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Polydiacetylene hydrogel self-healing capacitive strain sensor

An innovative polydiacetylene/polyacrylic acid/chromium ion hydrogel capacitive sensor employed for monitoring material strain, mechanical deformation and human motions.

Polydiacetylene hydrogel self-healing capacitive strain sensor†

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Strain sensors are used in varied applications, including personal healthcare monitoring, human–machine interaction, and artificial skin. Here, we report fabrication of a highly sensitive capacitive strain sensor comprising a self-healing polydiacetylene–polyacrylic acid–Cr³⁺ hydrogel. The dielectric hydrogel medium was prepared through a simple synthesis scheme from readily available ingredients. The elasticity and pronounced sensitivity of the composite hydrogel are attributed to the distinct components of the system. The Cr(H₂O)₆³⁺ complexes function as cross linkers, maintaining stability of the hydrogel framework through electrostatic binding to carboxylate moieties within both the polyacrylic acid and polydiacetylene, additionally facilitating incorporation of high concentration of water molecules essential for maintaining hydrogel elasticity. In parallel, polydiacetylene, employed here for the first time as a vehicle for strain sensing, endows the system with high intrinsic capacitance sensitivity to mechanical stimuli, further exhibiting a major contribution towards greater flexibility and resilience under high strains. The sensor exhibits high stretchability of 500%, and high sensitivity exhibiting a gauge factor (GF) of up to 160. Applications of the polydiacetylene–polyacrylic acid–Cr³⁺ capacitive hydrogel sensor for physiological strain monitoring are presented.

1. Introduction

Strain sensors have been implemented in various applications, including personal healthcare monitoring,1 wearable electronics,2 robotics,3 artificial skin,4 and others. Sensing platforms exhibiting high stretching capacities have been used, for example, to monitor large body movements such as shoulder- or arm-stretching and stooping.5,6 Strain sensors have been fabricated from different materials, such as silicone-based elastomers,5,6 rubbers,7,8 and others. The elastic polymer polydimethylsiloxane (PDMS) has been often used in physiological, skin-applied strain sensors due to good adhesion and deformation properties.9,10 PDMS, however, exhibits poor elasticity, limiting their practical applications.

Polymeric hydrogels, in particular, have been widely used as core components in strain sensors, as they exhibit elasticity and their mechanical properties can be tuned through modification of the chemical constituents.11,12 Hydrogels constitute a particularly attractive framework material in strain sensors, since their considerable water content furnishes high elasticity.12 Reported polymer hydrogel sensor media include double network hydrogels,13,14 nanocomposite hydrogels,15,16 triblock copolymer hydrogels,17,18 macromolecular microsphere composite hydrogels,19 and free-radical polymerization hydrogels.11 Polymeric hydrogels have been mostly employed in resistive strain sensors and as such in many instances have been interspersed with conductive fillers, such as metal nanowires,19,20 carbon nanotubes,21 conductive polymers,14,22,23 and others.23,24 Among reported strain sensors, resistive and capacitive strain sensors have been widely used. Resistance-based strain sensors convert applied mechanical deformations into recorded electric current (directly correlated to the resistance), whereas capacitive sensors measure the corresponding change of capacitance. While resistive strain sensors are, in general, highly stretchable, most of such sensors display nonlinear strain response and hysteresis behaviour in response to dynamic strains, which consequently limit their practical use.22–24 Capacitive strain sensors, in comparison, exhibit response linearity, however, they suffer from low sensitivity generally ascribed to the intrinsic parallel-plate capacitor structure.25

To date, however, a limited number of studies have reported improvement in sensitivity of the capacitive strain sensors. Capacitive-type strain sensors utilizing networks of carbon nanotubes and self-healing MXene (Ti₃C₂Tₓ)/polyvinyl alcohol (MXene/PVA) hydrogel as a stretchable electrode and a silicone-based elastomer as a stretchable dielectric layer have achieved
good sensor response at 100%,26 150%,27 or 200% strains.28 Capacitive strain sensors comprising conductive textile electrodes integrated with a silicone-based dielectric medium were also reported.29 A sensor in which the electrodes were assembled from wrinkled gold films featured reasonable sensitivity up to a maximum strain of 140%.30 Despite of the extensive work in this field, significant challenges remain, primarily complex synthetic pathways, insufficient sensitivity and recyclability, and mechanical instability.

