated with these types of actuators is relatively small and typically in the mN or single N unit range.

CNTs have shown promising characteristics when applied to actuator technology. They can either be used alone as an actuating devise (nano tweezers, gate systems) or as a filler material within polymers and ionic liquid mixtures, enabling

the creation of a layered actuating structure exhibiting displacements in the cm range, forces in the Newtonian range and reaction rates in the s to ms range. The principle of actuation is illustrated in Fig 13.3. Upon injection of electrodes from an external source, the ions within the polymer outer layers and supplied by the ionic liquid within, separate due to the repulsion between ion and electron. The separation leads to a concentration of ions on one side of the actuator layer, effectively swelling the material through ion intercalation. This swelling results in the laminate structure to bend. The direction is governed by the polarity of the external voltage supplied.

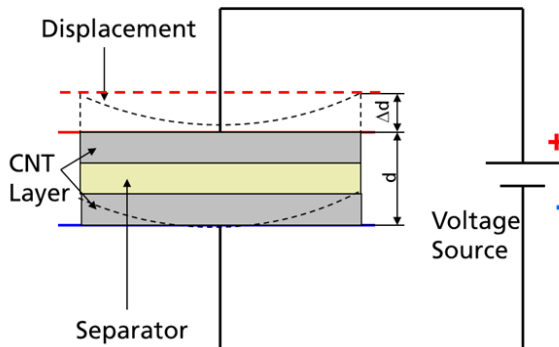


Fig. 13.3 Schematic principle of an actuator based on ionic electroactive polymers

Tri layer CNT based ionic actuators require low voltages (2V) and the strain produced can be in the range of 5.8% (triple layer solid state bending type actuator) [16, 17]. These actuators (triple layer solid state bending actuators) differ from the double layer bending actuators [18, 19] as they do not need to be immersed in an electrolyte solution since the electrolyte is embedded within the polymer matrix. However at the moment these demonstrate poor reproducibility from the point of view of actuation displacement. Current work undertaken at Fraunhofer IPA is focused on such CNT polymer hybrid actuator systems. The actuator class called A3D (Actuating Three Dimensional) actuators, which uses volumetric change generated by ion intercalation within the polymer chains and CNTs as well as the quantum-chemical based expansion due to electrochemical double-layer charging. From the three types of CNT based ionic polymer actuators described in this chapter (bilayer, trilayer and A3D) the only variation is the geometry and electrode material set up. For example long thin actuators generate a larger displacement, circular provide more force and ultrathin actuators move at a much higher frequency. Furthermore, the incorporation of many actuators into stacks with an aim of multiplying any given characteristic (force, displacement, speed) has also been studied. Lastly the interaction between contact electrodes and multiple actuator systems has been a governing parameter often neglected. A systematic approach (Fig. 13.4) must be taken in order to test, characterise and optimise each type of variable with an aim of producing, from an engineering point of view, a working func-

tional model mimicking real life applications. Thus by incorporating scientific findings with engineering principles the possibility to adopt CNT-polymer actuators for use in future soft robotics applications will be one step closer.

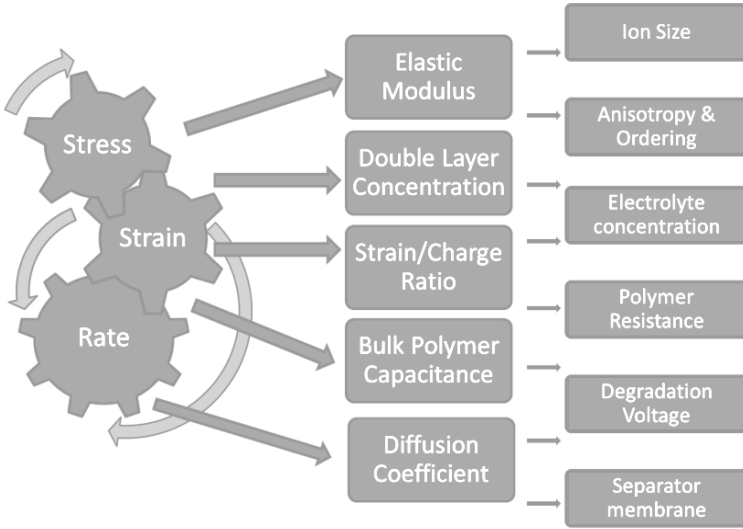


Fig. 13.4 Systematic approach for the testing, characterisation and optimisation of ionic electro-active polymers

