PEDOT: Fundamentals and Its Nanocomposites for Energy Storage

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Abstract  PEDOT, or poly(3,4-ethylenedioxythiophene), is among the most successful conducting polymer products because of its stable conductivity, colloidal processability, and rich assembly behavior. Since the very first patents on PEDOT filed in 1988, the material has been widely explored for decades in many applications. In this review, a comprehensive summary on the synthesis, processing and post-treatment of PEDOT will be presented for the sake of the discussion on PEDOT and its nanocomposites for energy storage. Knowing what PEDOT lends itself to the electrode materials is of importance to the rational design of energy storage devices that maximize the real-world performance. Based on these discussions, a roadmap for the development of PEDOT as promising multifunctional electrode component is presented.

Keywords  PEDOT; Energy storage; Nanomaterials; Capacitor; Battery

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INTRODUCTION

The practice of electropolymerizing aniline was reported as early as 1862,[11] and the product, polyaniline, has been studied over 150 years as one of the most important conducting polymers.[12,13] However, it was not until 1977 that the story of conducting polymers started officially when polyacetylene films were shown to experience a metal-insulator transition at dopant concentration around 1%.[14] The methodology established in those seminal papers was employed to create profuse conducting polymers by the synthesis and doping of conjugated polymers, such as polypyrrole,[6] polythiophene,[7] and polyaniline.[11] Nevertheless, one major challenge posed in front of the commercialization of conducting polymers is the insufficient half-life for conductivity originated from the poor stability of doped states.[8] The problem was not solved until the invention of PEDOT in late 1980s,[9] the best conducting polymer products ever; and from that point the technical situation was dramatically changed.

Based on the environmentally stable electrical behavior of PEDOT,[8,11] it has been continuously explored in almost all possible applications (Fig. 1): electrode materials,[10] including capacitors, batteries, and transparent conductive films; hole injecting materials in organic light emitting diodes[11] and organic field-effect transistors;[12] electrochromic materials;[13] functional coatings (e.g., antistatic coatings[14]); etc. The prerequisite of these applications is the abundant choices for the fabrication of PEDOT incorporated assemblies, involving fibers,[15] thin films,[16] and three-dimensional bulks[17] from both the in situ polymerization and post processing. At the core of PEDOT story, the delicate design of the molecular and crystalline architecture is what the whole PEDOT industry and research predicate on (Fig. 1), and it will be presented in this review as the backgrounds which are definitely critical for the understanding on all materials performance.

In this review we specifically focus on PEDOT nanocomposites for energy storage applications. In fact, energy storage based on conducting polymer materials like pseudocapacitive polyaniline is continuously studied and reviewed.[18-21] However, for one of the most stable conducting polymers—PEDOT, the systematic and in-depth review on the optimization of basic properties and device structure is still embraced, and we will show that PEDOT is a multifunctional material in energy storage devices and it is very promising for future explorations. For example, in electrochemical capacitors a representative composition of active carbon (AC)-based electrodes includes AC powders as active materials, Super-P™ as conductive fillers and polytetrafluoroethylene (PTFE) as binders,[22] what absolutely incredible is that PEDOT could function in energy storage devices as all the above components and plus, the current collector. In essence, the versatility of PEDOT is the result of the basic properties, e.g., stable conductivity and processability with the micellar system containing poly(styrene sulfonate) (PSS), which will be discussed through the review from the fundamental understanding to the prospective on optimizing related performances. The fabrication of PEDOT nanocomposites electrodes will be discussed based on the different synthesis pathways: in situ interfacial polymerization or colloidal mixing strategy, and the two methods both apply to solid electrolyte capacitors, electrochemical capacitors and batteries.
PEDOT: INVENTION, SYNTHESIS AND PROCESSING

The invention of PEDOT is not an overnight success, but full of laborious efforts. The initial compulsion to develop a successful conducting polymer product led to many attempts conducted by scientists from Bayer AG (Fig. 2), first on polypyrrole 2, then on polyacetylene 1. However, these projects were forced to terminate quickly because of either the potential risks of monomers (toxicity and volatility) or the instability of polymer products. From 1980s, the polycondensates workgroup in Bayer AG started the exploration on polythiophene 3. Unfortunately, the products also displayed poor stability in ambient environment resulted from the dedoping process.