Here we report construction of new sensitive and resilient strain sensors comprising, for the first time, polydiacetylene (PDA). PDAs are unique π-conjugated polymers exhibiting remarkable stimuli-responsive color transitions and fluorescence emission changes associated with structural transformations of the polymer backbone. Due to their unique physico-chemical properties, PDA systems have been used in varied optical sensing applications.31–39 PDAs have also manifested intriguing electronic properties; PDA domains generally form quasi-one-dimensional networks, giving rise to charge mobility generating p-type semiconductor properties,40–42 electrical conductance,43 and photo-induced conductivity.44 In most cases, however, PDA crystallites are nearly complete insulators (exhibiting electrical conductivity on the order of σ ≈ 10−12 S cm−1). This feature has been recently exploited in our laboratory to produce PDA-based capacitive gas sensors, in which a PDA/polymer composite constituted a highly effective dielectric medium.45

The capacitive strain sensor we developed comprises as the dielectric medium PDA, polyacrylic acid (PAA), and Cr3+ ions. Employing capacitance as the sensing platform has particular advantage, as capacitive sensors are robust, exhibit high intrinsic sensitivity and fidelity.16,46–48 The PDA–PAA–Cr3+ composite, prepared in ambient conditions through a simple synthesis scheme, forms a highly elastic, mechanically-resilient hydrogel, which furthermore exhibits self-healing properties. Self-healing gels, generally stabilized by dynamic covalent bonding within the gel framework, have garnered significant scientific and technological interest due to their intrinsic ability to repair after enduring damage.49–52 We demonstrate application of the self-healing PDA–PAA–Cr3+ hydrogel capacitive strain sensor for monitoring physiological motions.

2. Experimental section

2.1. Materials

Poly(acrylic acid) (PAA, average molecular weight: 450 kDa) was purchased from Sigma Aldrich. 10,12-Pentacosadiynoic acid from Alfa Aesar. Sodium carbonate from Frutarom, Ltd. Chromium(III) chloride hexahydrate purchased from Strem Chemicals Inc. (Newburyport, USA) absolute ethanol from Bio-Lab Ltd (Israel). Teflon molds (length: 30 mm, width: 10 mm and thickness: 3 mm) were prepared in-house.

2.2. Hydrogel synthesis

Polyacrylic acid (PAA)–Cr3+. 1 g of PAA was dissolved in 10 ml water and mixed with 1.25 ml aqueous CrCl3 (62.5 mg, 0.24 mmol) and 2 ml of ethanol and stirred for 15 min. The solution mixture was poured into the Teflon mold and kept for 20 h to form the hydrogel. For making the solution basic, 0.5 ml of Na2CO3 (25 mg, 0.24 mmol) aqueous solution was added prior to placing in the mold.

Polydiacetylene (PDA)–PAA–Cr3+. To obtain hydrogels with different weight ratios of PDA and PAA, 25 mg, 50 mg, 125 mg and 250 mg, respectively, of 10,12-pentacosadiynoic acid (the diacetylene monomer) dissolved in 2.0 ml of ethanol were mixed with 1 g PAA (dissolved in 10 ml of water) and 1.25 ml CrCl3 (0.24 mmol) and stirred for 5 min. Subsequently, 0.5 ml Na2CO3 solution (0.24 mmol) was added and the solution was further stirred for 5 min, then poured into the Teflon mold and kept for 20 h to form the hydrogel. The hydrogel was further irradiated with a UV lamp (254 nm) to induce PDA cross-linking in ambient atmosphere.

2.3. Characterization

Ultraviolet-visible (UV-vis) spectra of the composite thin films were recorded on an Evolution 220 UV-Visible spectrometer (Thermo Scientific, Madison, WI USA). Fourier transform-infrared (FTIR) measurements were performed on a Thermo Scientific Nicolet 6700 spectrometer (Madison, WI USA). Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-7400F scanning electron microscope (JEOL Ltd, Tokyo, Japan) operated and analyzed using the instrument software for freeze dried samples. Raman scattering measurements were performed on a LabRam HR-high resolution analytical Raman (Horiba Jobin Yvon, France). Excitation source was 633 nm laser and 50 × long-focal-length objective lenses were employed. Rheology experiments were carried out on an Advanced Rheometer AR 2000 (TA Instruments, New Castle, De USA) by cone and plate geometry in a Peltier plate. The cone diameter was 20 mm, cone angle 1°, and truncation 27 µm. Frequency sweep and strain sweep measurements were performed from 0.1 to 100 rad s−1 and between 0.5% and 1300% strains. Tensile stress-strain measurements were performed at room temperature using a universal mechanical tester (Instron 5965 instrument, Norwood, MA USA) equipped with a 10 N load cell. The uniaxial tensile test was performed on rectangular-shape specimens (10 mm in width, 3 mm in depth, and 30 mm in length). The initial distance between two clamps was 15 mm, and the constant stretching rate was 20 mm min−1. Capacitance measurements were conducted on a E4980A Precision LCR Meter (Keysight Technologies, Inc., Santa Rosa, CA, USA) interfaced with a personal computer.

