Application of intrinsically conducting polymers in flexible electronics

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Abstract

Intrinsically conducting polymers (ICPs), such as polyacetylene, polyaniline, polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene) (PEDOT), can have important application in flexible electronics owing to their unique merits including high conductivity, high mechanical flexibility, low cost, and good biocompatibility. The requirements for their application in flexible electronics include high conductivity and appropriate mechanical properties. The conductivity of some ICPs can be enhanced through a postpolymerization treatment, the so-called “secondary doping.” A conducting polymer film with high conductivity can be used as flexible electrode and even as flexible transparent electrode of optoelectronic devices. The application of ICPs as stretchable electrode requires high mechanical stretchability. The mechanical stretchability of ICPs can be improved through blending with a soft polymer or plasticization. Because of their good biocompatibility, ICPs can be modified as dry electrode for biopotential monitoring and neural interface. In addition, ICPs can be used as the active material of strain sensors for healthcare monitoring, and they can be adopted to monitor food processing, such as the fermentation, steaming, storage, and refreshing of starch-based food because of the resistance variation caused by the food volume change. All these applications of ICPs are covered in this review article.

KEYWORDS

biopotential electrode, conducting polymer, PEDOT, strain sensor, stretchable conductor, transparent electrode

1 | INTRODUCTION

Flexible electronic materials and devices have been garnering great attention because of their important application in many areas, such as flexible displays, healthcare monitoring, soft robotics, human-machine interfaces, and so on.1–3 A flexible electronic device requires the active materials and the electrodes to be mechanically stretchable. Although metals can have high mechanical flexibility when they are quite thin, their Young’s modulus is much higher than elastomers that are usually used as the substrate of flexible electronic devices. In addition, bulk metals do not have high transparency in the visible range, and thus they cannot be adopted as the transparent electrode of optoelectronic devices such as light-emitting diodes (LEDs) and solar cells. Flexible
LEDs and solar cells can be used for displays and energy supply, respectively, of flexible electronic systems. To emit or harvest light, at least one electrode of an optoelectronic device must be transparent. However, the conventional transparent conductors are oxides like indium tin oxide (ITO). They are too brittle to be as the flexible transparent electrode.

The promising flexible transparent conductors include conductive nanomaterials and intrinsically conductive polymers (ICPs). Metal nanowires particularly Ag nanowires and carbon nanotubes (CNTs) have been extensively studied as the flexible transparent electrode of optoelectronic devices. Their resistance depends on not only their intrinsic conductivity but also the contact resistance among the nanowires or nanotubes. The sheet resistance of CNT films is too low for the practical application, while the Ag nanowire electrodes have problems including high roughness, poor adhesion to substrate and performance degradation caused by surface oxidation. Graphene is also an interesting candidate for the transparent electrode because of its high mechanical flexibility and high transparency. Nevertheless, it is difficult to prepare a thin graphene film with high uniformity in large area. ICPs are promising candidates for the transparent electrode because they can have high mechanical flexibility and high intrinsic conductivity. Figure 1 presents the chemical structures of some representative ICPs, including polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS). The salient difference of ICPs from the conventional polymers is the conjugated backbone, and the conjugated backbone gives rise to not only high conductivity but also interesting optical properties of ICPs. For example, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives can have high transparency in the visible range. They can thus have potential application as the flexible transparent electrode. PEDOT:PSS is particularly important as the next-generation transparent electrode material owing to its high conductivity, high transparency in the visible range and solution processability.

Apart from the mechanical flexibility, the electrodes should be highly stretchable for stretchable electronic devices, such as stretchable strain sensors and soft robotics. However, the conventional conductors including metals, semiconductors, CNTs and graphene have very limited stretchability, while the conventional elastomers are not conductive. There are mainly two strategies to develop stretchable conductors. One way is to form stretchable nanocomposites by dispersing conductive nanofillers like metal nanowires, CNTs, graphene or ICP, into an elastomer like poly(dimethylsiloxane) (PDMS) or polyurethane (PU). The conductivity of the nanocomposites arises from the charge transport across the nanofillers, while the mechanical stretchability is due to the elastomeric matrix. The electrical and mechanical properties of the nanocomposites depend on the intrinsic properties of the matrix and fillers, the aspect ratio and the loading of the fillers, and the morphology of the composites. Another strategy is to enhance the mechanical stretchability of ICPs. Although the mechanical properties of ICPs can be improved by chemical modification such as the adoption of some soft side groups, the improvement in the mechanical stretchability is not too much because their mechanical properties mainly depends on the conjugated backbone. Recently, it was reported that plasticization with some organic molecules can greatly improve the mechanical stretchability of ICPs.

ICPs can have particular advantages over other conductors as the biomedical electrode. For example, biological signals such as biopotentials and neural stimulus are transduced via ionic transport process. The charge transport mechanism is remarkably different from that of the electronic transport of metals or semiconductors that are popularly used in electronic devices. Since ICPs are capable of both electronic and ionic conductions, they can be the ideal electrodes between biological tissues and electronic devices. ICPs have additional merits as biomedical electrode in terms of the mechanical properties. ICPs are soft materials, and they can form good mechanical contact to the soft tissues.

![Figure 1](image-url)

**Figure 1** Chemical structures of some representative intrinsically conducting polymers. (A) Polyacetylene (PA), (B) polypyrrole (PPy), (C) polyaniline (PANI), (D) polythiophene (PTh), and (E) (PEDOT:PSS, poly(3,4-ethylenedioxythiophene):polystyrenesulfonate) PEDOT:PSS
tissues. In contrast, metals or inorganic semiconductors are hard materials, and they can cause problems like inflammation on the soft tissues because of the problem in the mechanical matching, and those can affect the biological signals. The good biocompatibility of ICPs is another important merit for their application in bioelectronic systems.

In addition to the flexible and stretchable electrodes, ICPs have been investigated as the active materials of flexible strain sensors. The work principle of a strain sensor is the sensitivity of its resistance or capacitance to strain. Because the resistance of a nanocomposite is determined by the charge transport across the conductive nanofillers, it is very sensitive to the separation among the nanofillers and thus the strain applied to the nanocomposite. However, the application of the strain sensors with nanocomposites is affected by the toxicity of the nanomaterials. Because ICPs can have good biocompatibility and the resistance of ICP blends can be sensitive to strain, ICP blends have been investigated as the active materials of strain sensors as well. In addition, this principle can be adopted for food processing monitoring. For instance, the resistance of starch blended with an ICP can be sensitive to the volume expansion or shrinkage of the food. The starch/ICP blends can be thus exploited as strain sensors to monitor the starch-based food processing, such as fermentation, steaming, storage and refreshing.

ICPs can have important application in flexible electronics, including flexible transparent electrode of optoelectronic devices, stretchable electrodes for various devices, bioelectrodes, and strain sensors for healthcare and food processing monitoring. These applications are covered in this review article.

2 | ICPs as Flexible Transparent Electrode of Optoelectronic Devices

Some ICPs like PEDOT and its derivatives can have a small bandgap when in the neutral state, and they become transparent when in the oxidized state. PEDOTs particularly PEDOT:PSS are the most popular ICPs for transparent electrode. Because high conductivity is required for their application as the transparent electrode, great progress has been devoted to developing highly conductive PEDOT:PSS and PEDOTs doped with small anions.

2.1 | Conductivity enhancement of PEDOT:PSS by “secondary doping”

PEDOT:PSS is the most successful ICP in terms of the practical application, owing to its advantages over other ICPs, such as the solution processability, high conductivity and good thermal stability. The processability has been a big hurdle for the practical application of ICPs, as most of ICPs in the conductive state are intractable and insoluble in any solvent. PEDOT:PSS can be dispersed in water or some polar organic solvents, since PSS\(^-\) serve as a polymer surfactant to stabilize the hydrophobic PEDOT chains. A high-quality PEDOT:PSS film can be readily prepared by solution processing techniques like coating and printing. However, as-prepared PEDOT:PSS films from its aqueous solution have a very low conductivity of <1 S/cm. The low conductivity is attributed to the core-shell structure of PEDOT:PSS and the coiled conformation of PEDOT chains. To stabilize the conductive PEDOT chains in water, PSSH must be excessive. As a result, PEDOT:PSS has a core-shell structure in water with the hydrophilic PSS\(^-\) forming a shell for the core rich of conductive PEDOT, and this core-shell structure is conserved in the PEDOT:PSS films (Figure 2). The insulating shells block the charge transport across the cores, and it leads to low conductivity. In addition, PSSH as a soft polymer prefers to a coil conformation. Although the PEDOT chains with the conjugated backbone prefers to linear conformation, some PEDOT chains or segments have to adopt the coil conformation because they are attached to the PSSH chains through the Coulomb attraction. The coil

![Figure 2](image-url)
conformation causes the localization of the charge carriers, and it also leads to low conductivity.

