



Cite this: *Chem. Soc. Rev.*, 2015, 44, 6684

Nanostructured conductive polymers for advanced energy storage

Ye Shi,[†] Lele Peng,[†] Yu Ding, Yu Zhao and Guihua Yu*

Conductive polymers combine the attractive properties associated with conventional polymers and unique electronic properties of metals or semiconductors. Recently, nanostructured conductive polymers have aroused considerable research interest owing to their unique properties over their bulk counterparts, such as large surface areas and shortened pathways for charge/mass transport, which make them promising candidates for broad applications in energy conversion and storage, sensors, actuators, and biomedical devices. Numerous synthetic strategies have been developed to obtain various conductive polymer nanostructures, and high-performance devices based on these nanostructured conductive polymers have been realized. This Tutorial review describes the synthesis and characteristics of different conductive polymer nanostructures; presents the representative applications of nanostructured conductive polymers as active electrode materials for electrochemical capacitors and lithium-ion batteries and new perspectives of functional materials for next-generation high-energy batteries, meanwhile discusses the general design rules, advantages, and limitations of nanostructured conductive polymers in the energy storage field; and provides new insights into future directions.

Received 13th May 2015

DOI: 10.1039/c5cs00362h

www.rsc.org/chemsocrev

Key learning points

- (1) General synthetic approaches and fundamental properties of 1D, 2D, and 3D nanostructured conductive polymers.
- (2) Different categories of conductive polymer-based nanocomposites and their properties.
- (3) The design principle of nanostructured conductive polymers and composites as electrodes for electrochemical capacitors and lithium-ion batteries.
- (4) New perspectives of nanostructured conductive polymers as functional materials to enable the development of high-energy lithium batteries.

1. Introduction

Energy storage devices are becoming increasingly important for portable electronics, electrical vehicles, and grid scale storage for the best use of renewable energy sources, such as wind and solar. Among various types of energy storage systems, electrochemical energy storage (EES) devices are dominant and have attracted substantial scientific and technological interest. The key parameters to evaluate the performance characteristics of EES systems include energy density (W h kg^{-1} or W h L^{-1} , energy stored per unit weight/volume), power density (W kg^{-1} or W L^{-1}), specific capacitance (F g^{-1}), specific capacity (mA h g^{-1}), cycle life as well as cost and environmental safety. Lithium-ion batteries and supercapacitors are among the most promising EES devices which have found a wide range of applications. They share

similarities in design and energy-transformation processes that take place at the phase boundary of the electrode/electrolyte interface. However, they also exhibit unique distinct features. Lithium-ion batteries possess high energy density but have limitations of the cycle life and charge-discharge rate, while supercapacitors are known for their high power density and long cycle life, but at the expense of limited energy density.

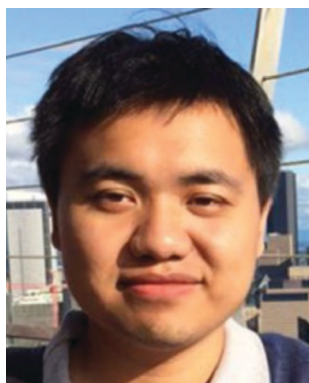
To significantly improve the performance of EES systems and meet ever-increasing energy requirements in various technologies, the exploitation of new materials and methods to tune/optimize the structure and properties of electrochemical materials is of particular importance. The rapid development of nanoscience and nanotechnology offers high potential for addressing critical challenges faced by many energy storage technologies. The nanoscale design of materials, processes and systems provides several advantageous features¹ including (1) new reactions which are not possible with bulk materials; (2) shortened pathways for charge/mass transport; and (3) better accommodation of the strain within electrodes induced by electrochemical reactions.

Materials Science and Engineering Program and Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA.

E-mail: ghyu@austin.utexas.edu

[†] These authors contributed equally to this work.

The adoption of conductive polymers provides another important class of materials for the new generation of EES devices. Conductive polymers are polymers with highly π -conjugated polymeric chains. Typical conductive polymers (Fig. 1a) include polyacetylene (PA, $3\text{--}1000\text{ S cm}^{-1}$), polyaniline (PANI, $0.01\text{--}5\text{ S cm}^{-1}$), polypyrrole (PPy, $0.3\text{--}100\text{ S cm}^{-1}$), polythiophene (PTh, $2\text{--}150\text{ S cm}^{-1}$), poly(phenylenevinylene) (PPV, $10^{-3}\text{--}100\text{ S cm}^{-1}$), *etc.* (significantly higher conductivities have been reported for these polymers, but not in the context of energy storage.) The conductivity of neutral conjugated polymers is rather low, usually in the range of $10^{-10}\text{--}10^{-5}\text{ S cm}^{-1}$. But they could be tuned in a wide range up to 10^4 S cm^{-1} through chemical or electrochemical redox reactions,² so-called “doping”. The resulting conductivity highly depends on the dopants used as well as the level of doping. This unique feature endows conductive polymers the ability to act as insulators, semiconductors and conductors. Doping is a reversible process, which makes the backbone of conductive polymer positive (p-doping) or negative charge



Ye Shi

Ye Shi is a Materials Science and Engineering graduate student at the University of Texas at Austin. He received BS and MS degrees in Polymer Science and Engineering at Zhejiang University. In fall 2013, he began graduate studies with Prof. Guihua Yu at the University of Texas at Austin, focusing on the synthesis and modification of conductive polymer nanomaterials and their applications in energy storage and functional devices.



Lele Peng

Lele Peng received his BS degree in Materials Science and Engineering from the University of Science and Technology of China (USTC) in 2012. He is currently pursuing his PhD in Materials Science and Engineering at University of Texas at Austin under the supervision of Prof. Guihua Yu. His current interests include the synthesis and characterization of 2D nanomaterials for energy storage and conversion, especially for lithium-ion batteries and high performance supercapacitors.



Guihua Yu

Dr Guihua Yu is an Assistant Professor of Materials Science and Engineering at the University of Texas at Austin. He received his BS degree with the highest honor in chemistry from the University of Science and Technology of China, earned his PhD in chemistry at Harvard University in 2009, followed by postdoc training at Stanford University. His research has been focused on the rational synthesis and self-assembly of functional organic nanostructures and two-dimensional nanostructured solids for advanced energy technologies, and fundamental understanding of the structure–property–performance relationship of these new synthetic nanoscale materials.

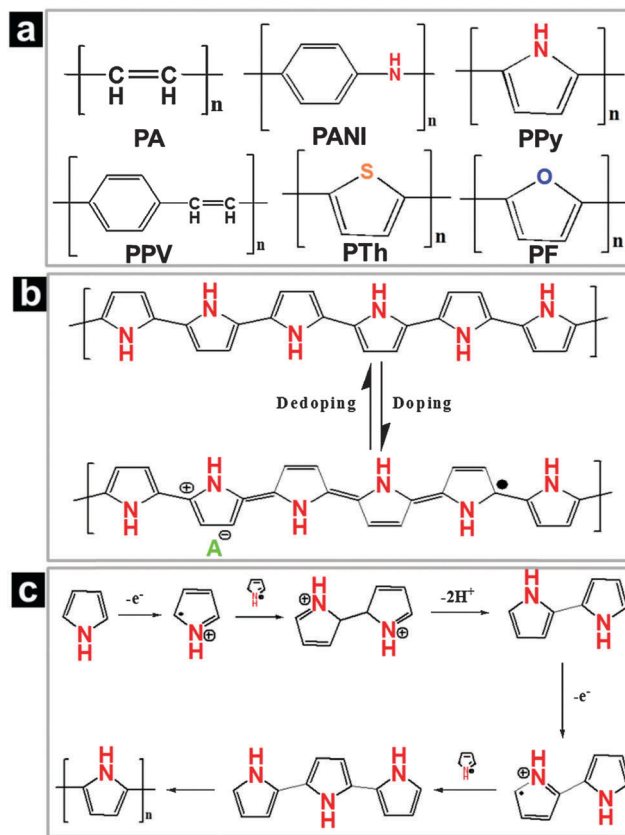


Fig. 1 (a) The chemical structures of typical conductive polymers; (b) the mechanism of the doping/dedoping process of PPy; (c) schematic illustration of the mechanism of polymerization of PPy.

carriers (n-doping). Therefore, counter ions with opposite charges would be entrapped or released from the polymer matrix to maintain the charge neutrality of the polymers. For example, the conductivity of PPy could increase from ~ 0.1 to 100 S cm^{-1} before (top panel of Fig. 1b) and after (bottom panel of Fig. 1b) doping, respectively.

The reversible doping–dedoping property endows conductive polymers with the ability to be applied in various devices, such as energy devices, sensors, and actuators.

The polymerization of conductive polymers involves an electrochemical process of oxidation, a chemical process of coupling and eliminating protons. The proposed mechanism of polymerization of PPy is shown in Fig. 1c.³ Firstly, the oxidation of one monomer generates a radical cation which couples with another radical cation and forms a dimer after the loss of two protons. The dimer could be further oxidized and coupled with radical cations to form oligomers. This propagation continues *via* the same sequence of oxidation, coupling, and deprotonation until the polymer is finally obtained. The oxidation step could be induced by various methods, such as chemical oxidation, the electrochemical process, photochemical initiation, *etc.* However, it should also be pointed out that complex polymerization mechanisms can be quite different for different conductive polymers.

