



Review Article

Polyaniline (PANI) based electrode materials for energy storage and conversion



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ARTICLE INFO

Article history:

Received 8 August 2016

Accepted 8 August 2016

Available online 15 August 2016

Keywords:

Polyaniline
Composites
Supercapacitors
Batteries
Electrocatalysts

ABSTRACT

Polyaniline (PANI) as one kind of conducting polymers has been playing a great role in the energy storage and conversion devices besides carbonaceous materials and metallic compounds. Due to high specific capacitance, high flexibility and low cost, PANi has shown great potential in supercapacitor. It alone can be used in fabricating an electrode. However, the inferior stability of PANi limits its application. The combination of PANi and other active materials (carbon materials, metal compounds or other polymers) can surpass these intrinsic disadvantages of PANi. This review summarizes the recent progress in PANi based composites for energy storage/conversion, like application in supercapacitors, rechargeable batteries, fuel cells and water hydrolysis. Besides, PANi derived nitrogen-doped carbon materials, which have been widely employed as carbon based electrodes/catalysts, are also involved in this review. PANi as a promising material for energy storage/conversion is deserved for intensive study and further development.

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1. Introduction

With the flying development of economy, supplying of energy cannot meet the increasing demand. The clean and efficient energy devices are desirable due to the energy and environment crisis [1]. Over the past decades, clean and sustainable energy technologies have been rapidly developed like solar energy, wind energy, biomass fuels and fusion power. On the other side, energy storage and conversion technologies have also been in the ascendant. Among them, supercapacitors, Li-ion batteries (LIBs) and fuel cells are “super stars” in the investigation fields [2].

The electrode materials play a significant role in the performance of the energy storage and conversion devices. Carbon

species, metal compounds and conducting polymers are the three main types used as electrode materials for energy storage devices. Carbon based electrodes (activated carbon, graphene, carbon nanotubes, etc.) with high conductivity and stability usually have excellent cycling stability and high power density as supercapacitor electrodes, battery anodes and the support for fuel cell and water hydrolysis catalysts. However, the energy density of carbon based electrodes for supercapacitors are usually low due to the limitation of energy storage mechanism. Metal compounds may exhibit excellent electrochemical performance in supercapacitors, batteries and fuel cells due to their high activity and good intrinsic electrochemical properties, but they still have problems like low conductivity, high cost and limited natural abundance.

Conducting polymers (CPs), like Poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (Ppy) and polyaniline (PANI), have attracted great interests in energy storage, sensors and electrochromic devices since the discovery in 1960 [3]. They have high conductivity and excellent capacitive properties. Their simple components (C, H, N or S) also indicate the high affordability. As displayed in the Ragone plot (Fig. 1), conducting polymers based devices (CP Device) show high specific capacitance compared with electrochemical double-layer supercapacitors, and

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Peer review under responsibility of Vietnam National University, Hanoi.

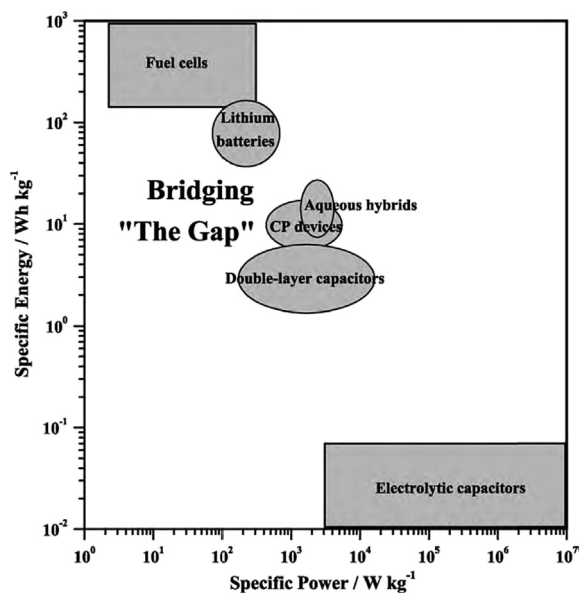


Fig. 1. Ragone Plots for capacitors, batteries and fuel cells [4]. Reproduced with permission.

have faster kinetics than most inorganic batteries, which can narrow the gap between inorganic batteries and carbon based capacitors, indicating the high potential of conducting polymers in energy storage [4]. The combination of conducting polymers and carbon materials, metal compounds is quite popular with excellent performance taking advantage of each component, like the Ppy/CNT/graphene foam composites shown superior performance in asymmetric supercapacitor [5]. Among the conducting polymers, polyaniline (PANi) generates most attention because it has the highest specific capacitance due to multi-redox reactions, good electronic properties due to protonation [6], and low cost for its infinite abundance. Moreover, it has better thermal stability and can be easily synthesized by chemical or electrochemical methods, resulting in powder or thin film [3].