2.4. Strain sensing studies

The sensor consisted of the hydrogel sample of and connecting the two ends of the hydrogel fixing the two silver wires using Cu adhesive tape and connected to the LCR meter to detect the capacitance change. Frequency sweep measurements were performed from 20 to 5000 Hz without applied strain. Capacitive reactance Xc, was inversely proportional to the signal frequency (f) and capacitance (C) [Xc = 1/(2πfC)] (f = 20 Hz, 500 Hz, 1000 Hz, 2000 Hz or 5000 Hz).16 Relative change in capacitive
reactance was calculated using the formula, \((\Delta X_C/X_{C0}) \times 10^2\) (\(\Delta X_C = X_C - X_{C0}\) and where \(X_C\) and \(X_{C0}\) denote the capacitive reactance with and without applied strain, respectively). We applied strain manually by stretching the hydrogel sensor to specific lengths and calculated the relative change in strain using the formula \((L_0 - L/L_0) \times 10^2\) where \(L_0\) and \(L\) represents the length with and without applied strain, respectively. We applied strains ranging from 0 to 500%. The indicated strain was confirmed by using a stretching length.

3. Results and discussions

3.1. Characterization of the polydiacetylene–polyacrylic acid–\(\text{Cr}^{3+}\) strain sensor

The self-healing PDA–PAA–\(\text{Cr}^{3+}\) strain sensor was designed to adhere to several requirements, including dielectric properties (essential for capacitive sensing), mechanical flexibility, elasticity, and withstanding high strains. Fig. 1 depicts the simple synthesis procedure of the PDA–PAA–\(\text{Cr}^{3+}\) hydrogel and its capacitive strain sensing capabilities. The diacetylene monomers (10,12-pentacosadiynoic acid) and PAA were mixed in water forming a flexible gel upon addition of \(\text{Cr}^{3+}\) ions and sodium carbonate. As illustrated in Fig. 1A, the hydrogel is maintained both by hydrogen bonding between the carboxylic moieties (blue dashed lines), and particularly through electrostatic attraction mediated by the hydrated \(\text{Cr}^{3+}\) complex (green dashed lines).

Previous fabrication methods of PAA-based hydrogels either utilized radical polymerization of acrylic acid monomers,\(^{13}\) or mixing the PAA solution with different alkaline earth and transition metal ions (\(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Sr}^{2+}, \text{Ni}^{2+}\) and \(\text{Zn}^{2+}\)).\(^{53}\) Whereas the latter strategies are generally easier to carry out, most metal ions give rise to hydrogels exhibiting low elasticity due to low concentration of embedded water.\(^{54}\) Borate ions have been used as cross-linking agents for polymers bearing hydroxyl (–OH) functional groups.\(^{21,28}\) Metal ions, however, constitute effective electrostatic cross linkers of polymers displaying carboxylic (–COOH) functional groups such as PAA. Notably, the use of \(\text{Cr}^{3+}\) ions here permits anchoring of greater water contents and concomitant elastic nature. Cross-linking of the polymeric framework via the \(\text{Cr(H}_2\text{O)}_3^{3+}\) complexes is critical for both gel stabilization, as well as for creating a host matrix embedding high concentration of water molecules essential for gel elasticity.\(^{12}\) The diacetylene–PAA–\(\text{Cr}^{3+}\) hydrogel appeared gelatinous, elastic, and could be easily molded (picture in Fig. 1A). Subsequent ultraviolet (UV) irradiation at 354 nm yielded the well-known dark blue conjugated polydiacetylene (PDA) network, indicating the occurrence of cross-linking of the diacetylene monomers within the composite material (photograph shown in Fig. 1A, right).

