THE LAYERS OF BIOLOGICAL COMPOSITE NANOMATERALS AS ELECTRODES IN AN ARTIFICIAL MUSCLE

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ABSTRACT

A brief analytical review of prototypes of artificial muscles is given, the possibilities of their use in medical practice are estimated. Actuators: pneumatic, hydraulic, based on materials with a shape memory effect and many others do not meet the requirements for their use in invasive medical practice. Ionic electroactive polymers and composite nanomaterials in biological materials and carbon nanotubes are promising. In particular, the composite nanomaterial from bovine serum albumin (BSA, matrix) and single-walled carbon nanotubes (SWCNT, filler) is considered in detail. The aqueous dispersion contained: 20 wt.% BSA and 0.5 wt.% SWCNT. After drying of the moisture, the composite nanomaterial had an approximate composition: BSA/2,2–2,4wt.% SWCNT. In the liquid state, the layers were irradiated with a laser until completely dried. The layers had a thickness of 0.5–50 µm. It should be noted that laser radiation does not overheat layers and does not lead to denaturing of albumin, and this process is much simpler than the deposition of metal layers on polymer substrates. Measurements showed: the maximum conductivity is ~ 100 S/m, the minimum surface resistance is ~ 1 kOhm. It is shown that these layers can perform the functions of electrodes in an ionic electroactive polymer artificial muscle. In view of the high biocompatibility and availability, the composite nanomaterial albumin/single-walled carbon nanotubes are promising as artificial muscles, both in non-invasive and invasive applications.

Keyword: artificial muscle, electroactive polymer, bovine serum albumin, carbon nanotube, composite nanomaterial, layers, conductivity

INTRODUCTION

Modern scientific research is focused on the development of various actuators. Actuators are needed for robotics, cosmonautics, underwater or distance works, industry, military, medicine. In medical practice, reproduction and control of movements is an important technological and engineering task. Actuators such as artificial muscles (AM) are developed. Such mechanisms can repeat natural muscle action: compression, stretching, torsion, free movement in different directions, lifting loads, movement. They are relevant for medicine for example, as artificial heart muscle patches, sphincter cuffs for various parts of the body (urethra, anal canal, lower esophagus). The spectrum of AM use as actuators is very wide (prostheses, exoskeletons, implantable drug delivery mechanisms, etc.). So, there is a task of creating light, biocompatible, reliable AM, and their activation should be safe for people (low power consumption, acceptable operating temperature). For this purpose, the properties of various materials are studied and the polymers and various composite nanomaterials are considered as the basic for the creation artificial muscles. The best materials for this purpose are electroactive polymers and composite nanomaterials containing carbon nanotubes (CNT). The latter deserve the greatest interest in the creation of AM, since the use of these nanomaterials allows achieving high strength, elasticity and electrical conductivity.

This article presents a brief analytical literature review, which describes the research and development of various drives and prototypes of artificial muscles, and also assesses the possibility of their use in medical practice. The focus is on nanomaterials containing biological polymer matrices.

PNEUMATIC ARTIFICIAL MUSCLES

McKibben artificial muscles (pneumatic artificial muscles, PAM) work by pumping fluid or gas under pressure into a chamber bounded by a rigid braid [1]. A new type of McKibben muscle uses paraffin which is heated to a temperature of 95 ° C and expands. They are not suitable for invasive medical use due to the high operating temperature, cumbersome, complex control system. McKibben AM have a great potential in external prosthetics, they have a high power density $P_m \geq 4$ kW/kg and the characteristics like human muscles [2]. For example, the McKibben AM external prosthesis provides sufficient torque for fast walking and climbing stairs [3]. The activate of hydraulic (fluid, GAM) artificial muscle is similar, but has its advantages: ductility, low weight, low maintenance and low cost [4]. PAM and GAM are designed as actuators for robotics and in various technical products, but in some cases they can be used to the movement of human limbs.

ELECTROACTIVE POLYMERIC

Electroactive polymers (EAP) have such characteristics as natural muscles, in particular, they are controlled by electrical impulses [5]. Usually EAP materials are divided into two main groups: electronic, activated by the electrostatic field and ionic, activated by the transfer of ions. EAP of the first group are high-voltage (≥ 1 kV), develop low power $P_m \leq 0.1$ kW/kg and have a high coefficient efficiency $CE \geq 90\%$. EAP of the second group are considered low-voltage (≤ 5 V), have high power and $CE \leq 20\%$. The materials of the first group for medical artificial muscles (prosthesis, implant) are unacceptable because of the danger of high tension. EAP of second group, for example, ionic polymer-metal composites, are promising for the development of various medical devices. Figure 1 shows principle of the action of EAP from an ionic polymer-metal composite (IPMC).

