Mechanically robust, photopatternable conductive hydrogel composites

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A B S T R A C T

Electrically conductive hydrogels (ECH) which are composites of hydrogels and conducting polymers, exhibit a powerful combination of biocompatibility and conductivity. They combine the high hydration and soft mechanical nature of hydrogel networks, with the electrochemical functionality of conducting components allowing precise control of properties. Interest in these materials has increased recently for applications in tissue engineering, biosensing, and flexible and implantable bioelectronics. Here, we demonstrate a dispersion of poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) in a photocurable poly(ethylene glycol)-diacrylate (PEG-DA) matrix to form functional hydrogels via a facile, fully aqueous, photopolymerization process. We report on effect of various compositions of the conducting polymer, tuning of mechanical and electrochemical properties, and the ability to micropattern the composite using photolithography. The electrical properties of the ECH are characterized by cyclic voltammetry, four-point probe, and conductive atomic force microscopy to reveal the competitive properties of the composite, with minimal leaching and stability over time. We further show how minute amounts of graphene dopant can be used to engineer mechanical and electrochemical properties. Overall, the graphene-hydrogel-conducting polymer composite structure enables optimization of various properties by synergistically integrating the electrochemical and mechanical properties of graphene and the PEDOT:PSS, with the biocompatibility and micropatterning of the soft hydrogel matrix.

1. Introduction

Electrically conductive polymeric hydrogels (ECHs) and their composites are of outstanding interest because of the ability to impart a hydrated and networked, three-dimensional (3D) architecture with electronic functionality [1,2]. ECHs describe hybrid networks fabricated from conventional, insulating hydrogel polymers combined with intrinsically conducting constituents. These include nanofibers [3], graphene/carbon nanotubes [4,5], metallic nanoparticles [6], or conducting polymers (CPs) [7]. With their flexibility and processibility, CPs have gained widespread interest for (bio)electronics applications [8]. CPs are synthetic polymers such as polypyrrole (PPy), poly(3,4-ethylene-dioxythiophene) (PEDOT), and polyaniline (PANI) with the ability to conduct electrons, while providing a suitable chemical structure that permits modifications and functionalization for various applications [9]. However, they are typically brittle and show poor resistance to protein adhesion, which limits their long term use in vivo. Incorporation into hydrogel matrices can mitigate this bio-incompatibility. Forming mechanically compliant and elastic composites with hydrogels offers the ability to form hydrated constructs that can conform to, or match the mechanical properties of soft tissue and extra-cellular matrix [10]. These can therefore interface biotic and electronic systems in novel ways such as conductive tissue stents [11], implantable biosensors and electrodes [12,13], conductive neural and cardiac cell cultures [14,15], and electronically stimulated drug delivery devices [16,17]. In addition, the ability to micropattern hydrogels can confer further advantages in defining precise areas for the stimulation of cells or sensing of signals [18].

Typically ECH composites using CPs are difficult to form – 3D hydrogel networks are cross-linked hydrophilic polymers with a high water content and elastic behavior. Once cross-linked these hydrophilic moieties imbibe water and swell to many times their original size, resulting in a tunably elastic material [19]. ECHs can be formed by creating a network of CPs throughout the hydrogel [20]. Conversely, CPs tend to be inherently rigid due to their conjugated backbone [21]. Their backbone is hydrophobic due to the presence of aromatic rings (causing π-π chain stacking). Synthetic hydrogel networks with the conducting polymers as the only polymer in the network can be formed via self-assembly or chemical crosslinking [10,12]. However, composite (or hybrid) systems consisting of more than one component offer the ability to provide precise control of properties. These can take different forms including incorporation of reactive monomers into the hydrogel network and copolymerization, forming an interpenetrating network (IPN) [22], a dispersion of one polymer within a network of another
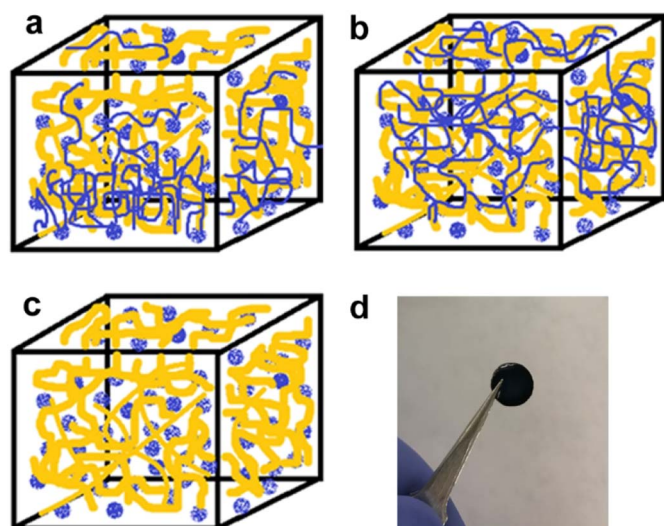
Fig. 1. Schematic of forming conductive polymer - hydrogel composites: (a) in situ electrochemical polymerization, (b) IPN of the CP and hydrogel, (c) dispersal of CP in the hydrogel matrix. In this study, we show that option (c) can form competitive mechanically stable hydrogels as seen in (d).