One possible approach to enhance the environmental stability of doped state is derivation. Scheme 1 shows the doped state of these polythiophene structure; the introduction of alkyl, especially alkoxy substituents (4 and 5) stabilizes the bipolaron structure. Moreover, these 3,4-disubstituted monomers also ensured the stereoregular polymerization, without the formation of branched structure via aβ-coupling. Prior to the invention of PEDOT, Hoechst AG obtained licensing of patent rights on alkoxide-substituted polythiophene, but the stability of these conducting polymers at doped state was also not satisfactory. Bayer AG scientists did is truly innovative and revolutionary: they introduced bicyclic ring systems to substituted polythiophene (6–8, Fig. 2). This unique rigid structure not only stabilizes the bipolaron, but also makes the planar crystalline phase more stable. Dioxolane derivative (3,4-ethylenedioxythiophene, EDOT, 7) then came in sight and thanks to the well-established synthesis protocol, scientists in Bayer AG succeeded. On April 22, 1988, the patent of PEDOT by Jonas, Heywang, and Schmidtberg was approved. The stability of doped PEDOT was later shown to be pronounced: conductivity of PEDOT film was largely retained after 1000 h aging test at 125 °C in air or 85% RH (85 °C).

Synthesis approach of EDOT monomer is simple and efficient from thioglycolic acid (Scheme 2a) and after optimization of production line, multi-ton scale of EDOT was produced annually by Bayer AG in 1990s. Polymerization of EDOT is also not complicated; generally, oxidative chemical polymerization and electrochemical polymerization are two mostly applied methods for preparing PEDOT.

The mechanism underlying the polymerization is similar to that for thiophene and pyrrole, i.e., the formation of radical cation as the very first step for the overall polymerization process (Scheme 2b). This step is rate-determining. In contrast, the following steps, i.e., coupling of radical cations (typically k ~ 10^8 L·mol⁻¹·h⁻¹) and the oligomer oxidation (for dimer, k ~ 10^3 L·mol⁻¹·h⁻¹) are considerably fast. Dimerization of EDOT catalyzed by acid is a side reaction similar to thiophene chemistry (Scheme 2b), and this might be the competition reaction during the polymerization because that H⁺ is released after coupling. Therefore, the low degree of polymerization (DP) induced by this side reaction in for instance, Fe(III) p-toluenesulfonate (Fe(Tos)_3) oxidation system, could be improved by the addition of organic base (e.g., imidazole). Nevertheless, this consensus was also achieved after a long debate the lowered polymerization rate resulted from the reduced reactivity of Fe(III) either by the increase of pH or coordination binding as the reason for higher DP was ruled out by very carefully designed control experiments. The optimization of this polymerization procedure, consequently, produced PEDOT materials with superior conductivity which will be discussed in the next part.

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Then we move to available reaction set-ups for the polymerization of EDOT (Fig. 3). Generally, EDOT monomers are prone to be polymerized under a relatively low oxidation potential\textsuperscript{32}. Chemical oxidants such as Fe(III) salts,\textsuperscript{31} Cu(II) salts,\textsuperscript{39} Ce(IV) salts,\textsuperscript{40} manganese dioxide,\textsuperscript{41} peroxides (technically important agent peroxodisulfates\textsuperscript{14,42}), and hypervalent iodine compounds\textsuperscript{43} or anode potential\textsuperscript{32} between 0.7 and 1.3 V versus Ag/AgCl could be implemented to the synthesis of PEDOT. These reactions are normally taken in organic media\textsuperscript{31} like propylene carbonate or acetonitrile due to the poor solubility of EDOT in aqueous system. However, in the presence of surfactants, oxidation polymerization of

**Scheme 1** Resonance structures of (a) alkyl- and (b) alkoxy-substituted polythiophene bipolaron (only one structural unit is shown). The bipolaron structure is more stable when alkoxy group is introduced because of the more available resonance structures in (b).