IPMC has the form of a sandwich, where layers of metal and EAP alternate. In the absence of an electrical voltage on the electrodes, the layers do not deform (fig. 1a, flat state), and after application of the voltage, the IPMC bends due to the migration of cations between the electrodes. When the voltage is turned off, the pressure gradient created during the previous activation will cause the electrolyte flow to the anode, and the IPMC drive will relax to a flat state.

Ion EAP is a functional material in the development and creation of AM [6]. The low-voltage operation (≤ 5 V) used in this EAP provides electrical safety, and the precious metals used (Au, Pd, Pt, etc.) provide an acceptable degree of biocompatibility. Already known AM based on ionic EAP: artificial sphincters of the lower esophagus, anal canal, urethra of the urinary canal and the heart muscle patch are created [7]. Also known the device for the eyelids (fig. 2) [8]. This device provides blink. It is assumed that the device will be combined with a normal movement of the face, which would ensure symmetrical control of the eyelids. The device was implanted in mice. The result of the histological examination showed the development of a minimal fibrous capsule surrounding the implants without signs of bacterial infection or inflammation.

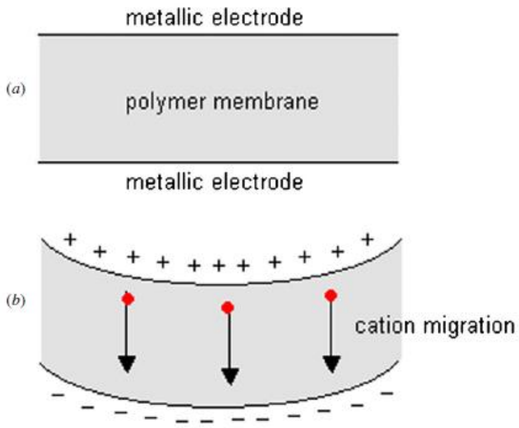

Fig. 1. Scheme of the IPMC action: a - voltage off; b - the voltage on, the migration of cations between the electrodes, and the bending of the IPMC [5]

For activation EAP AM, an electrolyte is required, which complicates the design of the device. New AM was developed, parts of it (electrolyte, electrodes) are enclosed in a hermetic and elastic material. This system is a prototype of AM, which can be used in any environment (in the air, in the liquid, in the human body) [9]. However, the medical prototype AM, which is widely used in practice, has not yet been created.

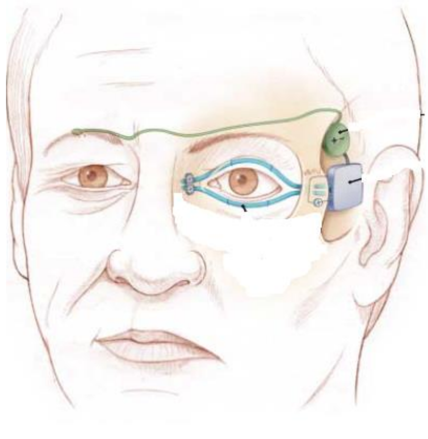

Fig. 2. Artificial muscle design for eyelid movement: the left upper eyelid is attached to the device and synchronized with a myoelectric sensor (green wire) with a normally functioning muscle to coordinate the blinking of the eyelids [8]

OTHER MATERIALS FOR ARTIFICIAL MUSCLES

The most accessible and simple is the actuator from twisted fibers of nylon and polyethylene. They shrink in length and expand in diameter when heated [10]. The actuator shows on fig. 3.

That type of actuators are activated by heating. The following values [10] have been achieved: the bulk energy density is 840 kJ/m^3, the energy density per unit mass is E_m ~ 530 J / kg, the power per unit mass is P_m ~ 1.0 kW/kg. Some indicators are at the level of the human heart muscle, for which P_m ~ 0.33 kW/kg. Inexpensive AM are made of nylon yarns [11,12]. For example, a twisted nylon bundle can lift the load more than 10 times heavier than a humans muscles with the same length and weight. However, this type of AM is not suitable for invasive prosthetics in the human body due to its high activation temperatures.