Compared with their bulk forms, nanostructured conductive polymers exhibit several advantageous properties, such as⁴ improved mechanical properties for strain accommodation, large surface areas, shortened pathways for charge/mass/ion transport, and, moreover, provides new exciting features including flexibility, and the mixed conductive mechanism which lowers the interfacial impedance between the electrode and the electrolyte.⁵ A variety of conductive polymer nanostructures have been developed and applied for a range of applications, such as energy conversion and storage devices, sensors and actuators, and bio-devices. Particularly, conductive polymer hydrogels with three-dimensional (3D) hierarchical porous frameworks developed recently are of great scientific interest because their intrinsic properties further increase the merits of conductive polymers for high-performance electrochemical devices.^{6,7}

Several review papers have been published in the past few years discussing nanostructured materials and conductive polymers and their applications in energy-related fields.^{4,8–10} In this review, we focus on the synthesis and characterization of different nanostructures of conductive polymers, and their promising applications and future opportunities in energy storage devices. For the synthesis and characterization, the conductive polymers are categorized by their structures: one-dimensional (1D) nanowires/nanorods/nanotubes, two-dimensional (2D) nanostructured films, 3D nanostructured polymers and their nanostructured composites. For their applications in energy storage field, we critically review the development of their applications and the general design rules for energy storage devices including supercapacitors and lithium-ion batteries, and their current limitations and future potential to advance energy storage technologies.

2. Nanostructures of conductive polymers

2.1 1D conductive polymer nanostructures

1D nanostructured conductive polymers are emerging as some of the important families of energy conversion and storage materials, due to their attractive electrical conductivity, good

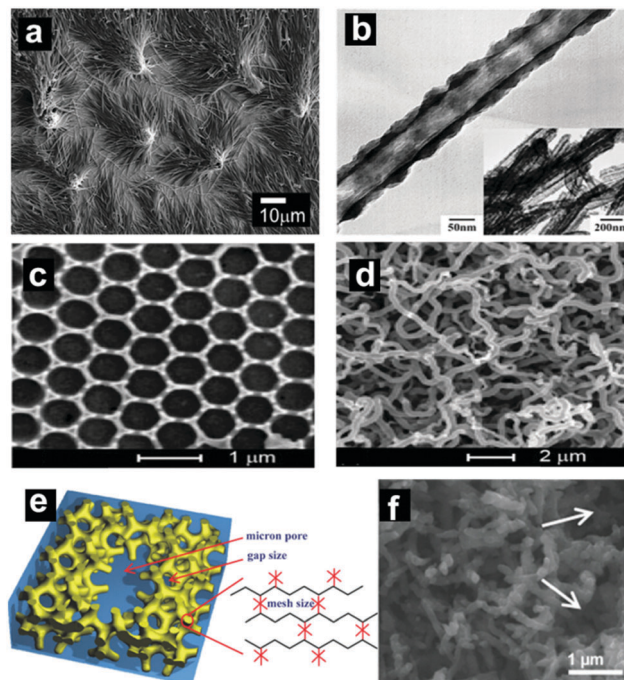


Fig. 2 (a) SEM image of PEDOT nanowires synthesized on a hard PTM template. Reproduced with permission from ref. 11. Copyright 2011 Elsevier Ltd. (b) The TEM image of the PPy nanotubes fabricated by reversed microemulsion polymerization. Reproduced with permission from ref. 12. Copyright 2003 The Royal Society of Chemistry. (c) The PPy network prepared using a template-free approach. Reproduced with permission from ref. 15. Copyright 2002 American Chemistry Society. (d) The PPy network prepared using a template-free approach. Reproduced with permission from ref. 16. Copyright 2008 American Chemistry Society. (e) A schematic of the 3D hierarchical porous nanostructure of the gelated PANI hydrogel. (f) The SEM image showing the interconnected network of dendritic PANI nanofibers. Reproduced with permission from ref. 6. Copyright 2012 Proceedings of the National Academy of Sciences of the United States of America.

mechanical properties, and unique electrochemical activity, as well as low cost, environmental benignity.³

To date, several strategies have been developed to synthesize 1D conductive polymer nanostructures, as referenced in recent review articles by Shi *et al.*² In general, the controlled synthetic strategies could be classified into two main categories: template-based methods (Fig. 2a)¹¹ and template-free methods mainly including self-assembly and electrospinning (Fig. 2b).¹²

The conventional hard template method is pioneered by Martin's group and has become a powerful tool for controllable synthesis of 1D conductive polymer nanostructures.¹³ Porous membrane materials, such as anodic aluminum oxide (AAO), block copolymers, porous silicate, mesoporous zeolites, and PTM are the most commonly employed templates. The dimension, aspect ratio and orientation of 1D polymer structures could be controlled either by adjusting the experimental parameters or by the template itself. Alternatively, pre-existing nanostructured materials could also be used as templates to guide the growth of 1D conductive polymer nanostructures. Other than hard templates, 1D conductive polymer nanostructures could also be obtained using the soft template method. The soft templates usually are made from mesophase

structures, such as surfactant micelles, liquid crystals, copolymers *etc.* The morphology of products is controlled by the nature and chain length of the surfactants as well as the concentrations of both polymer monomers and surfactants.

The template-based synthesis shows the advantages of universality and controllable dimensions. However, the synthesis quantity of the polymer nanostructures is limited by the size or amount of the template, thus limiting its large-scale fabrication. Moreover, the post treatment for template removal may destroy or harm the formed nanostructures and increase the processing cost. In contrast, the template-free methods using self-assembly or electrospinning are proved to be effective alternatives to prepare 1D conductive polymer nanostructures.³ The self-assembly method is induced by non-covalent forces between polymer chains, such as π - π stacking, dipole-dipole, hydrophobic, van der Waals forces, hydrogen bonding, electrostatic and ion-dipole interactions. PANI, PPy, and PEDOT have been successfully self-assembled to nanowires and nanotubes by a dopant induced micelle route. Electrospinning is another useful technique to synthesize 1D nanostructures. During synthesis, a high electrical field is applied between a polymer fluid and a conductive collector. The nanofibers are produced as the solvent is evaporated. More detailed information is presented in the review by Zheng *et al.*³

2.2 2D nanostructured films of conductive polymers

2D nanostructured films of conductive polymers are attractive for applications such as sensors and energy conversion and storage because they possess the unique features, such as controllable thickness, modifiable porosity and surface morphology, and processability over a large range of areas. The synthesis of such nanoscale thin films usually requires pre-treated substrates or well-defined surfaces.

The conductive polymer films are usually synthesized by electrochemical polymerization, spin coating, or layer-by-layer (LBL) techniques. Electrochemical polymerization is a widely used method to deposit ultra-thin films of conductive polymers on substrates and followed by introducing other molecules or particles which can act as functional components, such as conductive additives, reaction sites, catalysts and surface modifiers. For example, an ultra-thin (~ 55 nm) PPy-glucose oxidase (GOD) film has been fabricated by employing a simple electrochemical polymerization process in which a low current density and a long period was applied to an electrolyte-free monomer solution.¹⁴

To further increase the porosity and roughness of conductive polymer films, and thereby their surface area, networks of conductive polymers are fabricated by the interconnection of nanoscale domains or nanopores of conductive polymers on a substrate or surface. These resulting films have large surface areas due to their porous nature, which facilitates the diffusion of molecules and the interaction between molecules and exposed areas throughout the entire films. Their synthesis can be achieved using hard-template and soft-template methods and template-free electrosynthesis. Colloidal particles are commonly used as hard-templates to synthesize porous films of conductive polymers. For example, 2D PANI films with honeycomb (Fig. 2c)

structures are obtained by electrochemical polymerization of aniline monomers within the interstitial voids in assemblies of polystyrene nanospheres.¹⁵ Nanoporous conductive polymer films could also be synthesized using the soft template method. Template-free electrosynthesis has also been developed to synthesize nanoporous films of conductive polymers. The fabrication of a superhydrophilic PPy nanofiber porous film has been achieved using a template-free electrochemical approach in which phosphate buffer solution (PBS) is applied (Fig. 2d).¹⁶

2.3 3D nanostructured conductive polymers and their composites

2.3.1 3D nanostructured conductive polymers. 3D nanostructures have become a rapidly growing field of research, which have received considerable attention in the fields of electronics, photonics, and biomedical devices. Various 3D nanostructures of conductive polymers have been developed and reviewed in the recent literature.² A template-guided method is most widely adopted to generate 3D nanostructured conductive polymers. As 3D nano-networks, inverse opals of conductive polymers have been synthesized by polymerizing the corresponding monomers in the interstitial voids of PS colloidal arrays. Spheres and containers of conductive polymers with micro-level sizes have been prepared using gas bubbles or liquid droplets as templates. 3D nanoarrays which consist of highly ordered conductive polymer nanowires or nanotubes have been fabricated based on the hard templates, such as anodic aluminum oxide (AAO) or soft templates including various organic sulfonic acids.

