Research Article

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Nitrogen-Doped Carbon Quantum Dots-Gellan Gum As An Innovative Self-Healable Hydrogel Composite

Serbulent Turk[1,2*], Mahmut Ozacar[2,3]

ABSTRACT

Tension sensors can be widely applied to detect body movements and monitor physiological signals. Hydrogels with conductive properties draw attention among the studies in this field. However, their application is limited because hydrogels can be easily damaged during use. In this study, a self-healing conductive hydrogel was produced by adding nitrogen-doped carbon quantum dots (NCQDs) to gellan gum (GG) polymer. The self-healing property of the hydrogen bonds in the prepared polymeric matrix network to a certain extent and the conductivity were supported by the addition of NCQDs. The electrical recovery process of the hydrogel in the 1, 2, and 3 cut/healing cycles was illustrated by a visually designed LED bulb serial circuit. As a result of connecting the obtained 3D hydrogel to a real-time resistance change measurement system, the resistance changes in the cut/healing cycles were monitored. The duration of the total cut-healing process, including cut and contact time, was 2.12 s. In addition, a free-standing gel bridge was formed after joining the two cut pieces of cylindrical hydrogels. Due to the resulting hydrogel composite properties, it has promising potential in various applications such as personal health diagnosis, human activity monitoring, and human-motion sensors.

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Introduction

Self-healing and recovery after damage is an essential feature of living tissues. In nature, biological systems can self-heal at both the molecular level (DNA repair) and the macroscopic level (healing of a graze or broken bone in the skin). Inspired by such systems, self-healing materials have been developed for various applications. Self-healing hydrogels, which can regain their structure and function after damage, have been developed as “smart” soft materials that can extend the persistence time and have attracted great interest recently. As a typical soft material with good viscoelasticity, transparency and biocompatibility properties, self-healing gels are increasingly being

[1] Sakarya University, Biomedical, Magnetic and Semiconductor Materials Application and Research Center (BIMAS-RC), 54187 Sakarya, Turkey
[2] Sakarya University, Biomaterials, Energy, Photocatalysis, Enzyme Technology, Nano & Advanced Materials, Additive Manufacturing, Environmental Applications and Sustainability Research & Development Group (BIOENAMS R & D Group), 54187 Sakarya, Turkey
[3]Department of Chemistry, Faculty of Science & Arts, Sakarya University, 54187, Sakarya, Turkey
*Corresponding Author: Gülfidan Kuyumcu, e-mail: serbulentturk@sakarya.edu.tr

investigated for its potential applications in tissue engineering, biomedicine, artificial intelligence, wearable devices and soft robotics [1].

While self-healing materials can recover their original state by healing the damage done to them, this healing process is driven by thermodynamic parameters and depends on dynamic/reversible chemical bonds or physical interactions. These interactions allow the material to be cut into pieces and reassembled after contact, and mechanical properties are restored by restructuring the gel network after the rheological deformation treatment. This property extends the life of materials and makes them ideal candidates for applications with repeated mechanical stress. Compared to conventional hydrogels, self-healing hydrogels can recombine and regain their initial structures and functions once damage. Given their durability and long-term stability, self-healing hydrogels have emerged over the past few years as a promising material for many fragile hydrogels being used in preclinical or clinical trials. Looking at the hydrogels produced for use in the field of biotechnology and biomedicine; depending on the target tissue, self-healing hydrogels must conform to a wide variety of properties, including electrical, biological, and mechanical.