PANi can exist in different oxidation states: fully reduced leucoemeraldine (LE) ($y = 1$), half oxidized emeraldine base (EB) ($y = 0.5$) and fully oxidized pernigraniline (PE) ($y = 0$), as illustrated in Fig. 2 [7]. The intermediate PANi-EB has the highest stability and conductivity after the protonation. However, both LE and PE are insulators even after the protonation [6]. Usually, the PANi used in electrodes is a mixture of its three states and we are expecting for a highest portion of PANi-EB in the mixture to contribute to the best performance. PANi can be synthesized by the oxidation of monomer aniline through chemical or electrochemical methods [8]. Chemical polymerization can result in various morphologies, like nanofibers, nanorods, nanotubes, nanoflakes, nanospheres and even nanoflowers, through accurate control of oxidants or/and addition of additives [9,10]. Compared with chemical polymerization, the electrochemical polymerization is a much faster and environmentally benign polymerization process, which is free of oxidants and additives. Using simple setup, electrochemical polymerization can easily obtain film-shaped binder-free electrodes.

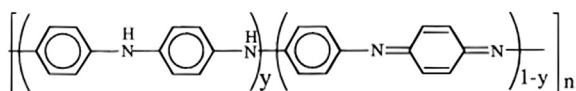


Fig. 2. The asymmetric chemical structure of PANi [7]. Reproduced with permission.

Nevertheless, the morphology of the PANi obtained from electrochemical deposition is usually limited to nanofibers, nanogranulars or thin film at the surface of substrates. Besides, the morphologies of PANi are greatly dependent on the properties of the substrates.

PANi has been widely used in energy storage and conversion devices, including supercapacitors, batteries and fuel cells. When used for supercapacitors PANi as the active material stores charge via redox reaction as the PANi transition between various oxidation states. It has been able to achieve specific capacitance as high as 950 F g^{-1} through the involvement of the entire volume in storage of charge, surpassing other conducting polymers that store charge solely on surface [11]. However, the pseudocapacitive processes involve the swelling, shrinkage and cracking of the polymer during doping/dedoping of charged ions, resulting in poor cycle stability. In addition, the degradation of PANi may occur at relatively high potentials due to the over-oxidation, which lead to relatively low working potentials of PANi electrode. These problems make it necessary to develop composite designs that couple other materials such as carbonaceous materials or metal oxides with the PANi matrix. Yan Jun and co-workers prepared an efficient supercapacitor electrode based on graphene nanosheets (GNSs), carbon nanotubes (CNTs) and PANi through a facile chemical in-situ method. The electrode shows very high specific capacitance (1035 F g^{-1} , 1 mV s^{-1}) and excellent stability (6% lost after 1000cycles) [12]. Similarly, when used for battery electrode fabrication, PANi also shows great enhancement in electrochemical performance via composite design which combines electroactive organic polymers and electroactive inorganic species to form single nanocomposite materials. This is an appealing way to merge the best properties of each of the components into a hybrid electrode material. The hybrid approach also allows the composite materials with synergic activity unattainable by the individual components. In the composite electrode smaller molecular or cluster inorganic species can be integrated and anchored in the PANi host matrix with enhanced structural stability, optimized porosity and improved electric conductivity, which lead to extra charge storage via improved charge transportation and kinetic behavior. Yang Liqun and co-workers prepared MoS_2/PANi nanowires as anode for LIB, illustrating high capacity of 1063.9 mAhg^{-1} , much higher than pure MoS_2 (684.9 mAhg^{-1}) [13].

Fuel cell is a promising energy conversion technology, which converts the chemical energy of fuels to electricity with high efficiency and without emission of greenhouse gases. However, the high cost and unsatisfied cycle life hinder the wide application and commercialization of fuel cells as a clean and sustainable power source. Up to now, the best electrochemical catalyst for both anode and cathode is Pt supported on porous carbon. Pt is expensive with limited availability while graphitic carbon support suffers from corrosive degradation. It is a great challenge to find a better electrode catalyst to replace Pt/C or to reduce the Pt loading with improved performance. This is true particularly for cathode catalyst to promote oxygen reduction reaction (ORR), which has high overpotential and requires much more (usually 4x) Pt than anode. Four classes of new ORR catalysts have been developed in recent years, including (i) Pt-M (M = Co, Ni, Cr, Fe, Mo, Bi) alloy catalysts with lower Pt contents, (ii) New-generation chalcogenides, (iii) Non-precious metal and heteroatomic polymer nanocomposites, and (iv) Metal-free carbon-based catalysts. PANi as supports for metal catalysts has several advantages, like the high flexibility, high conductivity, controllable morphologies and high dispersive ability to prevent the agglomeration of the active catalysts. Additionally, PANi can be employed as the carbon precursor to fabricate metal free non-precious catalysts [14], because of its low cost and high content of nitrogen, which may play important role in enhanced electrochemical activity.

In the past few years, more and more renewable energy is generated by intermittent solar and wind power sources added to the power grid. The need for grid balancing and energy storage increases. Although for less than a cycle or hourly energy storage, flywheel or battery is respectively the preferred option, power-to-gas (H_2) holds great significance for high volumes (gigawatt, terawatt hours) and long term energy storage, which converts surplus renewable electricity into hydrogen by rapid response electrolysis and its subsequent injection into the gas distribution network [15]. Hydrogen solutions have finally reached the top of energy agendas. Nevertheless, this program again requires low cost and effective electrocatalysts for water electrolysis, and PANi has shown promise as a useful electrode material, both for promoting hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [16].