As typical organic materials with intrinsic 3D structures consisting of networks of water-soluble polymer chains, hydrogels possess highly porous structures, excellent compatibility with other hydrophilic molecules, and tunable mechanical properties, leading to promising applications in energy storage electrode materials, sensors, drug delivery, *etc.*

3D nanostructured conductive polymer hydrogels (CPHs) have recently emerged as a novel class of polymeric materials that bring together the advantageous features of both hydrogels and organic conductors: taking advantage of the characteristics of nanomaterials, such as large effective surface areas, controllable sizes and structures as well as highly conducting and electrochemically active 3D frameworks (Fig. 2e). Traditional synthetic routes for CPHs include polymerization of conductive polymer monomers using multivalent metal ions or polymers in non-conductive hydrogel matrix which serve as templates.⁷ A typical procedure could be found in the review paper written by Yu *et al.*¹⁰ Another approach is to fabricate conductive polymer hydrogels through copolymerization of conductive polymer monomers with non-conductive hydrogel monomers.

A new synthetic approach for the synthesis of 3D CPHs has been reported recently, adopting phytic acid as the gelator and dopant in the synthetic process to form conductive hydrogel networks with tunable structures and interfaces.^{17,18} The framework of the as-prepared CPHs is free of insulating polymers, providing ideal 3D interconnected paths for electron transport. The obtained PANI hydrogel reaches a room-temperature conductivity of

0.11 S cm⁻¹ in wet state which is the highest reported value for conductive polymer hydrogels. Such 3D porous structures offer large open channels on the micro-scale and meso-scale pores (Fig. 2f). The swelling nature of conductive hydrogels provides additional effective surface areas between polymer chains and the solution phase to support more active reaction sites and anchoring sites for active molecules or ions. In addition, the as-prepared hydrogel could be applied *via* an ink-jet printing or spray coating technique to fabricate large-scale electrochemical device arrays that are potentially useful in many areas of technology from supercapacitors, lithium-ion batteries, sensors to other bioelectrodes.

2.3.2 Nanostructured composites based on conductive polymers. Nanostructured composites based on conductive polymers are of great technological importance due to the combination of the intrinsic properties of each component as well as the synergistic effect resulting from the hybrids. Moreover, the electrochemical activity, mechanical strength and conductivity, are tunable after incorporating one or more foreign components into conductive polymers using specific synthetic routes, such as surface and interface reactions, electrochemical synthesis, epitaxial growth, *in situ* polymerization, *etc.* Current research interest mainly focuses on the rational hybridization of conductive polymers with several important material systems, including cellulose and its derivatives, carbon nanomaterials, metal oxides and sulphides, and other functional materials like phosphates.

Due to the abundance of cellulose fibers in nature and ample variability of cellulose products, hybridization of conductive polymers with cellulose is of particular interest as the procedures for manufacturing these composites are relatively straightforward and inexpensive. Cellulose and its derivatives are regarded as suitable substrates for the *in situ* polymerization and post-deposition of thin layers of conductive polymers. In terms of fabrication methods, there are several general feasible strategies to realize the direct *in situ* polymerizations and layer-by-layer coating of cellulose fibers with conductive polymers. For example, the direct *in situ* chemical polymerization of PPy on cellulose fibers can be performed by employing oxidants. Detailed description can be found in the review article by Nyholm *et al.*¹⁰

The hybridization of conductive polymers with carbon nanomaterials often involves carbon nanotubes and nanofibers, graphene and graphene oxides, or activated carbon. Carbon nanomaterials play a critical role as the conductive framework, which facilitates the transport of charge carriers and helps conductive polymers sustain the strains during electrochemical processes. For example, single-walled carbon nanotube (SWCNT)-PANI composites have been synthesized *via* a typical initiator-assisted polymerization process, resulting in the formation of PANI nanofiber shells and SWCNT core nanostructures (Fig. 3a).¹⁹ Similarly, the composites composed of PANI-graphene oxide (RGO) have been prepared *via* the polymerization in the RGO suspensions.²⁰

Another important category of composite materials is the hybrids of transition metal oxides and conductive polymers. A number of transition metal oxides, such as ruthenium (RuO₂), iron (Fe₃O₄), vanadium (V₂O₅), manganese (MnO₂), cobalt (CoO_x)

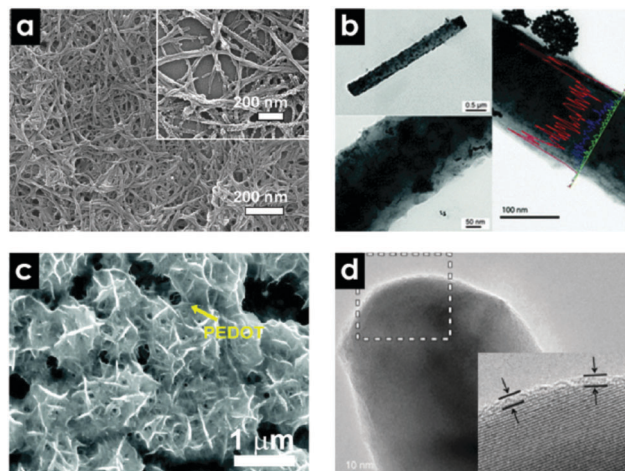


Fig. 3 (a) SEM image of SWCNT-polyaniline composite nanofibers. Reproduced with permission from ref. 19. Copyright 2011 American Chemical Society. (b) TEM image of MnO₂-PPy nanowires. Reproduced with permission from ref. 22. Copyright 2014 Royal Society of Chemistry. (c) SEM image of the graphene-MnO₂-PEDOT:PSS ternary electrode. Reproduced with permission from ref. 23. Copyright 2011 American Chemical Society. (d) TEM image of the PEDOT-LiFePO₄ composite. Reproduced with permission from ref. 26. Copyright 2011 Wiley-VCH Verlag GmbH & Co.

and other mixed TMOs, have been explored as additive electroactive materials for conductive polymers, due to the high chemical reactivity originated from their diverse transition oxidation states.²¹ For instance, binary composites made of MnO₂ and PPy were successfully fabricated *via* a redox exchange mechanism between KMnO₄ and the functional groups of PPy, which resulted in the deposition of MnO₂ nanoparticles into conductive polymer nanowires (Fig. 3b).²²

Similar design rules can be applied to fabricate the ternary hybrid structures. Such ternary hybrid systems are composed of carbon-based nanomaterials, transition metal oxides and conductive polymers. For example, a ternary hybrid material MnO₂-CNT-PEDOT-PSS has been proposed, in which CNTs provide a large surface for the deposition of hierarchical porous MnO₂ nanospheres and improve the electrical conductivity as well as the mechanical stability of the composite; PEDOT-PSS acts as an effective dispersant for MnO₂-CNTs structures and a binder material that helps in adhering and connecting MnO₂-CNTs particles in the film; and MnO₂ nanospheres serve as the active materials (Fig. 3c).²³ The specific examples will be discussed in details below.

Metal sulphides are another exciting class of materials, which can be hybridized with conductive polymers because of their unique physical and chemical properties (*e.g.*, higher electrical conductivity and mechanical and thermal stability than those of their corresponding metal oxides) as well as the rich redox chemistry.²⁴ Attaching conductive polymers, such as polyacrylonitrile (PAN) and PANI, to metal sulphides is an effective way to further improve the properties. For instance, pyrite FeS₂ embedded in a stabilized PAN matrix (PAN-FeS₂) was synthesized *via* two simple solid-state processes after thoroughly mixing the FeS₂ with PAN.²⁵

Apart from simple oxide-conductive polymer composites, other functional materials, like metal phosphates, can also form composites with conductive polymers. For example, olivine LiFePO_4 can polymerize with the conductive polymer PEDOT. Polymerization propagation requires the reinsertion of lithium into the partially delithiated LiFePO_4 as well as the transport of Li ions and electrons through the deposited polymer coating. In turn, these are also the functionality characteristics of an effective conducting coating for LiFePO_4 (Fig. 3d).²⁶

Current research interest mainly covers the rational design and synthesis of different conductive polymers with other material systems on the surfaces, but the chemical modification between them at the interface level is still unclear. Moreover, detailed investigations of different chemical compositions, morphologies, and phase structures of hybrid materials, which are crucial for fundamental understanding of the interface between foreign materials and conductive polymers are still critically needed.

3. Nanostructured conductive polymers for energy storage

3.1 Nanostructured conductive polymers as active electrodes for electrochemical capacitors

Electrochemical capacitors (ECs) with high power densities and long cycle lives are expected to be some of the most promising future power sources. As electrochemical systems involve ionic and electronic transport processes at the electrode surfaces and the interfaces between the electrode and the electrolyte solution, the electrode is the central component of an EC and largely dictates its ultimate performance.²⁷ In general, a high-performance EC electrode requires simultaneous minimization of the four primary resistances during electrochemical charge-discharge: (1) ion transport in the electrolyte, (2) ion transport in the electrode, (3) electrochemical reactions in the electrode and (4) electron conduction in the electrode and current collector (Fig. 4).²⁸

Conductive polymers have been explored as pseudo-capacitive materials due to their high charge density and low cost potential (compared with the relatively expensive metal oxides). It is possible to develop electrochemical devices with low equivalent series resistance (ESR) and high power. Although possessing high specific capacitance ($400\text{--}600\text{ F g}^{-1}$ in an acidic medium), conductive polymers for pseudocapacitors, such as PANI and PPy, often suffer from severe cycling stability problems (Fig. 5a and b).²⁹ The well-accepted reasons for these problems are the instable chemical structures and the low charge transfer of the conductive polymers. Generally, the polymer structures suffer from swelling and shrinking during charging and discharging processes, leading to the cycling instabilities of conductive polymers. Also, bulk films of conductive polymers have compact structures, which will block the penetration of electrolyte ions, hindering the high performance. Therefore, some effective strategies have been explored to sufficiently improve the cycling performance as well as to utilize the high capacitance of conductive polymers.

