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Photoinitiated chemical vapor deposition (piCVD) of composition tunable, ionically conductive hydrogels on diverse substrates

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PAPER

Photoinitiated chemical vapor deposition (piCVD) of composition tunable, ionically conductive hydrogels on diverse substrates

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Abstract

Ionically conductive hydrogels are finding prominence in a wide range of emerging devices and applications, including biopotential sensors, organic field effect transistors, biomedicine, and soft robotics. Traditionally, these gels are synthesized through solution-phase polymerization or solvent based swelling of a polymer network and then cast in place or adhered to an intended substrate after synthesis. These fabrication approaches place artificial limitations on the accessible chemical composition and ionic conductivity of the gels, and limit deployment of ionically conductive hydrogels in complex platforms. Here we present a modular method to create ionically conductive hydrogels on a variety of rigid, flexible, or filamentary substrates through a photoinitiated chemical vapor deposition (piCVD) process. First, a viscosity tunable precursor mixture of desired ionic composition and strength is created and coated onto a target substrate. Next, an acrylate film is grown directly on these coated substrates via piCVD. Since both the monomer and photoinitiator used during the piCVD process are miscible in the aqueous precursor mixture, polymerization occurs at both the surface of and within the precursor layer. Using this two-step strategy, we isolate a robust composite hydrogel with independently tunable ionic properties and physical structure. This method is compatible with most substrates and results in a conformal, persistent gel coating with excellent rehydration properties. Gels containing a variety of biocompatible salts can be accessed, without concomitant changes in physical structure and morphology. Ionic conductivities can be tuned between 1×10^{-5} – 0.03 S cm^{-1} by changing the ionic strength of the precursor mixture. Additionally, we show that the material retains its ion concentration and conductivity after washing. Finally, we deploy this material onto several different substrates and show that through this method the same gel can be manufactured in-place regardless of the intended substrate.

1. Introduction

Ionically conductive polymer gels have a wide range of potential applications from organic field effect transistors [1, 2], to strain-sensors [3–7], wearable electrodes [8, 9] and biosensor encapsulations [10, 11]. They consist of an interlinked polymer network that has been swollen with a solvent, typically water. Inside the gel, salts, ionic liquids and/or redox-active metal ions facilitate charge conduction, allowing some gels to store charge, or act as a stretchable, compliant conductor of charge [12–16]. More recently interest in ‘Second Skin’ materials that mimic the breathable, high strength, and ion-conductive

properties of human skin has increased, specifically in the application of wearable devices. Many of these devices increasingly make use of an ionically conductive polymer gel within the active layer, as the chemical and physical properties of hydrogel materials lends itself naturally to application in wearable and implantable devices [17–21].

These materials are synthesized through various methods, but most commonly through a cast-reaction method. This method means that ion gels must be either be formed in a mold, demolded and then independently adhered to their intended application or be cast on a surface capable of facilitating the gelation process [22]. This limitation means that

it is difficult to deploy these gels on porous and textured substrates, such as charge storage electrodes or fabrics, and substrates of unusual form factors, such as filamentary materials and pre-assembled robotics components. A few reports detail ‘sticker’ type hydrogel elements that can be applied to and removed from rigid and flat substrates [23–26], but this does not solve the underlying issue of interfacial/adhesion failure, which is the primary fracture point for devices assembled via straightforward ‘sticking’ of hydrogels onto active layers. Further, such hydrogel ‘stickers’ do not work as intended with flexible, textured, and filamentary substrates. What is needed is a method by which the ionic gel is manufactured directly on the surface of the intended substrate.

More recently, investigations into using a highly conformal initiated chemical vapor deposition (iCVD) techniques to form an ionic interface on the surface of a target substrate have been attempted [14, 27–29]. The results of these studies point to the ability of iCVD to provide high-performance conformal coatings for use in a wide range of potential applications. Previously, Gupta *et al* demonstrated that certain ionic liquids can be coated with acrylate polymers using iCVD [30, 31]. Using iCVD, the Gupta lab isolated a unique material that retained many of its ionic liquid capabilities, such as high conductivity, while also solidifying into a persistent gel material. Since this work, similar liquid templating techniques have also been shown to be useful in the production of metal-oxide layers [32] and previously-unachievable polymer structures [33, 34]. While these ionic liquid-based gels are interesting, their cytotoxicity precludes their use in wearable/implantable electronics and their high cost limits their practicality for soft robotics applications. Further, the chemistry used in the iCVD process, in particular the hydrophobic tert-butylperoxide radicals that serve as the polymerization initiator, cannot be easily translated to create water-based hydrogel systems, which are generally biocompatible and, therefore, more appropriate for biomedical and robotics applications.