This paper summarizes the recent progress on PANi based energy storage devices and beyond, including: (i) PANi based electrodes used in electrochemical supercapacitors, the composites with various carbon materials, blends with other polymers and hybrids with metal chalcogenides. (ii) PANi based electrodes used in lithium-ion batteries, lithium-sulfur batteries and sodium-ion batteries. (iii) PANi supported metal compounds and PANi derived porous carbon materials used as electrochemical catalysts for fuel cells or electrocatalysts.

2. Supercapacitors

Supercapacitors have high power density and long cycling stability. They are able to store much more energy than traditional capacitors because of the enlarged surface area of the electrode and the decreased distance between two charged layers. They can be divided into two categories: electrostatic double-layer supercapacitor (EDLC) and pseudocapacitor. EDLC stores electrical energy by the electrostatic adsorption and desorption of ions in the conductive electrolyte, thus creating the double layers at the electrode and electrolyte interface on both positive and negative electrodes (Fig. 3a). Porous carbon materials with low cost are usually used as double-layer supercapacitor electrode materials due to their high specific surface area and excellent mechanical and chemical stability. The electrochemical processes for charging and discharging can be expressed as: $E_{s1} + E_{s2} + A^- + C^+ \leftrightarrow E_{s1}^+ / A^- + E_{s2}^- / C^+$. Where E_{s1} and E_{s2} are the two electrode surfaces, A^- is anion coming from electrolyte, C^+ cation, and/represents for the electrode/electrolyte interface. During charging, the electrons travel through an external load from the negative electrode to the positive one. Cations in the electrolyte move towards the negative electrode while anions move towards the positive electrode, forming electrostatic double layers. During discharging the process is reversed. There is no electron transfer across the electrode and electrolyte interface, and no ion exchange between the two

electrodes in EDLC. In this way, the electrical energy is stored in the double-layer interface and can be estimated as $E = \frac{1}{2}(CV^2)$. Where E , C and V are the energy density, specific capacitance and voltage of the capacitor. The double layer capacitance can be expressed as $C = A \epsilon / 4 \pi d$. Where A is the area of the electrode surface, ϵ is the medium (electrolyte) dielectric constant, and d is the effective thickness of the electrical double layer. The double layer thickness d is typically a few tenths of nanometer and hence the specific capacitance is much higher than conventional capacitors.

Pseudocapacitor is another type of supercapacitor, which store energy through the redox reactions between electrode and electrolyte (Fig. 3b) [17]. Pseudocapacitance occurs together with static double-layer capacitance while the electron charge transfer is accomplished by electron adsorption, intercalation and very fast reversible faradaic redox reactions on the electrode surface. The adsorbed ions have no chemical bonds and chemical reaction with the atoms of the electrode since only a charge-transfer take place. The pseudocapacitors may show much (10–100x) higher capacitance than EDLCs of the same surface area, since the electrochemical processes occur both on the surface and in the bulk near the surface of the solid electrode. But they normally possess relatively low cycling stability and low conductivity in comparison with EDLC, which seemed to impede their wide application. To address these drawbacks, carbonaceous scaffold is usually added into the electrode for improving the performance. Pseudocapacitance strongly depends on the chemical affinity of electrode materials to the ions adsorbed on the effective surface of electrode. There are two types of materials exhibiting redox behavior for use as pseudocapacitor electrodes: one is transition metal oxides/chalcogenides and the other is conducting polymers [18].

Many transition metal oxides/sulfides, like RuO_2 , IrO_2 , V_2O_5 , Fe_3O_4 , Co_3O_4 , MnO_2 , NiO , MoS_2 and TiS_2 , generate faradaic electron-transferring reactions with low conducting resistance. These metal compounds undergo multiple oxidation states at specific potentials, leading to high capacitance. Ruthenium oxide (RuO_2) with aqueous H_2SO_4 electrolyte provides the best example, with a charge/discharge over a window of about 1.2 V per electrode. Excellent capacitance of $1340 F g^{-1}$ with several hundred-thousand cycles has been achieved on hydrous RuO_2 [19]. The redox reaction takes place according to: $RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x$ ($0 \leq x \leq 2$). During charge/discharge, H^+ ions are inserted-into or removed-from the RuO_2 lattice, without chemical bonding or phase transformation. The OH^- groups cling as a molecular layer on the electrode surface and remain in the region of the Helmholtz layer, while the Ru ions anchoring protons are reduced their oxidation state from +4 to +3.