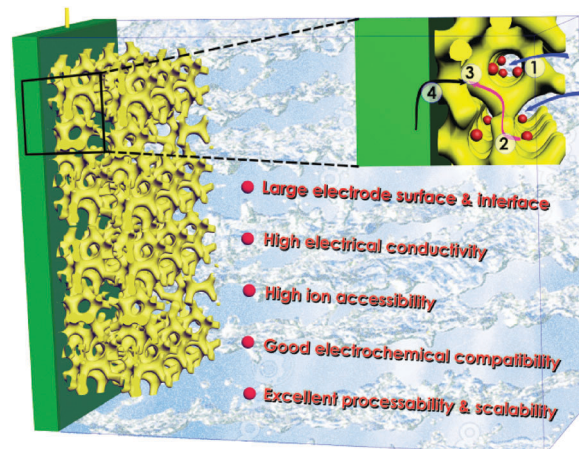


Fig. 4 Schematic of a high-performance EC electrode with the following desired characteristics: large electrode surface and interface, high electrical conductivity, high ion accessibility, good electrochemical compatibility, and excellent processability and scalability. The enlarged picture illustrates the four primary resistances in the electrode.

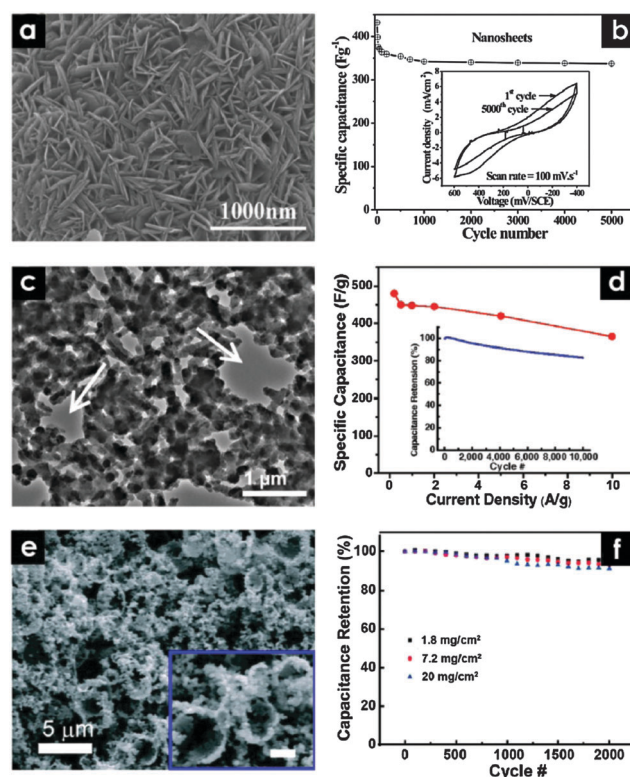


Fig. 5 (a and b) SEM image and electrochemical characteristics of the nanosheet of a PPy thin film. Reproduced with permission from ref. 29. Copyright 2012 Royal Society of Chemistry. (c and d) TEM image of the dehydrated 3D nanostructured PANI hydrogel, and its corresponding capacitive performance (specific capacitance versus current density). The inset shows the cycling performance of the 3D PANI CPHs. Reproduced with permission from ref. 6. Copyright 2012 Proceedings of the National Academy of Sciences of the United States of America. (e and f) SEM image and cycling performance of dehydrated polypyrrole hydrogel as supercapacitor electrodes. Reproduced with permission from ref. 17. Copyright 2014 Royal Society of Chemistry.

An interesting approach is the use of nanostructured cellulose and cellulose composites. For example, nanostructured cellulose–PPy composites prepared by chemical oxidation of pyrrole in the presence of nanostructured cellulose was used as supercapacitor electrodes. The cellulose fibers coated by a thin (30–50 nm) layer of PPy exhibited a high BET surface area of $\sim 100 \text{ m}^2 \text{ g}^{-1}$. The porous structure of the composites (which were found to contain about 67% of PPy) and thin PPy films ensured a rapid mass transport of the ions needed during the oxidation and reduction of PPy while the cellulose substrate provided good overall flexibility.¹⁰

Meanwhile, 3D nanostructured conductive polymers have been designed and applied to enhance the electrochemical performance of supercapacitor devices based on conductive polymers. PPy microcontainers, such as bowls and cups have been synthesized by electrochemical polymerization using gas bubbles as templates.² The unique structures show strong oxidation and reduction peaks in the CV test and a capacitance of $\sim 200 \text{ F g}^{-1}$ owing to the enhanced surface area. Conductive polymer (e.g. PPy and PANI) nanowire arrays provide a large surface area and an optimal ion diffusion path in the ordered nanowire structures, thus becoming promising materials for high-performance supercapacitors. For example, PPy nanowire arrays exhibited a capacitance of 566 F g^{-1} and retained 70% of its initial capacitance after hundreds of charge–discharge cycles.³⁰

Recently, 3D CPHs have emerged as a promising material platform for high performance ECs. 3D CPHs combine the unique properties of hydrogels with the electrical properties of metals or semiconductors, thus offering an array of features essential for high-performance EC electrodes: high electrical conductivity, large ion-accessible surface and interface areas, high ionic transport, and good processability and scalability (Fig. 4). 3D nanostructured PANI hydrogels showed great potential for high-performance ECs.⁶ The 3D continuous nanostructured framework favours fast ion transport during charging/discharging (Fig. 5c). The corresponding specific capacitance value yielded a high specific capacitance (480 F g^{-1} at 0.2 A g^{-1}) (Fig. 5d). In addition, the PANI hydrogel-based electrodes yielded a promising rate performance with only $\sim 7\%$ capacitance loss when the current density was increased by a factor of 10 as well as good cycling stability (Fig. 5d inset). The superior cycling performance achieved in the hydrogel electrode system confirms the unique advantages of the highly porous interconnected nanostructures in the CPHs that can accommodate the swelling and shrinking of the polymer network during intensive cycling processes. Recently, 3D nanostructured conductive PPy hydrogels were also demonstrated with structure-derived elasticity at an organic/aqueous biphasic interface.¹⁷ This strategy yielded PPy hydrogels with tunable porous nanostructures (Fig. 5e), leading to good mechanical properties and high performance with a specific capacitance reaching 380 F g^{-1} (Fig. 5f).

Many nanostructured conductive polymer-based ECs suffer from relatively low gravimetric and volumetric energy and power densities because conductive polymers can only work within a strict potential window. The swelling and shrinking of conductive polymers occurring during the electrochemical

cycling process always lead to fading of gravimetric and volumetric power densities. Composite materials are an important material platform for fabricating ECs with improved gravimetric and volumetric energy and power densities. As stated above, nanostructured composites based on conductive polymers are of great technological importance due to the combination of the intrinsic electrochemical properties of each component as well as the synergistic effect.

Given high electrochemical activity, conductive polymers often lead as active redox-reaction electrodes while carbon nanomaterials serve as conductive frameworks, which facilitate the transport of charge carriers and help conductive polymers sustain the strains during electrochemical processes. These features would facilitate addressing the cyclability problems of the conductive polymer-based electrodes. For example, Shi *et al.* fabricated the paper-like composite films of chemically converted graphene (CCG) and PANI-NF (G-PNF) electrodes for supercapacitors by simply filtrating stable aqueous dispersions of CCG–PANI-NF composites (Fig. 6a).³¹ The G-PNF film has several advantages over pure graphene or pure PANI-NF films, including the self-standing property and high flexibility of the G-PNF film and high conductivity to eliminate the need of conducting additives.

Another possible strategy is to employ nanostructured conductive polymers on graphene oxides as electrodes. The vertical nanowire array electrodes exhibit several advantages for energy

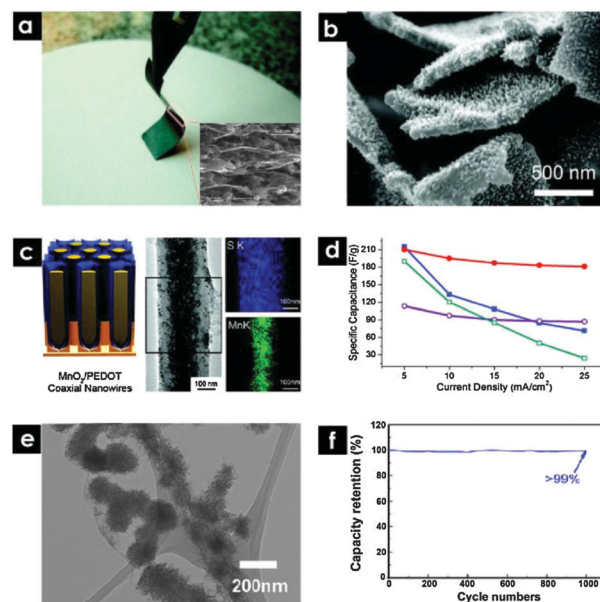


Fig. 6 (a) Photograph of a flexible G-PNF film. The inset shows the cross-section SEM image of a G-PNF film. Reproduced with permission from ref. 31. Copyright 2010 American Chemical Society. (b) SEM image of PANI-GO samples. Reproduced with permission from ref. 32. Copyright 2010 American Chemical Society. (c) SEM image of MnO_2 –PEDOT coaxial nanowires *via* the coelectrodeposition method on a porous alumina template. (d) Rate performance of the MnO_2 –PEDOT coaxial nanowires. Reproduced with permission from ref. 34. Copyright 2008 American Chemistry Society. (e) TEM image of PEDOT–PSS dispersed MnO_2 nanospheres *in situ* grown on fFWNTs. (f) Cycling performance of the ternary electrodes for supercapacitors. Reproduced with permission from ref. 36. Copyright 2010 American Chemistry Society.

