

# Conducting Polymer Coatings Prepared by Mixed Emulsions Are Highly Conductive and Stable in Water

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An aqueous emulsion of conducting polymer is commonly applied on a substrate to form a coating after drying. The coating, however, disintegrates in water. This paper reports a coating prepared using a mixture of two emulsions: an aqueous emulsion of conducting polymer, and an aqueous emulsion of hydrophobic and rubbery chains copolymerized with silane coupling agents. When applied on a substrate and dried, particles of the mixed emulsion merge into a continuous film. While the conducting polymer forms percolated nanocrystals, the silane groups crosslink the rubbery chains and interlink the rubbery chains to the substrate. The percolated nanocrystals make the coating highly conductive. The covalent network of hydrophobic polymer chains stabilizes the coating in water. The high conductivity and stability in water may enable broad applications.

## 1. Introduction

Conducting polymers usually do not melt or dissolve in solvents.<sup>[1,2]</sup> To fabricate devices, emulsions of conducting polymers have been synthesized for, for example, polyaniline, polypyrrole, and polythiophene.<sup>[3–7]</sup> The emulsions have been applied by spray, spin, cast, print, etc.<sup>[8,9]</sup> Upon drying, the conducting polymer forms a coating, which can function as an antistatic coating, electrode, interconnect, and chemical sensor.<sup>[10,11]</sup>

A type of polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), has been prepared commercially as an aqueous emulsion by forming a complex with polystyrene sulfonate (PSS).<sup>[9,12–15]</sup> When the PEDOT:PSS emulsion is applied on a substrate and dried to form a coating, PEDOT chains form percolated nanocrystals for electron transport, and PSS chains form a glassy matrix.<sup>[16–18]</sup> The dry PEDOT:PSS has a conductivity in the range of hundreds of  $S\text{ cm}^{-1}$ .<sup>[14,15]</sup> However, PSS chains are hydrophilic and uncrosslinked polyelectrolytes. Submerged in water, the coating disintegrates.<sup>[9,19,20]</sup> Efforts have been made

to stabilize coatings in wet environments. These works usually achieve conductivity up to several tens  $S\text{ cm}^{-1}$  (Table S1, Supporting Information).<sup>[19–24]</sup> For example, a crosslinked PSS stabilizes the coating in water, but decreases conductivity by orders of magnitudes.<sup>[19]</sup> As another example, an intermediate adhesive layer has been used to achieve strong adhesion of conducting polymer on diverse substrates. The coating has a conductivity of  $\approx 30\text{ S cm}^{-1}$ .<sup>[21]</sup> One exception is a work by Kim et al., showing the high crystalline PEDOT:PSS coating on a metal substrate is both highly conductive ( $\approx 4100\text{ S cm}^{-1}$ ) and stable in water.<sup>[20]</sup> However, the bonding between the coating and the substrate is purely based on the Van de Waals forces, which may

cause delamination if the substrate is deformed. The emulsion of PEDOT:PSS has been mixed with emulsions of other polymers to prepare films.<sup>[25–27]</sup> Such films can achieve high conductivity, but have not been demonstrated as stable coatings in water.

Here we present a method to prepare coatings of both high conductivity and stability in water. We prepare an aqueous emulsion of hydrophobic chains of poly(ethyl acrylate) (PEA), in which the PEA chains are copolymerized with silane coupling agents. In the aqueous environment, at room temperature, the PEA chains remain uncrosslinked for at least 6 months. We then mix two emulsions: the emulsion of silane-grafted hydrophobic elastomer PEA, and the emulsion of conducting polymer PEDOT:PSS. We spin-coated the mixed emulsion on a PDMS substrate (Figure 1a). As water evaporates, the emulsion particles merge into a continuous solid, in which PEDOT:PSS and PEA separate into two domains (Figure 1b). The silane groups condensate into siloxane linkages, which crosslink the PEA chains, and interlink the PEA chains to the PDMS substrate. When submerged in pure water, the coating is stable and has a conductivity of  $\approx 290\text{ S cm}^{-1}$ .