For conducting polymer pseudocapacitors, the electron charge storage is implemented by switching the polymer between two doping states (p-doping/n-doping) where electrolyte ions are

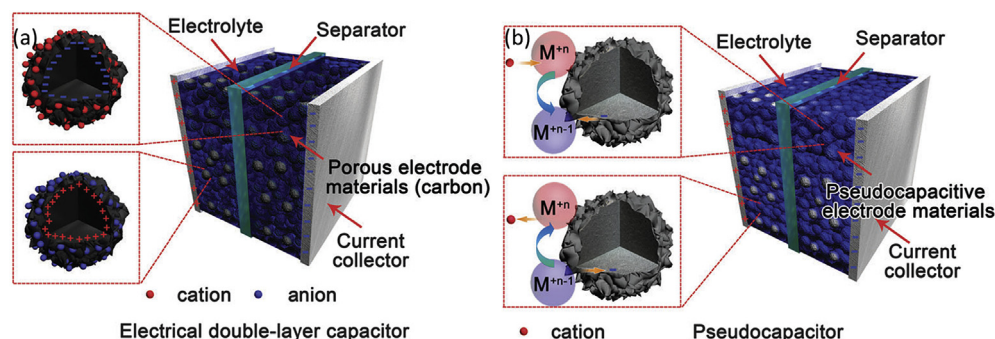


Fig. 3. Schematic diagram of (a) the electrochemical double-layer capacitors and (b) the pseudocapacitors [17]. Reproduced with permission.

inserted/extracted from the polymers' backbones. The conducting polymers become polycations during the charging process (oxidative p-doping). The positively charged polycations will attract the anions (like Cl^- in Fig. 4) in the electrolyte to intercalate into the polymer backbone for electroneutrality. Thus the conducting polymers are oxidized and they p-doped with anions ($(\text{P})_m + x\text{A}^- - xe^- \leftrightarrow (\text{P})_{x+m}(\text{A}^-)_x$) [20]. To the contrary, the conducting polymers are reduced and n-doped with cation (M^+) during discharge ($(\text{P})_m + y\text{M}^+ + ye^- \leftrightarrow \text{P}_{y-m}(\text{M}^+)_y$). Where $(\text{P})_m$ is the conducting polymer with conjugated double bonds, m is the degree of polymerization. A^- and M^+ are anions and cations, respectively. Unlike metal oxides, the entire polymer chains are exposed to the doping/depoting of ions during charge/discharge. This grants high capacitance but also lead to the damage of the polymer structure, shortening the polymers' overall life cycle. To improve the life cycle, conducting polymers and carbon supports are coupled, forming a hybrid electrode.

Usually, supercapacitors, including both EDLCs and pseudocapacitors, have lower energy density compared with batteries. Scientists have been investigating many routes to increase the energy density and trying to realize the ideal case: long cycling life, high power density and high energy density. The design of hybrid capacitors paves the way to supercapacitors with high capacitance and energy density. The combined devices based on the hybrid of carbon based EDLCs, pseudocapacitive electrodes, and even battery-type electrodes have shown rather good electrochemical

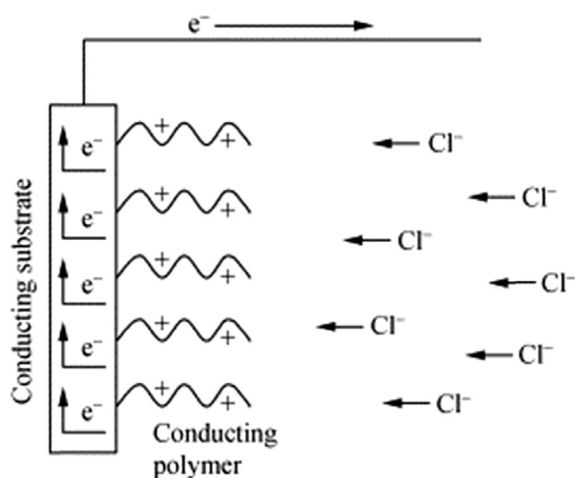


Fig. 4. Illustration of pseudocapacitive behavior of the conducting polymer during the charging process [18]. Reproduced with permission.

performance [17]. Here we will discuss the recent progress and innovations on PANi based pseudocapacitors in detail.

2.1. PANi and carbon composites

PANi based electrodes for supercapacitors have multi-redox reactions, high conductivity and excellent flexibility. Pure PANi could act as a supercapacitor electrode with high specific capacitance around 600 F g^{-1} in aqueous electrolyte due to its good pseudocapacitive properties [21,22]. Wang Kai and co-workers showed that PANi with unique nanowire structure as active material for supercapacitor could induce high capacitance of 950 F g^{-1} that was obtained through an electrochemical polymerization. As shown in Fig. 5, the PANi nanowire arrays could facilitate the electrolyte ions diffusion, resulting in high utilization of PANi and fast doping and de-doping process [11]. The excellent electrochemical performance is highly dependent on the PANi structures. Therefore, the inferior stability due to structural change and chemical degradation could result in cycling instability and poor rate performance. Moreover, the agglomerate morphologies of roughly synthesized PANi usually lead to the inefficient utilization of PANi. Fortunately, the high flexibility makes it possible for PANi to combine with other materials harmoniously. Carbon materials are suitable for the fabrication of PANi based composites due to their high stability, good conductivity and large surface area, which can reinforce the structures of PANi during the doping and depoting of counter ions.