**Scheme 2** (a) Synthesis protocol of EDOT, which is first established in Ref. \textsuperscript{30}. (b) Mechanism of oxidation polymerization of EDOT, in which a competition reaction (dimerization of EDOT catalyzed by proton acid) is shown.
EDOT could also be conducted in aqueous media. The practical problem existing in these dispersion or micellar media reaction is the formation of insoluble PEDOT powders or thin films on working electrode (Fig. 3a) which is not compatible with the post-processing or fabrication of PEDOT nanocomposites.

Development of in situ polymerization and vapor deposition polymerization (VDP) provides technically significant solutions to the preparation of PEDOT functional (composite) materials. In situ polymerization herein is defined as the direct polymerization of EDOT at interfaces or template molecules from dispersion usually along with the evaporation of solvents (Fig. 3b). Normally these systems are composed of oxidants and solvents after the addition of EDOT monomers, the mixture is processed on desired substrates or interfaces by spin casting or other methods before the gelation occurs. A special type of in situ polymerization is the template-assisted polymerization, in which PSS polyelectrolyte acts as the template for the growth of PEDOT and Na$_2$S$_2$O$_8$ as oxidant, producing processable PEDOT dispersions with PSS as stabilizer and dopant. Correspondingly, the commercial form of PEDOT products is PEDOT:PSS micellar system, currently under the trade name Clevios(TM) from Heraeus GmbH. Another strategy is VDP that eliminates the use of solvents and directly grows PEDOT crystalline phase at solid interfaces (Fig. 3c). In this approach EDOT monomers are vaporized and introduced into the deposition chamber with oxidants either on the substrate or in the vapor phase. The products have much higher crystalline degree and could be controlled to form thin films or nanofibrils under different deposition conditions. Furthermore, the highest conductivity till now (6259 S·cm$^{-1}$) in PEDOT films was achieved by optimizing the interconnection between PEDOT nanocrystals grown via VDP method.

Processing of PEDOT materials is exclusively based on PEDOT:PSS dispersion. Two major types of processing are employed to prepare PEDOT incorporated devices: bulk processing based on the shaping of PEDOT:PSS dispersion and the blending in colloidal system with nanomaterials. The first type involves coating techniques (dip, spray, spin, and blade), printing techniques (inkjet, screen, and gravure etc.) and recently developed gelation techniques which are very useful in the design and fabrication of thin films or patterned device structure. The latter is frequently employed to prepare PEDOT nanocomposites with metal oxides nanocrystal, two-dimensional materials, amorphous materials or molecular compounds (e.g., organic small molecules). We will discuss these processing techniques later in the part for energy storage devices with PEDOT nanocomposites.

**PEDOT: CONDUCTIVITY AND CAPACITIVE BEHAVIOR**

Without doubt understanding on the conductivity and capacitice behavior of PEDOT materials is crucial for the optimization on the performance of related PEDOT nanocomposites. In fact, in a majority of works commercialized PEDOT:PSS was employed as the starting material for the fabrication of electrode materials in energy storage devices. Therefore, the discussion on the conductivity issue will begin with PEDOT:PSS systems.

PEDOT:PSS dispersion is a typical micellar system, which consists of PEDOT polycations and PSS polyanions. We have mentioned before that PEDOT has a rigid bicyclic structure unlike flexible PSS chains; simultaneously, the mismatch of charges per unit length between PEDOT (one charge for unlike flexible PSS chains; simultaneously, the mismatch of charges per unit length between PEDOT (one charge for PEDOT and two charges for PSS) is the main drawback of PEDOT:PSS as an electrode material. Moreover, PEDOT:PSS is a weak electrolyte, the concentration of charge carriers is limited and the dissociation of PSS is very slow. In PEDOT:PSS, the dissociation of PSS is limited and the concentration of charge carriers is limited. The dissociation of PSS is very slow, the mobility of charge carriers is also low. Therefore, the conductivity of PEDOT:PSS is very low.

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ively poor especially when compared with oCVD grown PEDOT crystals, (2) PEDOT-rich domains are separated by PSS-rich domains. These two features are shown in the past twenty years to be responsible for the relatively poor conductivity and lots of post-treatment methods were proposed to improve the performance of assemblies processed from PEDOT:PSS.