An example of capacitive strain monitoring by the PDA–PAA–\(\text{Cr}^{3+}\) hydrogel is shown in Fig. 1B. In the experiment, the hydrogel was secured between adjacent silver electrodes by copper tape, forming a capacitor (pictures in Fig. 1B). The electrodes were connected to a conventional inductance–capacitance–resistance (LCR) meter, allowing continuous monitoring of the capacitance between the electrode plates. Importantly, while most previous studies utilizing hydrogel-based capacitive sensors employed hydrogels as the electrode material,\(^{55,56}\) the hydrogel here comprised the actual dielectric medium determining the sensing response.

The capacitance graph in Fig. 1B demonstrates that stretching the PDA–PAA gel gave rise to a dramatic decrease in the recorded capacitance (note the logarithmic scale of the Y axis, underscoring the pronounced capacitance change induced upon film stretching). Following strain release, the gel returned to its original non-stretched shape, displaying the initial capacitance value (Fig. 1B) underscoring the high elasticity of the PDA–PAA–\(\text{Cr}^{3+}\) hydrogel. The sensitivities of a PDA–PAA–\(\text{Cr}^{3+}\) hydrogel sensor exhibiting different weight ratios between PDA and PAA are depicted in Fig. S1 (ESI†). PDA–PAA–\(\text{Cr}^{3+}\) hydrogel with PDA:PAA weight ratio of 0.125 was used for subsequent characterization and capacitive sensing applications presented below.

Spectroscopic and microscopic characterization of the PDA–PAA–\(\text{Cr}^{3+}\) hydrogel is presented in Fig. 2. The Fourier transform infrared (FTIR) spectra in Fig. 2A illuminate the structural units of the PDA–PAA–\(\text{Cr}^{3+}\) composite hydrogel and their relationship with the starting materials. The pronounced band at 1696 cm\(^{-1}\), corresponding to the carbonyl units of the carboxylates in both PAA and diacetylene monomers, was diminished in intensity in PDA–PAA–\(\text{Cr}^{3+}\) (Fig. 2A, left arrow), likely due to decrease in interchain and intramolecular hydrogen bonding, following formation of the hydrogel assembly.\(^{49}\) The peak at 1636 cm\(^{-1}\) in PDA–PAA–\(\text{Cr}^{3+}\) is ascribed to the \(\text{H–O–H}\) bending of adsorbed...
between 1300–1400 cm$^{-1}$ respectively. The UV-vis spectrum of the final PDA–PAA–Cr$^{3+}$ hydrogel via linked lower in comparison to the PAA and diacetylene building blocks. The removal of water molecules adsorbed within the PDA–PAA–Cr$^{3+}$ framework is critical for maintaining high elasticity of such materials. Importantly, the pronounced broad signal at around 3400 cm$^{-1}$ in PDA–PAA–Cr$^{3+}$ (Fig. 2A, blue spectrum), assigned to symmetric O–H stretching vibrations of water molecules, is indicative of abundant water molecules embedded within the hydrogel framework. This feature is important as incorporation of water within flexible hydrogel constructs is critical for maintaining high elasticity of such materials. The thermal gravimetric analysis (TGA) trace in Fig. 2B corroborates the FTIR result, as the pronounced weight decrease around 80 °C corresponds to removal of water molecules adsorbed within the PDA–PAA–Cr$^{3+}$ hydrogel framework. Inclusion of water molecules in hydrogel frameworks is critical for maintaining elasticity. Indeed, previous studies have attested that elasticity of Fe$^{3+}$-stabilized hydrogels were closely linked to adsorbed water, whereas hydrogels cross-linked via Ca$^{2+}$ in which the contents of incorporated water was much reduced exhibited significantly lower flexibility.

The ultraviolet-visible (UV-vis) absorbance spectra in Fig. 2C illuminate the chromatic species formed, particularly confirming the occurrence of diacetylene polymerization in the composite hydrogel. Specifically, the UV-vis spectrum of PAA and Cr$^{3+}$ confirms formation of the hydrated chromium complex, yielding the absorbance peaks at around 410 nm and 570 nm, accounting for the $^{4}A_{2g} \rightarrow {^{4}T_{1g}}$ and $^{4}A_{2g} \rightarrow {^{4}T_{2g}}$ electronic transitions, respectively. The UV-vis spectrum of the final PDA–PAA–Cr$^{3+}$ hydrogel product, in particular, demonstrates formation of the conjugated “blue-phase” polydiacetylene network, accounting for the pronounced peak at 640 nm and shoulder at 580 nm. Raman scattering analysis in Fig. S2 (ESI†) further confirms diacetylene polymerization in PDA–PAA–Cr$^{3+}$.