2.1.1. PANi/Porous carbon composites

Porous carbon materials are popularly used to enhance the stability along with conductive PANi. They have large surface area, good chemical stability and easy processability, which can just make up the disadvantages of PANi. Furthermore, the double layer capacitance provided from such carbon materials and the pseudocapacitive contribution from PANi can further maximize the specific capacitance of the whole electrodes [23].

Activated carbon (AC) nanomaterials have gained much interest for the fabrication of PANi/carbon composites due to their high stability, good conductivity, high affordability and low cost. They are generally obtained from a variety of carbonaceous precursors by chemical conversion and physical activation, and commercially used as electrode materials for supercapacitors in nowadays [1]. The PANi/AC composites can be easily obtained through either chemical or electrochemical polymerization. The chemical method could realize the coupling of PANi and carbon during the polymerization of PANi in a mixture solution of aniline monomer and activated carbon powder. After the addition of oxidants, the in-situ polymerization happens and the PANi/carbon composites are

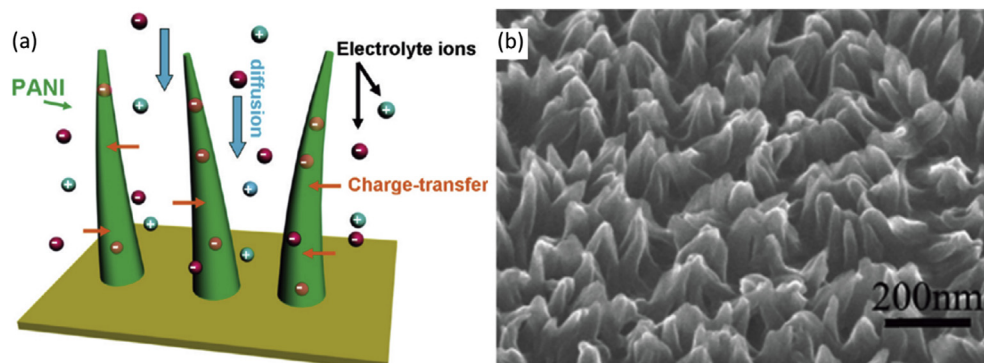


Fig. 5. (a) Schematic illustration of electrolyte diffusion paths in PANi nanowire arrays. (b) SEM image of as obtained PANi nanowire arrays [11]. Reproduced with permission.

achieved [24–26]. The size of AC particles has great effect on the morphology of PANi/AC. Small size AC particles could be wrapped in PANi matrix, while PANi could coat on the surface of AC when the carbon particle size is large. Surfactants can be used to control the morphology of the PANi/AC composites. In the electrochemical synthesis process, the activated carbon materials are usually coated on the stainless steel or graphite substrate and then act as the working electrode for PANi deposition, thus obtaining the PANi/carbon hybrids [27,28]. These PANi/AC composites show high specific capacitance of 200–700 F g⁻¹ due to the combination of both merits of high intrinsic pseudocapacitance of PANi and good stability of activated carbons.

Others kinds of porous carbon materials used are ordered mesoporous carbon (OMC) and ordered macroporous carbon, which are usually obtained by template (silica, CaCO₃, etc.) methods [29–34]. These ordered mesoporous/macroporous carbons are favorable for PANi/carbon composites because of their high specific surface area, unique structures as well as fast ionic transport. Their specific surface area can be as high as

1000–2000 m² g⁻¹. Fig. 6 illustrates a highly ordered mesoporous carbon (OMC) with a high specific surface area of 1703 m² g⁻¹ and a high mesopore volume around 4 nm. Highly flexible PANi grown on the large-surface OMC could induce high specific capacitance of 602.5 F g⁻¹ [33]. On macroporous carbon PANi could penetrate into the unique macropore structures and be coated on the inner and outer surface of carbon spheres [35]. The thin and porous PANi layer coated on the carbon surface resulted in high utilization of active materials and short ionic diffusion length. The nanostructured PANi is desired because of the high utilization of electrode materials with more exposed active sites of PANi. Well-ordered whisker-like polyaniline structure was synthesized on OMC with high electrochemical performance because of the facilitated ionic transport and improved PANi utilization [32,34]. The nanometer-sized PANi whiskers formed numerous “V-type” nanopores inside the active material (Fig. 7d) and thus yield a high electrochemical capacitance performance due to the fast penetration of electrolyte, decreased diffusion length and reduced energy/power loss, leading to high specific capacitance of 900 F g⁻¹. Other unique nanostructures like

