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Nanocomposite Hydrogels Reinforced by Carbon Nanotubes

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ABSTRACT
Hydrogels are three-dimensional (3D) network structure materials consisting of hydrophilic polymer chains, which are crosslinked to form matrices with high water content which swells but does not dissolve in water. They are characterized by tunable physical, chemical, biological properties, high biocompatibility and versatility in fabrication, which classified them as a promising materials in several fields. The soft and wet nature makes hydrogels ideal candidates for applications in soft robotics, smart lenses and artificial muscles. Recently, carbon nanomaterials, have been incorporated into various hydrogels, because of their superior electrical, mechanical, and thermal properties, which have been widely applied to sensors, actuators and barrier technologies. These unique physicochemical properties of carbon nanomaterials are highly desired for soft robots, enabling them to work in different environments and provide real-time feedback in order to achieve optimal human-robot and robot-robot interfaces. Carbon nanotubes (CNTs) are often used as reinforcing agents to enhance the mechanical properties of hydrogels. A new class of hydrogels, known as nanocomposite hydrogels were obtained by incorporating CNTs in hydrogel formulations, resulting as very tough and electrically conductive hydrogels. Herein, will be discussed more in detail the use of carbon nancomposite hydrogels in the applications as actuators and sensors, conductive hydrogels and tissue engineering and biomedicine.
Keywords - Applications, Carbon Nanotubes, Hydrogels, Nanocomposite

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I. INTRODUCTION

Nanotechnology is an interdisciplinary study which allows us to develop materials with new, interesting and useful properties [1]. Nanotechnology is necessarily a multidisciplinary field which encompasses and draws from the knowledge of several diverse technological fields of study including chemistry [2], physics, molecular biology, material science, computer science, and engineering [3-4]. Nanomaterials have dimensions below 100 nm and usually exhibit different chemical and physical properties than macroscopic objects based on the same material [5-6]. For a perspective of this scale at the atomic level, a hydrogen atom's diameter is on the order of an Ångström (1 Å = 0.1 nm). Thus, ten hydrogen atoms laid side by side would measure a distance of about 1 nm across. Nanomaterials are being used in a number of industries to improve product functionality for electronic, magnetic, optoelectronic, cosmetic, catalytic, biomedical, pharmaceutical, energy, and materials applications.

In the past decades, a new class of hydrogels, known as nanocomposite hydrogels [7] has been designed to improve mechanical performance. These gels, next to the polymeric network, contain inorganic particles, such as clay, graphene, carbon nanotubes (CNTs), or silica [8].

All nanomaterials composed of carbon atoms are termed as carbon-based or carbon nanomaterials. The era of carbon-based nanotechnology, as it is well-known, started from 1985 when the fullerene C60 was discovered. The rediscovery of carbon nanotubes and unexpected discovery of graphene gave a powerful impulse to the further development of carbon nanostructures [9]. Nanostructured allotrope forms of carbon have been intensively investigated in the past two decades because of their unique hybridization properties and sensitivity to perturbation during synthesis, allowing for fine manipulation of the material properties.

This review aims to provide an overview on recent progress in hydrogels and its nanocomposites with carbon nanotubes. Recent progress on the use of carbon nanotubes as nanofillers for the synthesis of nanocomposite hydrogels will be discussed in detail. It briefly describes the applications related to actuators and sensors, conductive hydrogels and tissue engineering and biomedicine.

II. CARBON NANOTUBES

Carbon nanotubes, discovered by Japanese scientist Ijima in 1991 [10], are another allotrope form of carbon with a cylindrical structure. CNTs

was discovered by an early experimental observation of carbon nanotubes by transmission electron microscopy (TEM). CNTs can be described as graphite sheets that are rolled up into cylindrical shapes. The length of CNTs is in the form of micrometers with a diameter of about 100 nm [11]. There are two types of CNTs that are classified according to the number of carbon layers present in them (Figure 1). Single-walled carbon nanotubes (SWCNTs) consist of single graphene layer with diameter varying between 0.4 and 2 nm and usually occurs as hexagonal-packed bundles. Multi-walled carbon nanotubes (MWCNTs) comprises of two or several cylinder, each made up of graphene sheets. The diameter varies from 1 to 3 nm [12].