Our group has previously reported that commercial water-based wound healing gels can be completely crosslinked with a various polymer networks via chemical vapor deposition to create persistent and rugged composite hydrogels that can be repeatedly swelled/deswelled and laundered without losing their ionic conductivity or mechanical fidelity [9–11]. In this work we show that photoinitiated chemical vapor deposition (piCVD) can be used to create composition tunable composite hydrogels from various poly(acrylic acid) based mixtures and vapor-deposited poly(hydroxy ethylene acrylate) (pHEA) (figure 1).

Using the process summarized in figure 1, a conformal and ionically conductive hydrogel can be created directly on the surface of any desired substrate, allowing ionically conductive hydrogels to be

deployed in complex and flexible platforms. We show that independent control of the composition of the precursor mixture and the piCVD deposition conditions enables access to hydrogels with a wide range of ionic conductivities (1×10^{-5} – 0.03 S cm^{-1}) without changing or compromising the morphology and physical structure of the hydrogel. Furthermore, the process described herein affords conformal hydrogel coatings on several flexible and filamentary substrates, which can be further elaborated into wearable electrodes.

2. Materials and methods

2.1. Materials

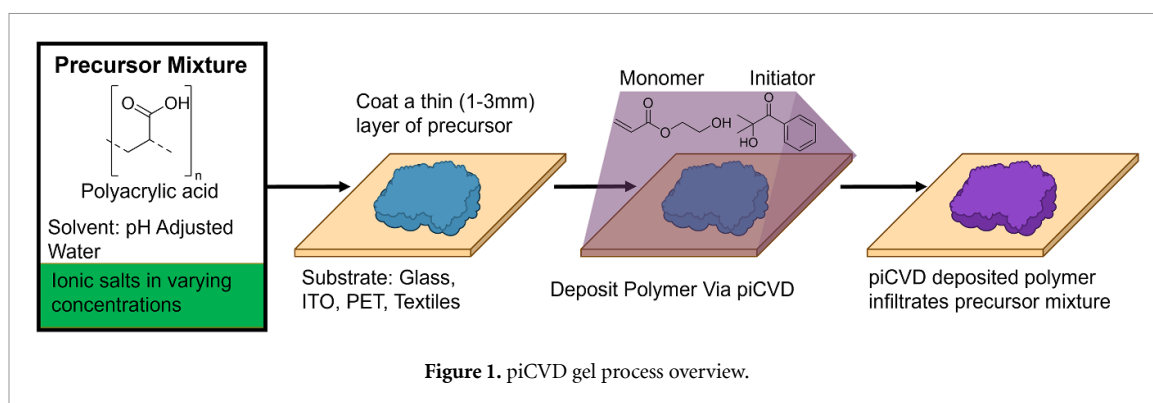
Polyacrylic acid (PAA), sold under the brand name Carbomer 940, was commercially supplied by Spectrum Chemical Mfg. Corp. Sodium chloride (NaCl), calcium chloride (CaCl_2), choline chloride (ChCl), glycerol, and sodium hydroxide (NaOH), all analytical grade, were sourced from Sigma Aldrich. 2-Hydroxyethylacrylate (HEA) and 2-hydroxy-2-methylpropiophenone (HMPP) were also sourced from Sigma Aldrich.

2.2. Precursor mixture

1 g of PAA was weighed out and placed in a beaker. While stirring vigorously with a homogenizer, 5 ml aliquots of DI water were added to the dry powder until a total 100 ml was added, allowing the powder to fully homogenize between each aliquot. Then 1 ml of glycerol was added to the mixture and incorporated using a homogenizer. Approximately ten drops or 200 μl of 2 M NaOH were added slowly while mixing to until the pH of the mixture was 7, as measured by an indicator testing strip. If a salt and or mixture additive was desired in the precursor mixture, the salt was weighed out and mixed with 100 ml of DI water prior to incorporation.