Wearable devices should maintain their structural properties after possible damages in the area where they are applied. After any damage, it can return to its original structural and functional state and add features that repair themselves, giving wearable devices more durability and a longer lifespan [2]. Due to this requirement, the self-healing feature in wearable devices has taken its place among the most sought-after features. In recent years, self-healable wearable devices, which can restore their functionality and structure after damage, have gained increasing interest [3–5]. Soft and flexible materials attract attention in the field of self-healing wearable devices. Self-healing materials as soft materials with properties such as biocompatibility and good viscoelasticity are frequently used in this field due to their potential applications in wearable devices, biomedicine, and artificial intelligence [6,7]. The field of materials with excellent electrical and biocompatibility properties and self-healing properties is still in its infancy. Based on this field, conductive hydrogels with good biocompatibility and high-water retention have attracted the attention of many researchers in recent years as promising materials [8–10]. Due to their conductivity and similarity to natural tissues, conductive hydrogels are applied in various applications such as biological tissue

engineering [11]. In addition, hydrogel-based wearable strain sensors connected to a wireless transmitter can wirelessly monitor and record body movements.

Gellan gum (GG) is a polymer that has potential applications in many areas recently due to its biocompatibility and functional reactive groups suitable for easy modification / functionalization of the polymer backbone. In fact, the major advantage of this biopolymer is its incredible versatility to be processed into new derivatives with different properties, making it possible to tailor its physicochemical and biological properties to suit the specific needs of a particular tissue [12] . GG is a versatile biopolymer that can be easily modified into new derivatives with different properties than the natural polymer, due to its free carboxyl and hydroxyl groups in its repeater unit. These different features, which are associated with high availability and low production costs, have made its application to different areas widespread. GG is an anionic microbial polysaccharide composed of repeat unit of two β-D-glucose, a β-D-glucuronic acid, and an α-L-rnasese tetrasaccharide. GG is capable of physical gelation. Upon temperature drop, a random helix transition takes place with more aggregation of helices leading to the formation of junctional sites. The sol-gel transition of GG polymer is ionotropic. Therefore, the presence of cations in polymeric environment is necessary for the formation of a stable hydrogel.

Adding conductive nanomaterials such as graphene, carbon nanotubes, and metallic nanoparticles to the conductive polymers network is one widely used approach to obtaining hydrogel-based electronic skin and strain sensors [13–15]. New studies are still needed to increase the wearable technology field's material diversity and introduce more suitable materials.

In this study, nitrogen-doped carbon quantum dots/gellan gum (NCQDs/GG) hydrogel was obtained as an innovative self-healing hydrogel composite that can be a promising candidate for wearable sensors. Rapid self-healing feature was observed as a result of the addition of NCQDs added to affect the fast self-healing capacity of the nanocomposite hydrogel. With the addition of NCQDs, which increases the self-healing property of the composite hydrogel, a composite hydrogel with also conductivity was obtained.

Material and Methods

As previously reported [16], N-doped carbon quantum dots were synthesized using a green and convenient "oil bath" strategy. Briefly, for this process, 2 g of urea powder and 10 g of sucrose powder were added to 20 mL of cooking oil preheated at approximately 250°C and mixed for 5 min. After cooling to room temperature, 30 mL of purified water was added to the reaction system to transfer the N-CQDs to the aqueous phase. It was then centrifuged (HETTICH) for 15 min at 11000 rpm to remove any clumped particles. The oil, which is the upper phase in the reaction system, was removed with the help of a separatory funnel. NCQDs synthesized in aqueous solution stored at 4°C were lyophilized using a lyophilizer (BIOBASE) to obtain solid products. As a lyophilization step, it was first frozen at −20°C for 24 hours, then frozen at −60°C for 12 hours, and then lyophilized in a low pressure environment for freeze-drying.

Pure water preheated to 85°C and in a closed environment was pre-prepared for the preparation of GG solutions. Then, 2.0% (w/v) Gellan gum (GG, Sigma Aldrich) was added to the preheated distilled water and the solution was stirred at 85° for 15 min. Then, for the preparation of NCQDS/GG hydrogels, 5% (wt) of pre-synthesized NCQDs were added and mixing was continued for another 15 min at 85°C in closed containers to ensure homogeneity. It was observed that the color of the solution changed with the addition of NCQDs during this time. Prepared solutions were poured into pre-prepared cylindrical and cube-shaped molds while hot to obtain 3D hydrogel shapes and left to cool at room temperature. After waiting for about 2 h at room temperature, the hydrogel samples were removed from the molds and made ready for analysis. For self-renewal characterizations, hydrogels were cut into two parts with a scalpel and the cut surfaces were joined. Real-time resistance changes of 3D NCQDS/GG hydrogels obtained using the Keithley 2612A Source Meter were analyzed during cut/healing cycles.