In terms of the factors for the low conductivity of PEDOT:PSS, the principle to enhance its conductivity is to induce a phase segregation of some PSSH chains from PEDOT:PSS and the conformational change of PEDOT chains from the coil structure to the expanded-coil or linear structure.\textsuperscript{25–28} This can enhance the conductivity of PEDOT:PSS, and it is called as “secondary doping.” The phase segregation can be achieved through the screening of the Coulomb attraction between the PEDOT polycations and the PSS polyanions and the disappearance of the Coulomb attraction by converting the PSS polyanions into neutral PSSH chains.\textsuperscript{29–31} Such a treatment can enhance the conductivity of PEDOT:PSS to 700–800 S/cm. The conductivity can be further enhanced by repeating the treatment. For instance, Leo et al. reported a conductivity of >1400 S/cm through the two-step treatments of PEDOT:PSS.\textsuperscript{32} EG is added into PEDOT:PSS aqueous solution in the first step, and the PEDOT:PSS films are treated in EG bath at 120°C in the second step. Apart from a single solvent, the conductivity of PEDOT:PSS can be enhanced through the preferential solvation with the cosolvent of two solvents, such as water/DMF (DMF: dimethylformamide), water/ethanol, water/(γ-butyrolactone), water/acetonitrile, water/acetone, and water/(isopropyl alcohol).\textsuperscript{33–37} The conductivity enhancement by the cosolvent treatment is much higher than a treatment with a neat component of the cosolvent. For example, the conductivity of a PEDOT:PSS film treated with neat water or DMF is less than 10 S/cm, while it increases to 1055 S/cm when it is treated with a cosolvent of 80 vol% DMF and 20 vol% water (Figure 3A). This cosolvent effect is attributed to the preferential solvations of PEDOT and PSS by the two solvents, respectively. Water prefers to solvate the hydrophilic PSS chains, while the organic solvents prefer to solvate the hydrophobic PEDOT chains. This can cause the phase segregation of some PSSH chains from PEDOT:PSS and thus the significant conductivity enhancement. In addition, the phase segregation can be induced by adding a surfactant into PEDOT:PSS aqueous solution, because the surfactant can partition the hydrophilic PSSH from the hydrophobic PEDOT chains as well.\textsuperscript{38–41}

Apart from a treatment with solvent, treating PEDOT:PSS with aqueous or organic solution of a common salt like ZnCl\textsubscript{2}, CuCl\textsubscript{2}, InCl\textsubscript{3}, or methyl ammonium iodide (MAI) can also significantly enhance its conductivity.\textsuperscript{37,42–46} The conductivity enhancement depends on the cations and anions of the salts. For example, the conductivity of a PEDOT:PSS film can be higher than 1800 S/cm after treated with a DMF/MAI solution (Figure 3B), while it is only 150 S/cm if it is treated with a DMF/NaI solution.\textsuperscript{37} The dependence of the conductivity on the ions is attributed to the interaction between the polyanions of PEDOT:PSS and the ions of the salts. If cations can have stronger bond to the PSS polyanions than the PEDOT polycations, the cations can substitute PEDOT polycations to balance the negative charge of PSS\textsuperscript{−}. This can induce the phase segregation of PSSH from PEDOT:PSS as well. The interaction between a cation and anion can be qualitatively assessed in terms of their softness parameters.\textsuperscript{47}

The phase segregation can be induced by converting PSS\textsuperscript{−} polyanions into neutral PSSH chains, because the Coulomb attraction becomes absent between PEDOT polycations and neutral PSSH chains. Since PSSH is an
acid with mild acidity ($pK_a = -2.8$), a stronger acid can protonate the PSS$^-$ polyanions and turn them into neutral polymer chains. Xia et al. reported that the conductivity of PEDOT:PSS can be enhanced to higher than 3000 S/cm after treated with sulfuric acid. Other labs confirmed the conductivity enhancement and reported that the conductivity can be higher than 4000 S/cm by using fumed sulfuric acid. In addition, the conductivity of PEDOT:PSS can be significantly enhanced when acids like organic carboxylic acids with their acidity lower than PSSH are used for the treatment. The driving force for the phase separation by the weak acids is ascribed to the repulsion between the hydrophobic PEDOT and hydrophilic PSSH chains.

There are two popular ways to perform the secondary doping of PEDOT:PSS. One is the addition of a chemical like a polar organic solvent or surfactant into PEDOT:PSS aqueous solution before coating, and the other is to use a solvent or solution to treat PEDOT:PSS films. The conductivity enhancements by the precoating or postcoating treatment is similar when a polar organic solvent like DMSO or EG is used for the secondary doping. However, the precoating secondary doping method cannot give rise to significant conductivity enhancement when the secondary doping is carried out with cosolvents, salts, or acids. Instead, the postcoating secondary doping method can saliently enhance the conductivity, because the concentration of the salts or acids in the solution for the postcoating treatment can be much higher than the direct addition of the salts or acids into PEDOT:PSS aqueous solution and the composition of the cosolvents can be well controlled. All the very high conductivities of PEDOT:PSS films in literature are achieved through the postcoating secondary doping method.

### 2.2 Highly conductive PEDOTs doped with small anions

PEDOT:PSS aqueous solution is usually prepared through the oxidative polymerization of the monomer, 3,4-ethylenedioxythiophene (EDOT), in water solution with sodium persulfate ($Na_2S_2O_8$) as the oxidant. The polymerization mechanism is briefly presented in Figure 4. In addition to PEDOT:PSS, great effort has been devoted to PEDOTs doped with small anions as well. Because they are insoluble after the polymerization, their conductivity mainly depends on the polymerization conditions. A couple of methods were reported to deposit thin films of PEDOTs doped with other counter anions, including the electrochemical polymerization, in-situ solution chemical polymerization, vapor phase polymerization (VPP), and oxidative chemical vapor deposition (OCVD). The conductivity of PEDOTs prepared by the electrochemical polymerization is less than 200 S/cm, much lower than by the other methods. Hence, electrochemical polymerization of EDOT is only briefly mentioned in this article.

#### 2.2.1 In situ solution chemical polymerization

The polymerization of EDOT proceeds through the formation of a covalent bond between the $\alpha$ carbons of two thiophene rings (Figure 4). Because protons are generated during the polymerization, the pH value of the solution can saliently affect the polymerization rate and thus the crystallinity of PEDOTs and their conductivity. Fe$^{3+}$ salts are the popular oxidant for the solution chemical polymerization. PEDOTs with high conductivity were reported by several labs. For example, Simonato et al. prepared PEDOT doped with trifluoromethanesulfonate (PEDOT:OTf) through the polymerization of EDOT in solvent with Fe(III)(OTf)$_3$ as the oxidant and block copolymer PEG-PPG-PEG on the substrate, and they observed a conductivity of 1200 S/cm. The conductivity can be greatly improved to 3600 ± 200 S/cm by adding N-methyl-2-pyrrolidone (NMP) with the loading of 7%–8% in the polymerization solution (Figure 5A). The NMP addition can enhance the conductivity of PEDOT:OTf because NMP as a proton scavenger causes the retardation of the polymerization and thus increases the crystallinity of PEDOT:OTf. The conductivity can be further enhanced to...
5400 ± 400 S/cm through the post-synthesis treatment with sulfuric acid. The acid treatment does not increase the crystallinity of PEDOT:OTf, but it may facilitate the charge transport through the amorphous region of PEDOT:OTf. As shown in Figure 5B, the PEDOT crystallites can be observed by high-resolution TEM (HRTEM). The stacking of the PEDOT chains is illustrated in Figure 5C. The HRTEM image indicates the π–π stacking distance of 3.46 Å and about 23 repeating EDOT units in the PEDOT chains in the crystallite.

Apart from Fe³⁺ salts, other oxidants were also studied for the polymerization of EDOT. For instance, Chen et al. polymerized EDOT using V₂O₅ as the oxidant for the polymerization of EDOT as the presence of methanesulfonic acid (MSA) and 2,6-di-tert-butylpyridine. They observed a conductivity of 1420 S/cm.63

2.2.2 | Vapor phase polymerization (VPP)

In the in-situ solution chemical polymerization, the monomer is dissolved in the solvent together with the oxidant. The monomer is in the vapor state in VPP, and the monomer vapor polymerizes at the surface of an oxidant solution like a Fe³⁺ salt on substrate. The PEDOT films can be directly deposited on various substrates by VPP. For example, Winther-Jensen et al. carried out the preparation of PEDOT:Tso thin films by VPP with Fe(Tso)₃ as the oxidant in ethanol and pyridine as the polymerization retardant. They observed a conductivity of >1000 S/cm in 2004. Fabretto et al. reported that pyridine can be replaced with water vapor in the VPP. In addition, to have fast diffusion of monomer/oxidant during the polymerization, they modified the oxidant by dispersing Fe(Tso)₃ in the block copolymer of PEG-PPG-PEG and obtaining a liquid-like thin film of the oxidant. This can greatly improve the conductivity to 2500 S/cm. The liquid-like oxidant can give rise to the PEDOT thin films with better uniformity. Crispin et al. prepared the PEDOT:OTf films through the VPP of EDOT on PEG-PPEG-PEG consisted of Fe(OTf)₃ and then treated them with sulfuric acid, and they observed a conductivity of 4500 S/cm.