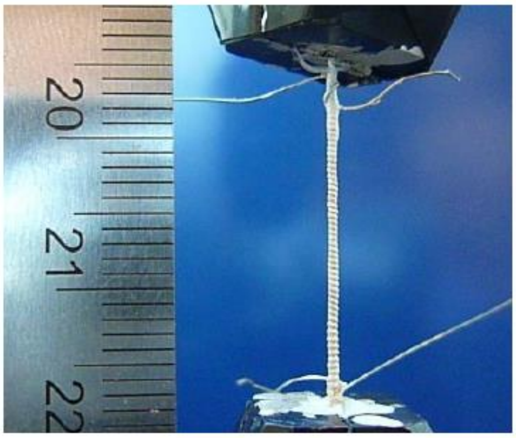

Fig. 3. Optical image of silver nylon actuator [10]

Numerous drives are created on the shape memory effect. They develop high power (P_m ~ 4 kW/kg) and are actively used for robotics [13]. Despite that alloys with shape memory develop very high specific powers, their limit of elastic deformation is limited to 4% and they have a high operating temperature ($\geq$ 50 °C) [14]. The same level of operating temperature is required for a drive based on niobium nanofibers impregnated with wax [15]. Obviously, the actuators considered in [13–15] cannot be invasively used as AM in the human body.

Currently, AM prototypes cannot to simultaneously perform complex deformations that make natural muscles: bending, squeezing, elongation, etc. Recently, it has been established that a single-layered lattice microstructure of onion epidermal cells under the influence of an electrical voltage (50–1000 V) can simultaneously participate in complex deformation [16]. This direction is at the initial stage of the study and it is difficult to determine its future prospects.

ARTIFICIAL MUSCLES CONTAINING CARBON NANOTUBES

The unique mechanical and electrical properties of carbon nanotubes (CNT) make them excellent candidates for developing and creating AM medical applications. For example, up to 1% of CNT in the polymer matrix increases the conductivity of it by more than 10 orders of magnitude. At the same time, the coefficient of thermal conductivity increases by several orders of magnitude and by 10–30 % the modulus of elastic modulus. Such an amazing increase physical characteristics of a composite material after the addition of CNT is because of extremely high values of electrical, mechanical, and thermophysical parameters of the nanotubes themselves. AM with CNT have advantages over conducting polymeric muscles, both in the activation rate and in the lifetime of the device (more than 140000 strain cycles without loss of properties). However, pure CNTs produce a small tensile action (usually ≈ 0.2%), have low efficiency (≈ 0.1%), mechanical stress averages 1 MPa [17].

An airgel of CNT, sometimes called frozen smoke (frozensmoke), is a material with a very low density [18]. The layers expand by high voltage (1–5 kV) with a strain rate – $3.7 \cdot 10^4$ %/s, energy destiny – E_m ~ 30 J/kg. They also have a very wide range of operating temperatures of 80-1900 K and can develop a force more than 30 times the force produced by natural muscles of the same section. The main parameters (mechanical, energy, temperature) for CNT layers are good for the implantable AM, but for practical implementation it is necessary to solve some problems, such as: encapsulation, increase in safety level, biocompatibility.

These problems can be solved by using a composite nanomaterial, which includes a biological polymer as a matrix and CNT as a filler. In [19], a nanomaterial containing a biological polymer of chitosan (CS) and single-walled CNT (SWCNT) in an amount of 25 wt.%. Figure 4 shows the images of the layers of this nanomaterial in the absence of applied voltage (fig. 4a) and deformation by electric voltage of 5 V (fig. 4b).