Results and Discussion

One of the techniques in which the electrical self-renewal of the sample is demonstrated is to place the prepared sample into a series circuit [17–20]. As shown in Figure 1, a series circuit consisting of a light-emitting diode (LED) indicator and a commercial 3 V dry cell was set up to demonstrate the electrical recovery process of the hydrogel

visually. It is known that GG has good conductivity due to the ions such as Na^+, K^+, Ca^{2+} in its content and is effective in a led circuit in an established circuit [21]. The prepared hydrogels, which were divided into two parts and subjected to cut/healing processes 1, 2, and 3 times and integrated into the circuit, are shown in Figure 1a, b and c, respectively. It has been observed that when the bifurcated parts of the hydrogels with different cut/healing cycles come into contact with each other, the series circuit is completed, and the LED emits light of equivalent brightness. In addition, since it is known that human soft tissue has electrical conductivity [22], the conductivity of the hydrogels obtained for the biomedical field is also important.

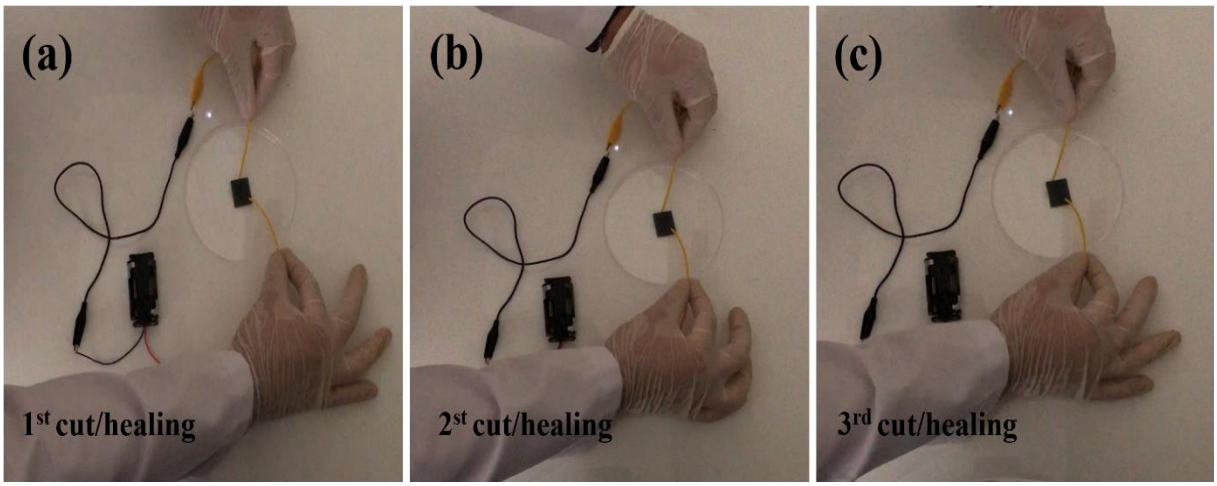

Fig 1 Self-healing behavior of a series-connected hydrogel in a designed LED lamp circuit after cut/healing operations. (a) after 1st cut/healing, (b) after 2nd cut/healing, and (c) after 3rd cut/healing