2.3. Precursor coating and piCVD process

Using 3 ml of precursor mixture a 1.5 mm layer of the precursor mixture was doctor bladed onto the surface of a desired substrate in a $25 \times 25 \text{ mm}$ square, which was then placed inside the piCVD reaction chamber. Attached to the chamber via a needle valve and a $1/4$ turn shutoff valve was a single vial containing HEA and HMPP mixed in the ratio desired for deposition (Usually 10:1 by mass). The vial and the inlet line were wrapped in a heating tape and a k -type temperature probe was taped to the bottom of the reactant vial. A rotary vacuum pump and liquid nitrogen (LN2) vapor trap were used to pump the piCVD chamber to a pressure of 200 mTorr, the reactant vial was evacuated before closing both valves and setting the heating tape PID controller to a temperature of $110 \text{ }^\circ\text{C}$. Once the temperature controller read $110 \text{ }^\circ\text{C}$, a 5 min heat soak was allowed. Then, a 365 nm UV LED source (Darkbeam SK68 365 nm) was placed over the quartz



chamber window and turned on, exposing the chamber to UV light. After this the 1/4 turn valve was opened completely and the needle valve was opened 1/8th of a full turn from the closed position. After 1 min, the needle valve was opened completely. After the desired deposition time (typically 10 min) the UV source was turned off, and the needle valve closed, and the LN₂ vapor trap re-charged. Heating tape was removed from the vial and the chamber allowed to pump off any residual or unreacted monomer and initiator vapor for 5 min. Then the chamber could be opened to the atmosphere and the sample removed. Samples were then washed with 20 ml of methanol, isopropanol, and deionized (DI) water to remove any unreacted material unless otherwise specified.

2.4. Composite hydrogel characterization

Electrochemical impedance spectroscopy (EIS) measurements were performed using Scribner Zplot (Solartron Analytical 1252 A, SI 1287) and analyzed using the circuit fitting feature in Zview 4. A custom 3d printed clamp was adapted for sample containment by adding two square platinum electrodes (figure S3). Samples were gently clamped between the two electrodes and analyzed at a 20 mV potential sweep from 10 Hz to 300 kHz. (figure S4) Data was then fit to a model Randle's circuit (figure S5) and the conductivity of the gels extracted using a method previously reported [13].

Ca²⁺ containing ion samples were soaked in a beaker using 500 ml of DI for 10 min stirring with a magnetic stir bar at 500 RPM.

Scanning electron microscope (SEM) images were collected on a FEI Magellan 400 using beam settings of 1 kV and 13 pA. Atomic composition and atom maps were obtained using energy dispersive x-ray spectroscopy (EDX), performed with an EDX accessory to the SEM. For EDX measurements beam settings of 15 kV and 50 pA were used (Oxford Instruments EDX).

Confirmation of reaction completion was performed via Fourier transform infrared spectroscopy (FTIR, Bruker Alpha II) (figure S1).

3. Results and discussion

3.1. piCVD process

Here we report a technique to deposit polymer layers onto a viscous, salt-containing precursor mixture, resulting in a composite hydrogel with unique combinatorial properties of both the precursor mixture and the deposited polymer layer. Previous work reported by Bradley and Gupta has shown that a similar polymer deposition process, iCVD can be conducted on the surface of high viscosity liquids to result in films with tunable surface morphologies [34], encapsulate ionic liquids [30], and form unique polymer-ionic liquid gels [35]. In these examples, a thermally generated peroxide radical was used to initiate the polymerization reaction. In contrast, for the work presented here, a UV-light initiated radical initiates the reaction (figure 2) instead of a hot filament above the deposition site, which enables new chemistries and allows use of fragile substrates. In our system (figure 2), the gas phase polymerization reaction consists of a type 1 Norrish reaction where the photoinitiator HMPP is excited by UV light, resulting in homolysis and the production of two radical species. This reaction happens readily in the gas phase and requires only low intensity UV light (on the order of 35 mW) to be initiated. The wavelength compatibility of this specific chemistry makes it possible for this reaction to be initiated by commercially available 365 nm UV LEDs powered by cheap, commercial AA batteries, significantly lowering the previously-reported power requirement for photoinitiated chemistry [36]. This homolysis then initiates a radical polymerization forming polymer on the substrate. In this process, the polymerization proceeds both in the gas phase, on the surface of the substrate, and in the case of miscible polymers and liquid substrates, inside the liquid phase [30]. This combination of process is what leads us to call the new gel a combination of the precursor mixture and the deposited polymer.