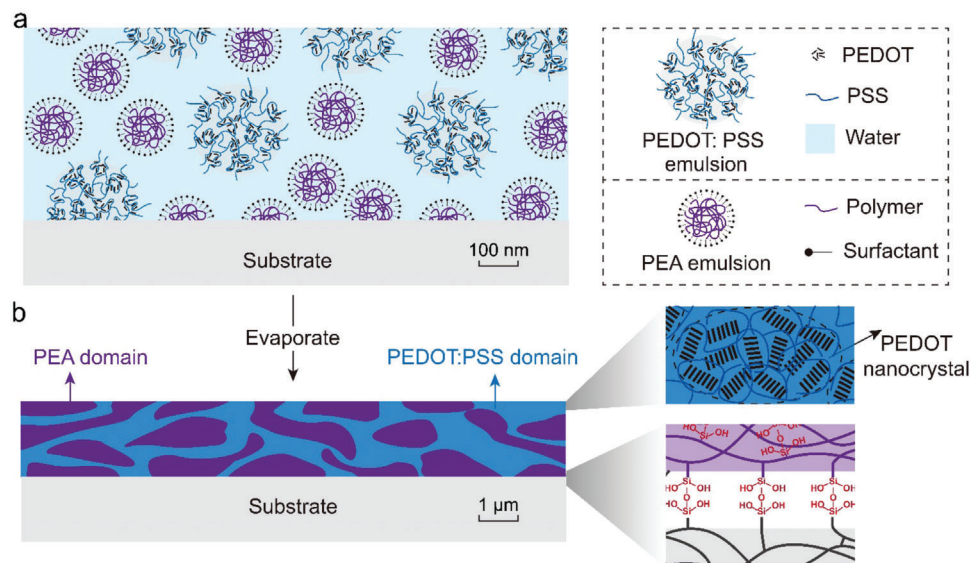
The structural evolution from PEDOT:PSS emulsion to dry PEDOT:PSS coating has been reported before. Each particle in the PEDOT:PSS emulsion consists of two polymers, PEDOT and PSS, as well as water molecules and dissolved ions.<sup>[13]</sup> PEDOT is a hydrophobic and positively charged polyelectrolyte, whereas PSS is a hydrophilic and negatively charged polyelectrolyte. The PEDOT and PSS form a polyelectrolyte complex, and PEDOT forms clusters of a diameter  $\approx 5\text{ nm}$ .<sup>[28]</sup> An emulsion particle has a diameter of 10–300 nm.<sup>[16,29,30]</sup> In effect, an emulsion particle is a hydrogel, in which PEDOT clusters function as crosslinks by hydrophobic interactions, and PSS forms a hydrophilic polymer network (Figure 1a). The emulsion

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**Figure 1.** A conducting coating prepared using a mixed emulsion. a) The emulsion of PEDOT:PSS and the emulsion of silane-grafted PEA are mixed, and then spin-coated on a PDMS substrate. b) Upon drying, the PEDOT:PSS forms one continuous domain, and PEA forms another continuous domain. PEDOT chains pack into percolated nanocrystals. The silane groups condensate to crosslink the PEA chains, and to interlink the PEA chains to the PDMS substrate.

particles do not coagulate because individual emulsion particles have a PSS-rich exterior, which stabilizes a cloud of counterions in water, so that emulsion particles repel one another. When PEDOT:PSS is dried, the PEDOT clusters turn into nanocrystals, and PSS chains turn into a glassy matrix (Figure 1b). The PEDOT nanocrystals are embedded in the PSS matrix and form a percolated network, which conducts electrons. When the coating is submerged in water, PSS chains rehydrate. The PSS-rich exterior of the individual emulsion particles is insufficiently crosslinked by the PEDOT nanocrystals, so the coating disintegrates in water. Crosslinking PSS chains can stabilize the coating in water, but decrease conductivity by orders of magnitude, probably because the crosslinked PSS interferes with the formation of a percolated network of PEDOT nanocrystals.<sup>[19]</sup>