storage devices compared with disordered networks. Firstly, each nanowire is electrically connected to the conductive substrate such that all the nanowires contribute to the storage capacity. Secondly, the nanowire arrays have direct 1D electronic pathways allowing for efficient charge transport and reduced ion-transport length that result in high rate performance. Lastly, the inter-space between the oriented nanowires can accommodate volume changes without the initiation of fracture in bulk or micron-sized materials. Wei *et al.* reported conductive PANI nanowire arrays grown vertically on graphene oxide (GO) sheets by dilute polymerization of aniline monomers on the GO substrates (Fig. 6b).³² The PANI nanowire–GO composites showed a synergistic effect when used as supercapacitor electrodes, yielding a specific capacitance of 555 F g^{-1} at a discharge current density of 0.2 A g^{-1} . These results indicated that optimizing the structures at the nano-scale is an effective way to improve practical capacitance and cycling stability of conductive polymer-based electrodes.

Compared to conductive polymers or carbon–conductive polymer composites, hybrids of conductive polymers and pseudocapacitive transition-metal oxides like RuO_2 , NiO , and MnO_2 would have higher electrochemical activities due to their high energy density and large pseudocapacitance from metal oxides.³³ Lee *et al.* introduced a simple one-step method to synthesize the binary composites based on MnO_2 –PEDOT coaxial nanowires by co-electrodeposition on a porous alumina template (Fig. 6c).³⁴ The core MnO_2 provides high energy storage capacity, while the highly conductive, porous, and flexible PEDOT shell facilitates the electron transport and ion diffusion into the core MnO_2 and significantly protects it from structurally collapsing and breaking. The coaxial nanowires exhibited high specific capacitance and good capacitance retention. The coaxial nanowires preserved 85% of their specific capacitance as the current density increases from 5 to 25 mA cm^{-2} . Liu *et al.* reported a 3D CoO –PPy composite electrode with very high capacitance and good rate capability. 3D nickel foam with large uniform macropores and high electrical conductivity was employed as the current collector to ensure the efficient electrolyte penetration and thus fast ion diffusion; PPy was integrated into the nanowire array to enhance the conductivity of the 3D electrode (Fig. 6d). The binary electrodes still maintain a good electrochemical reversibility of 99.86% Coulombic efficiency even after 2000 cycles, and the as-fabricated asymmetric supercapacitors deliver a high energy density of 43.5 W h kg^{-1} at a power density of 87.5 W kg^{-1} .³⁵

Other important material models for high performance EC electrodes are the ternary composites based on conductive polymers. Liu *et al.*³⁶ developed a ternary MnO_2 –CNT–conductive polymer composite as high performance EC electrodes (Fig. 6e). They found that the synergistic effects arising from the combination of MnO_2 , functionalized few-walled carbon nanotubes (fFWNTs) and the commercial PEDOT–PSS conductive polymer could effectively utilize the full potential of all the desired functions of individual component. The ternary MnO_2 –CNT–conductive polymer composite exhibited not only the high specific capacitance and stable capacitance at high current density, but also showed great potential for use in power applications. Such an electrode

design provides the possibility to solve the potential problems such as the dense morphology and the intrinsically poor electrical conductivity of transition metal oxides.

The synergistic effect was also observed in the hybrids of two pseudocapacitive materials with tailored structures. Wang *et al.* designed a two-step method to synthesize a ternary nanocomposite of graphene– Fe_2O_3 –polyaniline (GFP) in which the PANI was synthesized *via in situ* polymerization of aniline. Such a nanostructure of ternary composite with the well-dispersed Fe_2O_3 nanoparticles anchored firmly on the GE sheets and protected by PANI films is advantageous to address the poor cycling problems and offer a direct short pathway for charge/electrode diffusion. The GFP composite exhibited an excellent cycling life, with a decrease in capacitance of only 8% after 5000 cycles. Moreover, GFP showed an enhanced energy density of 107 W h kg^{-1} at a power density of 351 W kg^{-1} and 17 W h kg^{-1} even at a higher power density of 4407 W kg^{-1} .³⁷

Pseudocapacitors often suffer instability issues from both the transition metal oxides and the conductive polymers, which hinder their practical applications in long-term storage devices. TMOs often lack stability due to mechanical stress or by undergoing soluble transition states, while conductive polymers often suffer from limited cyclability due to the swelling and shrinking of electroactive polymers during charging/discharging processes. These instability limitations lead to the poor cycling performance of the hybrid composite electrodes. Effective strategies to minimize/alleviate the instability issues include rational nanostructuring of electrodes to better accommodate structural changes and chemical integration and/or modification with carbon-based framework materials to improve structural and chemical stability. As example, recently developed 3D CPHs that possess highly porous structures, large surface areas, and tunable mechanical properties originated from the crosslinking structure and swelling nature, have been known to exhibit attractive electrochemical properties as EC electrodes due to the capability to accommodate the swelling and shrinking of the polymer network during intensive cycling processes. Nanocomposite electrodes made of 3D CPHs as material frameworks with other pseudocapacitive materials would be a novel and promising material system for next generation EC devices.

Conductive polymers and their composites also find numerous applications in flexible energy storage, especially solid-state flexible supercapacitors, due to their mechanical flexibility, conformability, versatility and ease in fabrication into composites. Conductive polymers, and their composites with carbon, metal oxides and ternary composites have been demonstrated as flexible electrodes for high performance solid-state flexible supercapacitors. Meng *et al.* developed a flexible solid-state SC device using PPy–Au as the electrode and a PVA/ HClO_4 gel as the electrolyte and separator.³⁸ The PPy–Au electrode achieves an excellent specific capacitance of 270 F g^{-1} at a low current density of 0.6 A g^{-1} . Fan and co-workers developed an all-solid-state paper-like polymer supercapacitor based on the PANI–CNT composite film electrodes.³⁹ This device showed a high specific capacitance of 31.4 F g^{-1} (counting weight of entire device) with

excellent cycle stability. Gao and co-workers fabricated a flexible supercapacitor based on PPy–MnO₂–carbon fiber hybrid structures,⁴⁰ which showed a high specific capacitance of 69.3 F cm⁻³ at a discharge current density of 0.1 A cm⁻³ and an energy density of 6.16 × 10⁻³ W h cm⁻³ at a power density of 0.04 W cm⁻³. Another approach is to apply cellulose, which is widely known for its intrinsic mechanical strength and flexibility, as a suitable substrate material to reinforce brittle conductive polymers, such as PPy, PANI, *etc.* Detailed descriptions of the use of conductive polymers as electrodes in flexible supercapacitors are beyond the scope of this tutorial article, but can be extensively found in other literature reports.^{10,27}

Although outstanding properties of new conductive polymer-based electrode materials have been reported, true performance of actual devices need be more carefully evaluated. Firstly, energy and power densities per weight of the active material alone may not give a realistic picture of the performance of the actual devices because the weight of the other device components also needs to be taken into account.⁴¹ Especially for porous conductive polymers, the weight of the electrolyte within the pores should be taken into account while comparing the gravimetric energies and power densities. The influence of the electrolyte within the porous structure could be demonstrated by comparing the volumetric energies and power densities of different materials. One example is that the PPy@cellulose electrode material after compression showed much higher volumetric energy and power density when compared to the same material before compression because the undesired “electrolyte dead weight” was eliminated.⁴² Another example is that the volumetric energy of an electrode based on a carbon aerogel with 90% porosity is 20% that of a carbon electrode with just 50% porosity.⁴¹ Secondly, the mass loading should meet the requirements for realistic applications, or the reported data would be of little value. The ability to predict the performance of an electrode with high mass loading by testing one with a small amount of material is still very poor.⁴¹ These two considerations apply to both supercapacitors and lithium-ion batteries.

3.2 Nanostructured conductive polymers as active electrodes for lithium-ion batteries

Lithium-ion batteries are extensively investigated as essential energy storage devices due to their high theoretical capacity, relatively light weight, enhanced safety, and low toxicity. Conductive polymers have been explored as electrode materials since 1980s and a comprehensive review has been conducted by Haas *et al.*⁵ Conductive polymers can serve as both anodic and cathodic materials, while they are commonly used as cathodes in lithium-ion batteries. Different conductive polymers show quite different energy densities and power densities due to their chemical structures and physical properties. For example, PPy-based electrodes exhibit energy densities of ~10–50 W h kg⁻¹ and power densities of 5–25 kW kg⁻¹; PANI-based electrodes exhibit energy densities of 50–200 W h kg⁻¹ and power densities of 5–50 kW kg⁻¹; PTH-based electrodes exhibit energy densities of 20–100 W h kg⁻¹ and power densities of 5–50 kW kg⁻¹.¹⁰ Conductive polymers show several advantages, such as good processibility, low cost, convenient molecular modification, and

light weight when applied as electrodes. However, poor stability during cycling and low conductivity in reduced state inhibit their further applications in lithium-ion batteries.