These post-treatments were referred to as secondary doping, which was conceptualized by MacDiarmid et al. in the research on polyaniline. Different from primary doping, secondary doping produces permanent effects on the increase of conductivity, even with the dopants removed. Briefly, secondary dopants mainly function by initiating changes in the composition and microstructure of conducting polymers, whereas primary doping only introduces charges on the polymer chain. In PEDOT:PSS system, secondary dopants were found to influence significantly the crystallinity and counterions, which brings improvement in conductivity. Major dopants share the common features including high boiling point (bp), high dielectric constant (polarity), and good solubility in water; and the examples are: polyols (glycerol, ethylene glycol, sorbitol, etc.), high bp solvents (dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), acetonitrile, etc.), and polar solvents (alcohols, tetrahydrofuran (THF) etc.).

Generally, the secondary dopants are added to PEDOT:PSS system and the colloidal dispersion is subsequently coated to the substrate. During the drying process (Fig. 4b), as water is evaporated from the system, high bp or polar dopants are concentrated to induce the phase separation between PSS-rich and PEDOT-rich domains by swelling PSS phase and then the conducting networks form, in which the positive Gibbs energy in original emulsion system is compensated. In contrast, drying process without the presence of high bp agents lacks enough time to reach a thermodynamic equilibrium state, namely, in dried films the PEDOT-rich cores are still separated, and this will have impact on the conductivity behavior. Basically, conductivity in PEDOT:PSS system mainly conforms to variable range hopping (VRH) transport model,

$$ R(T) = R_0 \exp \left[ \frac{T_0}{T} \right] $$

where $R$ is the resistance ($R_0$ is the value at infinite temperature) and $T$ stands for temperature (K). $T_0$ is the energy barrier between localized states that is inversely proportional to localization length $\xi$ and density of states $N(\xi)$. The phase separation in PEDOT:PSS has shown to increase $\xi$ and make the conductivity higher at specific temperature. Furthermore, Kemerink et al. also showed that the VRH transport could change from 3D model ($\alpha \approx 0.25$) in pristine PEDOT:PSS to quasi-1D model ($\alpha \approx 0.5$) in secondary doped samples, which could be explained from the elongated chain morphology caused by phase segregation.

In addition to the pre-mixing and coating procedure, post-treatment using secondary dopants was also frequently employed. In these practices, a special type of secondary dopant is sulfuric acid, and as an inorganic strong acid, it has the power to protonate PSS chains and further replace PSS in PEDOT-rich cores (Fig. 4c). We have shown in Fig. 4a that the mismatch in both chain flexibility and charge density leads to the poor crystallinity in PEDOT phase, but when PSS counterions are replaced by small anions, higher order crystalline phase could form. Lee et al. reported the highest conductivity value in $H_2SO_4$ processed PEDOT:PSS films (4380 $S \cdot cm^{-1}$). They found that in the presence of concentrated $H_2SO_4$, PSS components were significantly reduced and PEDOT chains assembled to fibrous crystalline structure spontaneously. It is also worth noting that secondary dopants could be used not only to improve the conductivity, but also for the gelation of PEDOT:PSS dispersion (e.g., $H_2SO_4$, DMSO, and metal ions due to the cross-linking effects.
by expanded PEDOT-rich domains.

We have discussed the structural characteristics in PEDOT:PSS and the related secondary doping approaches for the enhancement in conductivity. Now we turn to the conductivity behavior in other PEDOT systems. As mentioned before, the charge transport in PEDOT:PSS follows a VRH model because of the existence of thick PSS layers between PEDOT crystalline region. However, this model is possibly not applicable in PEDOT with small counterions. Simonato et al. presented a comprehensive analysis on the conductivity of in situ polymerized PEDOT:trifluoromethanesulfonate (OTf) films. The authors found that the prepared PEDOT films do not conform to VRH transport model for the nonzero conductivity at $T \to 0$ K, rather to follow a metallic conductivity behavior that is rare in polymeric materials.