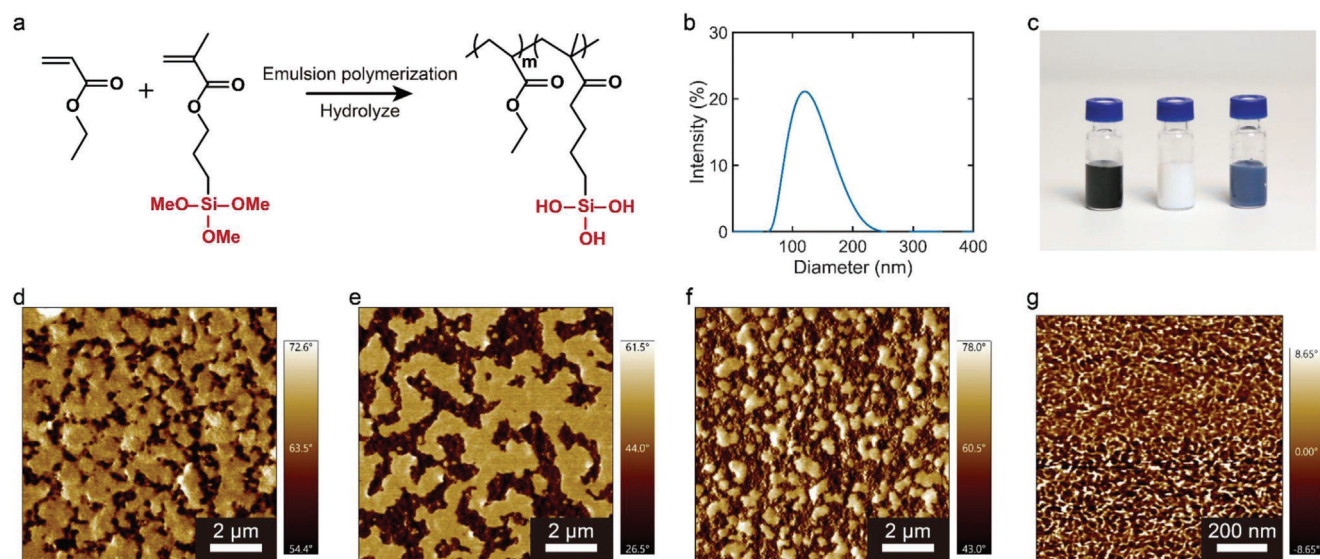
By contrast, when a mixture of PEDOT:PSS emulsion and PEA emulsion is dried, the dissimilar emulsion particles come into contact. In the dried coating, PSS is a glassy polymer, PEDOT is a crystalline polymer, and PEA is a rubbery polymer. The PSS chains are not crosslinked and are continuous. The PEDOT nanocrystals embedded in PSS are much smaller than the emulsion particles. Consequently, the PEDOT nanocrystals in the coating prepared by the mixed emulsion can form a percolated network just as in the coating prepared by pure PEDOT:PSS (Figure 1b). That is, the formation of the percolated nanocrystals of PEDOT is not interfered by the presence of the hydrophobic and rubbery PEA chains, so that the coating has a high conductivity. Subsequently, the silane groups condensate into siloxane linkages, which crosslink the PEA chains, and interlink the PEA chains to the PDMS substrate. The PEA network prevents the PSS from swelling excessively and detaching from the substrate, so that the coating is stable in water. For example, after being submerged in water for 1 week, a coating of 80 wt% PEDOT:PSS and 20 wt% PEA remains stable, and has a conductivity of  $\approx 290 \text{ S cm}^{-1}$ .

## 2. Results and Discussion

The PEA emulsion is prepared by emulsion copolymerization of ethyl acrylate (EA) and a small amount of silane coupling agent, 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) (Figure 2a). EA is the monomer of PEA. TMSPMA contains methylsilyl groups  $-\text{Si}-(\text{OCH}_3)_3$ , which can hydrolyze in water to form silanol groups  $-\text{Si}-(\text{OH})_3$ . After polymerization, an emulsion of linear, hydrophobic, rubbery polymers is formed. The solid content of the emulsion is  $\approx 26.8 \text{ wt}\%$ . Scanning electron microscopy (SEM) shows that the emulsion particles are spheres of diameter  $\approx 100 \text{ nm}$  (Figure S1, Supporting Information), consistent with the size distribution obtained from dynamic light scattering (DLS) (Figure 2b). The PEA emulsion does not precipitate when stored at room temperature for at least 6 months, suggesting that the silanol groups have not condensated. The DLS of PEDOT:PSS shows two peaks at  $\approx 30$  and  $\approx 300 \text{ nm}$  (Figure S2, Supporting Information).

We cast the PEA emulsion to form a film, which is then kept at  $65^\circ \text{C}$  overnight. The silanol groups condensate into siloxane linkages, crosslinking the rubbery PEA chains (Figure S3, Supporting Information). As TMSPMA-to-EA molar ratio increases, the modulus increases, but the toughness decreases (Figure S4, Supporting Information). In subsequent experiments, the TMSPMA-to-EA ratio is fixed at  $10^{-3}$ .