The adoption of nanostructured conductive polymers can partly overcome this problem, owing to their high surface and faster diffusion kinetics of Li ions. Cheng *et al.*⁴³ synthesized ordered PANI nanotubes doped with HClO₄ and utilized them as positive electrode materials which showed better performance than the commercial PANI powders in lithium-ion batteries (Fig. 7a). The Li–PANI battery achieved a high practical discharge capacity of 75.7 mA h g⁻¹ and retained 95.5% of the highest discharge capacity after 80 cycles. However, the capacity and power density is still relatively low and the stability of organic materials remains a serious problem (Fig. 7b).

The realizable capacity of conductive polymers is usually low and decreases gradually upon charge–discharge cycling.⁴⁴ To overcome this problem, redox-active components are doped into a polymeric matrix or linked to polymer chains where they can act as counterion dopants to enhance the electronic conductivity and function as redox-active sites to enhance the capacity. Goodenough *et al.*⁴⁵ covalently anchored ferrocene groups to the PPy backbone,

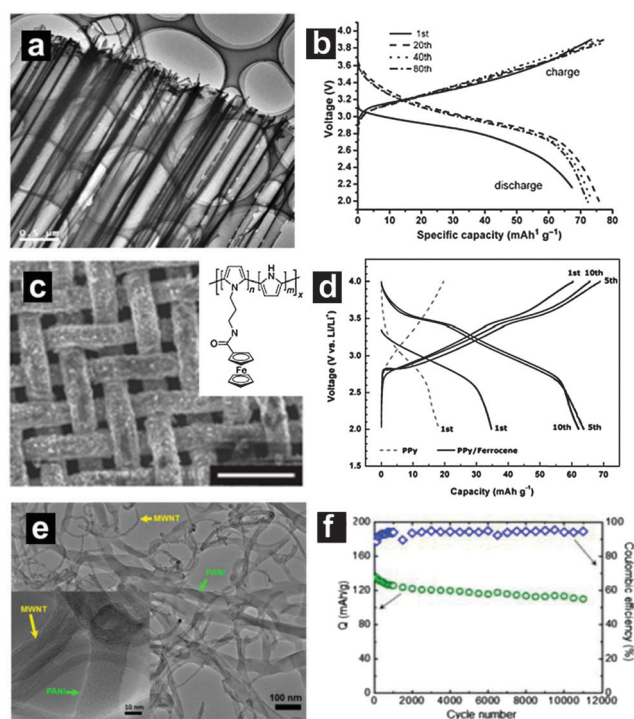


Fig. 7 (a) TEM image of ordered HClO₄-doped PANI nanotubes; (b) cycling characteristics of half cells fabricated by HClO₄-doped PANI nanotubes at a current density of 20 mA g⁻¹. Reproduced with permission from ref. 43. Copyright 2006 Wiley-VCH Verlag GmbH & Co. (c) SEM image of the PPy–ferrocene polymer deposited on a stainless-steel mesh; the inset shows the chemical structure of the pyrrole/[(ferrocene) amido-propyl]pyrrole copolymer; (d) charge–discharge curves of PPy and PPy–ferrocene polymer cathodes. Reproduced with permission from ref. 45. Copyright 2007 Wiley-VCH Verlag GmbH & Co. The TEM image (e) and cycling performance (f) of vacuum-assisted layer-by-layer PANI–carbon nanotube electrodes. Reproduced with permission from ref. 46. Copyright 2014 American Chemical Society.

thus increasing the specific capacity and rate capability, as well as lowering the overpotential at high discharge rates (Fig. 7c and d). Recently, Yang *et al.*⁴⁴ developed PPy and PTh polymers with a greatly enhanced redox capacity of 140 mA h g⁻¹ and excellent cyclability by doping with Fe(CN)₆⁴⁻ anions which serve as counterion dopants to ensure electronic conduction of the polymer and function as redox mediators to facilitate the charge transfer between the polymer and electrolyte.

Another strategy to improve the performance of conductive polymer-based electrodes is the development of nanostructured composites with carbon materials, such as graphene and carbon nanotubes. Incorporation of carbon nanomaterials can improve the electrical conductivity as well as the mechanical properties of the conductive polymer matrix. Hammond *et al.*⁴⁶ adopted a vacuum-assisted layer-by-layer technique to achieve electrodes consisting of PANI nanofibers and multiwall carbon nanotubes (Fig. 7e). The electrostatic interactions and vacuum force help to form an interpenetrating network of nanofibers and nanotubes, resulting in the electrodes with a high specific capacity of 147 mA h g⁻¹ and excellent charge-discharge stability over 10 000 cycles (Fig. 7f). The excellent performance originates from the carbon nanotubes and redox active PANI nanofibers that store charges through both electrical double layer and faradaic mechanisms. Manthiram *et al.*⁴⁷ synthesized graphene nanosheets and PANI nanocomposites in which PANI could limit the formation of the SEI layers and help to enhance lithium-ion conduction and electron transport during cycling. The nanocomposites show improved cyclability with a capacity retention of 84% in 40 cycles.

Nanostructured conductive polymers have provided several attractive features in all polymer batteries, such as flexibility, light weight, and facile processing and fabrication, thus becoming excellent candidates for flexible and stretchable batteries. The nanostructured conductive polymer-based batteries also show potentially high power densities, owing to enhanced ion/mass transport in nanostructured electrodes. However, when compared to inorganic materials and redox active polymers, the relatively low capacity and poor cycle life of conductive polymers still need to be overcome. Recent advances in research have exploited some promising strategies. The conductive polymers could be modified with redox active groups or incorporated with redox polymers to enhance the storage capacity. Nanocomposites based on conductive polymers and carbon-based materials can improve the mechanical and conductive properties.

3.3 Nanostructured conductive polymers as functional materials for Li-ion batteries

Besides being used as active energy storage electrodes, nanostructured conductive polymers can also serve other important functions in energy storage devices.⁵⁰ Conductive polymers are commonly used as modification materials to enhance the performance of other cathode and anode materials. For example, Co₃O₄ anodes suffer from poor rate capabilities due to their low intrinsic electronic conductivity. Recently, Co₃O₄-PANI core-shell nanowire arrays were synthesized by directly electrochemical depositing PANI on the Co₃O₄ nanowire array backbones and the composite anodes exhibited superior Li-ion storage capability

compared to the bare Co₃O₄ nanowires arrays.⁴⁸ Olivine LiFePO₄ is also appropriate for polymerization of the conductive polymer PEDOT. The LiFePO₄-PEDOT composites exhibited greatly improved rate capability (125 mA h g⁻¹ at 10 C) and power density.²⁶

As the modification materials for anodes or cathodes, nanostructured conductive polymers have some important advantages, such as providing effective paths for electronic transport and Li ion diffusion, enhanced conductivity and electrochemical activity, but some shortcomings are also associated, such as an increase in undesirable reactions and potentially more complicated processing procedures.

Nanostructured polymers can also function as binder materials, which hold the active materials together in the electrodes of Li-ion batteries, offering multiple advantageous features: a continuous electrically conductive framework, binding with the hosted active materials, and porous space for volume changes upon repeated Li⁺ insertion/de-insertion, thus allowing significant improvements in the stability of the electrode materials. Traditional binders used in Li-ion batteries such as polyvinylidene fluoride (PVDF) adhere the active materials and other conducting additives together to hold the mechanical integrity while conductive additives ensure the conductivity of the entire electrode. However, this classic binder system cannot work well in materials with large volume changes, such as alloy-type electrodes (silicon, germanium, *etc.*), because high stress generated during the lithiation/delithiation process would delaminate the polymer layer coated on the surface of active materials. And because the conductive additives have no mechanical binding force, they tend to aggregate during volume expansion, resulting in the destruction of electric connections, as schematically illustrated in Fig. 8a. In contrast, nanostructured conductive polymers may have the practical application in high-capacity alloy-type anodes owing to their distinctive characteristics, as demonstrated in Fig. 8b: (1) good electronic conductivity inherited from the conductive polymer framework, (2) good mechanical adhesion and ductility with tolerance of large volume changes, and (3) good electrolyte uptake to warrant high ionic conductivity.⁴⁹

Recently, a dynamic three-phase interline electropolymerization (D3PIE) method has been used to synthesize a free-standing PEDOT film which supports LiFePO₄ particles and acts as the cathode material for batteries (Fig. 9a).⁵⁰ The PEDOT-LiFePO₄ film shows high conductivity, flexibility and porosity and achieves high electrochemical performance with a discharge capacity of ~160 mA h g⁻¹ at the C/10 rate. The conductive polymer PEDOT:PSS could also be applied on sulfur particles to effectively trap the polysulfides and minimize the dissolution of polysulfides. A notable improvement in the performance of Li-S batteries was achieved.⁵¹

Liu *et al.*⁵² developed a promising conductive polymer binder which can be cathodically doped in reducing environments for silicon anodes. They introduced two functional groups to tailor the lowest unoccupied molecular orbital (LUMO) electronic states and the mechanical binding force. Based on the designed electronic and mechanical properties, the tailored polymer binder achieves both high conductivity for electron conduction and mechanical integrity, resulting in high