In our process, we begin with a commercially available polymer network, PAA is widely used in the

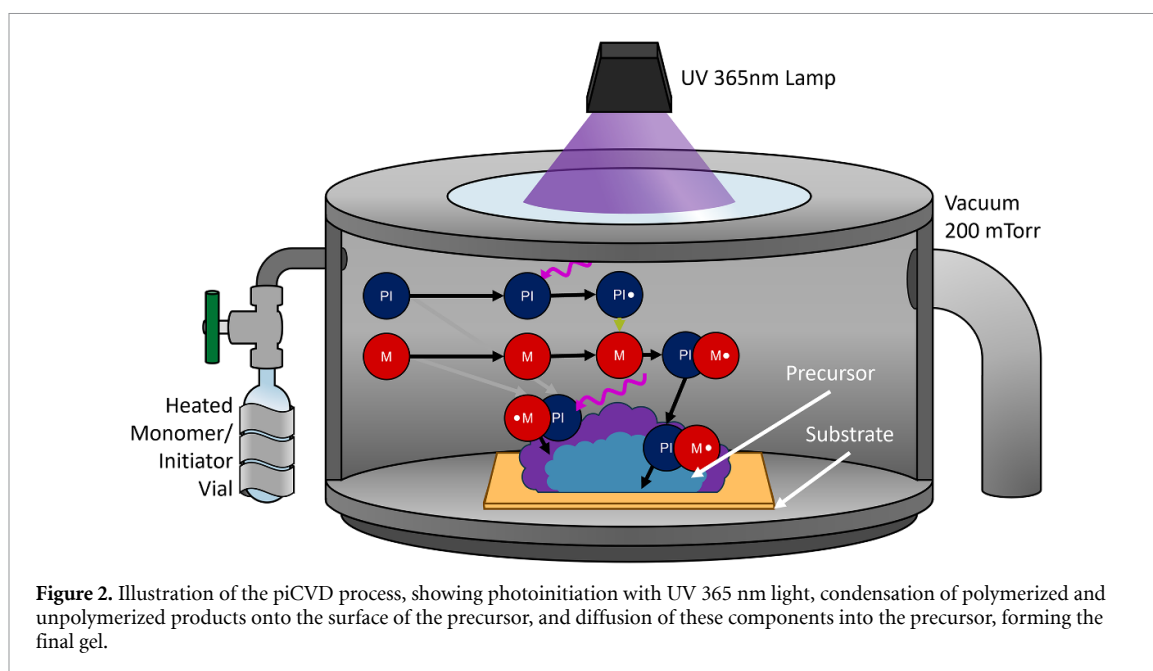


Figure 2. Illustration of the piCVD process, showing photoinitiation with UV 365 nm light, condensation of polymerized and unpolymerized products onto the surface of the precursor, and diffusion of these components into the precursor, forming the final gel.

cosmetics industry to produce hand sanitizers, burn treatments, and other topical gel formulations [37]. It consists of a highly crosslinked carboxylic acid network, easily swelled by solvents like water, methyl and isopropyl alcohol, and ethylene glycol. When simply dissolved into these solvents, the polymer can thicken these solutions, forming a solution with a viscosity of 50 000 mPa*s with only 0.5 wt % polymer. However, the real thickening action of this polymer happens when the pH of the solution is lowered with some base, the base pH of a .5 wt % solution in water is around 2–3, but when this is brought to a neutral pH of 7 the solution thickens due to carboxylic deprotonations resulting in a higher degree of hydrogen bonding. To this spreadable gel, a myriad of salts, dyes, drugs, and other active ingredients can be added. The ionic strength of the solution influences also influences the overall viscosity, allowing the precursor to be further tuned for different substrate applications. The precursor formed is stable enough to be deposited onto the surface of a hard substrate like glass or PET, as well as porous substrates such as fabrics without wetting the surfaces.