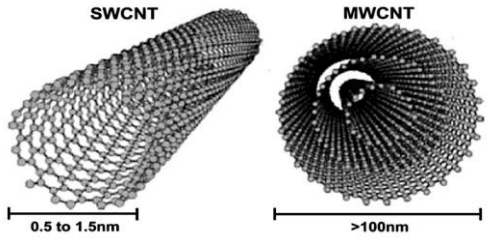

Fig. 1. Representation of single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). [13]

The unique structure of CNTs results in many extraordinary properties. CNTs exhibit excellent chemical and physical properties such as high tensile strength, ultra-light weight, special electronic structures and high chemical and thermal stability. In addition to their extraordinary properties, the density of CNTs is around 1.33–1.4 g/cm^3 [14], which is half of the density of aluminium (2.7 g/cm^3), making them very attractive for lightweight applications. CNTs belong to a promising group of nanomaterials. Because of these exceptional properties, scientists have developed an immense interest in these nanomaterials. These include applications in high-strength composite materials, scanning probe microscopy, field emission sources, nanoelectronics, nanoelectromechanical systems (NEMS), nanorobotics, chemical sensors, bio-nanotechnology, and energy storage. Furthermore, the main applications of carbon nanotube include biomolecule, drug, and drug delivery to the targeted organs, biosensor diagnostic and analysis [15].

Recently, carbon nanomaterials, such as carbon nanoparticles [16-17], carbon nanotubes [18-20], [21-22], and graphene oxide (GO)[23-24], have been incorporated into various hydrogels, because of their superior electrical, mechanical, thermal properties, high mechanical strength, high specific area, and low mass density [25] which have been widely applied to sensors [26], actuators [27-28], and barrier technologies [29-30]. These unique physicochemical properties of carbon nanomaterials are highly desired for soft robots, enabling them to work in different environments and provide real-time feedback in order to achieve optimal human-robot and robot-robot interfaces. Nevertheless, the incompatibility between "hard" carbon nanomaterials and "soft" hydrogels has been a huge challenge towards full utilization of their intrinsic physicochemical properties in the fabricated soft robots [31].

CNTs are often used as reinforcing agents to enhance the mechanical properties of hydrogels. By incorporating CNTs in hydrogel formulations, it is possible to obtain very tough [32-33] and electrically conductive hydrogels [34-36]. CNT-based nanocomposites represent a versatile platform for developing hydrogels with multiple responsive properties and remarkable mechanical performance. However, there is a concern about the toxic effects of CNTs and, therefore, hydrogel biocompatibility. Studies reported CNT toxicity that seemed to be dose-dependent, but which could be reduced when CNTs are functionalized and incorporated in networks [37]. Most of the reported CNT-based nanocomposite hydrogels contain covalent cross-links between CNTs and polymer chains, or between polymer chains, with CNTs being only physically embedded in the network [33, 34, 38-40].

III. HYDROGELS

Both natural and synthetic polymers have been broadly used for the synthesis of hydrogels [41]. The primary natural polymers exploited for fabrication of hydrogels are biodegradable materials such as fibrin [42], collagen [43], hyaluronic acid [44] and alginate [45], that are able to mimic natural tissue constructs [46]. However, their mechanical strength is essentially poor and their composition may vary from one hydrogel to the other. On the other hand, hydrogels that are made of synthetic polymers such as poly(ethylene glycol) (PEG)[47], poly(acrylamide) (PAM)[48] and poly(vinyl alcohol) (PVA)[49] possess controllable chemical and mechanical features. However, they need to be modified to become bioactive by incorporating adhesive molecules upon polymerization [50].

Hydrogels, which are a three-dimensional (3D) network of cross-linked hydrophilic polymer chains with high water content (up to 90 wt%), are highly elastic and soft materials. If these hydrogels contain stimuli-responsive polymer, they can produce drastic changes in their volume in response to environmental stimuli, such as heat, light, and magnetic and electric fields. Particularly, hydrogel

actuators, converting the energy received from outside into mechanical motion, can exhibit soft and flexible motions similar to that of living creatures. Owing to the flexibility, biocompatibility, and stimuli sensitivity advantages of hydrogels, they can be utilized in a wide variety of applications, including drug delivery, smart window and soft actuators [51].