We pour the PEA emulsion, the PEDOT:PSS emulsion, and ethylene glycol into a tube, and shake the tube on a vortex mixer for 10 s. Ethylene glycol is commonly used to enhance conductivity.<sup>[14,15]</sup> The PEDOT:PSS emulsion is dark blue, the PEA emulsion is white, and a mixed emulsion is light blue (Figure 2c). The mixed emulsion is spin-coated on a glass substrate and dried. The weight percentage of PEDOT:PSS in the dried coating,  $W_{\text{PEDOT:PSS}}$ , is set by the amounts of the two emulsions (Table S2, Supporting Information). Atomic force



**Figure 2.** The preparation and characterization of the coating. a) The synthesis of a PEA emulsion of linear, hydrophobic, rubbery polymers. b) The distribution of the diameters of the particles in the PEA emulsion measured by dynamic light scattering. c) Photos of the PEDOT:PSS emulsion, PEA emulsion, and the mixed emulsion. The AFM images of coatings of  $W_{\text{PEDOT:PSS}}$  = d) 40%, e) 60%, f) 80%. g) The AFM image of pure PEDOT:PSS.

microscopy (AFM) shows PEDOT:PSS domains (dark area) and PEA domains (bright area). The two types of domains are bicontinuous when  $W_{\text{PEDOT:PSS}} = 40\%$  (Figure 2d) and  $W_{\text{PEDOT:PSS}} = 60\%$  (Figure 2e). The PEDOT:PSS domains are continuous but PEA domains become discontinuous when  $W_{\text{PEDOT:PSS}} = 80\%$  (Figure 2f). The transition between  $W_{\text{PEDOT:PSS}} = 60\%$  and  $80\%$  is consistent with the percolation threshold of spheres.<sup>[31]</sup> At a higher resolution, the AFM image of pure PEDOT:PSS shows percolated PEDOT nanocrystals (bright area) (Figure 2g).

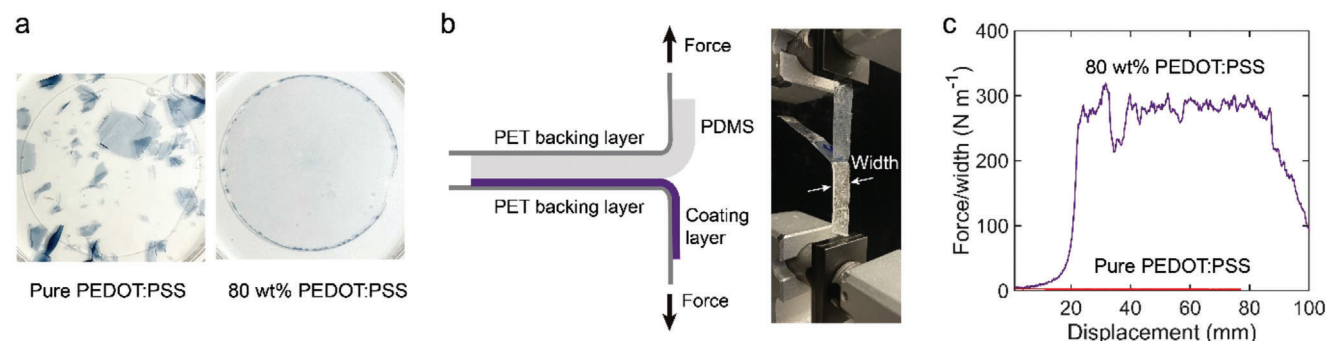
For a single emulsion, the film-formation process is usually illustrated by three stages.<sup>[32]</sup> In stage I, upon evaporating water, the emulsion particles become concentrated and come into contact. In stage II, these particles deform and coalesce to form a void-free film driven by surface tension. In stage III, these particles further coalesce and fuse through chain diffusion. For a mixed emulsion, the two types of emulsion particles with the same exteriors (e.g., same surfactant) and similar sizes usually form a random dispersion when mixed. This random arrangement persists throughout the drying process until the particles come into contact.<sup>[33]</sup> In the case of the mixed emulsion of PEA and PEDOT:PSS, the exteriors and the sizes of the two species particles are different, so aggregations of particles of the same species may happen in the liquid state.<sup>[34]</sup> Upon evaporation, the aggregation persists when a void-free film is formed (stage II). In stage III, the energy of mixing drives phase separation, while the condensation of silanol groups and the glass transition of the PSS chains arrest the phase separation. This competition equilibrates the phases.

A PDMS substrate is prepared by pouring on a silicon wafer the liquid PDMS precursor, which forms a liquid film of thickness  $\approx 1$  mm. The liquid is cured at  $65^\circ\text{C}$  for 1 day. The PDMS substrate is exposed to oxygen plasma to produce silanol groups on the surface, and is spin-coated with the mixed emulsion of PEA and PEDOT:PSS. The sample is heated at  $90^\circ\text{C}$  for 5 min for the water to evaporate from the emulsion without forming vapor

bubbles inside the coating. The sample is then kept at  $140^\circ\text{C}$  for 5 h for the silanol groups to condensate to crosslink PEA chains and interlink PEA chains to the PDMS substrate. The coating is gradually cooled to room temperature, after which the dry coating has a thickness of  $\approx 0.5\ \mu\text{m}$ . The coating is submerged in water to leach out all soluble components. The coating is kept in fresh water before further testing.