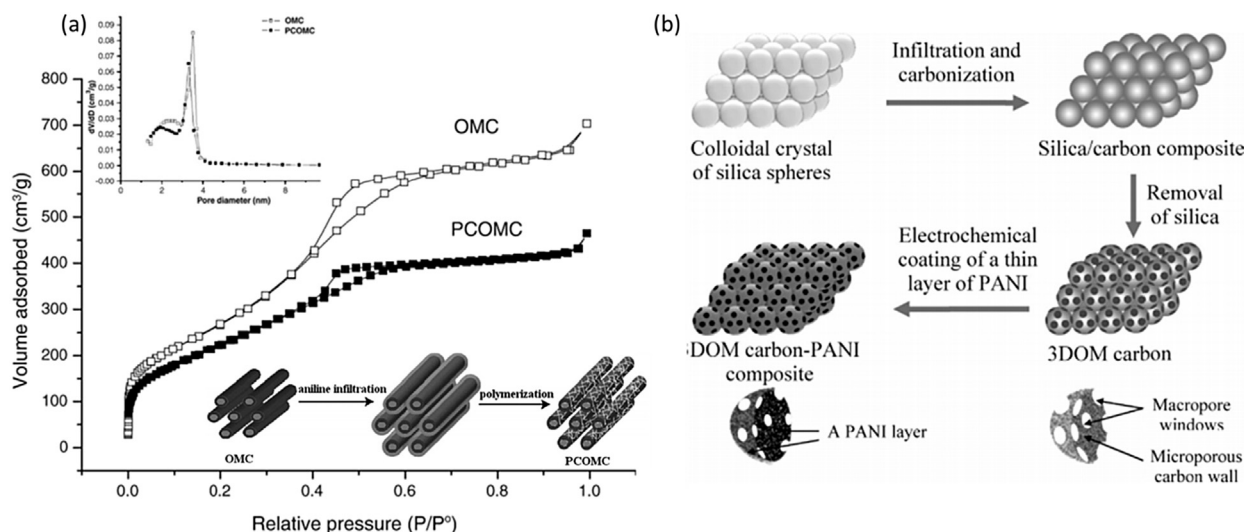


Fig. 6. (a) N₂ adsorption and desorption isotherms of ordered mesoporous carbon materials (OMC) and insets are the corresponding pore size distribution and the schematic of experimental routes [33]. (b) Preparation of three-dimensionally ordered macroporous (3DOM) carbons and 3DOM-PANI composites [35]. Reproduced with permission.

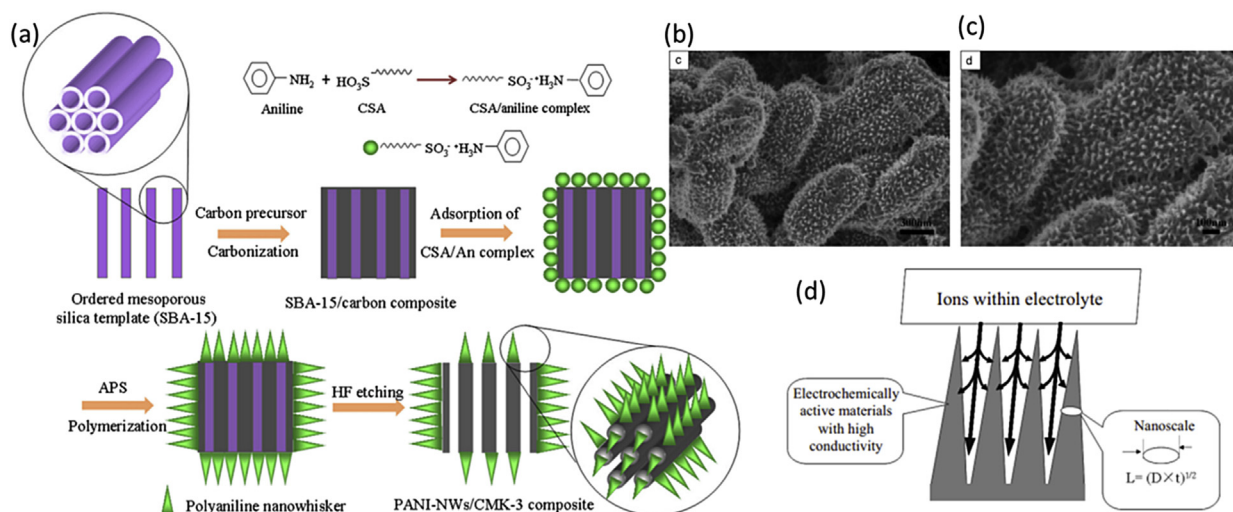


Fig. 7. (a) The schematic experimental preparation of PANi nanowhiskers (PANI-NWs) and ordered mesoporous carbon (CMK-3) composite. (b), (c) The low and high magnification SEM images of PANi-NWs/CMK-3 [34]. (d) Schematic representation of the reduced diffusion length with whisker-like channels [32]. Reproduced with permission.

nanofasciculi, nanowires and nanofibers of PANi were also synthesized on the surface of OMC with high specific capacitance of $473\text{--}747\text{ F g}^{-1}$ [29,30,35].