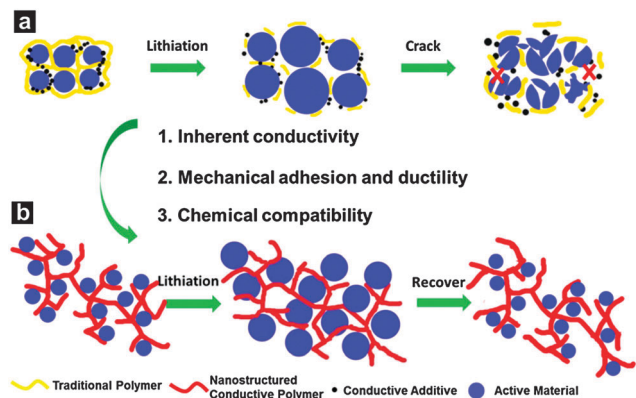


Fig. 8 (a) Traditional approach using a conductive additive and a polymer as a mechanical binder may result in broken electric contacts. (b) A nanostructured conductive polymer, which plays multiple functions, as a conductor and a binder, could maintain both electrical and mechanical integrity of the electrode during cycling.

specific capacity and stable cycling performance. In their following work,⁴⁹ other functional groups were introduced into polyfluorene type conductive polymers. The designed PFEM-Si electrodes achieved full-capacity cycling of Si with excellent rate performance.

In addition to molecular tailoring of conductive polymers, the micro/nano structure design is another efficient way to enhance their performance as electrode binders. Zhang *et al.*⁵³ developed PPy nanotubes as conductive matrices to support sulfur cathodes in lithium-sulfur batteries (Fig. 9b). The PPy nanotubes were synthesized by a self-degraded template method and the sulfur was incorporated by a co-heating process. The PPy-S composites

exhibited nearly a constant capacity of $\sim 650 \text{ mA h g}^{-1}$ after 80 cycles (Fig. 9c). The enhanced performance could be mainly attributed to the improved conductivity of PPy nanotube-based composites, favorable distribution of nanosized sulfur in the PPy matrix and excellent retention of the polysulfides within the electrode.

Recently, we adopted *in situ* polymerization of the PANI hydrogel, to form a bi-functional conformal coating that binds to the Si surface and also serves as a continuous 3D pathway for electronic conduction (Fig. 9d).⁵⁴ The crosslinker, phytic acid can potentially enhance the interactions between the Si particle surface and binder material *via* hydrogen bonding and electrostatic interaction. There are several key features of these unique Si-conductive hydrogel electrode systems. First, the porous hydrogel matrix possesses a large pore volume that can effectively accommodate the volume change of the Si nanoparticles. Second, the highly conductive and continuous 3D conductive polymer hydrogel framework as well as the conformal conductive coating surrounding Si nanoparticles provide good electrical connection to the particles. Third, the 3D nanostructured conductive polymer hydrogel reduces the weight fraction of the binder and conducting filler of a battery and improves the SEI interface between the electrode and the electrolyte. The Si-PANI electrode also exhibits superior cycling performance, *i.e.*, $\sim 91\%$ capacity was retained after 5000 cycles (Fig. 9e). We further extended the conductive polymer-based electrode to a ternary system which integrates Si nanoparticles and CNTs into a 3D PPy framework.¹⁸ The 3D nanostructured ternary electrode also exhibited a high reversible capacity and excellent cycling performance.

Compared to traditional binder systems, nanostructured conductive polymers show several advantageous features. First,

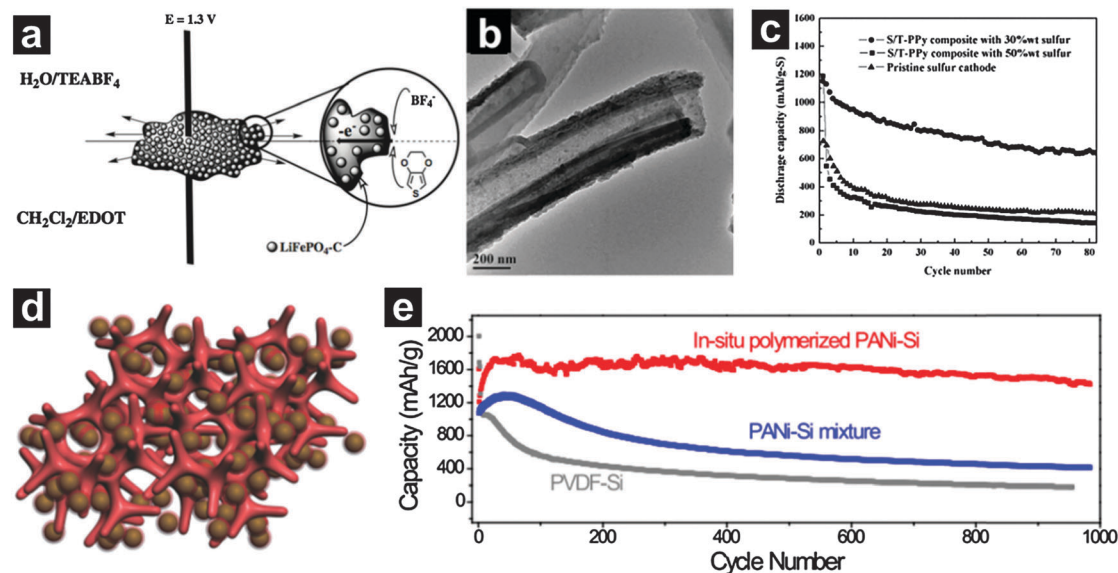


Fig. 9 (a) Schematic of the D3PIE method of dynamic growth with LiFePO_4 at the water/dichloromethane interface. Reproduced with permission from ref. 50. Copyright 2013 Elsevier Ltd. (b) The TEM image of the sulfur-PPy nanotube composites with 30 wt% sulphur. (c) Cycling performance of the sulfur-PPy nanotube composites and pristine sulphur. Reproduced with permission from ref. 53. Copyright 2011 Elsevier Ltd. (d) A schematic of 3D porous Si nanoparticle-conductive polymer hydrogel composite electrodes. (e) Electrochemical performance of the *in situ* polymerized Si-PANI composite electrodes at a charge-discharge current of 1.0 A g^{-1} , showing a stable capacity of $\sim 1500 \text{ mA h g}^{-1}$ after 1000 cycles (red line). Reproduced with permission from ref. 54. Copyright 2013 Nature Publishing Group.

the gravimetric energy density could be potentially enhanced because no conductive additives are needed and the loading of binders could be as low as 10 wt% of the electrode material (vs. 20–30% for commercial samples). Second, the porous nanostructure provides efficient paths for the diffusion of the electrolyte, thus enhancing the power density. Third, conductive polymer binders could be uniformly coated on the surface of active materials, thus achieving a better electrical contact. Although progress has been made towards using nanostructured conductive polymers to be used as binder materials, some limitations prohibit their practical application. First, the mechanical strength of conductive polymers is not high enough to hold large amount of active materials on the current collector, resulting in the relatively low mass loading of active materials. Second, the volumetric capacity and energy density is lower than that of other polymer-based electrodes, such as an SiNP–alginate electrode due to the nano-porous structure of the whole electrode which leads to inferior packing. In addition, the conductivity still needs to be further enhanced for better high-rate performance.

Several potential methods could be adopted to solve these problems and thus further improve the performance of nanostructured conductive polymer-based electrodes. Surface chemical modification or molecular-level modification could be applied to enhance the mechanical and electrical properties of nanostructured conductive polymers along with surface passivation to avoid undesirable reactions. Hybrid conductive polymers could also be synthesized to combine the advantages of each component. Finally, the chemical modification of the conductive polymer/active material interface could improve their electrical and chemical contacts.

4. Summary and outlook

Following the rapid development of synthetic strategies, a variety of nanostructured conductive polymers and conductive polymer-based composites have been obtained. These polymeric nanomaterials not only maintain attractive properties of bulk conductive polymers with efficient and reversible redox activity, light weight and facile processability, but also offer additional important features, such as much larger active surface areas and improved electrical, electrochemical and mechanical properties that are critically important for broad applications in energy conversion and storage, sensors, biomedical devices, etc.

From the aspect of energy storage applications, nanostructured conductive polymers can serve as active electrode materials in supercapacitors and lithium batteries as well as superior binder materials in next-generation high-energy Li-ion batteries. This class of materials possess intrinsic conducting frameworks that promote the transport of charges, ions, and molecules; and large interfaces between the electronic transporting phase (electrode) and the ionic-transporting phase (electrolyte) which would facilitate the high rate capability. Furthermore, the intermolecular polymeric bonding provides chemical and mechanical robustness to the frameworks, which make them important electrochemical components in fabricating flexible energy storage devices that may complement rapid

development of flexible and wearable electronics. Nanostructured conductive polymers are also attractive functional materials for high-energy Li-ion batteries because of their high electronic conductivity, mechanical adhesion and ductility with tolerance of large volume changes, chemical compatibility, and electrolyte uptake for ionic transport.