The scanning electron microscope (SEM) image of a representative freeze-dried PDA–PAA–Cr$^{3+}$ hydrogel in Fig. 2D reveals the microporous PAA framework critical for retaining stretching capabilities. Importantly, the SEM micrograph further shows typical planar PDA sheets latched onto the pore “walls” (indicated by the arrows in Fig. 2D), confirming that UV-induced diacetylene polymerization occurred within the PAA host matrix. The mechanical properties of the PDA–PAA–Cr$^{3+}$ hydrogel were also studied (Fig. 3). Fig. 3A examines the strain profiles of different gel constructs through application of uniaxial tensile analysis. The tensile stress/strain curve of PAA/CrCl$_3$ mixture (Fig. 3A, black curve) corresponds to a soft polymeric material, exhibiting a maximum tensile strength of less than 0.25 kPa and a fracture strain (also defined as “elongation at break”) at approximately 500%.

Addition of around 20 mM Na$_2$CO$_3$, however, considerably increased the tensile stress of the hydrogel to 7 kPa while reducing the fracture strain to around 380% (Fig. 3A, red curve). The significantly higher tensile stress attained by the PAA–Cr$^{3+}$ hydrogel following addition of Na$_2$CO$_3$ is attributed to deprotonation of the carboxylic residues in the presence of the weak base, thereby contributing to more pronounced electrostatic interactions between COO$^-$ units and Cr(H$_2$O)$_6$$^{3+}$ which strengthen the PAA framework.
This result underscores the important role of the Cr(H_2O)_6^{3+} complex in formation and stabilization of the gel framework. Incorporation of the diacetylene monomers in PAA–diacetylene–Cr^{3+} yielded an elastic gel exhibiting a tensile stress of around 5 kPa and a strain fracture of 530% (Fig. 3A, green curve).

The greater elasticity recorded for PAA–diacetylene–Cr^{3+} is likely due to the extensive electrostatic/hydrogen bonding network between the PAA and diacetylene constituents, partly mediated by the hydrated chromium complex (e.g. scheme in Fig. 1A). Notably, two-minute UV irradiation, which gave rise to PDA formation through cross-linking of the diacetylene monomers, significantly increased both the tensile strength (reaching approximately 7 kPa), and particularly the strain fracture (to more than 800%, Fig. 3A, dark blue curve). This simultaneous enhancement of both mechanical resilience and elasticity of the hydrogel underscores the significant structural role of the cross-linked PDA network in the composite material. Interestingly, Fig. 3A demonstrates that increasing the duration of UV irradiation to five minutes produced a gel exhibiting a tensile stress that was similar to the lesser irradiated gel, albeit displaying a lower fracture strain (740%; Fig. 3A, light blue curve). This result likely accounts for higher gel rigidity induced by more extensive polymerization, further stressing the significant impact of the PDA network upon the mechanical properties of the PAA–PDA–Cr^{3+} hydrogel.

The mechanical properties of the materials were further investigated using rheology analysis (Fig. 3B). As illustrated in Fig. 3B, the storage modulus (G′, filled circles) was higher than the loss modulus (G″, open circles) in the frequency range of 0.1 to 100 rad s^{-1} for all samples examined, accounting for the formation of stable gels. Similar to the tensile stress/strain analysis in Fig. 3A, the rheology data demonstrate that diacetylene polymerization through UV-vis irradiation enhanced gel stability (higher storage modulus in case of PDA–PAA–Cr^{3+} hydrogels in both UV irradiation durations, Fig. 3B, dark blue/light blue datapoints). Furthermore, echoing the tensile strain/stress experiment in Fig. 3A, the rheology analysis also attests to the higher rigidity of PAA–PDA–Cr^{3+} UV-irradiated for 5 minutes, reflected in the higher storage modulus (light blue vs. dark blue solid circles).