In this example, secondary dopants N-methyl-2-pyrrolidone (NMP) and $H_2SO_4$ were also used in the synthesis and post-treatment steps, respectively. NMP was proved to improve the crystallinity of PEDOT, which led to the quasi-1D metallic conductivity of $8 \times 10^4$ S·cm$^{-1}$ inside PEDOT grains. On the other side, $H_2SO_4$ treatment was proved to have no impact on crystallinity, but it improved the disordered metallic charge transport in amorphous region greatly, henceforth making the conductivity higher (up to 5400 S·cm$^{-1}$). Other than the delicate control on the microstructure of crystalline and amorphous phase, alignment and orientation of PEDOT crystalline phase were also demonstrated to influence the carrier mobility in PEDOT materials. For instance, Gleason et al. reported that the face-on stacking configuration in polycrystalline PEDOT:Cl thin films could maximize the carrier mobility and therefore the conductivity.

As a summary of the discussion on conductivity of PEDOT materials, we put a broad comparison of the conductivity values for different PEDOT systems in Fig. 5. At the top of the plot, single-crystal PEDOT nanowire holds the highest conductivity: 8797 S·cm$^{-1}$, then the polycrystalline phase in which interface as barriers lowered the conductivity. PEDOT:PSS systems could be doped using high bp agents, polar solvents or proton acids to achieve conductivity of several thousand S·cm$^{-1}$. At the same time, PEDOT bipolaron could also undergo dedoping to give insulating neutral materials. The highly tunable conductivity in PEDOT materials should be promising for the design of functional devices.

For energy storage applications, one of the most important properties of electrode materials is capacitive behavior. Generally, the electrical conductivity reflects the electron transport which is critical to the availability of electrochemical interface and ion transport dictates the accessibility and rate of the electrochemical process. Capacitor behavior is manifested in the electrochemical reaction at these interfaces that mainly comprises two types: the electric double-layer (EDL) adsorption of ions and the redox reaction (pseudocapacitive or battery-type reactions). In this part we mainly focus on the capacitive behavior of PEDOT, and in the following part the architecture of electrodes that is important to the ion transport will be considered.

In conducting polymers, both pseudocapacitive and EDL behavior...
capacity could contribute to the electrochemical activity.\cite{18} Pseudo-capacity mainly originates from doping and dedoping of conducting polymers, which is well-characterized in polyaniline.\cite{51} EDL capacity stems from the adsorption of ions on conducting polymer surface, and for all electrode materials this type of capacity is available. PEDOT is presenting both of the behaviors in energy storage systems; however, which one is dominant is still without a consensus.\cite{83,85} The typical cyclic voltammetry of PEDOT:PSS thin films in 0.1 mol·L\(^{-1}\) KCl electrolyte is shown in Fig. 6.\cite{82} In which the potential window of PEDOT (> 1.2 V) is much larger than that of polyaniline and polypyrrole. Peaks located at −0.7 V (versus Ag/AgCl) are attributed to the injection of holes/electrons (forward/backward) into the electrode\cite{85} and this corresponds to the \(p\)-type doping/ dedoping of PEDOT chains. The capacity in the range of −0.3−0.5 V was traditionally attributed to the redox reaction of PEDOT but shown by Zozoulenko et al.\cite{82} that a pure electron/ion diffusion at PEDOT domains and the PSS domains could also result in such capacitive behavior. Similar trends were also observed in \textit{in situ} polymerized PEDOT,\cite{84} and the redox peaks are not conspicuous as polyaniline and polypyrrole at a large range of potential window.

Based on the discussion above, PEDOT is not a characteristic pseudocapacitive-type material for the specific capacity is relatively low (theoretical value 210 F·g\(^{-1}\)) when compared with e.g., polyaniline (720 F·g\(^{-1}\) by theory).\cite{18} The major capacitive features of PEDOT are the fast electrochemical response resulted from high electrical conductivity and broad potential window. The former is used to build high rate electrochemical capacitor for line-filtering applications\cite{91} and the latter is promising for the construction of asymmetric capacitor devices.\cite{84} Another important advantage of incorporating PEDOT into the energy storage device is the pronounced electrochemical stability, which is attributed to the excellent stability of bipolaron structure. In the next part we will go through the typical energy storage systems based on PEDOT nanocomposites, from the fabrication strategies to the specific applications.