As can be concluded the use of electronic and ionic EAPs materials bring many challenges when used alone. It is therefore important to realise that the combination of EAPs with CNTs can lead to new and improved properties which could be specifically designed or tailored for use in soft robotics. The addition of highly electrically conductive and extremely strong CNT within a polymer based matrix would inevitably increase electrical conductivity and the Young's modulus of the resultant actuator material (conductivity from 500 S/cm to 700S/cm) and mechanical strength (from 170MPa to 255 MPa), properties which are highly desirable when selecting suitable materials for soft actuator systems. In addition, the increase in stiffness will decrease the creep tendency of polymers, enabling for more reproducible and accurate actuation [20]. Although further research is needed within the domain of CNT based ionic actuators, the potential has already been shown mainly through functional models: bending actuators (Fig. 13.5a), breaking systems (Fig. 13.5b), suction and dispensing capability (Fig. 13.5c) all validate their functionality and applicability within the soft robotic domain.

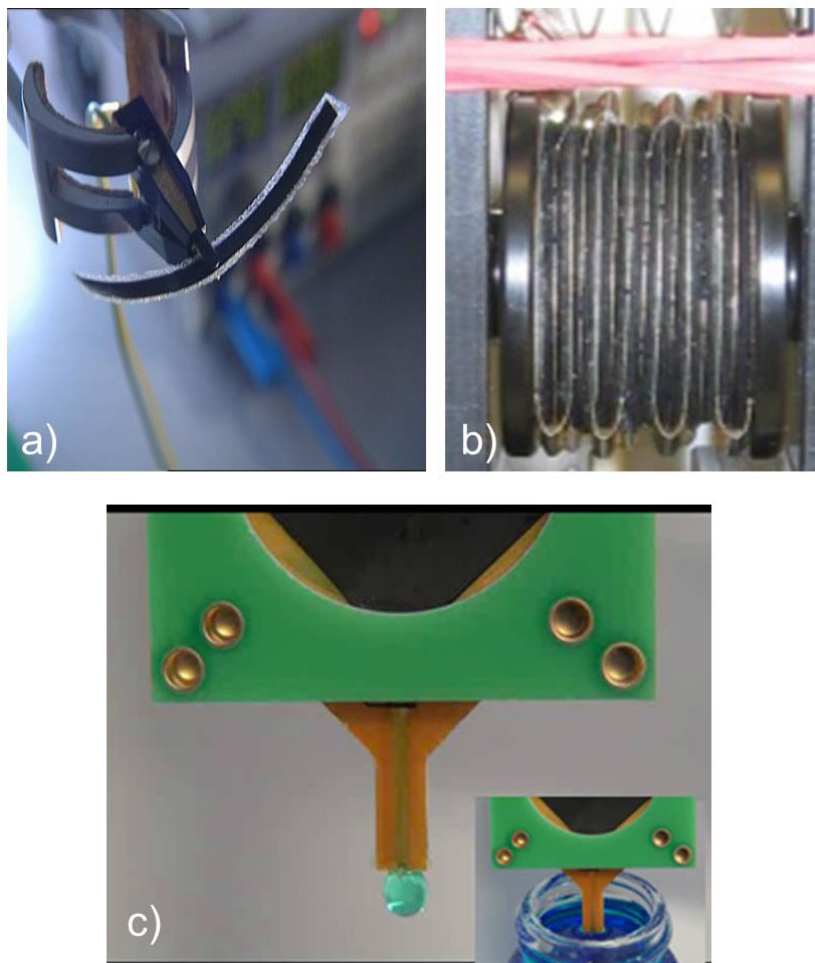


Fig. 13.5 a) Trilayer CNT based actuators mimicking gripping functionality b) Stack of round trilayer CNT-ionic actuators integrated to function as a disk brake c) CNT based actuator system for liquid handling devices; developed at Fraunhofer IPA and AIST Kansai