Cho et al. used the VPP method to grow single-crystal PEDOT nanowires by using FeCl₃ solution in nanoscale channels. The PEDOT nanowires have a cross-sectional dimension of 95 x 100 nm. They can exhibit an average conductivity of 7619 S/cm and the highest conductivity of up to 8797 S/cm.

2.2.3 | Oxidative chemical vapor deposition (oCVD)

The oCVD of PEDOTs is a modification of the VPP methods. Apart from the EDOT vapor, the oxidant is in the vapor state as well in oCVD. The conductivity of the PEDOTs by oCVD depends on the chemical structure and pressure of the oxidant and the deposition temperature. When FeCl₃ is used as the oxidant, the conductivity of PEDOT:Cl by oCVD can be up to 180 S/cm at the deposition temperature of 100°C. As shown in Figure 6A, the conductivity depends on the deposition temperature. The deposition temperature affects the pressure of the oxidant vapor. By increasing the deposition temperature to 300°C and a postdeposition treatment with hydrobromic acid (HBr), the PEDOT thin films can exhibit a conductivity of 6259 ± 1468 S/cm and a remarkably high carrier mobility of 18.45 cm²/(Vs).

The oxidant vapor pressure is a crucial factor for the conductivity of PEDOTs by oCVD. In a recent study by Gleason et al., SbCl₅ that is liquid at room temperature was adopted as the oxidant. They also introduced water vapor as the proton scavenger of the polymerization.
The polymerization can take place at much lower temperature than that with FeCl₃. As shown in Figure 6B, THE conductivity of PEDOT:Cl depends on the vapor pressure of SbCl₅. Deposited at 140°C and 100 ppm of the SbCl₅ pressure to its saturation pressure at this temperature, the PEDOT:Cl thin films can exhibit a conductivity of 7520 ± 240 S/cm.

2.3 | ICPs as transparent electrode of devices

The highly conductive PEDOTs doped with PSS⁻ or other anions can have important application as flexible transparent electrode of optoelectronic devices, such as organic LEDs (OLEDs), organic solar cells (OSCs), and perovskite solar cells (PSCs). In fact, a key challenge for flexible optoelectronic devices lies in the flexible transparent electrode, because the conventional transparent conductors like ITO and aluminum-doped zinc oxide (AZO) are brittle materials. A transparent electrode should have high transmittance in the visible range while low sheet resistance. In addition, highly conductive PEDOTs are also studied as the electrodes of transparent heaters.

2.3.1 | OLEDs

OLEDs have been becoming more and more popular in displays such as TVs and mobile phones. Flexible OLEDs can be used even in wearable devices and intelligent systems. Highly conductive PEDOT:PSS can be used as the flexible transparent electrode of OLEDs. For example, Kim et al. prepared highly conductive PEDOT:PSS thin films through a post treatment with methanol solution of benzoic acid. The treated PEDOT:PSS film can exhibit a conductivity of higher than 1500 S/cm. They fabricated OLEDs with the structure of glass/PEDOT:PSS/1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) as the hole-transport layer/4,4-bis(N-carbazolyl)-1,1′-biphenyl:tris(2-phenylpyridine)iridium(III) [CBP:Ir(pp y)₃] as the emitting layer/2,2′,2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole) (TPBi) as the electron transport layer/LiF/Al. The OLEDs can exhibit a luminance of 1000 cd/m² at the bias of 5.9 V, and its maximum current efficiency is 25.3 cd/A. The luminance of the flexible OLEDs can remain at 83% of the initial value after 1400 bending cycles at a bending radius of 5 mm.

2.3.2 | OSCs

Highly conductive PEDOTs were studied as the transparent electrode of OSCs that convert light into electricity as well. Xia et al. investigated OSCs with sulfonic acid-treated PEDOT:PSS films as the transparent electrode and poly(3-hexylthiophene):phenyl-C₆₁-butryric acid methyl ester (P3HT:PCBM) as the active layer in 2012. The photovoltaic performance the OSCs is similar to the control devices with ITO as the transparent electrode. Nonfullerene OSCs can exhibit much higher photovoltaic efficiency than the ones with fullerene or its derivatives. Flexible nonfullerene OSCs were demonstrated as well. For example, Ge et al. reported an efficiency of 12.35% for flexible OSCs with PEDOT:PSS treated with β-maltose that has a conductivity of 2626 S/cm as the transparent electrode and polyethylene

FIGURE 6 (A) Variation of the conductivity of PEDOT:Cl thin films with the deposition temperature of oCVD with FeCl₃ as the oxidant. The conductivities along the face-on and edge-on directions were measured. The face-on and edge-on directions are illustrated in the inset. Reproduced with permission. Copyright 2018, American Association for the Advancement of Science. (B) Variation of the conductivity of PEDOT:Cl thin films with the ratio of the SbCl₅ vapor pressure to its saturation pressure at the deposition temperature of 90 or 140°C with or without water. W-A indicates the presence of water vapor during the polymerization. Reproduced with permission. Copyright 2021, Wiley. oCVD, oxidative chemical vapor deposition; PEDOT, poly(3,4-ethylenedioxythiophene)
terephthalate (PET) as the substrate. The photovoltaic performance is comparable to the control OSCs with ITO as the transparent electrode (Figure 7). After these flexible OSCs were bent at the bending radius of 4 mm for 1000 cycles, they can exhibit a photovoltaic efficiency of around 92% of the original efficiency.

2.3.3 | PSCs

PSCs have received great attention since its discovery in 2011 because of their high photovoltaic efficiency. They have a similar architecture to OSCs with the active layer sandwiched between two electrodes. Highly conductive PEDOT:PSS thin films were investigated as the transparent electrode of flexible PSCs. For example, Sun et al. observed a photovoltaic efficiency of 8.1% on flexible PSCs with PEDOT:PSS films treated with methanesulfonic acid as the transparent electrode in 2015.

Hu et al. reported that blending di[bis(trifluoromethylsulfonyl) imide] (Zn(TFSI)$_2$, chemical structure shown in Figure 8A) can enhance both the conductivity and flexibility of PEDOT:PSS, and they thus called Zn(TFSI)$_2$ as a conductivity and flexibility enhancer (CFE). The PEDOT:PSS:CFE thin films can exhibit a conductivity of >4000 S/cm and transmittance over 80% from 400 to 900 nm. They fabricated flexible PSCs with PEDOT:PSS:CFE on PET as the transparent electrode (Figure 8). The power conversion efficiencies are 19.0% and 10.9% at the aperture areas of 0.1 and 25 cm$^2$, respectively, which is comparable to control PSCs on rigid substrate.

2.3.4 | Transparent heater

PEDOTs were also studied as the electrodes of transparent heaters that generate heat from electricity through the Joule effect. Transparent heaters can be used to defrost the windows of aircraft, vehicle, refrigerators, and so on. Simonato et al. studied the application of PEDOT:OTf, pristine PEDOT:PSS, PEDOT:PSS treated with EG, and PEDOT:OTf treated with sulfuric acid as the electrodes of transparent heaters. They found that PEDOT:OTf treated with sulfuric acid can exhibit a sheet conductivity and flexibility of PEDOT:PSS, and they thus called Zn(TFSI)$_2$ as a conductivity and flexibility enhancer (CFE). The PEDOT:PSS:CFE thin films can exhibit a conductivity of >4000 S/cm and transmittance over 80% from 400 to 900 nm. They fabricated flexible PSCs with PEDOT:PSS:CFE on PET as the transparent electrode (Figure 8). The power conversion efficiencies are 19.0% and 10.9% at the aperture areas of 0.1 and 25 cm$^2$, respectively, which is comparable to control PSCs on rigid substrate.

**Figure 7** (A) Schematic architecture of flexible OSCs with a PBDB-T-2Cl:IT-4F active layer and the chemical structure of the active materials. (B) Energy levels of the materials of the OSCs. (C) Current density ($J$)-voltage ($V$) curves of flexible OSCs with PEDOT:PSS (PH1000) treated with d-glucose, d-sucrose, d-glucitol or d-maltose on PET as the transparent electrode. (D) Photovoltaic efficiencies of the flexible OSCs. Reproduced with permission. Copyright 2019, Royal Society of Chemistry. OSC; organic solar cell; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):polystyrenesulfonate
resistance of 57 Ω/sq and transmittance of 87.8% and the corresponding heater can show a heating rate of 1.6°C/s and a steady-state temperature of 138°C under 12 V bias. Similar performance can be achieved by using PEDOT:PSS treated with EG as the transparent electrodes.