**PEDOT AND ITS NANOCOMPOSITES FOR ENERGY STORAGE**

PEDOT in nanocomposite electrode materials takes four roles: current collector, active materials, conductive fillers and binders. These roles deeply rely on the excellent electrical conductivity, stable electrical performance and the interfacial properties in composites such as PEDOT:PSS. In this part we will discuss major types of energy storage devices that employ PEDOT nanocomposites based on the classification of different electrode fabrication methods.

**Polymerization of EDOT in Nanomaterials Architecture**

Polymerization of EDOT in nanomaterials architecture includes both the \textit{in situ} oxidation or electrodeposition of EDOT in colloidal system\cite{84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99,100} and the VDP growth of polycrystalline PEDOT (Fig. 7),\cite{90,100} and it is a widely employed strategy for the construction of PEDOT nanocomposites for energy storage applications. Normally, EDOT could be polymerized both on the surface of 0D\cite{85,86,92,93,94,95,96,97,98,99,100} or in the nanoconfinement interface in a template architecture.\cite{93,94} \textit{In situ} polymerizations of EDOT on the surface of colloidal sulfur,\cite{85} Prussian nanocrystals,\cite{86} silicon nanowires,\cite{87} vanadium pentoxide (\(V_{2}O_{5}\)) nanowires,\cite{88} reduced graphene oxide (rGO) sheets,\cite{84,90} and layered double hydroxide (LDH) sheets\cite{92} were reported for the construction of electrochemical capacitors and battery systems (Fig. 7a); and the examples of polymerization in nanoconfined space include alumina-templated growth of PEDOT nanowires,\cite{93,94} and formation of semi-penetrating networks with poly(ethylene oxide) (PEO) (Fig. 7b).\cite{98} A special compositing technique was developed for MnO\(_{2}\)/PEDOT (Fig. 7c): the \textit{in situ} reduction of KMnO\(_{4}\) at PEDOT surface could introduce MnO\(_{2}\) nanocrystals without a conspicuous oxidation damage.\cite{86,94} As for VDP growth of crystalline PEDOT, porous materials like cellulose paper\cite{99} or droplet containing FeCl\(_{3}\) nanocrystal\cite{100} could be used as substrates (Fig. 7d); these methods are simple and elegant for the fabrication of PEDOT electrodes.

Performing the \textit{in situ} polymerization is discussed in the synthesis of PEDOT. Either electrochemical deposition using nanomaterials as anodes\cite{84,85,86,87,88,91,92,93,94,95} or the \textit{in situ} chemical oxidation\cite{85,86,88,90,91,92,93} could be employed. The reaction media might be both organic and aqueous systems containing surfactants, and note that if chemical polymerization ap-

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**Fig. 6** Cyclic voltammetry of PEDOT:PSS thin films: (a) experimental results in 0.1 mol·L\(^{-1}\) KCl and (b) simulation results using a two-phase, 2D modeling approach. (Reproduced with permission from Ref. \cite{82}; Copyright (2017) Wiley-VCH.)

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Conductive fillers

Generally, in electrochemical capacitors, the combination of PEDOT with pseudocapacitive-type materials such as metal oxides/hydroxides (MnO₂, LDH),[86,92,94] small organic molecules,[58] and some of the covalent organic framework (COF)[97] materials provides a solution for the poor electrical conductivity of these electrochemical active species, making more electrochemical interfaces available for the charge storage. For instance, hematite (α-Fe₂O₃) is a pseudocapacitive material with poor conductivity (ca. 10⁻¹⁴ S·cm⁻¹),[96] which will severely deteriorate both the power and energy density of the device. Lu et al.[96] developed an in situ polymerization method on the surface of Ti-doped hematite for the preparation of core/shell hematite/PEDOT nanocomposites that exhibit significantly improved electrochemical performance (Figs. 8a and 8b). On the other hand, however, as the active material despite that PEDOT has the promising electrical conductivity, the ionic conductivity should also be improved. Smoukov et al.[95] designed a semi-penetrating network of PEDOT and PEO by polymerizing EDOT monomers in cross-linked PEO matrix, and in this prototype the excellent ion mobility and soft nature of PEO chains bring improvement on the capacitance, cycling stability and flexibility of the device.