13.3 Touch Sensors

In a certain way a touch sensor can be described with the inverse function principle of an electric actuator. Whereas an electric actuator moves or changes its shape due to electrical stimuli, a touch sensor converts an externally generated mechanical pressure on its surface into an electronic signal. However this statement is only partially correct as it describes a resistive touch sensor where two electrically conductive films are separated by a thin insulating layer. Voltage is applied to one

of the conductive films and sensed by the other conductive film. When mechanical pressure is applied on the top conductive layer, the electrical resistance is measured at the location of the contact of the conductive layers. For applications in displays the conductive layer has to be transparent. Since a few years another type of touch sensor is used in many applications such as smartphones and tablet computers: capacitive touch sensors. Capacitive touch sensors are stimulated by the detection of a close object, which has a dielectric different from air. In touch panels in display devices the human body capacitance of the finger generates the stimuli [21]. As the electrical field is changed by the iron in the red blood cells of the nearby finger, a capacitance meter inside the device detects the change of the electrical field lines. One of the major advantages of capacitive touch sensors over resistive touch sensors is the possibility to allow multi-touch functions. However, in applications for soft robotics, there is not always an object that has a dielectric other than air. There also are capacitive touch sensors, which react on pressure. The key component is the same as for any other capacitive sensing system: a plate capacitor [21]. The change of the detected capacitance occurs not due to an external field of an object but due to the change of the distance between the two capacitor plates caused by the mechanical pressure of the object.

Lu et al. have recently given a comprehensive overview on flexible and stretchable electronics for the usage in soft robotics [22]. One of the potential applications is a tactile sensing artificial skin (electronic skin, E-skin). For soft robotics it is obligatory that such components base on a bendable and stretchable carrier material such as silicones. As mentioned above, touch sensors consist of conductive layers, which should not be brittle or heavy for the usage in soft robotic components. Indium tin oxide does not fulfil these criteria due to its high brittleness. Metallic wires are bendable but not stretchable. On the other side, CNT networks exhibit excellent performance not only with regard to bendability but also to expansibility. Hence, the coating of thin conductive CNT networks onto flexible substrates such as silicones offer promising potential for the realisation of haptic sensing in soft robotics. However, as mentioned in the introduction section, there are still enormous challenges concerning the purifications of the CNTs and the coating process onto the substrate. Due to the resistances at the junctions in a CNT network, the overall sheet resistance is much higher as one expects from the high intrinsic conductivities of metallic CNTs. Hybrid structures could overcome the drawbacks of the sole materials. Recently we have developed a transparent flexible film based on silver nanowires (AgNWs) and CNTs [23]. It is reported that the mechanical flexibility as well as the electrical performance of silver nanowire networks can be improved by a top layer of CNTs [24]. Fig. 13.6 shows an atomic force microscope image of a conductive AgNW/CNT hybrid film. The CNTs enhance the overall conductivity by creating electrical bridges between the AgNWs.

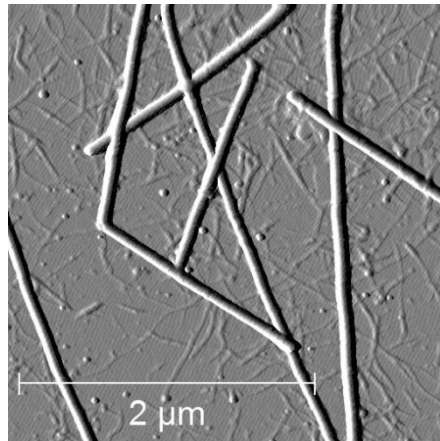


Fig. 13.6 Atomic force microscopy image of a silver nanowire/carbon nanotube hybrid network

13.4 Conclusions and Perspectives

Components for soft robotic devices demand novel materials with improved mechanical and electrical properties. With conventional stiff and brittle materials the goal of creating soft robots cannot be achieved. Therefore novel materials have to be investigated in an interdisciplinary research environment. These materials will be one of the essential driving forces for the development of future robotic components. Due to their extraordinary mechanical robustness and outstanding electronic properties, nanostructured carbon materials offer high potential for the production of mechanically flexible components in soft robotics. The biggest challenge for the realisation of these devices is the integration of the materials into or onto the carrier material. However, recent developments have shown that both new actuators and touch sensors can be developed and improved with the usage of carbon nanotubes.

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