3 | CONDUCTING POLYMERS AS STRETCHABLE CONDUCTORS

Stretchable conductors are crucial materials for the stretchable electronics. However, the conventional conductors including metals, semiconductors, ICPs, CNTs, and graphene have limited mechanical stretchability. On the contrary, polymers in the rubbery state can have high mechanical stretchability because of the recoiling and slippage of the polymer chains. Although ICPs are polymers, their glass transition temperature is higher than the room temperature due to the rigid conjugated backbone. In addition, to have a high conductivity, an ICP should have high crystallinity, while the crystallinity can lower the mechanical stretchability of polymers. The strategies to develop stretchable ICPs include the plasticization or blending with a soft polymer or elastomer.

3.1 | Stretchable ICPs by plasticization

The stretchability of a polymer is related to the mobility of the polymer chains. The polymer chains can have high mobility when the temperature is higher than its glass transition temperature. A popular way to lower the glass transition temperature is through plasticization. This method has been studied for ICPs as well, but the plasticization mechanism of ICPs is very different from the conventional polymers like polyvinyl chloride that have a neutral and saturated backbone.

He et al. investigated the plasticization of PEDOT:PSS with a series of organic molecules (Figure 9). They found that the plasticization depends on the chemical structure of the plasticizers. A compound with two or more -OH groups such as D-sorbitol, glycerol, malic acid, 1,2,6-hexanetriol, or triethylene glycol can significantly enhance the mechanical stretchability of the PEDOT:PSS films (Figure 10). The elongation at break can be enhanced from less than 10% for the pristine PEDOT:PSS films to higher than 50%. In contrast, when the compounds with only one or no hydroxyl group are adopted as the additives, the elongation at break increases much less. The effects of these compounds on the Young’s modulus and the tensile strength are consistent with that on the elongation at break. They found that the plasticization mechanism is related to the Hansen solubility parameter (HSP, δh) of the additives with multiple -OH groups (Figure 10D). Higher the δh value of a plasticizer, longer elongation at break of PEDOT:PSS. They attributed the plasticization mechanism to the destruction of hydrogen bonds among the chains of poly(styrenesulfonic acid) (PSSH) by the plasticizers. In addition, these compounds can induce secondary doping of PEDOT:PSS and can enhance its conductivity to higher than 1000 S/cm.

Other compounds were also studied as the plasticizer of PEDOT:PSS. For example, Bao et al. reported that Zonyl that is a neutral fluoro-surfactant and ionic liquids can also plasticize PEDOT:PSS. The plasticization mechanism is not clearly provided, but it should be different from that of the plasticizers by He et al. because of their different interactions to PEDOT:PSS. Ionic liquids can enhance the conductivity of PEDOT:PSS to
higher than 3000 S/cm, while Zonyl only slightly affects the conductivity.

3.2 Stretchable ICP blends

When a rigid polymer is dispersed in a soft polymer matrix, the polymer blends can be mechanical stretchable. Because PEDOT:PSS can be dispersed in water or some polar organic solvents, the blends of PEDOT:PSS with another polymer can be easily formed by solution mixing.105–112 For example, Li et al. prepared the blends of PEDOT:PSS with a soft polymer like poly(ethylene glycol) (PEG), poly(ethylene oxide) (PEO), or PVA (chemical structure shown in Figure 11A) that is soluble in water as well.106 The elongation of break of the PEDOT:PSS blends with PEG (MW = 20,000, MW: molecular weight) or PEO (MW = 100,000) is 20%–30%. This is higher than not only PEDOT:PSS but also neat soft polymers, because the blends can lower the crystallinity of the soft polymers. The PEDOT:PSS blends with PVA (MW = 89,000) or with PEO (MW = 1,000,000) can...
exhibit elongations at breaks of ~55% and ~37%, respectively, at the soft polymer loading of 66.7 wt%.

The soft polymers can enhance the conductivity of PEDOT:PSS as well through the secondary doping. The PEDOT:PSS blends with PEG (MW = 20,000) at the PEG loading of 50 wt% can show a conductivity of about 100 S/cm. The addition of polar organic solvents like EG or DMSO can further increase the conductivity. The blends of PEDOT:PSS with 66.7 wt% PVA (MW = 89,000) can exhibit a conductivity of 172 S/cm and elongation at break of 47%.

These soft polymers are not elastic, and their crystallinity can lower the mechanical stretchability as well. Some thermoplastic elastomers can be dispersed in water or organic solvents, and they can be used to form stretchable conductive blends with PEDOT:PSS. A popular elastomer for this purpose is waterborne polyurethane (WPU). WPU can form uniform structure with PEDOT:PSS in the blend films arising from the strong interaction between them. Because of the formation of the continuous phases of both components, the PEDOT:PSS/WPU blends are conductive and stretchable. As shown in Figure 11B, THE neat WPU can have an elongation at break of higher than 700%, and the elongation at break of the blends is always higher than that of neat PEDOT:PSS. The elongation at break decreases while the Young's modulus increases with the increasing PEDOT:PSS loading (Figure 11C). The conductivity of PEDOT:PSS/WPU films almost linearly increases with the PEDOT:PSS loading (Figure 11D). The blend films at the PEDOT:PSS loading of 20 wt% can have an elongation at break of 33% and a conductivity of 77 S/cm.

In addition to WPU, PU that can be dispersed in polar organic solvents was adopted to the blends with PEDOT:PSS as well. But phase separation can be observed in these PEDOT:PSS/PU blends because PEDOT:PSS is less dispersible in organic solvents than in water.

### 3.3 ICPs as stretchable electrode

ICPs with high mechanical stretchability and high conductivity can be used as the electrode of stretchable devices and systems. For example, stretchable electrodes are needed for soft robotics. A dielectric elastomer soft actuator has structure with a dielectric elastomer layer sandwiched between two
compliant electrodes. When a high voltage is applied to the two electrodes, positive and negative charges are generated at the two interfaces between the dielectric elastomer layer and the two electrodes. These charges at the two sides of the dielectric elastomer layer can induce a Coulomb attraction on the dielectric elastomer layer and thus mechanical deformation.\textsuperscript{117} The electrodes should be compliant so that they can follow the electromechanical movement of the dielectric elastomer layer. Carbon grease is conventionally used for the compliant electrodes. Nevertheless, it is not convenient to handle the liquid carbon grease, and carbon grease is opaque as well.

Li et al. demonstrated that PEDOT:PSS/WPU blends can be used as the compliant and transparent electrodes of dielectric elastomer soft actuators.\textsuperscript{109} As shown in Figure 12A, PEDOT:PSS/WPU blends are assembled with a dielectric elastomer (VHB) layer for a soft actuator, and two actuators are integrated into a soft robot. The soft robot can show electromechanical response to the voltage applied (Figure 12B). Varying the voltage can move the soft robot forward or backward or rotate (Figure 12C). As both the PEDOT:PSS/WPU electrodes and the dielectric elastomer layer have high mechanical stretchability, the actuators can exhibit a high area strain of 200\% under a voltage (Figure 12D). In addition, the soft actuators can have a transmittance of 85.5\% at the wavelength of 550 nm because all the materials are highly transparent. As a result, the soft robot is camouflage.

In addition, the stretchable ICPs can be used as wearable heater for thermotherapy. Thermotherapy is a useful approach to treat diseases like arthritis, joint injuries, stiff muscles, and injuries to the deep tissue of the skin.\textsuperscript{118–120} Zhou et al. reported that PEDOT:PSS/WPU films can be used for thermotherapy and the temperature can be controlled by controlling the voltage.\textsuperscript{108}

Another important application for stretchable ICPs is for electromagnetic interference (EMI) shielding, which is needed to screen the noise in stretchable electronics. The EMI effect is related to the resistance and the microstructure of the materials.\textsuperscript{121,122} Li et al. studied the EMI effect of PEDOT:PSS/WPU within the X-band range.\textsuperscript{107} The EMI shielding effectiveness increases with the increasing PEDOT:PSS loading, and it reaches 62 dB for the PEDOT:PSS/WPU film with the PEDOT:PSS loading of 20\% and thickness of 0.15 mm. Because of the high mechanical stretchability, the EMI shielding effectiveness of PEDOT:PSS/WPU is not affected by stretching.

4 ICPS AS BIOELECTRONIC ELECTRODE

Bioelectric signals such as biopotentials and neural information have very low amplitude and appear at low frequency. Thus, the contact between the biological tissue and electrodes can significantly affect the signal quality. The tissue/electrode contact is related to the both the electrical and their mechanical properties. In principle, ICPs can be a perfect material for the bioelectric electrodes because of their unique advantages including electronic and ionic conduction, soft nature and good biocompatibility.