Fig. 3C highlights the self-healing properties of the PAA–PDA–Cr^{3+} hydrogels. The strain alternation experiment in Fig. 3C demonstrates effective viscoelasticity recovery of the PDA/PAA/ Cr^{3+} hydrogels, underscoring their self-healing capabilities. Initially the hydrogel was placed under a low 0.5% strain for 200 sec at room temperature for which G′ > G″. Fig. 3C shows that upon applying a high strain of 1300% for 200 s, the gel became viscous (i.e., G″ > G′). Notably, after returning the strain back to 0.5%, the gel rapidly healed, almost returning to its initial viscoelastic profile, reflecting the well-established self-healing feature of the material.17,41 Fig. S3 (ESI†) visually illustrate the self-healing properties of PDA–PAA–Cr^{3+} demonstrating that the hydrogel not only completely healed within a relatively short time, but also maintained high stretchability.

The self-healing properties of the PDA/PAA/Cr^{3+} are attributed to the dynamic cross-linking nature of the electrostatic interactions among carboxylate groups of PDA/PAA and Cr^{3+}, and hydrogen bonding interactions between carboxylic groups of PAA and PDA (schematic description in Fig. S4, ESI†). We also assessed the stability of the PDA/PAA/Cr^{3+} hydrogel. Water evaporation adversely affected device performance after several days, however sealing the device with an adhesive tape significantly enhanced the long-term stability of the device (Fig. S5, ESI†).

3.2. Capacitive sensing applications

Fig. 4–6 present practical applications of the PDA–PAA-based capacitor for strain monitoring. Fig. 4 shows stretch-dependent...
Maxwell–Wagner polarization induced within mesoscale dielectric networks in affecting sensor sensitivity. Specifically, while a hydrogel sensor comprising only PDA–PAA–Cr\textsuperscript{3+} gave rise to small capacitance change upon stretching and did not resort to its initial length (Fig. 4A), the PAA–diacetylene–Cr\textsuperscript{3+} construct was much more elastic (fully reversible) and displayed a capacitance change of 3.4 nF upon stretching by approximately 300% [Fig. 4B]. The polymerized hydrogel PDA–PAA–Cr\textsuperscript{3+}, however, exhibited a higher capacitance change, of around 4.0 nF upon application of the same strain (Fig. 4C), underscoring the significance of the conjugated PDA network in affecting sensor sensitivity.

In general, stretch-induced decrease in capacitance corresponds to the well-known inverse relationship between electrode distance and capacitance. The results presented in Fig. 4, however, attest to the significant contribution of PDA to strain-dependence capacitance transformations. We previously demonstrated that PDA constitutes a remarkable dielectric medium, displaying pronounced capacitance changes induced by external stimuli, specifically gas adsorption.\textsuperscript{45} In the PDA–PAA–Cr\textsuperscript{3+} hydrogel presented here, greater strain applied likely disrupted the interfaces between the PDA assemblies and PAA framework. This transformation is expected to result in decrease of the Maxwell–Wagner polarization induced within mesoscale dielectric boundary layers within inhomogeneous dielectric materials, and concomitant reduction in dielectric permittivity (\(\varepsilon_r\)) and capacitance.\textsuperscript{61–63}

Fig. 5 illustrates application of the PAA–PDA–Cr\textsuperscript{3+} hydrogel for capacitive sensing of different strains underscoring its elastic nature. In the experiment, the PAA–PDA–Cr\textsuperscript{3+} film was subjected to stretch/release cycles in distinct elongations (Fig. 5A), and the respective capacitive reactance changes were recorded (Fig. 5B). The strain-dependent capacitive reactance changes summarized in Fig. 5B highlight the reversibility and sensitivity of the PAA–PDA–Cr\textsuperscript{3+} hydrogel sensor. In particular, note the exceptional dynamic range of the capacitive sensing platform (recorded capacitance changes were in the order of hundreds-of-thousand percent, Fig. 5B).

Relationships between the strain and capacitive reactance change of the sensor are depicted in Fig. 5C and D. The graphs, indicating strain sensing from 20% to almost 500%, reflect both the resilience of the PAA–PDA–Cr\textsuperscript{3+} hydrogel withstanding pronounced stretching, as well as the intrinsic sensitivity of the capacitive hydrogel sensor in wide strain variability. Fig. 5C shows the variation of capacitive reactance under low strains of 20–130%, displaying an almost linear response (\(R^2 = 0.979\)) of capacitive reactance vs. strain. In higher strains (130–500%), the variation of capacitive reactance (\(\Delta X_C/X_{C0}\)) increased nonlinearly with the applied strain (Fig. 5D). The non-linear dependence of capacitive reactance is attributed to the plasticity of the PDA–PAA hydrogel,\textsuperscript{21,54,64} and strain-dependent disruption of physical association between the PDA domains and PAA framework.