In pure water, a coating of pure PEDOT:PSS disintegrates, whereas a coating of a mixed emulsion remains intact (Figure 3a). The adhesion between the dried coating and PDMS is characterized by peel test. The test sample has four layers: two backing layers, a PDMS layer, and an adhesive layer (Figure 3b). The PDMS layer is bonded to one backing layer by Crazy glue on one side, and bonded to the other backing layer through the adhesive layer on the other side (see Experimental Section). The width of the sample is  $\approx 10$  mm, and the crosshead rate is  $1\ \text{mm s}^{-1}$  throughout all the tests. Following the literature, we use rigid polyester film as the two backing layers.<sup>[35]</sup> Pure PEDOT:PSS has negligible interaction with the PDMS (Figure 3c, Figure S5, Supporting Information). For a dried coating of mixed emulsion, as the displacement between the crossheads increases, the force first increases, and then plateaus. The toughness is twice the plateau force divided by the width of the sample. Coatings of  $W_{\text{PEDOT:PSS}} = 0, 20, 40, 60, 80\%$  all achieve a toughness of  $\approx 600\ \text{N m}^{-1}$  (Figure S4, Supporting Information). In these cases, cracks grow within PDMS, so the adhesion toughness is expected to exceed the toughness of the pure PDMS.<sup>[35]</sup>

We characterize the conductivity of a coating submerged in water. Four probes are equally spaced and contact the coating (Figure 4a). When a current  $I$  is applied between the outer two probes, the voltage  $V$  between the inner two probes is recorded (see Experimental Section, Table S3, Supporting Information). The thickness  $T$  of the coating is measured by AFM in the dry state (Figure S6, Supporting Information). When the size of the sample is much larger than the spacing of the probes, the



**Figure 3.** Stability and adhesion of the coating. a) In pure water, a coating of pure PEDOT:PSS disintegrates, whereas a coating of mixed emulsion remains intact. b) Schematic and photo of the 180° peel test. c) Force/width is measured as a function of displacement.

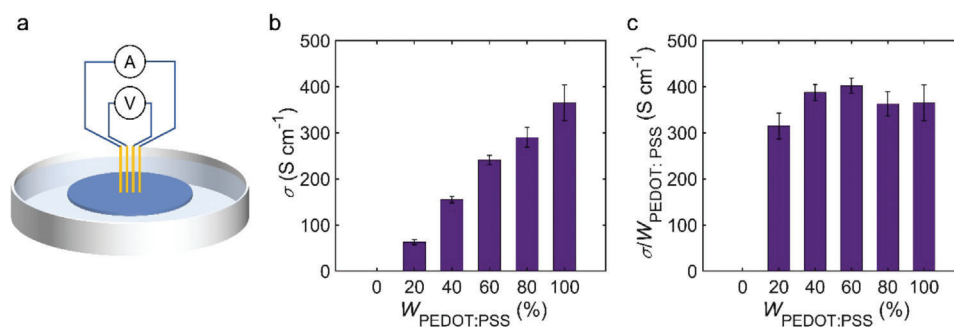
conductivity can be calculated by  $\sigma = \ln(2)I/(\pi VT)$ .<sup>[36]</sup> The conductivity increases linearly with the weight fraction of PEDOT:PSS (Figure 4b). Pure PEA is an insulator, and pure PEDOT:PSS disintegrates in water. To gain the conductivity of the pure PEDOT:PSS coating, we conduct the measurement in the dry state. The conductivity increases linearly with the weight fraction of PEDOT:PSS (Figure 4b). The ratio  $\sigma/W_{\text{PEDOT:PSS}}$  remains roughly constant, even when  $W_{\text{PEDOT:PSS}}$  is as low as 20% (Figure 4c). The conductivities measured in water and in the dry state have little difference (Figure S7, Supporting Information).

We further study the fracture of the coating. A PDMS strip is cut from the coated PDMS with a coating of  $W_{\text{PEDOT:PSS}} = 80\%$ . The sample is subject to loading and unloading with increasing maximum strain. During the tensile tests, the coating is continually sprayed with water to remain wet. After each cycle, the surface of the sample is submerged in water for 1 min, dried, and then imaged in a microscope (Figure 5a). When the maximum strain is less than 100%, no crack forms (Figure 5b,c). At a strain of  $\approx 140\%$ , cracks form.