4.1 ICPs as epidermal biopotential dry electrode

Epidermal biopotentials such as electrocardiography (ECG), electromyography (EMG), and electroencephalography (EEG) are vital for the diagnosis and treatment of various diseases.\textsuperscript{123–126} Long-term monitoring of these signals are often required. They are usually detected by placing electrodes on skin. The contact between the electrodes and skin can significantly affect the biopotential signals. Although Ag/AgCl gel electrodes are very popular in clinical setting for the epidermal biopotential detection, they are not suitable for long-term monitoring owing to the evaporation of the liquid phase of the gel electrolyte and skin irritation caused by the gel electrolyte. In addition, high noise mainly due to the motion artifacts appears during the physical movement.

Great effort has been devoted to replacing the gel electrodes with dry electrodes for biopotential detection.\textsuperscript{127–129} Although both dry contact electrodes and dry capacitive noncontact electrodes have been studied, the capacitive noncontact electrodes are not a good option because of the poor signal quality during physical movement. Several types of dry contact electrodes with different materials were reported in literature, including metal thin films, conductive polymers composites and ICPs. To have high signal quality, the dry contact electrodes should be mechanical stretchable, highly conductive and their contact to skin should not be affected during physical movement. In terms of these criteria, metal thin films are not good materials for the dry contact electrode because they are not stretchable and their contact to skin can be deteriorated during physical movement.\textsuperscript{130} Conductive polymer composites consisted of an elastomer matrix and conductive nanofillers such as metals, nanotubes, nanowires, and nanosheets.
have been extensively studied as the dry contact electrode.\textsuperscript{131–134} Nevertheless, they give rise to bio-potential signals with high noise particularly during physical movement. This is related to the small effective contact area between the conductive nanofillers and human skin as the conductive nanofillers are usually a few percent of the composite. In addition, a physical movement can generate motion artifacts due to the mechanical mismatch between a composite electrode and skin. The toxicity of the nanofillers is also a big concern for the composites as the epidermal contact electrode.\textsuperscript{135,136}

If an electrode is stretchable and self-adhesive to skin, it can follow the deformation of the skin during physical movement and thus always form conformal contact to skin. Because bio-inspired micro-pillar or sucker-like structures could enable the adhesion to skin, they were adopted for polymer composite patches as adhesive dry electrodes.\textsuperscript{137–139} However, these adhesion by these bio-inspired structures to the skin is prone to secreted sweat or dirt on the skin. Additionally, the users can feel uncomfortable for the suction after a long-term use.

ICPs have been studied as the dry electrode for bio-potential detection as well. For example, PEDOT:PSS
films coated on flexible substrate like polyimide foil or ethyl cellulose or paper were investigated as the dry electrodes for the ECG or EMG detection.\textsuperscript{124,140,141} However, they cannot give rise to high quality biopotential signal because they are not self-adhesive to skin and cannot form conformal contact to skin.

Recently, Zhang et al. reported that the blends (PWS) of PEDOT:PSS, WPU and D-sorbitol can be high-performance epidermal biopotential electrode. PWS can have high conductivity, high mechanical stretchability and self adhesion to skin conditions, and all the components are biocompatible.\textsuperscript{142} As shown in Figure 13A,B, THE PWS films are adhesive to skin, and they can adapt to the grooves of the wrinkles. They also do not cause any irritation to skin. The impedance using the PWS dry electrodes is even lower than that using the conventional Ag/AgCl gel electrodes because PWS has a conductivity higher than the Ag/AgCl gel electrolyte by 5–6 orders by magnitude.

As shown in Figure 14A, THE PWS dry electrode can give rise to high quality ECG signals when the user is in static (Figure 14A), quite similar to that using the Ag/AgCl gel electrodes. In addition, the PWS dry electrodes can be used for long-term ECG monitoring (Figure 14B).\textsuperscript{142} There is no remarkable change in the signal quality even after a continuous use for 24 h. In fact, the PWS electrodes can be used for much longer duration like one month or even longer. Because of the self adhesion to skin, the PWS electrodes can always form conformal contact to skin even during physical movement. As shown in Figure 14C, AN electrical vibrator is used to induce the muscle movement. The self-adhesive PWS electrodes can produce high-quality signals even under vigorous vibration (Figure 14D). In contrast, high noise is observed, and the curves are twisted, when the electrodes are only slightly adhesive or not self-adhesive.

### 4.2 ICPs as neural interface

A neural interface is used for the communication between neurons and machine. This can be used for the treatment of a variety of diseases including Parkinson’s disease, epilepsy, depression, blindness, deafness, sleep apnea, obesity, urinary and fecal incontinence.\textsuperscript{143} The interface between the excitable tissue and the electrode is crucial for the signal quality and the activation of neural cells. Although metals like Pt and Ir or semiconductors like ITO are often used as the electrode, there is usually a

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**FIGURE 13** (A) Photos demonstrate the adhesiveness of PWS films to various skins including a smooth skin, hairy rough skin, deformed wet skin, and stretched porcine skin. (B) A cross-section SEM image of a PWS film that replicates a rough skin surface. (C) Impedance spectra with a commercial Ag/AgCl gel electrode and PWS dry electrodes on dry and wet skins, and (D) the corresponding impedances at 10, 100, and 1000 Hz. Reproduced with permission.\textsuperscript{142} Copyright 2020, Nature Publishing Group. PWS, blend of PEDOT:PSS, WPU and D-sorbitol; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):polystyrenesulfonate; WPU, waterborne polyurethane
significant fluid gap at the interface between the soft tissues and implanted hard electrode, and the hard electrode can also cause inflammation. Due to the soft nature of ICPs, coating a layer of ICPs on a hard conductive substrate can reduce the mechanical mismatch between the tissue and electrode and thus reduce the inflammation. This can thus greatly improve the signal quality and the communication between the neuron and machine. ICPs including PPy, PTh, PANi, and PEDOT have been studied for the neural interface. However, there is a problem related to the poor adhesion of ICPs to the hard conductive substrate,
and this can cause problem for long time use. Methods have been developed to enhance the adhesion of ICPs to metal or semiconductor substrate. For instance, Martin et al. added an anchor layer between the hard conductive substrate and the ICP layer to improve the adhesion. They demonstrated that a polymer of EDOT with a carboxylic acid group (EDOT-COOH) can serve the anchoring layer between ITO and PEDOT in 2015. The thin layer of P(EDOT-COOH) does not block the charge transfer between ITO and the PEDOT layer. Later in 2017, they found that the polymer of an amine-functionalized EDOT (EDOT-NH₂) can greatly improve the adhesion of PEDOT to various conductive substrates like Pt, Ir, and ITO. As shown in Figure 15, the impedance with P(EDOT-NH₂)/PEDOT is comparable to that with PEDOT, and it is significantly lower than the bare electrode in the low frequency range. The improvement in the adhesion of PEDOT is further evidenced by the ultrasonication study. When the electrodes are ultrasonicated for 1 h, the PEDOT and P(EDOT-NH₂) layers remain intact, whereas the PEDOT layer at the absence of P(EDOT-NH₂) delaminates from the substrate only after the sonication for a few seconds.

Apart from coating an ICP layer to conductive substrate, the contact between tissue and electrode can be improved by directly depositing an ICP layer on tissue. For instance, Martin et al. directly polymerized PEDOT within the brain tissue. The PEDOT chains form a conductive network, and this can decrease the impedance by 1–2 orders by magnitude.
ICPs were investigated as the active material for flexible strain sensors. Because ICPs are conductive materials, their blends with a soft or elastic polymer can show a resistance sensitive to the tensile strain. However, a normal ICP film on a flexible substrate usually exhibits a resistance not very sensitive to the tensile strains. Their sensitivity is below 5 at 20% strain.

Fan et al. observed that PDMS embedded with strong acid-treated PEDOT:PSS can show a sensitivity of 22 at 20% strain. The high sensitivity is attributed to the formation of PEDOT/PDMS composites at the interfaces. But the resistance increase becomes irreversible after 400 cycles. Later in 2018, they found that the resistance cyclability can be greatly improved by using a triple-layer structure of (PVA–PEDOT:PSS blends)/(highly conductive PEDOT:PSS)/PDMS (Figure 16A). The strain sensors can show a sensitivity of 26, 70, and 100 at the strains of 10%, 20%, and 30%, respectively. The high sensitivity is ascribed to the formation of fine cracks in the highly conductive PEDOT:PSS films when a strain is applied and the reconnection of the conductive networks assisted by PVA-PEDOT:PSS after the release of the strain. They demonstrated the application of the strain sensors to monitor various physical movements, such as the motions of joints like knee, finger, elbow, and palm (Figure 16C–F).
5.2 Strain sensors with ICPs for food processing monitoring

Stretchable strain sensors have been extensively studied for healthcare monitoring. They can be used in other areas that can have salient geometric change like structural damaging monitoring. The resistance variation of a strain sensor is caused by the strain-induction separation among the conductive fillers. Starch-based food can experience a remarkable change in the volume during food processing. If a conductive material is mixed into the starch-based food, the resistance variation can indicate the volume change of the food during food processing.