To further investigate the electrical recovery of the hydrogel, the NCQDs-GG hydrogel was connected to a real-time resistance change measurement system, and the resistance changes in the cut/healing cycles were monitored. As shown in Figure 2, the strength of the hydrogel was recorded over three cut/healing cycles performed with the polyester film slice. The hydrogel was repeatedly completely bifurcated at the same location, and the two separate pieces were soon joined together. Figure 2b shows the time evolution of real-time resistance change during the self-healing process. It was observed that the resistance of the hydrogel attached to the analyzer increased rapidly when cut by the polyester film slice. Then, the resistance value decreased rapidly with the removal of the polyester film. The resistance change of the hydrogel was observed to be relatively stable during the cut/healing cycle. The duration of the total cut/healing process,

including cut and contact time, was observed as 2.12 seconds. In Table 1, comparisons of the sample in the current study with some of the hydrogels in the literature are given. Overall, the results show that the hydrogel with added NCQDs has reproducible electrical self-healing property. Thanks to this feature, the hydrogel obtained for wearable electronics devices becomes an interesting material.

Samples with self-healable feature are materials that have the ability to regain their previous properties after cutting. In this respect, there are visuals in the literature showing that cylindrical samples can form a gel bridge without disintegrating after self-healable [28–31].

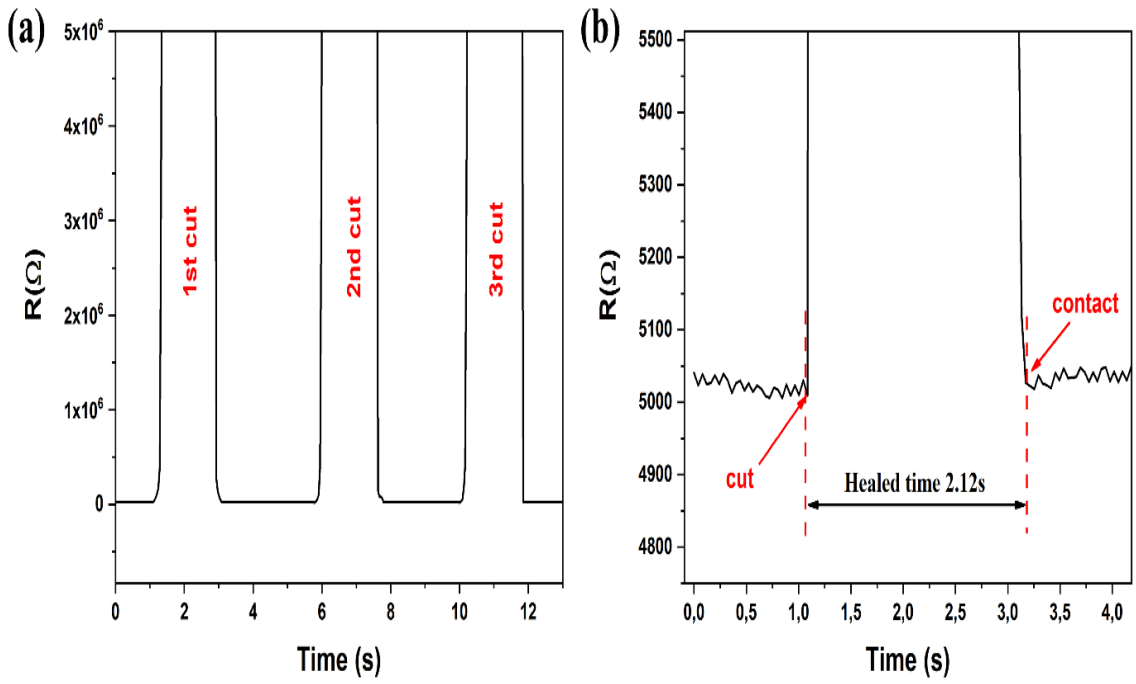

Fig 2 Time evolution of self-healing process by Real-time resistance measurements for NCQDs/GG hydrogel. (a) co-located cut/healing cycles, (b) regional magnified self-healing process

As shown in Figure 3, the two pieces separated after cutting were joined together, and the two bottle caps formed a free-standing gel bridge. Thus, it has been observed that they stick together as a single piece of self-healing gel.