In the piCVD reaction chamber, a layer of precursor consisting of 1 wt% PAA in water, and 0.5 wt% NaCl, was coated onto the surface of a substrate and a deposition performed, forming a layer of densely interconnected polymer networks. This layer is then rinsed with methanol isopropanol and DI water to remove any unreacted components confirmed by ATR-FTIR (figure S1). The material formed this way retains the ionic conductivity of the precursor mixture and can be tuned using salt identities, concentrations, and the conditions in the deposition reaction. In previous works, using the iCVD technique, we found the material generated in this process to

be useful in producing a wearable, biomarkers sensing device [9]. In this device, a similar gel material was used as an ionically conductive medium for water-retainment and skin contact, helping the device to achieve low-noise sensing of multiple biological signals. We hypothesize that this material conducts these biopotentials through physical ion transfer, acting as a mediator layer in transducing biopotentials into electrical signals that can be analyzed for health marker information. The piCVD process allows for further material modifications, presenting variables that allow for the tuning of several aspects of the gel.

3.2. Composite gel characterization

We chose to use electrical impedance spectroscopy to characterize variations in the through-plane ionic conductivity of gels fabricated under differing piCVD conditions. This measurement has been reported for other hydrogel materials and can be measured reliably to generate understanding of how the process conditions affect the final product. These measurements were conducted using a custom-built Pt–Gel–Pt cell to minimize interfacial resistance due to oxidation (figure S3). A 20 mV potential and a frequency sweep of 10 Hz–300 kHz were used and Nyquist and Bode plots generated. (figure S4) From these plots an equivalent circuit was generated, this circuit was identified as the Randles circuit (figure S5). From this equivalent circuit, along with the area of the electrodes and the thickness of the samples, the ionic conductivity was determined using a previously reported equation [15]. Each sample was prepared using the piCVD method described above and dried completely. Then, each sample was tempered for a period of at least 24 h in a 100% humidity environment to ensure that each sample was similarly hydrated.

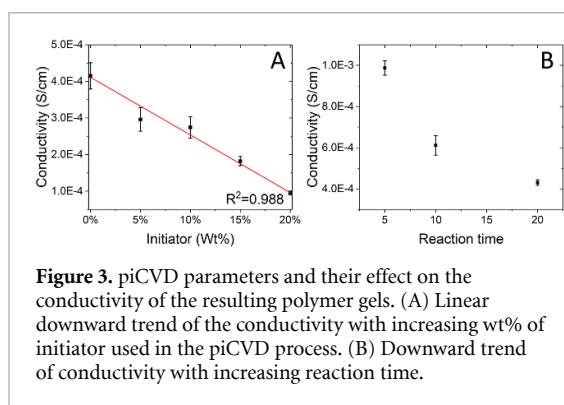


Figure 3. piCVD parameters and their effect on the conductivity of the resulting polymer gels. (A) Linear downward trend of the conductivity with increasing wt% of initiator used in the piCVD process. (B) Downward trend of conductivity with increasing reaction time.

The first process variables explored were the parameters of the piCVD deposition. Linear control over the ionic conductivity could be achieved by modulating the amount of photoinitiator used during the deposition process (figure 3(A)). At very high initiator concentrations, this relationship became nonlinear, ostensibly resulting in increased ionic conductivities, though these increases were unreliable and variable across different deposition batches (figure S7). The influence of deposition time was also investigated. Keeping all other variables constant, samples were allowed to sit under UV exposure for time periods of 5, 10 and 20 min. Upon measuring the conductivity of these samples, a trend was identified: an increase in reaction time resulted in a decrease in the observed ionic conductivity of the composite hydrogel (figure 3(B)) due to higher cross-linking within the hydrogels, consistent with previous reports [9–11, 36]. However, at short deposition times (5 min), the isolated composite hydrogels were fragile and could not be repeatedly and reliably swelled/dried. Therefore, we concluded that a deposition time of 10 min was optimal for isolating hydrogels that were both physically robust and ionically conductive.