This concept was recently verified by Zhang et al. They demonstrated the application of stretchable strain sensor to monitor the processing of starch-based food. This is significant because starch-based foods like bread and steam bun are very popular on earth and processing conditions can significantly affect the food quality. The stretchable strain sensors were prepared by adding PEDOT:PSS into starch. PEDOT:PSS is biocompatible, and it can be uniformly dispersed in starch owing mainly to the hydrogen bond between them. The chemical structure of PEDOT does not change during the food processing such as fermentation, steaming, storage and refreshing. As a result, the PEDOT:PSS/starch blends are conductive, and their resistance changes with the volume variation of the food during processing.

As shown in Figure 17, the volume of wheat powder expands during fermentation. The presence of 0.3 wt% PEDOT:PSS does not affect the fermentation and volume variation of the starch-based food. The food volume can expand by 1.9 times, while the resistance of the PEDOT:PSS/starch blends can increase by 2.8 times (Figure 17C). The resistance variation is caused mainly by the volume expansion instead of the pH variation, because the pH value of the food only decreases from 5.2 to 4.7 during the fermentation.

The volume of the starch-based food expands during steaming as well. The resistance variation of the PEDOT:PSS/starch blends follow the volume change (Figure 17D). When the steaming starts, the temperature increases, and the food volume increases. Correspondingly, the resistance of the PEDOT:PSS/starch blends increases. When the food volume expands to the maximum, that is, the mature of the steaming, the resistance of the blends increases to the maximum as well. The temperature cools down after the steaming completion. The food volume shrinks, and the resistance of the steamed bread drops correspondingly.

The resistance of the PEDOT:PSS/starch doughs can be used to monitor the food storage and refreshing as well. Hence, these sensors can be helpful in finding the optimal conditions for food processing. This can lead to the best food quality at low energy consumption.

6 CONCLUSION AND OUTLOOK

ICPs can have important application in flexible electronics because they combine the merits of metals and plastics, such as high conductivity, high mechanical flexibility, low price, easy materials processing, and good biocompatibility. Flexible transparent electrode is urgently needed for flexible optoelectronic devices because the conventional transparent conductive oxides are brittle materials. PEDOTs with high conductivity can be used as the transparent electrodes. A variety of “secondary doping” methods have been developed to enhance the conductivity of PEDOT:PSS, and the conductivity can be more than 4000 S/cm. Various methods were demonstrated for the preparation of highly conductive PEDOTs doped with small anions as well. Very impressive conductivity of higher than 7000 S/cm was reported for PEDOT thin films. They were demonstrated as the transparent electrode of optoelectronic devices, including OLEDs, OSCs, PSCs, and transparent heaters. ICPs have limited mechanical stretchability because of their rigid conjugated backbone. The methods to improve their mechanical stretchability mainly include the plasticization and blending with a soft polymer or elastomer. Owing to their good biocompatibility, ICPs can have important biomedical application, such as dry electrode for biopotential monitoring and neural interface. An ICP blend self-adhesive to skin can always form conformal contact to skin and thus give rise to high-quality biopotential signals. Blends of ICPs can show a resistance sensitive to strain and they can be used as the active material of strain sensors for healthcare monitoring. This principle was recently demonstrated to monitor starch-based food processing as well.

Compare with other conductors, ICPs have unique advantages in flexible electronics because of their soft nature and mixed ion-electron conduction. Their properties such as conductivity and mechanical stretchability have been continuously improved. Apart from the electrical and mechanical properties, there are other requirements in terms of the application. For example, ICPs can be used as the interface on skin or in tissue. To acquire high-quality signal for long term, they should always have good contact to skin or cells for long term. Thus, they should be self-adhesive and good stability in the biological environment. There are tremendous opportunities for ICPs in flexible electronics, but much more efforts from materials scientists, chemists, physicists and biologists are needed.

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CONFLICT OF INTERESTS
The authors declare no conflict of interest.
REFERENCES

1. Wang C, Yokota T, Someya T. Natural biopolymer-based biocompatible conductors for stretchable bioelectronics. Chem Rev. 2021;121(4):2109-2146.

2. Song E, Li J, Won SM, Bai W, Rogers JA. Materials for flexible electronic systems as chronic neural interfaces. Nat Mater. 2020;19(6):590-603.

3. Tee B, Ouyang J. Soft electronically functional polymeric composite materials for a flexible and stretchable digital future. Adv Mater. 2018;30(47):1802560.

4. Chen ZH, Fang R, Li W, Guan J. Stretchable transparent conductors: From micro/macromechanics to applications. Adv Mater. 2019;31(35):1900939.

5. McLellan K, Yoon Y, Leung SN, Ko SH. Recent progress in transparent conductors based on nanomaterials: Advancements and challenges. Adv Mater Technol. 2020;5(4):1900939.

6. Li D, Lai WY, Zhang YZ, Huang W. Printable transparent conductive films for flexible electronics. Adv Mater. 2018;30(10):1704738.

7. Jeon I, Yoon J, Ahn N, et al. Carbon nanotubes versus graphene as flexible transparent electrodes in inverted perovskite solar cells. J Phys Chem Lett. 2017;8(21):5395-5401.

8. Lian L, Dong D, Feng D, He G. Low roughness silver nanowire flexible transparent electrode by low temperature solution-processing for organic light emitting diodes. Org Electron. 2017;49:9-18.

9. Ricciardulli AG, Yang S, Wetzelaer GJAH, Feng X, Blom PW. Hybrid silver nanowire and graphene-based solution-processed transparent electrode for organic optoelectronics. Adv Funct Mater. 2018;28(14):1706010.

10. Lee JH, Jeong YR, Lee G, et al. Highly conductive, stretchable, and transparent PEDOT:PSS electrodes fabricated with triblock copolymer additives and acid treatment. ACS Appl Mater Interfaces. 2018;10(33):28027-28035.

11. Bießmann L, Saxena N, Hohn N, Hossain MA, Veinot JGC, Müller JAH, Feng X, Blom PW. Effective approaches to improve the electrical conductivity of PEDOT:PSS: A review. Adv Mater Interfaces. 2020;7(4):1900654.

12. Chen J, Yu Q, Cui X, et al. An overview of stretchable strain sensors from conductive polymer nanocomposites. J Mater Chem C. 2019;7(38):11710-11730.

13. Youn JH, Jeong SM, Hwang G, et al. Dielectric elastomer actuator for soft robotics applications and challenges. Appl Sci. 2020;10(2):640.

14. Yu Y, Zeng J, Chen C, et al. Three-dimensional compressible and stretchable conductive composites. Adv Mater. 2014;26(5):810-815.

15. Hong S, Lee S, Kim DH. Materials and design strategies of stretchable electrodes for electronic skin and its applications. Proc IEEE. 2019;107(10):2185-2197.