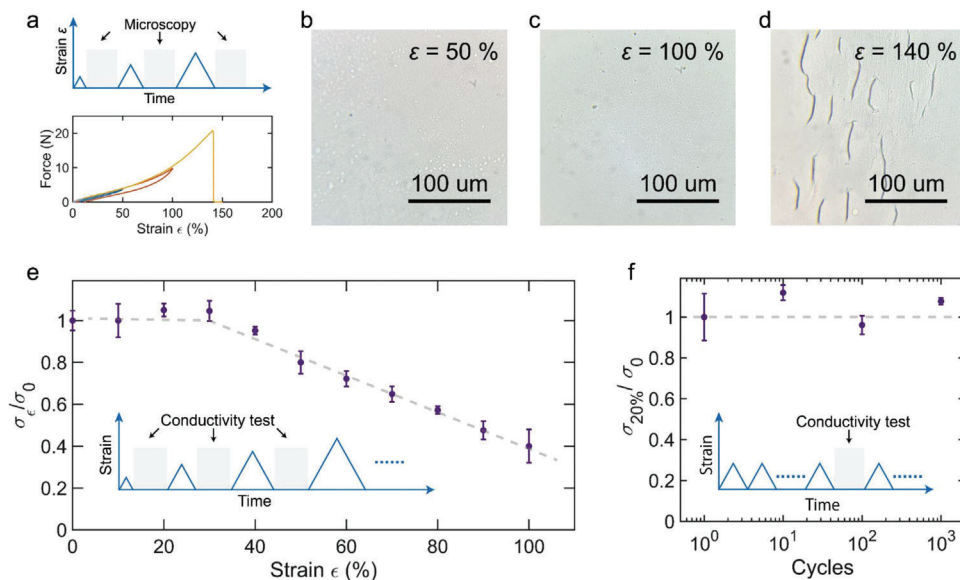
These observations can be interpreted as follows. A free-standing PEDOT:PSS film fractures at a strain of 2%–10%.<sup>[18,37]</sup> A PEDOT:PSS coating on PDMS forms cracks at a strain of  $\approx 50\%$ .<sup>[38]</sup> The coating of mixed emulsion forms cracks at a strain of  $\approx 140\%$ . Both PEDOT and dry PSS are brittle at room temperature. When PEDOT:PSS is under loading, stress is concentrated at flaws, leading to brittle fracture. The stress concentration is alleviated when PEDOT:PSS on PDMS. In this work, be-

sides the stress deconcentration by the PDMS substrate, PSS is hydrated and becomes partially mobile. The PEDOT:PSS domain can be treated as a composite, where brittle PEDOT is embedded in the hydrated PSS chains. This type of composite is known to be ductile.<sup>[39]</sup>

Although the coating remains intact until the fracture strain, the percolated structures of PEDOT may damage before the coating fractures. We subject a coating to loading, unloading, and reloading, with each reloading increasing strain by 10%. The initial conductivity  $\sigma_0$  of the coating is measured. After each unloading, the conductivity  $\sigma_\epsilon$  of the coating is measured, where  $\epsilon$  is the last applied strain.  $\sigma_\epsilon/\sigma_0$  and  $\epsilon$  are plotted in Figure 5e. No notable decline in  $\sigma_\epsilon/\sigma_0$  is observed when  $\epsilon < 30\%$ . The conductivity starts to decrease when  $\epsilon \approx 30\%$ , before the visible cracks are formed. At  $\epsilon = 100\%$ , the conductivity decreases to 40% of the initial conductivity. We further conduct a fatigue test. A sample undergoes cyclic loading and unloading at a constant strain  $\epsilon = 20\%$ . After several cycles, the conductivity is measured (Figure 5f). There is no noticeable decline in  $\sigma_{20\%}/\sigma_0$  after 1000 cycles. Based on the above data, the PEDOT percolated structures can sustain at least 20% strain without any noticeable damage over cycles. Similar results are observed on the coating of  $W_{\text{PEDOT:PSS}} = 60\%$  (Figure S8, Supporting Information). Aqueous emulsions are environmentally friendly and easy to apply in diverse manufacturing methods. As a demonstration, we use mixed emulsion to fabricate an interconnect of complex shape (Figure S9, Supporting Information).