Hydrogels are characterized by tunable physical, chemical, biological properties, high biocompatibility and versatility in fabrication, which classified them as a promising materials in several fields. The soft and wet nature makes hydrogels ideal candidates for applications in soft robotics [52-55], smart lenses [56-57], manipulators [58-59] and artificial muscles [60-61].

In spite of these significant features exhibited by the hydrogels, they still possess many shortcomings, for instance, poor mechanical strength, low strain, low thermal stability, which have restricted their optimal and efficient realization in various fields of science and technology. Unfortunately, most conventional hydrogels are fragile and weak. A major problem is the inhomogeneous distribution of crosslinks and mesh size in the network [62]. The poor mechanical properties have prevented conventional hydrogels from practical applications. A great of trials have been made by scientists and researchers into redesigning and developing new hydrogels with improved and unique properties. In some cases, nanoparticles are functionalized to form covalent bonding or host-guest recognition with polymer chains. Upon loadings, the interactions between polymer chains and nanoparticles gradually rupture to dissipate energy [63].

Hydrogels have been actively investigated considering their high reconfigurability/deformability, low material stiffness, and more importantly, their outstanding biocompatibility, high conformability, as well as intrinsic interfacial adhesion [64-66]. Multifunctional soft robots require enhanced capabilities in mechanical stability, tensile sensation, and stimuli responsiveness which could be achieved by different approaches such as polymer modification, dual-crosslinking strategies, and nanomaterial reinforcement of hydrogels [67-68].

III. I NANOCOMPOSITE HYDROGELS

Nanocomposite (NC) hydrogels can be elongated to more than 1000% of their primary length, and tolerate ~90% compression [7]. Numerous synthetic routes have been developed to synthesize NC hydrogels. However, to tune mechanical properties, nanomaterials have been introduced into polymer networks either via physical crosslinking or covalent integration. Polymer monomers in physical crosslinking are crosslinked by nanomaterials via physical interactions during their polymerization. In contrast, in the covalent integration, nanomaterials facilitate chemical crosslinking using methods like click chemistry and radical polymerization [69]. Various nanoparticles including ceramic [70], carbon-based [71] and metallic nanomaterials [72] have been incorporated into hydrogel networks to achieve nanocomposites with tuned physical properties and functionality [73].

Chen et al in 2015 prepared a new type of fully physically cross-linked Agar/hydrophobically associated polyacrylamide (HPAAm) DN gels by a simple one-pot method. The Agar/HPAAm DN gel consisting of the hydrogen-bond crosslinked agar gel as the first network and the hydrophobically crosslinked HPAAm gel as the second network. Use of ductile, nonsoft HPAAm gel as the second network can not only effectively dissipate energy and thus greatly enhance the mechanical properties, but also introduce superior self-recovery and self-healing properties via reversible network reconstruction. At the optimal formulation, Agar/HPAAm gels showed high mechanical strength and toughness, comparable to conventional chemically linked DN gels and superior to hybrid-linked DN gels. More importantly, due to its unique physically, reversible network structures, the gels can sufficiently and quickly reconstruct the gel network structures, leading to rapid self-recovery and self-healing from softening and damages without any external stimuli at room temperature.

Xia et al in 2017 have prepared an open porous microgel with high hydrophilicity and great injectability based on double bonded poly-(L-glutamic acid)-g-2-Hydroxyethyl methacrylate (PLGA-g-HEMA) and maleic anhydride-modified chitosan (MCS), with diameter of 200-300 μm, pore diameter of 38 μm, and porosity of 88.3%. The storage modulus of 30 mg/ml of microgel dispersions is 2000 Pa, which is similar to that of the native adipose tissue. The spheroidal stem cell shape and extensive cell-cell connections can be formed in the present microgels to promote adipogenic differentiation and realize adipose tissue regeneration. After injection in vitro, the microgels can maintain high stem cell viability up to 14 days. The extensive Oil Red O staining is observed after adipogenic induction for 14 days. After 12 weeks post-implantation, adipose tissues can be regenerated well. Blood vessels are formed in the neo-generated tissues. The degradation rate of microgels roughly matches with the adipose tissue formation rate.