16. Kayser LV, Lipomi DJ. Stretchable conductive polymers and composites based on PEDOT and PEDOT:PSS. Adv Mater. 2019;31(10):1806133.
co solvent engineering in polymer photovoltaic cells. J Mater Chem. 2011;21(13):4927-4936.
35. Thomas JP, Leung KT. Mixed co-solvent engineering of PEDOT:PSS to enhance its conductivity and hybrid solar cell properties. J Mater Chem A. 2016;4(44):17537-17542.
36. Putra IR, Wei TC, Hsiao PH, Chen CY. Simple co-solvent treated PEDOT:PSS films on hybrid solar cells with improved efficiency. IEE J Photonol. 2020;10(3):771-776.
37. Yu Z, Xia Y, Du D, Ouyang J. PEDOT:PSS films with metallic conductivity through a treatment with common organic solutions of organic salts and their application as transparent electrode of polymer solar cells. ACS Appl Mater Interfaces. 2016;8(18):11629-11638.
38. Fan B, Mei X, Ouyang J. Significant conductivity enhancement of conductive poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate) (PEDOT:PSS) films by adding anionic surfactants into polymer solution. Macromolecules. 2008;41(16):5971-5973.
39. Vosgueritchian M, Lipomi DJ, Bao Z. Highly conductive and transparent PEDOT:PSS films with a fluorosurfactant for stretchable and flexible transparent electrodes. Adv Funct Mater. 2012;22(2):421-428.
40. Zhang W, Zhao B, He Z, et al. High-efficiency ITO-free polymer solar cells using highly conductive PEDOT:PSS/surfactant bilayer transparent anodes. Energy Environ Sci. 2013;6(6):1956-1964.
41. Yeon C, Kim G, Lim JW, Yun SY. Highly conductive PEDOT:PSS treated by sodium dodecyl sulfate for stretchable fabric heaters. RSC Adv. 2017;7(10):5888-5897.
42. Fan Z, Du D, Yu Z, Li P, Xia Y, Ouyang J. Significant enhancement in the thermoelectric properties of PEDOT:PSS films through a treatment with organic solutions of inorganic salts. ACS Appl Mater Interfaces. 2016;8(35):23204-23211.
43. Kadem B, Cranton W, Hassan A. Metal salt modified PEDOT:PSS as anode buffer layer and its effect on power conversion efficiency of organic solar cells. Org Electron. 2015;24:73-79.
44. Zhao Z, Wu Q, Xia F, et al. Improving the conductivity of PEDOT:PSS hole transport layer in polymer solar cells via Copper(II) Bromide salt doping. ACS Appl Mater Interfaces. 2015;7(3):1439-1448.
45. Zhu Z, Song H, Xu J, Liu C, Jiang Q, Shi H. Significant conductivity enhancement of PEDOT:PSS films treated with lithium salt solutions. J Mater Sci: Mater Electron. 2015;26(1):429-434.
46. Li X, Liu Z, Zhou Z, et al. Effects of cationic species in salts on the electrical conductivity of doped PEDOT:PSS films. ACS Appl Polym Mater. 2021;3(1):98-103.
47. Marcus Y. On enthalpies of hydration, ionization potentials, and the softness of ions. Thermochim Acta. 1986;104:389-394.
48. Xia Y, Sun K, Ouyang J. Solution-processed metallic conducting polymer films as transparent electrode of optoelectronic devices. Adv Mater. 2012;24(18):2436-2440.
49. Zhang L, Yang K, Chen R, et al. The role of mineral acid doping of PEDOT:PSS and its application in organic photovoltaics. Adv Electron Mater. 2020;6(1):1900648.
50. Kim N, Kee S, Lee SH, et al. Highly conductive PEDOT:PSS nanofibrils induced by solution-processed crystallization. Adv Mater. 2014;26(14):2268-2272.
51. Hosseini E, Kollath VO, Karan K. The key mechanism of conductivity in PEDOT:PSS thin films exposed by anomalous conduction behaviour upon solvent-doping and sulfuric acid post-treatment. J Mater Chem C. 2020;8(12):3982-3990.
52. Wang C, Sun K, Fu J, et al. Enhancement of conductivity and thermoelectric property of PEDOT:PSS via acid doping and single post-treatment for flexible power generator. Adv Sustain Sys. 2018;2(12):1800085.
53. Mengistie DA, Ibrahim MA, Wang PC, Chu CW. Highly conductive PEDOT:PSS treated with formic acid for ito-free polymer solar cells. ACS Appl Mater Interfaces. 2014;6(4):2292-2299.
54. Ouyang J. Solution-processed PEDOT:PSS films with conductivities as indium tin oxide through a treatment with mild and weak organic acids. ACS Appl Mater Interfaces. 2013;5(24):13082-13088.
55. Xia Y, Ouyang J. Significant conductivity enhancement of conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) films through a treatment with organic carboxylic acids and inorganic acids. ACS Appl Mater Interfaces. 2010;2(2):474-483.
56. Fan X, Xu B, Liu S, et al. PEDOT:PSS electrodes using mild acids for high conductivity and improved stability with application to flexible organic solar cells. ACS Appl Mater Interfaces. 2016;8(22):14029-14036.
57. McCarthy JE, Hanley CA, Brennan LJ, Lambertini VG, Gun’ko YK. Fabrication of highly transparent and conducting PEDOT:PSS films using a formic acid treatment. J Mater Chem C. 2014;2(4):764-770.
58. Groenendaal L, Jonas F, Freitag D, Pielartzik H, Reynolds JR. Poly(3,4-ethylenedioxythiophene) and its derivatives: Past, present, and future. Adv Mater. 2000;12(8):481-494.
59. Jonas F, Morrison JT. 3,4-polyethylenedioxythiophene (PEDT): Conductive coatings technical applications and properties. Synth Met. 1997;85(1):1397-1398.
60. Pei Q, Zuccarello G, Ahlskog M, Inganäs O. Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue. Polymer. 1994;35(7):1347-1351.
61. Gueye MN, Carella A, Massonnet N, et al. Structure and dopant engineering in polydop thin films: practical tools for a dramatic conductivity enhancement. Chem Mater. 2016;28(10):3462-3468.
62. Yao H, Fan Z, Li P, et al. Solutionally processed intrinsically conductive polymer films with high thermoelectric properties and good air stability. J Mater Chem A. 2018;6(47):24496-24502.
63. Chen R, Sun K, Zhang Q, et al. Sequential solution polymerization of poly(3,4-ethylenedioxythiophene) using V2O5 as oxidant for flexible touch sensors. JScience. 2019;12:66-75.
64. Murugan AV, Kale BB, Kwon CW, Campet G, Vijayamohan K. Synthesis and characterization of a new organic–inorganic poly (3,4-ethylene dioxythiophene) PEDOT/V2O5 nanocomposite by intercalation. J Mater Chem. 2001;11(10):2470-2475.
65. Guo CX, Sun K, Ouyang J, Lu X. Layered V2O5/PEDOT nanowires and ultrathin nanobelts fabricated with a silk reel-in-like process. Chem Mater. 2015;27(16):5813-5819.
66. Winther-Jensen B, Winther-Jensen O, Forsyth M, MacFarlane DR. High rates of oxygen reduction over a vapor phase–polymerized PEDOT electrode. Science. 2008;321(5889):671-674.
OUYANG

79. Kovacik P, del Hierro G, Livernois W, Gleason KK. Scale
82. Drewelow G, Song HW, Jiang ZT, Lee S. Factors controlling
81. Gharahcheshmeh MH, Robinson MT, Gleason EF,
67. Laforgue A, Robitaille L. Production of conductive PEDOT
80. Wu D, Zhang J, Dong W, et al. Temperature dependent
81. Wang W, Xu D, Huang A, et al. Controllable vapor phase
74. Evans D, Fabretto M, Mueller M, Zuber K, Short R,
75. Li B, Lopez-Beltran H, Siu C, et al. Vapor phase polymerized
72. Li B, Skorenko KH, Qiu H, et al. Effects of interfacial
81. Li B, Lopez-Beltran H, Siu C, et al. Vaper phase polymerized
85. Chen H W, Lee J H, Lin B Y, Chen S, Wu S T. Liquid crystal
81. Jang H, Kim MS, Jang W, Son H, Wang DH, Kim FS. Highly
89. Ouyang J, Chu CW, Chen F, Xu Q, Yang Y. Highly conductive
97. Hu X, Meng X, Zhang L, et al. A mechanically robust conducting
98. Lee JW, Heo JH, Im SH, Park OO. Reproducible dry stamping
93. Jamal MS, Bashar MS, Hasan AKM, et al. Fabrication techniques
95. Li X, Chen W, Wang S, et al. One-source strategy boosting
doped-hole free transport layers for highly efficient and stable
70. Wang W, Xu D, Huang A, et al. Controllable vapor phase
76. Rosseel T, Detry J M, Vanmechelen E, et al. Effect of structure
directed growth of high conductivity PEDOT from liquid-like oxant layers during vacuum vapor phase polymerization. J Mater Chem. 2012;22(30):14889-14895.
77. Brooke R, Franco-Gonzalez JF, Wijeratne K, et al. Vapor phase synthesized poly(3,4-ethylenedioxythiophene)-trifluoromethanesulfonate as a transparent conductor material. J Mater Chem A. 2018;6(43):21304-21312.
78. Cho B, Park KS, Baek J, Oh HS, Lee YEK, Sung MM. Single-crystal poly(3,4-ethylenedioxythiophene) nanowires with ultrahigh conductivity. Nano Lett. 2014;14(6):3321-3327.
79. Kovacik P, del Hierro G, Livernois W, Gleason KK. Scale-up of oCVD: Large-area conductive polymer thin films for next-generation electronics. Mater Horiz. 2015;2(2):221-227.
80. Wang X, Zhang X, Sun L, et al. High electrical conductivity and carrier mobility in oCVD PEDOT thin films by engineered crystallization and acid treatment. Sci Adv. 2018;4(9):eaat5790.
81. Gharahcheshmeh MH, Robinson MT, Gleason EF, Gleason KK. Optimizing the optoelectronic properties of face-on oriented poly(3,4-ethylenedioxythiophene) via water- assisted oxidative chemical vapor deposition. Adv Funct Mater. 2021;31(14):2008712.
82. Drewelow G, Song HW, Jiang ZT, Lee S. Factors controlling conductivity of PEDOT deposited using oxidative chemical vapor deposition. Appl Surf Sci. 2020;501:144105.
83. Mirabedin M, Vergnes H, Caussé N, Vahlas C, Caussat B. An out of the box vision over oxidative chemical vapor deposition of PEDOT involving sublimed iron trichloride. Synth Met. 2020:266:116419.
84. Volk AA, Kim JS, Jamir J, Dickey EC, Parsons GN. Oxidative molecular layer deposition of PEDOT using volatile antimony(V) chloride oxidant. J Vac Sci Technol A. 2021;39(3):032.
85. Chen HW, Lee JH, Lin BY, Chen S, Wu ST. Liquid crystal display and organic light-emitting diode display: Present status and future perspectives. Light: Sci Appl. 2018;7:17168.
86. Kang HS, Kim DH, Kim TW. Organic light-emitting devices based on conducting polymer treated with benzoic acid. Sci Rep. 2021;11:3885.
87. Song W, Fan X, Xu B, et al. All-solution-processed metal-oxide-free flexible organic solar cells with over 10% efficiency. Adv Mater. 2018;30(26):1800075.
88. Ouyang J, Chu CW, Chen F, Xu Q, Yang Y. Highly conductive PEDOT:PSS film and its applications in optoelectronic devices. Adv Funct Mater. 2005;15(2):203-208.
89. Fang J, Kim MS, Jang W, Son H, Wang DH, Kim FS. Highly conductive PEDOT:PSS electrode obtained via post-treatment with alcoholic solvent for ITO-free organic solar cells. J Ind Eng Chem. 2020;86:205-210.
90. Cao D, Song Y, Peng J, et al. Interface bonding engineering of a transparent conductive electrode towards highly efficient and mechanically flexible ITO-free organic solar cells. J Mater Chem A. 2019;7(18):11460-11467.
91. Zhang J, Liu F, Chen S, Yang C, Zhu X, Zhu D. High-performance polymer solar cells achieved by introducing side chain heteroatom on small-molecule electron acceptor. Macromol Rapid Commun. 2019;40(1):1800393.
92. Yan C, Barlow S, Wang Z, et al. Non-fullerene acceptors for organic solar cells. Nat Rev Mater. 2018;3(3):18003.
93. Liu M, Johnston MB, Snaith HJ. Efficient planar heterojunction perovskite solar cells by vapour deposition. Nature. 2013; 501(7467):395-398.
94. Jamal MS, Bashar MS, Hasan AKM, et al. Fabrication techniques and morphological analysis of perovskite absorber layer for high-efficiency perovskite solar cell: A review. Renew Sustain Energy Rev. 2018;98:469-488.
95. Li X, Chen W, Wang S, et al. One-source strategy boosting dopant-free hole transporting layers for highly efficient and stable CsPbI2Br perovskite solar cells. Adv Funct Mater. 2021;31(21):2010696.
96. Sun K, Li P, Xia Y, Chang J, Ouyang J. Transparent conductive oxide-free perovskite solar cells with PEDOT:PSS as transparent electrode. ACS Appl Mater Interfaces. 2015;7(26):15314-15320.
97. Hu X, Meng X, Zhang L, et al. A mechanically robust conducting polymer network electrode for efficient flexible perovskite solar cells. Joule. 2019;3(9):2205-2218.
98. Lee JW, Heo JH, Im SH, Park OO. Reproducible dry stamping transfer of PEDOT:PSS transparent top electrode for flexible semitransparent metal halide perovskite solar cells. ACS Appl Mater Interfaces. 2020;12(9):10527-10534.
99. Gueye MN, Carella A, Demadrille R, Simonato JP. All-polymeric flexible transparent heaters. ACS Appl Mater Interfaces. 2017; 9(32):27250-27256.
100. He H, Zhang L, Yue S, Yu S, Wei J, Ouyang J. Enhancement in the mechanical stretchability of PEDOT:PSS films by compounds of multiple hydroxyl groups for their application as transparent stretchable conductor. Macromolecules. 2021;54(3):1234-1242.
to provide context to potential health effects. *ACS Nano*. 2017;11(9):8849-8863.