**Figure 4.** The conductivity of PEDOT:PSS coating on PDMS substrate. a) The schematic of the conductivity measurement. b) The conductivity  $\sigma$  of the coating increases with PEDOT:PSS content. c)  $\sigma/W_{\text{PEDOT:PSS}}$  is approximately constant for all  $W_{\text{PEDOT:PSS}}$ .



**Figure 5.** The fracture and conductivity of the coating under uniaxial tension. The coating of  $W_{\text{PEDOT:PSS}} = 80\%$  is on a PDMS substrate. a) The schematic of the testing process (upper), and the corresponding force and strain (lower). b–d) The microscopic images of the surface of the coating after each unloading. e) A coating is subject to loading, unloading, and reloading, with each reloading increasing strain by 10%. The ratio of the conductivity after each unloading  $\sigma_{\epsilon}$  to the initial conductivity  $\sigma_0$  and strain  $\epsilon$  are plotted. f) The conductivity of the coating is measured when it is subject to cyclic loading and unloading at a constant amplitude of strain of 20%.

### 3. Conclusion

This paper reports a method to prepare a coating of high conductivity and stability in water. We mix two emulsions: an emulsion of conducting polymer, and an emulsion of hydrophobic and rubbery chains copolymerized with silane coupling agents. When spin-coated on a PDMS substrate and dried, PEDOT:PSS and PEA separate into two domains. The PEDOT nanocrystals form a percolated structure for electron transport. The silanol groups condensate into siloxane linkages, which crosslink the PEA chains and interlink the PEA chains to the PDMS substrate. The two domains have a feature size on the order of micrometers. The coating has a high conductivity of  $\approx 290 \text{ S cm}^{-1}$ , which remains undiminished after 1000 cycles of 20% strain. This method for preparing highly conductive and stable coatings by mixed emulsions opens possibilities for the use of conducting polymers in diverse fields, such as biological sensing, electrode interfaces, and flexible electronics.

### 4. Experimental Section

**Materials:** PEDOT:PSS (739332), ethyl acrylate (E9706), ammonium persulfate (APS, 248614), 3-(trimethoxysilyl)propyl methacrylate (440159), sodium dodecyl sulfate (SDS, 436143) were purchased from Sigma Aldrich and used without further purification. Sylgard 184 was purchased from Dow Corning.

**The Emulsion Polymerization:** In a 500 mL round-bottom flask (VWR International, 10536), 168 g water, 0.415 g SDS, and 0.164 g APS were added in sequence, and stirred to form a transparent solution. Separately, 72 g of EA was mixed with different amounts of TMSPMA at TMSPMA-to-EA molar ratios of 0, 0.001, 0.002, and 0.01. The resulting mixture was then transferred to the flask, along with a magnetic stirrer. Nitrogen was bubbled through the solution for 10 min, and the flask was subsequently sealed using a septum stopper (VWR International, 89029). After vigorous

hand-shaking for 30 s, the flask was placed into an 80 °C oil bath, and the solution was stirred at 300 rpm. The stopper was subsequently removed from the flask, and the flask was immediately sealed using a balloon (VWR, 470003-968). The reaction was allowed to proceed overnight, and the resulting emulsion was transferred to a plastic jar (McMaster-Carr, 4188T45) for storage.

**DLS:** DLS tests were conducted using a Zetasizer Nano ZS machine. The opaque PEA emulsion was diluted with water until the emulsion was almost transparent. Zetasizer Software (Version 7.13) was used to analyze the data. The input included the test temperature  $T$ , and the viscosity  $\eta$  of water. In the experiment, tests were carried out at 298 K, and the water's viscosity was 0.0089 poise. The Zetasizer Nano ZS machine determined the particle size by measuring the Brownian motion of the particles in the sample. The relationship between the size of a particle and its speed due to Brownian motion is defined in the Stokes-Einstein equation,  $D = kT/(6\pi\eta r)$ , where  $D$  is the diffusivity of the particle which is measured by the machine,  $k$  is the Boltzmann constant, and  $r$  is the hydrodynamic particle diameter.

**SEM:** The images were conducted using a scanning electron microscope (Hitachi SEM, SU8230). All the samples were coated with a 5-nm-thick Pt/Pd layer using a metal sputter (Cressington Scientific Instruments, 208HR) before proceeding to imaging.

**PEA Film Preparation:** 18 g of the PEA emulsion was poured into a PTFE dish of a diameter of 80 mm (VWR, 89026). The dish was heated on a hot plate at 50 °C for 12 h and then transferred to an oven at 65 °C for 2 days. The PEA film was peeled off, and stored in the atmosphere at room temperature for further testing.