Binders

As for battery systems, one of the major challenges for the poor cycling stability is the loss of mechanical integrity of the active materials during repeated volumetric change.[58] A typical example is alloying anodes in lithium-ion battery (LIB). The most promising candidate—silicon,[102] has a theoretical Li storage capacity that is over ten times higher than that of graphite anodes but also coupled with up to 400% volume expansion during the lithiation process. Consequently, the destructive mechanical stress could cause fracture of brittle silicon anodes, which leads to the deterioration of the device performance. Cui et al.[87] employed in situ electropolymerized PEDOT as the protective coating for Si nanowire anodes (Figs. 8c–8e), and for both its functions of mechanical protection and electrical connection, the LIB device with PEDOT showed 80% capacity retention after 100 cycles, in a sharp contrast to only 30% retention of pure Si nanowire anodes.

Another than the improvement of mechanical integrity in electrode materials, PEDOT coatings have another important function in an exclusive battery system—Li-S batteries.[103] Sulfur as a promising high capacity cathode material over binary or ternary metal oxides in traditional LIBs also has disadvantages such as the diffusion and shuttling of polysulfides in the battery.[103] Wang et al.[96] therefore explored the potential of PEDOT coating to minimize the diffusion of polysulfides entrapped in Prussian blue nanocubes (Figs. 8f and 8g). They found that PEDOT provides further physical confinement together with chemical bonding effects which significantly reduce the shuttling of polysulfides and the nanocomposites electrodes presented an exceptional Coulomb efficiency even after 200 cycles.

Colloidal Processing of PEDOT in the Presence of PSS for Nanocomposites Electrodes

The requirement for a facile fabrication technology of conducting polymer or its nanocomposites electrode is satisfied in PEDOT materials because of the mature colloidal processable PEDOT:PSS dispersion products.[50,51,54,55,58,104−110] Basically, a vast array of nanomaterials, including 2D materials (rGO)[54,104,105] MXene[106] etc.), powder and nanocrystals (ruth-

![Fig. 7 General strategies for the fabrication of PEDOT nanocomposites. (a) In situ polymerization of PEDOT on the surface of nanomaterials (0D, 1D, and 2D for example); (b) nano-confined synthesis of PEDOT in either solid or soft matter templates; (c) post-growth of nanomaterials on PEDOT surface; (d) VDP growth of PEDOT crystalline phase; (e, f) examples of colloidal processing of PEDOT:PSS.](https://doi.org/10.1007/s10118-020-2373-2)
enium dioxide (RuO$_2$), MnO$_2$, Si nanoparticles etc.) and small organic molecules could be mixed homogeneously with PEDOT in the presence of dispersers such as PSS (Fig. 7e), and these colloidal nanocomposite dispersions are compatible with various processing approaches such as spin, spray and blade coating, which are very promising for the scalable production of electrodes in rich forms. Furthermore, based on the gelation chemistry of PEDOT:PSS dispersions, it could be directly transformed to hydrogel bulks, films or fibers by the addition of gelators (Fig. 7f).

For the improvement of materials performance, critical post-treatments such as soaking in H$_2$SO$_4$ or DMSO are necessary to enhance the conductivity of processed electrodes, which have been already discussed in the previous part.

**Active materials**

Now we turn to specific examples of the colloidal processing methods. When PEDOT is directly employed as the electrode materials, we have mentioned before that the fast electrochemical response and broad potential window are the major features. Therefore, PEDOT electrodes or the nanocomposites with highly conductive materials could be used for ac line filtering applications. In order to efficiently smooth the ripples in dc voltage busses, higher capacitance and lower total impedance should be satisfied in EDL capacitor, given that PEDOT electrodes have a relatively low impedance, Shi et al. implemented a rational design on the microstructure of thin PEDOT films to make the areal capacitance to be simultaneously optimized (Figs. 9a and 9b). In this example, a piece of porous cellulose paper was used as the template for the deposition of PEDOT:PSS and the subsequent concentrated H$_2$SO$_4$ treatment removed cellulose, producing a thin PEDOT electrode with fast diffusion kinetics. They demonstrated that owing to the optimized microstructure, areal capacitance of the device could reach 0.99 mF·cm$^{-2}$ at 120 Hz while maintaining the resistor-capacitor time constant less than 200 μs, making it highly promising in ac line filtering. A practical ac line filtering device was also demonstrated by Shi et al., in which rGO and PEDOT were mixed to prepare a film-based electrode that displayed rapid electrochemical response and was therefore capable of transforming the sinusoidal signal to flat output (Figs. 9c−9e).