In addition to varying the conditions of the piCVD reaction, the characteristics of the precursor mixture could also be changed. To study the effect that different additives might have on the ionic conductivity, two experiments were performed. In the first, the identity of the salt was changed, for this, sodium chloride, calcium chloride, and choline chloride were selected. Sodium chloride served as a baseline as all other tests were run using a precursor mixture that consisted of 0.5 wt% NaCl or 75 mmol. Gels containing calcium chloride, and choline chloride were made at identical concentrations. The resulting measurements place calcium chloride as the most conductive, owing to its increase in number of ions when compared to sodium chloride. The choline chloride is less conductive than the NaCl sample due to the increase in the interaction size of the choline ion, this makes the choline ion slower in the polymer gel, and therefore less conductive (figure 4(A)). Finally, the salt concentration in the precursor was modulated. Of all

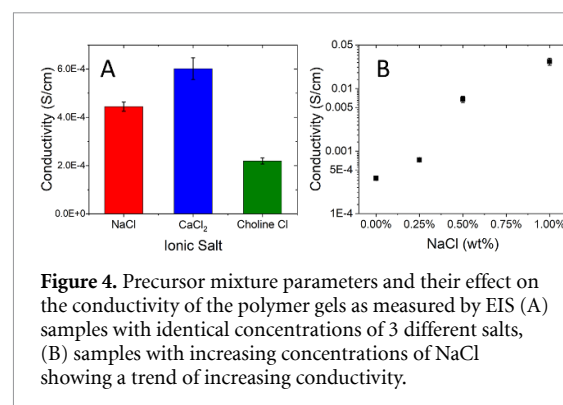


Figure 4. Precursor mixture parameters and their effect on the conductivity of the polymer gels as measured by EIS (A) samples with identical concentrations of 3 different salts, (B) samples with increasing concentrations of NaCl showing a trend of increasing conductivity.

the variables explored, concentration had the largest effect on the conductivity. It was found that varying the concentration of the salt present in the precursor mixture could increase the conductivity of the gel a full order of magnitude for only a doubling increase in the concentration of NaCl. This increase in conductivity is due to the increase in conductive species in the gel, like the increase in conductivity of the calcium chloride sample (figure 4(B)). This relationship shows that the piCVD gel formed through this reaction inherits the ionic characteristics of the precursor mixture.

3.3. Composite gel morphology and substrate compatibility

These gel samples were then analyzed through scanning electron microscopy, to look for any morphology changes that may reinforce our understanding of how different reaction conditions and precursor recipes lead to different conductivities. It was found that the polymer layer formed in these reactions remained visually consistent across a wide range of reaction conditions. Qualitatively, these gels had equivalent properties regardless of starting composition, meaning that the ionic conductivity of these gels can be tuned without the fear that the morphology or structure of the final composite hydrogel will change substantially (figure 5). In addition, EDX analysis of the gel showed that the ions present in the hydrogel are stable against erosion or leeching, remaining in the film even after 10 min of soaking in DI water. (figure 6).

To show the wide substrate compatibility of our gel formation process, we coated three different substrates with a composite hydrogel following the process summarized in figure 1. Glass, cotton muslin fabric and a braided nylon thread were chosen to show a range of substrate morphologies. For both the planar glass and fabric substrates, the precursor mixture was observed to spread evenly across the substrate surface; a coating thickness of 1 mm was used for both substrates. The thread was dip-coated with the precursor PAA gel mixture to a final coating thickness of 1 mm. Then, each substrate was coated with pHEA using the piCVD process. In all cases, the composite