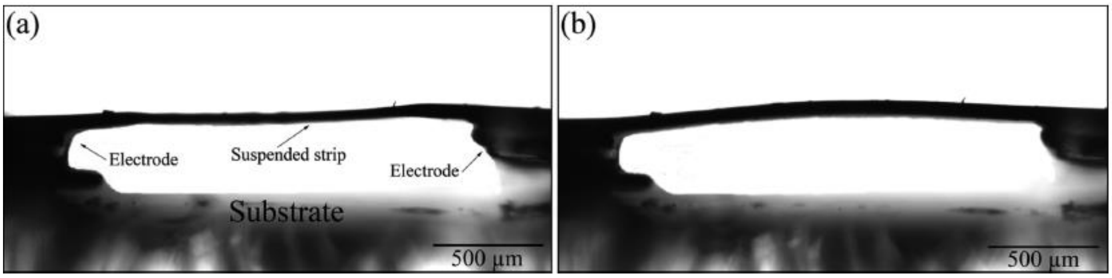

Fig. 4. Optical images of the lateral view of the suspension strip: a – voltage is not applied to the electrodes; b – 5 V applied to the electrodes [19]

The electrothermal method of generating mechanical motion, the ease of control and the biocompatibility of layers of composite nanomaterials such as SWCNT/CS indicate are good for development AM based on them. Apparently, the complication of the nanomaterial composition in order to increase the conductivity will significantly reduce the existing concentration of 25 wt. % SWCNT. As a result, proposed AM will be safety and biocompatible.

In [20] presents, a composite nanomaterial in the form of a nanogel containing cholesterol (HC), boric acid (BA), hyaluronic acid (GA) and multi-walled CNT (MWCNT). When the MWCNT filaments are placed in the nanogel and contact with a small amount of glucose occurs, a redistribution (change) of the internal charge of the anions occurs, the nanotubes repel each other and the nanomaterial swells. Such actuator provides torsional motion that is sensitive to glucose. This process is demonstrated in fig. 5. Such AM can also serve as glucose sensors (range 55–100 mM), which automatically release the drug if necessary.

In a liquid electrolyte, twisted CNT filaments can generate rotational motion and shortening of the length. Such AM are able to lift cargo 25 times heavier than can be lifted by a human skeletal muscle of the same size [21]. A low voltage of ≤ 5 V applies for work. A new type AM with the addition of CNTs at a concentration of ≤ 10% provides high performance without immersion in the electrolyte [22]. The drive mechanism is the swelling of rubber when exposed to a non-polar solvent. The calculated *CE* value is ~ 16 %, which is close to the *CE* value ~ 20 % for human muscle tissue [23].

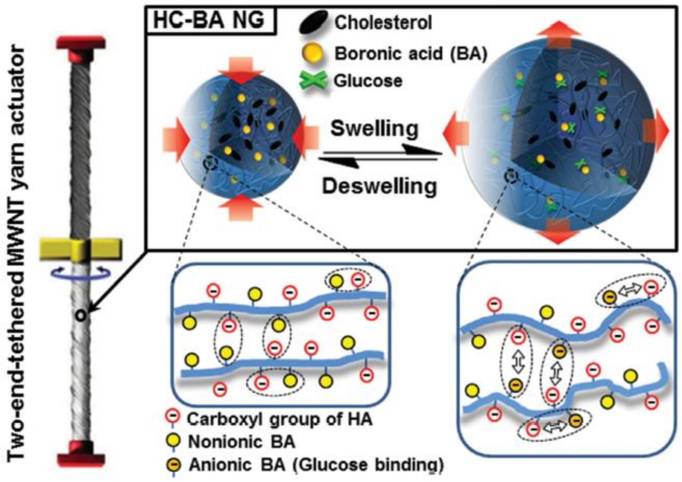

Fig. 5. Self-guided drives from MWCNT in the electrolyte containing HC-BA NG [20]

High power, fast response and low supply voltage are advantages for the considered types of AM with CNTs [19–22], but there is a difficulty in converting rotational motion into other forms of motion.

COMPOSITE NANOMATERIALS CONTAINING BIOLOGICAL PROTEINS AND CARBON NANOTUBES

In [24] studied the electrical conductivity of a composite nanomaterial containing a matrix of their bovine serum albumin (BSA) and a filler of single-walled carbon nanotubes with a concentration – *C* ~ 3 wt.% SWCNT. A nanomaterial had components: bovine serum albumin (BSA) – firm "AMFESCO" (USA); single-walled carbon nanotubes (SWCNT) – firm "UglerodChg" from the Moscow region (Russia). Their external views are shown in fig. 6.

SWCNT were obtained by electric arc synthesis and had a diameter ~1.5 nm, length ≥ 1μm. They were in the form of a water paste (2.5 wt.% SWCNT) and carboxylated (functionalized). For individual SWCNTs, a specific surface is achieved ~1300 m^2/g, However, they are highly aggregated and their specific surface area drops to 200÷400 m^2/g. In these cases, the average sizes of nanotubes could have orders of magnitude: diameter – 3÷4 nm, length – 1÷10 μm.