**Binders and conductive matrix**

PEDOT:PSS based electrode could also serve as the supportive matrix for electrochemical active materials. In fact, this offers profuse opportunities for capacitive materials that cannot be directly applied in an energy storage device. Based on colloidal processing approach, Chen et al. fabricated a
nanocomposite electrode of sulfur heterocyclic quinone small molecules and PEDOT:PSS binder that showed ability for Li$^+$ storage (Figs. 9f–9h), and the resultant LIB delivers a high discharge capacity of 292 mAh·g$^{-1}$ in the 1st cycle at 0.1C. In addition to the hosting of capacitive materials, it is more intriguing to prepare homogeneous PEDOT nanocomposites in colloidal suspension. Jang et al.\(^{[54]}\) reported the preparation of ternary composite electrodes PEDOT:PSS/rGO/RuO$_2$ for high performance electrochemical capacitor, and the fabrication process was interesting: the mixing process of PEDOT and rGO was completed in the presence of excess PSS as the disperser, and rGO nanosheets, which are prone to aggregate, were reduced from graphene oxide also in the presence of PSS. This example is the excellent representative for the colloidal processing of PEDOT composites electrodes: through this strategy, a wide range of nanomaterials could be mixed with PEDOT for the further versatile processing methods.\(^{[50],[107],[108]}\)

**SUMMARY AND PROSPECTS**

The roadmap for the design of PEDOT incorporated energy storage devices is illustrated in Fig. 10. We have discussed the
critical roles of PEDOT structure in electrode materials: as the active materials, the excellent rate capacity is promising in ac line filtering or power smoothing applications; as the conductive filler, it provides a good electrical contact in the bulk electrodes, making as many as the electrochemical interfaces accessible; when combined with PSS, the material as binders improves the mechanical integrity and selectively restricts the dissolution and diffusion of active materials (especially in the case for small molecules like polysulfides). Moreover, the intrinsic properties such as conductivity of PEDOT could be improved via the control of polymerization conditions or secondary doping of PEDOT:PSS. These strategies have been well-established in the past decades, and for the future development of PEDOT nanocomposites for energy storage, two possible directions are discussed below.

First one is based on the design of the microstructure of PEDOT electrodes (Fig. 10). There is an increasing demand on the special properties of energy storage devices in addition to good electrochemical performances. For instance, the ongoing flexible and especially stretchable electronics needs the new design of electrode materials and for PEDOT-rich materials, the poor stretchability is a severe limitation. Therefore, the novel design of microstructures in PEDOT-based electrodes is crucial for the achievement of these special properties, rather than mixing PEDOT in e.g., elastomer matrix which is normally combined with inferior electrochemical performance. Bao et al. presented an elegant method for finely tuning the interaction of PEDOT and PSS in the bulk material by adding small molecule plasticizers, and the modified PEDOT:PSS films displayed up to 7-fold improvement in failure strain without sacrificing the conductivity. However, in energy storage devices, this type of structural engineering should be explored closely in the future.

The other possible direction is the derivation of PEDOT (Fig. 10). Generally, introducing functional groups on the six-member ring in PEDOT unit and the addition of polymer blocks are two approaches for derivation. These attempts have been conducted continuously, and the new functions realized through the derivation include self-doping of PEDOT chains, enhancement of energy storage capacity, and sensing of target chemicals. In energy storage systems, these strategies should be studied further for the maximization of the excellent properties in PEDOT and the introduction of new capabilities.

In conclusion, despite PEDOT based materials have been studied over 30 years, there are still many things to explore in this old system, e.g., the crystalline structure in in situ polymerized PEDOT, and we envision that, understanding of these fundamental issues should be inspirational for the development and application of PEDOT incorporated functional devices, not only in energy storage.

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