Table 1 Comparison of the contents and cut/healing properties of some hydrogel studies in the literature with the current study

Hydrogel	Component	Cut/Healing Time	Ref.
L4S90	•[2-Methacryloyloxy) ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide •2- hydroxyethyl methacrylate •Laponite XLG	11s (including cut time)	[23]
PVA/PDA	•Polyvinyl alcohol •Polydopamine	250 ms (including cut time)	[24]
PVA-PDA-pRGO	•Polyvinyl alcohol •Polydopamine •Graphene oxide	4.2 s (after the contact moment)	[25]
CSH	•Polypyrrole •Poly(acrylic acid) •Chitosan	30 s (including cut time)	[26]
SWCNT	•Single wall carbon nano-tube •Graphene •Silver nanowire	3.2 s (after the contact moment)	[27]
NCQDs/GG	•Gellan Gum •Nitrogen-doped carbon quantum dots	2.12s (including cut time)	This study

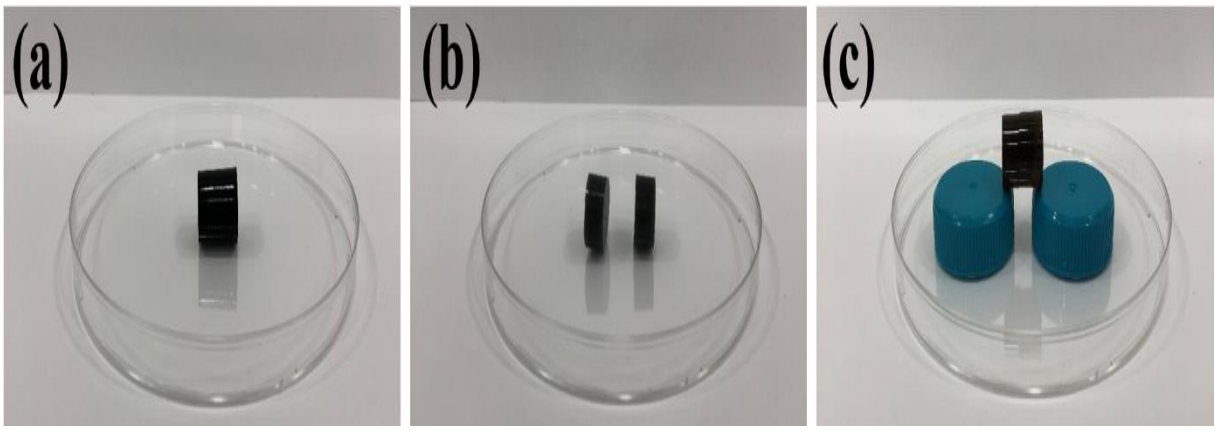

Fig 3 (a) Obtained cylindrical hydrogel (b) cut hydrogel blocks (c) self-healing cylindrical hydrogel sample able to form a bridge

Conclusion

In summary, an innovative self-healable NCQDS/GG hydrogel was produced by adding NCQDs to the hydrogel medium. It was observed that the conductive hydrogel was able to regenerate itself after the cut/healing cycles returned to their initial resistance. It was observed that the obtained hydrogels had reproducible self-healing properties after 2.12 s. For these reasons, there is great potential for the application of the NCQDS/GG hydrogel as a wearable body motion tension sensor to monitor body movements.

For future studies, it is planned by our group to analyze the recovery times in environments where external environmental conditions such as body sweat are imitated. In addition, the evaluation of sensitivity in the perception of under-eye, neck and pulse movements by using the existing hydrogel with an innovative composition is considered to be of great importance in terms of adding an additional innovation to the literature. By varying the NCQDs ratios in its content, hydrogels with adjustable conductivity can also be prepared and used in application areas such as drug-delivery system, bone regeneration, stimulation of tissue growth, artificial muscle.

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