Fig. 6 (ESI\textsuperscript{†}) presents the capacitance evolution in response to the excitation frequency, underscoring a typical frequency-dependent capacitive characteristics, which are due to the interactions of the electric field with induced charge carriers in the samples.\textsuperscript{45,61} Specifically, the PDA–PAA–Cr\textsuperscript{3+} hydrogel capacitive strain sensor performance increased as the frequency decreases from 1000 Hz to 20 Hz at the same applied strain (Fig. S7, ESI\textsuperscript{†}).

The strain sensitivity of the PDA–PAA–Cr\textsuperscript{3+} capacitive hydrogel sensor was further evaluated by calculation of the gauge factor (\(S\)), defined according to:\textsuperscript{16}

\[
S = \frac{(\Delta X_C/X_{C0})/\varepsilon}{[(X_C - X_{C0})/X_{C0}]/\varepsilon}
\]  

in which \(\varepsilon\) is the applied strain, \(X_C\) and \(X_{C0}\) are the capacitive reactance with and without applied strain, respectively. The gauge factors calculated for the datapoints in Fig. 5C and D were 4.8 in a strain of 100%, increasing to 33.4 in 500% strain (the strain factors calculated for the entire capacitive reactance values are presented in Fig. S8 (ESI\textsuperscript{†}) at 1000 Hz).

The calculated gauge factors were 3 and 161 at 20 Hz for 100% and 500% strains, respectively (Fig. S9 and S10, ESI\textsuperscript{†}). These values are significantly better compared to varied previously-reported hydrogel-based resistive-based strain sensors,\textsuperscript{2,14,20,22,65–67} and also compared to soft capacitive strain sensors.\textsuperscript{46} While some strain sensors do exhibit high gauge factors (~60–3700), their stretching capabilities have been generally limited (0.2–100%),\textsuperscript{68–74} whereas the PDA–PAA–Cr\textsuperscript{3+} hydrogel strain sensor displayed significantly high stretchability of up to 500%. The sensitivity of the PDA–PAA–Cr\textsuperscript{3+} hydrogel sensor is significantly higher than most reported capacitive...
strain sensors, in which hydrogels were used as electrodes and VHB tape as the dielectric material, as we employ the hydrogel as the dielectric medium yielding high sensitivity.

Fig. 6 illustrates application of the PAA–PDA–Cr$^{3+}$ capacitive sensor for physiological strain monitoring. In the experiment outlined in Fig. 6A, the PDA–PAA–Cr$^{3+}$ gel device was placed upon the index finger and the capacitance changes induced upon bending and unbending of the finger were monitored. Such an application has practical implications. The substantial and relatively uniform capacitance changes apparent in the graph in Fig. 6A highlight the capability of the PDA–PAA–Cr$^{3+}$ gel sensor to closely track the bending/unbending motion. Similar remarkable strain sensing performance was apparent when employing the PAA–PDA–Cr$^{3+}$ hydrogel for monitoring wrist motion (Fig. 6B).

4. Conclusions

This work presents fabrication of a new polydiacetylene-based self-healing hydrogel employed as a capacitive strain sensor, displaying high sensitivity and mechanical resilience. The PDA–PAA–Cr$^{3+}$ hydrogel was synthesized from readily available building blocks through a simple scheme. The hydrogel is stabilized through electrostatic interactions mediated by embedded Cr(H$_2$O)$_6^{3+}$ complexes and hydrogen bonding between carboxylate moieties within the PDA and PAA framework. The PDA units, in particular, play important role in enhancing hydrogel stability, elasticity, and capacitive response. We show that the capacitance of the PAA–PDA–Cr$^{3+}$ hydrogel underwent pronounced changes upon stretching; the significant sensitivity, high gauge factor, and dynamic range make the PAA–PDA–Cr$^{3+}$ system an excellent strain sensing platform. We demonstrate use of the PAA–PDA–Cr$^{3+}$ hydrogel for monitoring physiological motion, pointing to varied applications in healthcare, wearable sensors, and others.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