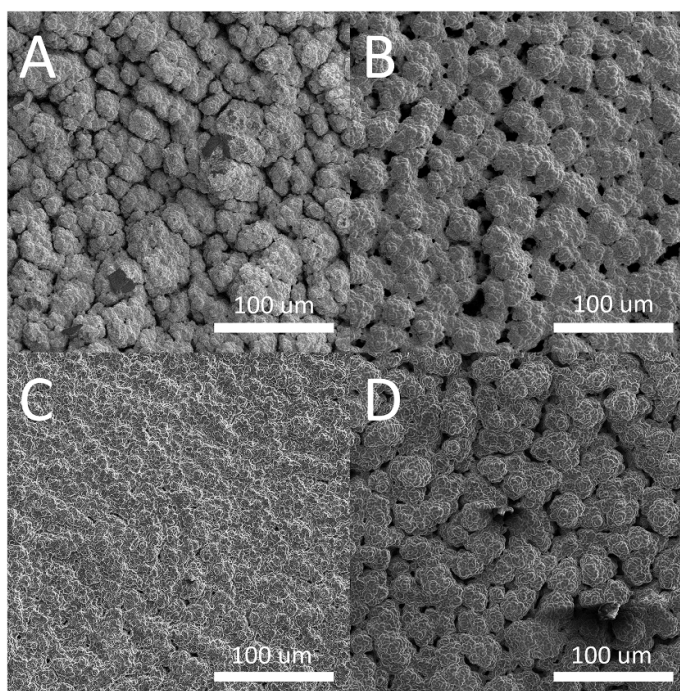


Figure 5. Scanning electron microscopy images of piCVD gels under different process conditions. (A) Sample made with 0 wt% initiator vial ratio. (B) Sample made with 20 wt% initiator vial ratio. (C) Sample made with 0 wt% NaCl precursor mixture. (D) Sample made with 1 wt% NaCl precursor mixture. All other process conditions are identical.

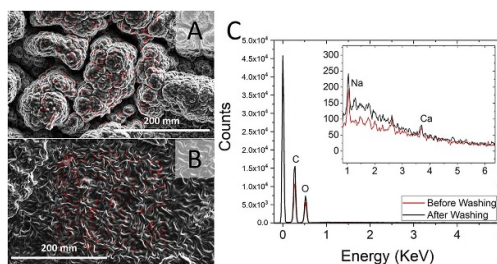


Figure 6. Electron dispersive spectroscopy of a gel sample before and after soaking in water, showing the persistence of ions trapped in the gel. (A) As-deposited gel sample, red pixels represent calcium EDX signals. (B) Gel sample after soaking and stirring in water, red pixels represent calcium EDX signals (C) EDX signal plots showing presence of sodium and calcium ions before and after soaking.

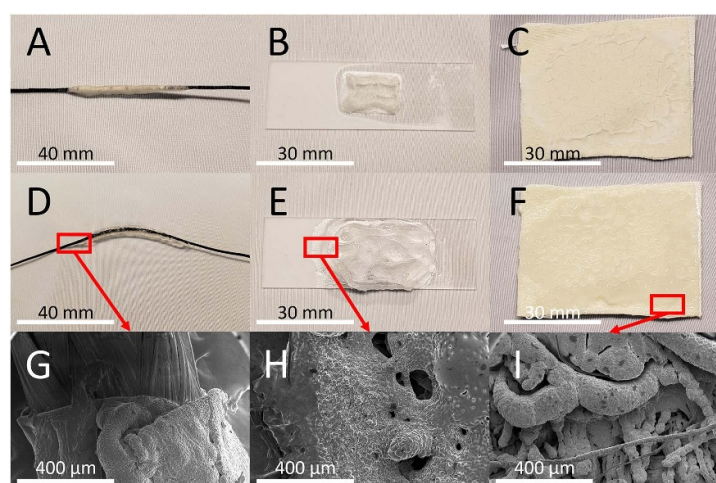


Figure 7. Examples of piCVD gels on different substrates, showing conformal coating abilities and swelling. (A), (D) Example of a piCVD gel on a braided nylon fiber showing high optical clarity in swelled state. (B), (E) Example of a piCVD gel on a glass slide. (C), (F) Example of a piCVD gel on a cotton muslin fabric. (G)–(I), Scanning electron microscopy images of material and gel interfaces.

gel formed normally, and in the case of the fiber the gel was fully formed over the entire coated circumference thanks to the high conformality of the piCVD deposition process (figure 7). This experiment shows that this gel can be used regardless of the chosen substrate which makes it an easily deployable material in many different applications.

4. Conclusions

Here we report a new piCVD method for the creation of persistent, conformal, ionically conductive composite hydrogels on the surface of a wide variety of substrates. The ionic conductivity of the composite hydrogels can be tuned by changing the deposition conditions of the piCVD process, or by changing the components and concentrations of the precursor mixture. Gels containing a variety of biocompatible salts can be accessed, without concomitant changes in physical structure and morphology. Ionic conductivities can be tuned between 1×10^{-5} – 0.03 S cm^{-1} by changing the ionic strength of the precursor mixture. Additionally, we show that the material retains its ion concentration and conductivity after washing. Finally, we deploy this material onto several different substrates and show that through this method the same gel can be manufactured in-place regardless of the intended substrate.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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