The composite BSA / SWCNT nanomaterial was prepared according to a route map, some of it steps are: the preparation of an aqueous dispersion based on BSA and SWCNT and its dispersing; preparation of substrates; Deposition of BSA/SWCNT dispersion onto substrates; application of water paste from SWCNT to substrates; irradiation of layers by a laser when they were in a liquid state; sample drying; electrical and temperature measurements. The aqueous dispersion contained: 20 wt.% BSA and 0.5 wt.% SWCNT. After drying the moisture, the composite nanomaterial had an approximate composition: BSA/2,2-2,4wt.% SWCNT. It should be noted that laser radiation does not overheat the layers and does not lead to denaturing of albumin, and this process is much simpler than the deposition of metal layers on polymer substrates.The process of preparation of BSA/SWCNT samples, and measurement of electrical properties are shown on fig. 7.

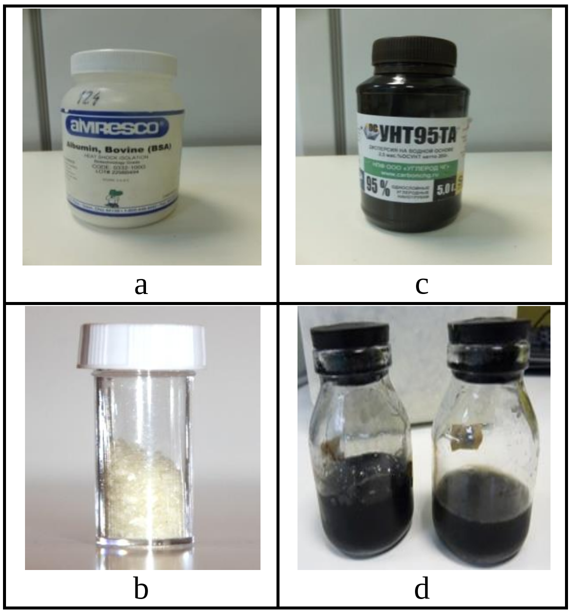

Fig. 6. Composite parts of composite nanomaterial BSA/SWCNT: a – BSA; b – BSA (powder); c –SWCNT; d – aqueous dispersion BSA/SWCNT [24]

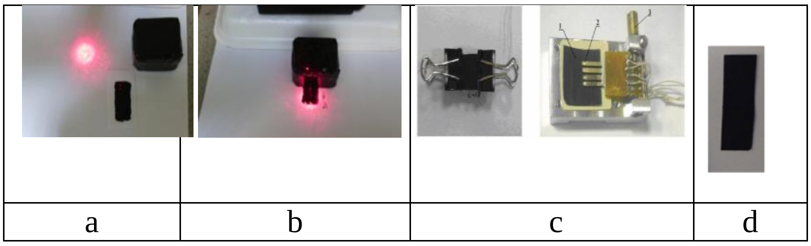

Fig. 7. The preparation process, measurements and appearance of the samples: a – BSA/SWCNT layers, laser radiation, opaque box; b – laser irradiation of half the layer, when the second half is closed by a light-proof box; c – electrical resistance measurements; d is the finite form of the layer [24]

The sample consisted of layers in the liquid state deposited on the substrates. Half was covered with a light-tight hollow box (fig. 3f , right-hand part), and the other half of the layer was laser irradiated (LI). This process ended when the layers became completely dry. In this case, the other half of the layer remained in the liquid state (not dried). In the experiment, a medical laser with the following characteristics was used: generation wavelength 810 nm; continuous mode of radiation; the specific power LI on the surface of the layer ~ 100 W/m^2.

Control samples were those not exposed to LI. The thickness of the layers was in the region 0.2÷50 μm. Figure 8 shows typical dependencies of the given conductivity on temperature for different layers: SWCNT (triangular markers); BSA/SWCNT (round markers). Видно, что для всех слоев наблюдаются полупроводниковый тип поведения. In this case, for SWCNT layers, the conductivity σ_0 ~ 70 kS/m at a temperature t = 25 °C approximately three orders of magnitude greater than value σ_0 ~ 100 S/m for composite nanomaterial layers BSA/SWCNT. However, the last value is many orders of magnitude greater than the BSA conductivity, for which $\sigma_0 \le 1\mu$S/m. Obviously, the enormous effect of a small concentration (C ~ 3 wt.%) carbon nanotubes growth of the electrical conductivity of bovine serum albumin (fig. 8).