[23], (Fig. 1) or the physical combination of two polymers (such as coating or layering) [15]. The synthesis methodology can significantly alter the properties and applications of the resultant material, and each have their own advantages ranging from stability, to ease of fabrication. For instance, ECHs with physically or ionically entrapped CPs are easy to prepare. However, they are generally thought to result in leaching of the conductive component leading to a drop in electroactivity [24]. Other electroactive hydrogels such as PEDOT with functional pendant groups bearing double bonds have been reported, but tend to involve complex synthesis procedures [25]. Here we show that dispersions of CPs within low molecular weight hydrogels (small mesh sizes) can provide competitive electroactivity with high temporal stability, while providing additional advantages including facile synthesis, tunable mechanical properties, and photopatternability.

Poly (ethylene glycol) (PEG)-based hydrogels have been extensively studied owing to their high biocompatibility [26], ability to incorporate adhesion sequences and growth factors [27], resistance to protein adhesion, and the ease of regulating mechanical properties. PEG monomers with functional acrylate and methacrylate groups allow this material to be used as a printable ink via photolithography [28]. Here, we demonstrate composite hydrogels formed from polyethylene glycol diacrylate (PEG-DA) with interspersed poly (ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). This forms a functional material that is not only electrochemically active, but can also be micropatterned using photolithography to form high resolution ECH architectures. The acrylate moieties of the PEG-DA crosslink, trapping dispersed nanoparticles of PEDOT:PSS within the matrix. (Fig. 1c) The advantage of this strategy is the ease of fabrication, aqueous processing, and printability through photolithography. In addition, these soft hydrogels can be mechanically tuned by the addition of minute amounts of graphene dopant (reduced graphene oxide or rGO). This dopant is formed by a benign reduction procedure under room temperature and aqueous conditions. The rGO dopant itself contributes to higher electroactivity, while conferring mechanical strength. Thus, electrochemically active hydrogels can be produced that are highly robust, while being hydrated and flexible. The combination of biofriendly materials together with their tunable mechanical properties, high electroactivity, and importantly, ability to be patterned, allows the fabrication of a wide variety of functional bioelectronics devices such as sensors and tissue scaffolds.

2. Experimental section

2.1. Materials

Poly(ethylene glycol)-diacrylate (PEG-DA, MW 575 Da), Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS, high conductivity grade, 3.0–4.0 wt%, 655201 Aldrich) dispersion, PEDOT:PSS dry re-dispersible pellets (Aldrich), 3,4-Ethylenedioxythiophene (EDOT, Aldrich), 3-(trichlorosilyl) propyl methacrylate (TPM, Aldrich), and Poly(sodium 4-stryene sulfonate) (PSS, MW 70,000, Aldrich) were used as received. Darocur 1173 as photoinitiator was obtained from Ciba Specialty Chemicals.

2.2. Reduction of graphene oxide

Graphene oxide (GO) was reduced using a benign protocol at room temperature following an earlier report [29]. Briefly, 4 mg/ml GO solution (University Wafer, South Boston, MA) was first diluted. 5 mg of ascorbic acid (Fisher Scientific, Asheville, NC) per 1 mg of GO was added and stirred at room temperature for 1 h. The reduction of GO to rGO was confirmed by UV–Vis absorption spectra which shifted from 230 nm to 262 nm.

2.3. Fabrication of composite PEG-DA/PEDOT:PSS hydrogels and photolithography

Dispersions of PEDOT:PSS were added to PEG-DA along with 1% (w/w) photoinitiator to form precursor solutions with compositions ranging from 5% to 25% of the conducting polymer. Doping with the rGO solution was performed at a concentration of 0.125 and 0.25% (w/w). Solutions were drop cast in molds and polymerized via exposure to UV light at $20\,mW.cm^{-2}$ at 365 nm for ~5 s (Lumen Dynamics OmniCure 1000). The slabs were peeled from the molds to obtain 1 cm disks for dynamic materials testing. To form microstructures, the ECH solution was spin coated on TPM functionalized Si or glass substrates. Photopolymerization was achieved through a chrome photomask, whereby the polymer behaves as a negative photoresist material and crosslinks in the presence of light. Structures were developed by washing with copious amount of DI-H$_2$O (18 MΩ-cm, Millipore) to remove un-polymerized precursor.

2.4. SEM imaging

ECH films and microstructures were imaged using scanning electron microscopy (SEM) on a Jeol JSM LV-5610 SEM. Cross-sectional images were obtained following cryo-fracturing of films.

2.5. Hydration

To determine the effect of PEDOT:PSS wt% on hydration and swelling of the hydrogel, 50 μl of precursor solutions with varying concentrations of PEDOT:PSS were cast and exposed to form slabs. The slabs were weighed, hydrated for 24 h and reweighed. Slabs were then placed in an oven for 24 h until completely dehydrated and weighed.

2.6. Mechanical analysis

ECH samples were cast into disks as described above. The diameter of the disks was measured using digital calipers (Fowler & MSK); heights of samples were directly measured using Dynamic Mechanical Analysis (DMA) (RSA3 TA Instruments, New Castle, DE). Each hydrogel disk was placed on the sample platform, adjusted so that the upper and lower stage plates were in full contact. The gap distance between the upper and lower plates was decreased at a rate of 0.0005 mm/s to provide pseudo steady-state conditions by minimizing time dependent and viscoelastic effects. Each sample was run until failure or risk of