Though numerous studies have been conducted on the synthesis and application of nanostructured conductive polymers, advanced experimental and simulation/modelling studies are still needed to help researchers acquire a deeper understanding of the fundamental knowledge concerning the nanostructured conductive polymers, such as the effects of nanostructures on charge transfer and surface chemistry of nanostructured conductive polymers. State-of-the-art *in situ* and *ex situ* microscopic and spectroscopic techniques are also needed for studying fundamental electrochemistry of rationally synthesized conductive polymer nanostructures as well as electrochemical dynamics of hybrid inorganic–organic interfaces. Such studies will not only provide insights into the intrinsic properties of conductive polymers from the molecular scale to the macroscopic level, but will also promote the development of a wide range of techniques from chemical modification of conductive polymers to device fabrication for optimized performance. With delicate control over their electrical, electrochemical, thermal and mechanical properties, nanostructured conductive polymers with unprecedented multi-functionality, such as self-healing, multi-stimuli-responsive properties could be further developed, opening up significant opportunities for many other technologies. Exciting future advances will require great effort and continued innovation that will be best afforded by interdisciplinary research across chemistry, physics, and materials engineering.

Acknowledgements

G.Y. acknowledges the financial support of a faculty start-up grant from the University of Texas at Austin, 3M Non-tenured Faculty award, and the Welch Foundation grant F-1861.

Notes and references

- 1 A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon and W. van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366–377.
- 2 C. Li, H. Bai and G. Shi, *Chem. Soc. Rev.*, 2009, **38**, 2397–2409.
- 3 Z. Yin and Q. Zheng, *Adv. Energy Mater.*, 2012, **2**, 179–218.
- 4 Q. Zhang, E. Uchaker, S. L. Candelaria and G. Cao, *Chem. Soc. Rev.*, 2013, **42**, 3127–3171.
- 5 P. Novák, K. Müller, K. S. V. Santhanam and O. Haas, *Chem. Rev.*, 1997, **97**, 207–282.
- 6 L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C.-K. Tee, Y. Shi, Y. Cui and Z. Bao, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 9287–9292.
- 7 Y. Zhao, B. Liu, L. Pan and G. Yu, *Energy Environ. Sci.*, 2013, **6**, 2856–2870.
- 8 R. Ramya, R. Sivasubramanian and M. V. Sangaranarayanan, *Electrochim. Acta*, 2013, **101**, 109–129.

- 9 M. S. Islam and C. A. J. Fisher, *Chem. Soc. Rev.*, 2014, **43**, 185–204.
- 10 L. Nyholm, G. Nyström, A. Mihranyan and M. Strømme, *Adv. Mater.*, 2011, **23**, 3751–3769.
- 11 Y.-Z. Long, M.-M. Li, C. Gu, M. Wan, J.-L. Duvail, Z. Liu and Z. Fan, *Prog. Polym. Sci.*, 2011, **36**, 1415–1442.
- 12 J. Jang and H. Yoon, *Chem. Commun.*, 2003, 720–721.
- 13 C. R. Martin, *Acc. Chem. Res.*, 1995, **28**, 61–68.
- 14 S. J. Killoran and R. D. O'Neill, *Electrochim. Acta*, 2008, **53**, 7303–7312.
- 15 S. Han, A. L. Briseno, X. Shi, D. A. Mah and F. Zhou, *J. Phys. Chem. B*, 2002, **106**, 6465–6472.
- 16 J. Zang, C. M. Li, S. J. Bao, X. Cui, Q. Bao and C. Q. Sun, *Macromolecules*, 2008, **41**, 7053–7057.
- 17 Y. Shi, L. Pan, B. Liu, Y. Wang, Y. Cui, Z. Bao and G. Yu, *J. Mater. Chem. A*, 2014, **2**, 6086–6091.
- 18 B. Liu, P. Soares, C. Checkles, Y. Zhao and G. Yu, *Nano Lett.*, 2013, **13**, 3414–3419.
- 19 Y. Liao, C. Zhang, Y. Zhang, V. Strong, J. Tang, X.-G. Li, K. Kalantar-zadeh, E. M. V. Hoek, K. L. Wang and R. B. Kaner, *Nano Lett.*, 2011, **11**, 954–959.
- 20 J. Zhang, J. Jiang, H. Li and X. S. Zhao, *Energy Environ. Sci.*, 2011, **4**, 4009–4015.
- 21 H. Wang and H. Dai, *Chem. Soc. Rev.*, 2013, **42**, 3088–3113.
- 22 Z. Gui, J. Duay, J. Hu and S. B. Lee, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12332–12340.
- 23 G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Lett.*, 2011, **11**, 4438–4442.
- 24 C. Tan and H. Zhang, *Chem. Soc. Rev.*, 2015, **44**, 2713–2731.
- 25 S.-B. Son, T. A. Yersak, D. M. Piper, S. C. Kim, C. S. Kang, J. S. Cho, S.-S. Suh, Y.-U. Kim, K. H. Oh and S.-H. Lee, *Adv. Energy Mater.*, 2014, **4**, DOI: 10.1002/aenm.201300961.
- 26 D. Lepage, C. Michot, G. Liang, M. Gauthier and S. B. Schougaard, *Angew. Chem., Int. Ed.*, 2011, **50**, 6884–6887.
- 27 X. Lu, M. Yu, G. Wang, Y. Tong and Y. Li, *Energy Environ. Sci.*, 2014, **7**, 2160–2181.
- 28 H. Zhang, X. Yu and P. V. Braun, *Nat. Nanotechnol.*, 2011, **6**, 277–281.
- 29 D. P. Dubal, S. H. Lee, J. G. Kim, W. B. Kim and C. D. Lokhande, *J. Mater. Chem.*, 2012, **22**, 3044–3052.
- 30 J. Huang, K. Wang and Z. Wei, *J. Mater. Chem.*, 2010, **20**, 1117–1121.
- 31 Q. Wu, Y. Xu, Z. Yao, A. Liu and G. Shi, *ACS Nano*, 2010, **4**, 1963–1970.
- 32 J. Xu, K. Wang, S.-Z. Zu, B.-H. Han and Z. Wei, *ACS Nano*, 2010, **4**, 5019–5026.
- 33 G. Wang, L. Zhang and J. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 797–828.
- 34 R. Liu and S. B. Lee, *J. Am. Chem. Soc.*, 2008, **130**, 2942–2943.
- 35 C. Zhou, Y. Zhang, Y. Li and J. Liu, *Nano Lett.*, 2013, **13**, 2078–2085.
- 36 Y. Hou, Y. Cheng, T. Hobson and J. Liu, *Nano Lett.*, 2010, **10**, 2727–2733.
- 37 X. Xia, Q. Hao, W. Lei, W. Wang, D. Sun and X. Wang, *J. Mater. Chem.*, 2012, **22**, 16844–16850.
- 38 F. Meng and Y. Ding, *Adv. Mater.*, 2011, **23**, 4098–4102.
- 39 C. Meng, C. Liu, L. Chen, C. Hu and S. Fan, *Nano Lett.*, 2010, **10**, 4025–4031.
- 40 J. Tao, N. Liu, W. Ma, L. Ding, L. Li, J. Su and Y. Gao, *Sci. Rep.*, 2013, **3**, 2286.
- 41 Y. Gogotsi and P. Simon, *Science*, 2011, **334**, 917–918.
- 42 Z. Wang, P. Tammela, P. Zhang, M. Strømme and L. Nyholm, *J. Mater. Chem. A*, 2014, **2**, 16761–16769.
- 43 F. Cheng, W. Tang, C. Li, J. Chen, H. Liu, P. Shen and S. Dou, *Chem. – Eur. J.*, 2006, **12**, 3082–3088.
- 44 M. Zhou, J. Qian, X. Ai and H. Yang, *Adv. Mater.*, 2011, **23**, 4913–4917.
- 45 K. S. Park, S. B. Schougaard and J. B. Goodenough, *Adv. Mater.*, 2007, **19**, 848–851.
- 46 M. N. Hyder, R. Kaviani, Z. Sultana, K. Saetia, P.-Y. Chen, S. W. Lee, Y. Shao-Horn and P. T. Hammond, *Chem. Mater.*, 2014, **26**, 5310–5318.
- 47 A. V. Murugan, T. Muraliganth and A. Manthiram, *Chem. Mater.*, 2009, **21**, 5004–5006.
- 48 X. Xia, D. Chao, X. Qi, Q. Xiong, Y. Zhang, J. Tu, H. Zhang and H. J. Fan, *Nano Lett.*, 2013, **13**, 4562–4568.
- 49 M. Wu, X. Xiao, N. Vukmirovic, S. Xun, P. K. Das, X. Song, P. Olalde-Velasco, D. Wang, A. Z. Weber, L.-W. Wang, V. S. Battaglia, W. Yang and G. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 12048–12056.
- 50 N. D. Trinh, M. Saulnier, D. Lepage and S. B. Schougaard, *J. Power Sources*, 2013, **221**, 284–289.
- 51 Y. Yang, G. Yu, J. J. Cha, H. Wu, M. Vosgueritchian, Y. Yao, Z. Bao and Y. Cui, *ACS Nano*, 2011, **5**, 9187–9193.
- 52 G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V. S. Battaglia, L. Wang and W. Yang, *Adv. Mater.*, 2011, **23**, 4679–4683.
- 53 X. Liang, Y. Liu, Z. Wen, L. Huang, X. Wang and H. Zhang, *J. Power Sources*, 2011, **196**, 6951–6955.
- 54 H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nat. Commun.*, 2013, **4**, 1943.