Takashima et al. in 2012 have prepared a photoresponsive supramolecular actuator which

reminiscent of a natural muscle by integrating host–guest interactions and photoswitching ability in a hydrogel. They demonstrated that an intelligent supramolecular actuator could be formed using a main chain with a sufficient length and an adequate number of guest molecules to generate reversible crosslinks between αCD and the Azo units. A photoresponsive supramolecular hydrogel with α-cyclodextrin as a host molecule and an azobenzene derivative as a photoresponsive guest molecule exhibits reversible macroscopic deformations in both size and shape when irradiated by ultraviolet light at 365nm or visible light at 430 nm. Moreover, photoresponsive materials have many general applications, including remotely controlled materials and medical devices. They believe that these stimulus-responsive stretching properties may eventually be used in stents and drug delivery carriers to selectively release drugs. αCD–Azo gels may realize photoresponsive embolization application, where photoresponsive αCD–Azo gels will be introduced into the vessels around a tumour using catheter techniques, and optical fibres will provide the photostimuli. It is hypothesized that the introduced gels will embolize the blood stream in arbitrary vessel positions controlled by photostimuli using optical fibres.

III. I. I Carbon Nanotubes Nanocomposite Hydrogels

Within the past few decades, inorganic (e.g. silica, clay, carbon nanotubes)—organic (polymer) nanocomposites have attracted many attentions as they hold promise for properties that cannot be realized by their microcomposite counterparts. Presently, CNTs nanoparticles are one of the widely used inorganic components embedded in the matrices of polymeric hydrogels in order to enhance their inherent properties. In fact, the CNTs have found a place as nanofillers in the fabrication of nanocomposite hydrogels due to the fact that CNTs have some excellent properties, such as regular pore structure, high conductivity, excellent electrochemical stability, well-defined one-dimensional structure, low mass density, high mechanical strength, and high specific area [74].

IV. APPLICATIONS OF CARBON NANOTUBES NANOCOMPOSITE HYDROGELS

Owing to the flexibility, biocompatibility, and stimuli sensitivity advantages of hydrogels, they can be utilized in a wide variety of applications, including drug delivery, smart window [75-78] and soft actuators [79-80]. There are various types of external stimuli including pH, light, heat, magnet field and ion strength.

Carbon nanotubes nanocomposite hydrogels have a diverse applications such as actuators, biofuel, tissue engineering, effluents treatment, sensors, solar cells, biomedicine, conductivity, etc.

IV.I Actuators and Sensors

According to a study [81], the first synthetic actuators were polyelectrolyte gels which were found to undergo substantial, and reversible, dimensional change. These reversible changes in gel volume can be triggered chemically by immersing the gel in a different solvent, by changing the solution pH, or by altering the solution salt concentration. They explained that the mechanism of gel actuation can be understood by considering the operating forces that maintain the gel in the swollen state. The actual changes in gel volume responsible for actuation arise from a coil-globule transition of individual molecular segments in the crosslinked network. However, in another study [82], it was stated that the MWNTs nanocomposite hydrogels developed through a simple hydrogelation with PVA were actually the first actuators to be synthesized. The MWNTs/PVA nanocomposite hydrogel fabricated in their study exhibited excellent actuating properties.

Exceptional properties of carbon nanotubes such as high tensile strength, light weight, fast electron transfer kinetics, high biocompatibility, helps in protein immobilization. Furthermore, large surface area, chemical inertness, large number of antibacterial and antifungal properties, can be used as protein carriers, contains exposed functional groups makes them tremendously attractive in various biosensor applications [83]. Multi-walled carbon nanotubes possess significant potential in biosensors due to their ease in supporting protein immobilization while maintaining protein inherent activity [84].