Porous carbon nanospheres (PCNSs) and hollow carbon spheres (HCSs) have also been used in fabricating PANi/C composites [36–38]. PCNSs and HCSs have unique pore structures, such as ultrahigh surface area and suitable pore sizes, contributing to short ionic paths, large electrochemical active areas and high specific capacitance. The PCNSs synthesized by the pyrolysis of polypyrrole showed a specific capacitance as high as 320 F g^{-1} [38]. With the coating of PANi, the electrochemical performance of PANi/PCNS was greatly enhanced with a higher capacitance of 584 F g^{-1} by taking advantages of each component. PANi/OMCs based electrodes usually show better performance than PANi/PCNSs. This is because the coating of PANi on the PCNSs and HCSs may cover and block a large portion of micropores, even some mesopores, which could hinder the electrolyte from infusion. In addition, the coverage of PANi on smaller sized pores in PCNSs and HCSs decreased the double-layer capacitance contribution, which is high compared with that of common carbon materials.

Besides active carbon and ordered mesoporous carbon materials, there are biomass (wood, bitch, bamboo, etc) derived porous carbon materials used for the PANi/C composite electrodes [39,40]. After high temperature pyrolysis, such biomass carbon materials could be excellent support and current collector for the deposition of polyaniline because of their high porosity and large pore sizes, which are superior to powered carbon. The disadvantages of such carbon materials are the impurities, which come from the inorganic salts or oxides in the biomass.

2.1.2. PANi/graphene composites

Graphene has caused extensive concern in supercapacitors due to its good thermal stability excellent electronic properties and

high theoretical specific surface area ($2630\text{ m}^2\text{ g}^{-1}$) [41]. This dramatically high surface area can help to improve the dispersion of PANi, which could tremendously enhance the utilization of PANi and result in much higher specific capacitance. Large sheets of 2-D graphene can improve the stability by holding every PANi component together on the large surface tightly. Additionally, the conductivity of the composite could be enhanced due to the intact contact of each PANi component to a conducting surface.

Graphene shows a specific capacitance of around 100 F g^{-1} in aqueous (acidic, neutral, alkaline), organic, and even ionic liquid electrolytes [41,42]. When combined with PANi, the capacitance reaches 1046 F g^{-1} , as PANi contributes most to the capacitance due to pseudocapacitive properties [43]. Graphene used in energy storage is usually synthesized following the Hummer's method or modified Hummer's method due to the high yields and low cost. This result in graphene oxide (GO) [44]. The composites of PANi and GO can be prepared through chemical in-situ polymerization or electrochemical co-deposition. Various morphologies of the composites can be obtained from chemical method, like nanofiber or flocculent structures, the nanostructure of which is beneficial to fast charge transfer, and thus high specific capacitance [45,46]. As show in Fig. 8a and b, the growth of PANi on GO is highly dependent on the concentration of aniline monomer. When the concentration is low ($<0.05\text{ M}$), PANi tends to dispersedly grow on GO, while the nucleation will happen in the solution when the concentration is high ($>0.06\text{ M}$). This growth mechanism was used as a guidance to optimize the products. The flocculent PANi/GO composites showed a high specific capacitance of 555 F g^{-1} and high capacitance retention of 92% after 2000 cycles due to the synergistic between layered GO sheets and pseudocapacitive PANi. Electrochemical co-deposition is a facile method and the obtained PANi/GO composites also show good electrochemical performance, high specific capacitance ($C_{sp} > 640\text{ F g}^{-1}$) and long cycling stability ($\sim 90\%$ after 1000