High conductivity values were obtained in samples of layers subjected to LI in thin layers with thicknesses of 0.5 μm and 1.4 μm. The conductivity is ~ 6 times higher than in the layers dried in without LI. The following indicators were achieved for the layers: SWCNT – σ_0 ~70 kS/m; BSA/SWCNT – σ_0 ~100 S/m. In the latter case, the minimum surface resistance was of the order of ~ 1 kOhm.

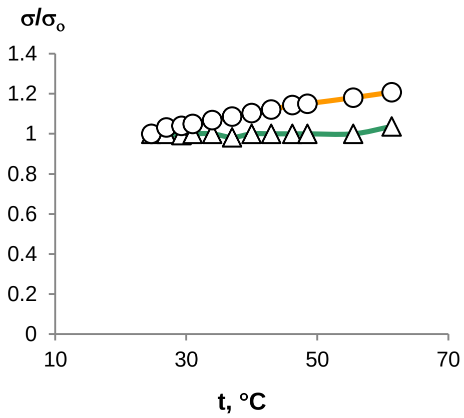

Fig. 8. A typical dependence of σ/σ_0 and t or different samples: Δ – SWCNT layers; o – BSA/SWCNT layers, σ_0 ~100 S/m [24]

Thus, the layers of the composite nanomaterial BSA/3wt.% SWCNT have high values of conductivity, more than 10 orders of magnitude higher than the conductivities of pure layers from BSA. It is also believed that the composite nanoscale materials has an acceptable degree of biocompatibility, since they are mainly composed of the biological material of albumin (≥ 97 wt.% BSA). The components of this composite nanomaterial are inexpensive, the BSA/SWCNT material itself is not difficult to prepare, and it maintains stability under long-term storage under normal conditions. Therefore, it can replace precious metals (Au, Pt, etc.), which are currently used in artificial muscles [5–9].

CONCLUSIONS

From the analysis of literature sources, the following conclusions can be drawn:

• pneumatic and hydraulic AM produce the highest specific power ($P_m \ge$ 4 kW/kg) and are suitable for robotics and for external prostheses of human limbs. However, it is impossible to use them as an invasive implant because of their inconvenient energy supply and insufficient biocompatibility;

• AM from ionic electroactive polymers give the following parameters: power – P_m ~ 1.0 kW/kg, energy – E_m ~ 530 J/kg and efficiency – $CE \le 20\%$ at human level

(P_m ~ 0.33 kW/kg, E_m ~ 39 J/kg, CE ~ 20%). However, components (electrolytes, polymers, electrodes) of construction, high cost, very limited life of existing prototypes of AM do not meet the requirements for their application in medical practice;

• nylon and polyethylene AM, shape memory materials have operating temperatures ≥ 50 °C and, undoubtedly, their use as a medical invasive implant is impossible;

• the main parameters (mechanical, energy, temperature) for CNT layers are acceptable for the creation of implantable AM, but for practical implementation it is necessary to solve some problems, including: encapsulation, increase in safety level, biocompatibility.

• layers of composite nanomaterial BSA/SWCNT obtained by laser technologies have high values of specific conductivity (~ 100 S/m), which is more than 10 orders of magnitude higher than pure layers from BSA. It is believed that this composite nanomaterial possesses an acceptable degree of biocompatibility, since they consist mainly of albumin biological material (≥ 97 wt.% BSA) and a negligible fraction of carbon nanotubes (≤ 2.5 wt.% CNT). The components of this composite nanomaterial are inexpensive, the layers of the BSA/SWCNT nanomaterial themselves are easy to prepare, and it maintains stability under long-term storage under normal conditions. Therefore, it can replace precious metals (Au, Pt, etc.), which used in electroactive polymers artificial muscles.

Thus, active research especially in the field of improving the characteristics of actuators based on ionic electroactive polymers and composite nanomaterials wich includes carbon nanotubes, will create an invasive muscle for medical invasive purposes. About 10 million people die of heart failure around the world, so creating an artificial muscle as an auxiliary part instead of a damaged cardiac node will save many lives.

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