IV.II Conductive hydrogels

Conductive hydrogels have aroused wide attention in recent years due to their promising applications for wearable sensors [85-87], supercapacitors [88-91], medical diagnosis [92-94], etc. For example, recently, a highly stretchable supercapacitor assembled from polypyrrole-incorporated gold nanoparticle/carbon nanotube (CNT)/poly(acrylamide) (GCP@PPy) hydrogel was developed by Chen et al in 2019 [95], which performed excellent supercapacitor performance under complex mechanical deformations.

Recently, hydrogels with shape memory function has been expected to display the great potentials in soft actuators, intelligent robots, etc.

[96-98]. Shape memory hydrogel could transform from a temporary shape to its performant shape in response to external stimulus, such as thermal, electric, magnetic, light or chemical, etc. [99-102].

Recently, Hsiao et al., in 2020 [18] fabricated a conductive hydrogel by integrating pristine multi-walled carbon nanotubes (MWNTs) into gelatin solution followed by the introduction of a crosslinking agent (i.e., glutaraldehyde). Gelatin served as not only the polymer backbone for the formation of hydrogels but also a stable, non-covalent surfactant that could be adsorbed on the sidewalls of pristine MWNTs, resulting in effective dispersion of MWNTs in aqueous gelatin solution prior to crosslinking. The formation of imine derivatives (Schiff base bonds) between gelatin and glutaraldehyde was as result of crosslinking reaction. After large-area printing, the MWNT-gelatin paste (containing glutaraldehyde) continued to crosslink, and an MWNT-integrated gelatin hydrogel (abbreviated as MW-hydrogel afterward) was obtained. The MW-hydrogels were highly deformable (e.g., 100% stretching, >90° bending, 360° twisting) and mechanically durable. Within the resulting MW-hydrogels, MWNTs served as a commercially available and highly conductive carbon-based nanofillers. Owing to the high aspect ratio of MWNTs (diameter ~5 nm, length ~15 μm), the MW-hydrogels only required a low MWNT loading to achieve the percolation network with high electrical conductivity. In addition, with embedded MWNT networks, the electrical resistances of conductive MW-hydrogels were responsive to various mechanical deformations, including tension/compression, twisting, and bending, enabling their applications in electronic robotic skin to monitor the actuations of soft robots in real time. Also, with high water content, the MW-hydrogels exhibited high efficiency of heat regulation and were further utilized as flame-retardant skin for a soft robotic gripper, which could manipulate and rescue irregularly shaped objects from a fire scene. Direct additive manufacturing such as doctor blading was adopted to obtain large-area or patterned conductive MW-hydrogels, which could facilitate their wide adaptations to various robotic and actuation systems.

Recently, Zhang et al. in 2019 [103] prepared a highly tough and conductive hydrogel with good shape memory behavior via constructing the catechol-Fe^{3+} interactions in the poly(vinyl alcohol) (PVA) hydrogel matrix. The hydrophobic 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1-spirobisindane (TTSBI) was introduced to provide the catechol ligands for Fe^{3+}. The fabricated TTSBI-2@Fe^{3+}-12 nanocomposite hydrogel performed great toughness (9.23 MJ/m^3), large tensile strength (3.25 MPa) and high extensibility (752%). The distinguished mechanical performance of the composite hydrogel was contributed by the synergy of nanophase separation structure formed by TTSBI in PVA matrix, strong hydrogen bonding interaction between PVA and TTSBI, and metal coordination interaction of catechol-Fe^{3+}. The introduced Fe^{3+} also imparted good conductivity to the hydrogel. Moreover, the mechanical and conductive properties of the composite hydrogel could be flexibly regulated by the pH value. The conductive hydrogel showed excellent sensitivity to stretching, bending, twist, and compression. In addition, the hydrogel exhibited multiple-stimuli responsive shape memory behaviors. This work offers a hierarchical self-assembly strategy to fabricate functional hydrogel with tailored mechanical, conductive properties and shape memory behavior for a series of promising applications such as flexible wearable electronics and intelligent actuators.

IV.III Hydrogels for Tissue Engineering and Biomedicine

Tissue engineering is an approach involving the design of tissue constructs with the capability of mimicking native tissue in vitro. These constructs are subsequently implanted in vivo to regenerate damaged tissue functionality and to help millions of people who suffer from diseases, or impaired organs [104]. This method combines scaffolds, cells, and growth factors in which the cells are cultured on the scaffold and grown. Subsequently, this tissue construct is implanted at the site of injury without the need for multiple surgeries, thereby reducing the costs, risks, and recovery time associated with conventional treatments [105].