**PDMS Substrate Fabrication:** The base and the curing agent of Sylgard 184 were added in a cup at a ratio of 15:1. In a mixer (ARE-250; Thinky), the mixture was mixed at 2,000 rpm for 1 min and degassed at 2,200 rpm for another minute.  $\approx 7$  g of the obtained precursor was poured onto a 100-mm diameter wafer and left in an oven at 65 °C overnight for curing. Upon curing, the precursor formed a PDMS disk with a diameter of  $\approx 100$  mm and a thickness of  $\approx 1$  mm on the wafer.

**Plasma Treatment:** The Anatech Barrel Plasma System (Anatech LTD) was used for performing oxygen plasma. The power was set to 150 W, and the exposure time was 10 s.

**180° Peel Test:** A PET backing layer was placed on a glass sheet, poured with the emulsion, and covered with a plasma-treated PDMS. The emulsion formed a layer of liquid sandwiched between the PET backing layer and the PDMS. The assembly, consisting of the glass sheet, PET backing layer, emulsion layer, and PDMS, was put in a vacuum sealer bag (FoodSaver), and vacuumed and sealed by a vacuum sealer machine (FoodSaver V4400). The bag was stored in an oven at 65 °C for 3 days. The laminate of PDMS, emulsion, and PET was lifted off from the glass sheet, and cut into several rectangular-shaped samples, each with a width of 10 mm. The PDMS face of each sample was glued to another PET backing layer using crazy glue (406, Henkel Loctite). A crack was initiated along the coating using a razor blade. The two backing layers were pulled by a tensile tester (Instron 5966).

**AFM:** Clean micro cover glass (VWR International, 48368095) was treated with plasma, and used as a substrate. PEA emulsion, PEDOT:PSS emulsion, and ethylene glycol were mixed, and spin-coated on the cover glass at a speed of 300 rpm for 2 min. The coating was heated at 90 °C for 5 min, then 140 °C for 2 h. After cooling, the coating was subject to AFM measurements in ambient air using a Cypher AFM (Asylum Research).

**Thickness Measurements:** A portion of the coating on the PDMS substrate was carefully removed using a blade. A scanning area of 30 μm × 30 μm was selected to include both coated and bare PDMS regions. The height profile of this area was measured through AFM topographic imaging, and the step decrease in height was regarded as the thickness of the coating.

**Coating Fabrication:** The PDMS substrate was exposed to oxygen plasma, and then spin-coated with the mixed emulsion of PEA and PEDOT:PSS. The sample was heated at 90 °C for 5 min and then kept at 140 °C for 5 h. The formed coating had a diameter of ≈100 mm and a thickness of ≈0.5 μm. The coating was gradually cooled to room temperature, and then submerged in water to leach out all soluble components. The coated PDMS was peeled off from the wafer, and was kept in fresh water before further testing.

**Conductivity Measurement:** Electrodes were purchased from McMaster (5949T15). Each electrode had a round tip of diameter ≈0.52 mm and was coated in gold. The tip was connected with the rest of the electrode with a spring of maximum force ≈1.36 N. Four tips were aligned in a line with an equal interval of ≈2 mm. A total force of ≈2.35 N applied by a dead weight was applied to compress the tips on the surface when tests were conducted. A current was applied between the outer two probes using a current source (Dr. Meter, PS-305DM), and the voltage *V* between the inner two probes was measured with a multimeter (Fluke 8846A). For the measurement of dry coating, the electrodes were dip-coated with a layer of ethylene glycol.

**Preparation of Sample for Stretching:** A PDMS strip of width ≈20 mm and length ≈80 mm was cut from the coated PDMS. Parts of the coating were carefully removed using a blade, so that only a rectangular-shape area of width ≈20 mm and length ≈40 mm in the middle of the strip remained coated. The uncoated area was for gripping when loaded on Instron. The coated area was for conductivity tests.

**Fabrication of an Interconnect of Complex Shape:** A mask was made by cutting a plastic film with a laser cutter. The mask was used to cover the PDMS substrate. The uncovered area of PDMS was exposed to plasma, and then cast with the mixed emulsion. After the emulsion dried, the mask was removed from the PDMS.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Author Contributions

G.Z. conceived and designed the study. G.Z. developed the synthesis method. G.Z., Z.C., and C.H.A. conducted the experiments. G.Z. and Z.S. wrote the manuscript. Z.S. supervised the research. All authors discussed the result and commented on the manuscript.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

adhesion, coatings, conducting polymers, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), water stability

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