137. Kim T, Park J, Sohn J, Cho D. Jeon S. Bioinspired, highly stretchable, and conductive dry adhesives based on 1D–2D hybrid carbon nanocomposites for all-in-one ECG electrodes. *ACS Nano*. 2016;10(4):4770-4778.

138. Chun S, Kim DW, Baik S, et al. Conductive and stretchable adhesive electronics with miniaturized octopus-like suckers against dry/wet skin for biosignal monitoring. *Adv Funct Mater*. 2018;28(32):1805224.

139. Chandra D, Yang S. Stability of high-aspect-ratio micropillar arrays against adhesive and capillary forces. *Acc Chem Res*. 2010;43(8):1080-1091.

140. Bihar E, Roberts T, Saadaoui M, Hervé T, De Graaf JB, Malliaras GG. Inkjet-printed PEDOT:PSS electrodes on paper for electrocardiography. *Adv Healthc Mater*. 2017;6(6):1601167.

141. Zucca A, Cipriani C, Tarantino S, et al. Tattoo conductive polymer nanosheets for skin-contact applications. *Adv Healthc Mater*. 2015;4(7):983-990.

142. Zhang L, Kumar KS, He H, et al. Fully organic, skin-compliant, self-adhesive and stretchable dry electrodes for long-term motion-robust epidermal biopotential monitoring. *Nat Commun*. 2020;11:4683.

143. Green R, Abidian MR. Conducting polymers for neural prosthetic and neural interface applications. *Adv Mater*. 2015;27(46):7620-7637.

144. Cui X, Wiler J, Dzaman M, Alschuler RA, Martin DC. In vivo studies of polypyrrole/peptide coated neural probes. *Biomaterials*. 2003;24(5):777-787.

145. Bidez PR, Li S, Macdiarmid AG, Venancio EC, Wei Y, Lelkes PI. Polyaniline an electroactive polymer, supports adhesion and proliferation of cardiac myoblasts. *J Biomat Sci Polym Ed*. 2006;17(1-2):199-212.

146. Wang LC, Wang MH, Ge CF, et al. The use of a double-layer platinum black-conducting polymer coating for improvement of neural recording and mitigation of photoelectric artifact. *Biosens Bioelectron*. 2019;145:111661.

147. Wei B, Liu J, Ouyang L, Kuo CC, Martin DC. Significant enhancement of PEDOT thin film adhesion to inorganic solid substrates with EDOT-acid. *ACS Appl Mater Inter faces*. 2015;7(28):15388-15394.

148. Ouyang L, Wei B, Kuo CC, Pathak S, Farrell B, Martin DC. Enhanced PEDOT adhesion on solid substrates with electrografted (PEDOT-NH₂). *Sci Adv*. 2017;3e1600448(3).

149. Richardson-Burns SM, Hendrickx JL, Martin DC. Electrochemical polymerization of conducting polymers in living neural tissue. *J Neural Eng*. 2007;4(2):L6-L13.

150. Irfan MS, Gill YQ, Ullah S, Naeem MT, Saeed F, Hashmi M. Polyaniline-NBR blends by in situ polymerization: application as stretchable strain sensors. *Smart Mater Struct*. 2019;28(9):095024.

151. Tjahyono AP, Aw KC, Tracas-Sejdic J. A novel polypyrrole and natural rubber based flexible large strain sensor. *Sens Actuat B Chem*. 2021;316:34-437.

152. Losaria PM, Yim JH. A highly stretchable large strain sensor based on PEDOT-thermoplastic polyurethane hybrid prepared via in situ vapor phase polymerization. *J Ind Eng Chem*. 2019;74:108-117.

153. Liu N, Fang G, Wan J, Zhou H, Long H, Zhao X. Electrospun PEDOT:PSS–PVA nanofiber based ultrahigh-strain sensors with controllable electrical conductivity. *J Mater Chem*. 2011;21(47):18962-18966.

154. Fan X, Xu B, Wang N, et al. Highly conductive stretchable all-plastic electrodes using a novel dipping-embedded transfer method for high-performance wearable sensors and semi-transparent organic solar cells. *Adv Electron Mater*. 2017;3(5):1600471.

155. Fan X, Wang N, Wang J, Xu B, Yan F. Highly sensitive, durable and stretchable plastic strain sensors using sandwich structures of PEDOT:PSS and an elastomer. *Mater Chem Front*. 2018;2(2):355-361.

156. Vertuccio L, Guadagno L, Spinelli G, Lamberti P, Tucci V, Russo S. Piezoresistive properties of resin reinforced with carbon nanotubes for health-monitoring of aircraft primary structures. *Compos B Eng*. 2016;107:192-202.

157. Zhu JW, Zhang B, Li RKY, Dang AM. High-performance strain sensors based on functionalized graphene nanoplates for damage monitoring. *Compos Sci Technol*. 2016;123:32-38.

158. Zhan Z, Lin R, Tran VT, et al. Paper/carbon nanotube-based wearable pressure sensor for physiological signal acquisition and soft robotic skin. *ACS Appl Mater Interfaces*. 2017;9(43):37921-37928.

159. Zhang L, Li J, Yue S, He H, Ouyang J. Biocompatible blends of an intrinsically conducting polymer as stretchable strain sensors for real-time monitoring of starch-based food processing. *Adv Funct Mater*. 2021;31(30):2102745.

160. Zhu F. Influence of ingredients and chemical components on the quality of Chinese steamed bread. *Food Chem*. 2014;163:154-162.

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