Many patients around the world suffer from organ failure, tissue damage or disease, they require surplus quantities of tissues or organs for replacement. However, due to the shortage of donors, still many wait for the suitable transplant [106]. To address this issue, researchers started focusing towards tissue engineering and regenerative medicine, where hydrogels play a major role in providing the three dimensional microenvironment for the cells [107-108]. The 3D polymeric scaffolds used for this specific purpose should be biodegradable, biocompatible and also, should contain biofactors to enhance the cell adhesion and proliferation [109].

Hydrogels have been recognized as crucial biomaterials in the field of tissue engineering, regenerative medicine, and drug delivery applications due to their specific characteristics. These biomaterials benefit from retaining a large amount of water, effective mass transfer, similarity to natural tissues and the ability to form different

shapes. The hydrogels provide the flexibility by modifying their polymeric network or cross linking density or methods; however, they can be tuned to respond to a physical, chemical or biological stimuli [110].

In recent years, flexible hydrogel strain sensors have shown potential applications in artificial intelligence, such as medical monitoring, human motion detection, and intelligent robotics. It is a challenge for flexible strain sensors with stretchable and efficient healing to ensure stable sensing under repeated deformations or damage. Self-healing capacity refers to a material's ability to automatically repair damage and recover to its original structure and properties [111-112].

Recently, the metal ion cross-linked hydrogels have gained enormous interest because of its excellent properties like self-healing, fast recovery, biocompatibility and high mechanical properties combined with multi-stimuli responsiveness. In the review article [113], the recent trends in the development of metal ion cross-linked hydrogels for tissue engineering and biomedical applications have been summarized.

In the research carried out by Mao et al. in 2019 [114], a highly stretchable, self-healing, and strain-sensitive sensor was prepared from a hydrogel with a dual network structure, consisting of acrylic acid (AA), graphene oxide (GO), iron ions (Fe^{3+}), and ammonium persulfate (APS) via one-step *in-situ* polymerization without a chemical crosslinker. The composite polyacrylic acid (PAA)-GO hydrogel showed dual crosslinking effect: (i) ionic coordination bonding between Fe^{3+} ions and the carboxylic functional groups of PAA and GO and (ii) hydrogen bonding between the polar functional groups of PAA and the oxygen-containing functional groups of PAA and GO. Because of dynamic double-crosslinked networks, the PAA-GO hydrogel exhibited superior stretchability (1185.53% elongation at break) and self-healing property (88.64% healing efficiency) as well as electrical self-healing performance. Moreover, strain-sensitive conductive hydrogels can be used as flexible sensors to monitor body motions (e.g., bending of fingers, wrists, and elbows) by detecting change in electrical signal and can be used as wearable sensors and for personal health monitoring.

Recent publications have been focused on ferric (Fe^{3+}) ion based cross-linking. Fe ion- catechol (F-C) cross-linked hydrogels were used to develop biomimetic materials inspired from the mussel. The combination of catechol and iron chelation offers enhanced hardness and extensibility to the hydrogels. With this combination, Waite and his colleagues reported a pH-responsive hydrogel by modifying the poly(ethylene glycol)[115] with L-dihydroxyphenylalanine (DOPA) containing catechol groups where *mono*-, *bis*- and *tris* catechol forms containing Fe^{3+} ions were used to develop pH-dependent crosslinking of hydrogels [116]. Similarly, in another work, they varied the different metal ions to modulate the mechanical properties of the hydrogels by adjusting the pH values [117-118].

V. CONCLUSIONS

Among numerous composite hydrogel systems, carbon nanotubes-based nanocomposite hydrogels have gained significant attention due to their high mechanical strength, effective surface area, and high electrical conductivity. The well-demonstrated features of CNTs advocate them as one of the most promising nanofiller for diverse applications such as regenerative medicines, tissue engineering, drug delivery devices, implantable devices, bio-sensing and bio-robotics.

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