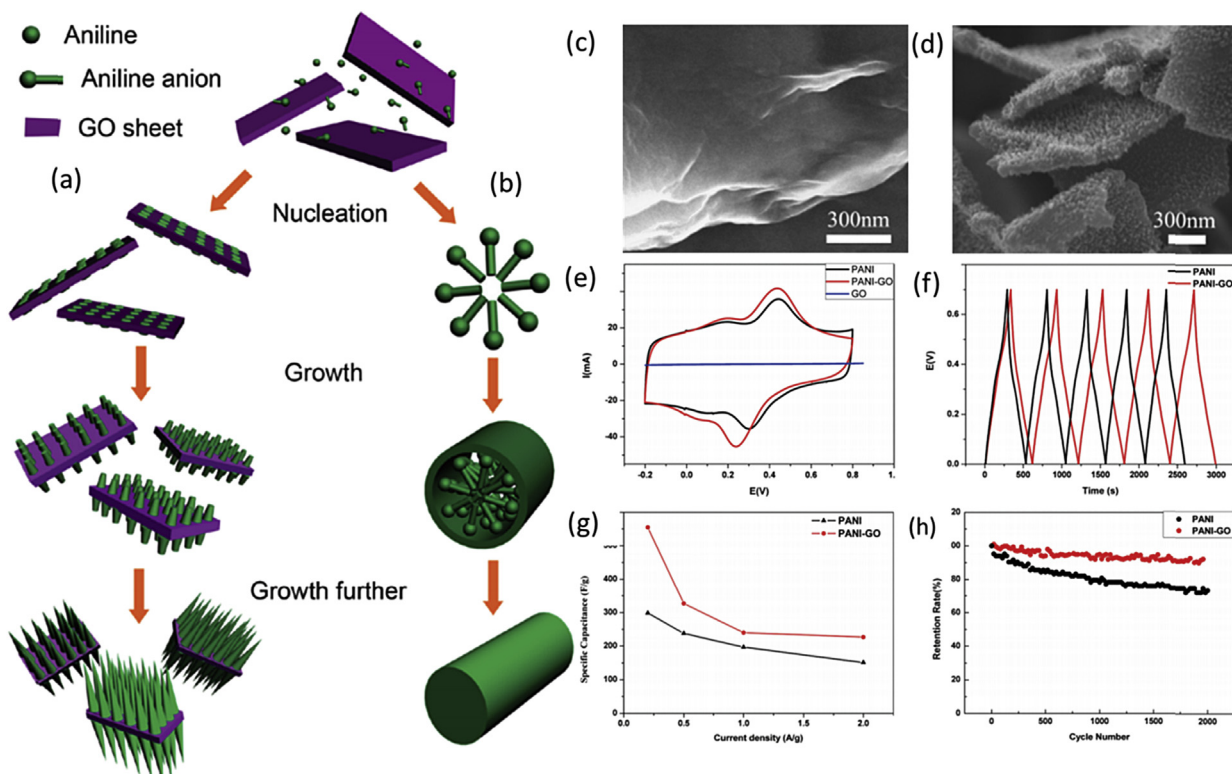


Fig. 8. The schematic of (a) growth mechanism of PANi on the surface of GO and (b) nucleation of PANi in solution. SEM images of (c) GO and (d) PANi/GO reacted for 24 h. (e–h) the electrochemical performance of PANi and PANi/GO [46]. Reproduced with permission.

cycles) reported [46,47]. However, the morphologies of PANi/GO composites synthesized by electrochemical polymerization are sterile and the structure design is more difficult for special purpose.

Many works have made progress on PANi/Graphene by reducing GO to reduced-graphene-oxide (rGO) in order to enhance the conductivity. The reduction could be realized through the use of reductant like hydrazine, sodium borohydride, or a heating process in inert gas around 400 °C [43,48,49]. The PANi/rGO composites show 3x better electrochemical performance compared with PANi/GO, 480 F g⁻¹ to 158 F g⁻¹ as illustrated in Zhang Kai's work [48]. There are two main routes for the synthesis of PANi/rGO composite, one is a reduction process of GO to rGO first and then combined with PANi. However, scientists found that rGO tends to be agglomerate during the reduction. Therefore, many researchers synthesized the composites of PANi/GO first and then reduced them to PANi/rGO following a re-doping process of PANi to improve the utilization of rGO [43]. The properties of the PANi/G composite capacitors strongly depend not only on morphology and loading mass ratio of PANi on graphene surface, but also on the connecting (non-covalent or covalent) mode between PANi and graphene. Compared to non-covalent connecting, covalent connecting is stronger and might have positive impact on the capacitance and cycle life of the composite. Recently a new strategy has been developed to induce covalent connecting between PANi and functional-rGO (frGO) via selection of surface functionality of rGO, such as aminophenyl-rGO and nitrophenyl-rGO. The functionalization of rGO to frGO was performed through solvothermal reaction or furnace heating with ammonia gas flow [50,51]. The functional group may affect the morphology and conductivity of PANi and thus improve the supercapacitor performance. Vertical PANi nanowires array grown on nitrophenyl-group-modified rGO (frGO) showed higher thermal stability, higher specific capacitance

and longer cycle life than the two nanocomposites connected by van der Waals force (PANi-GO and PANi-rGO). A large-scale conjugated system was found to form between PANi and frGO, which could improve charge transfer significantly and enhance the capacitive performance [51].

Besides traditional PANi/GO, PANi/rGO and PANi/frGO composites, new types of 3-D graphene foam (GF) or graphite paper have been prepared for the fabrication of PANi based free-standing electrodes [52–55]. Bin Yao and co-workers deposited PANi onto the pencil-drawing graphite paper and the obtained free-standing electrodes with excellent mechanical properties, as shown in Fig. 9g. The electrode is highly flexible so that the CV curves in Fig. 9g have no difference with the bending angle change. The G/PANi paper based supercapacitors have high energy density, good cycling stability and high coulombic efficiency that can light a red LED (Fig. 9f). PANi nanowire arrays on 3D graphene (rGO-F/PANi) electrodes also showed promise for flexible and wearable device applications. Fig. 10a schematically shows the skillful experimental process for preparation rGO-F/PANi electrode. The rGO-F/PANi based symmetric supercapacitor achieved high capacitance of 790 F g⁻¹ due to the facilitated electrolyte ions diffusion in the porous carbon network structures (Fig. 10c), as well as the improved utilization of PANi with nanowire structures (Fig. 10e). The 3D rGO films could also be obtained by the vacuum filtration or free-dry methods with the assistance of certain organic additives and the polymerization of PANi could be conducted to obtain PANi/3D-rGO free standing electrodes [52,53]. Graphene was also used to fabricate the 3D kitchen sponge based porous carbon structures for PANi deposition. And the as received sponge/PANi/Graphene (GnP) composites were used to fabricate supercapacitors with outstanding performance [54], in which ordinary macroporous, low-cost and recyclable kitchen sponges were used as porous

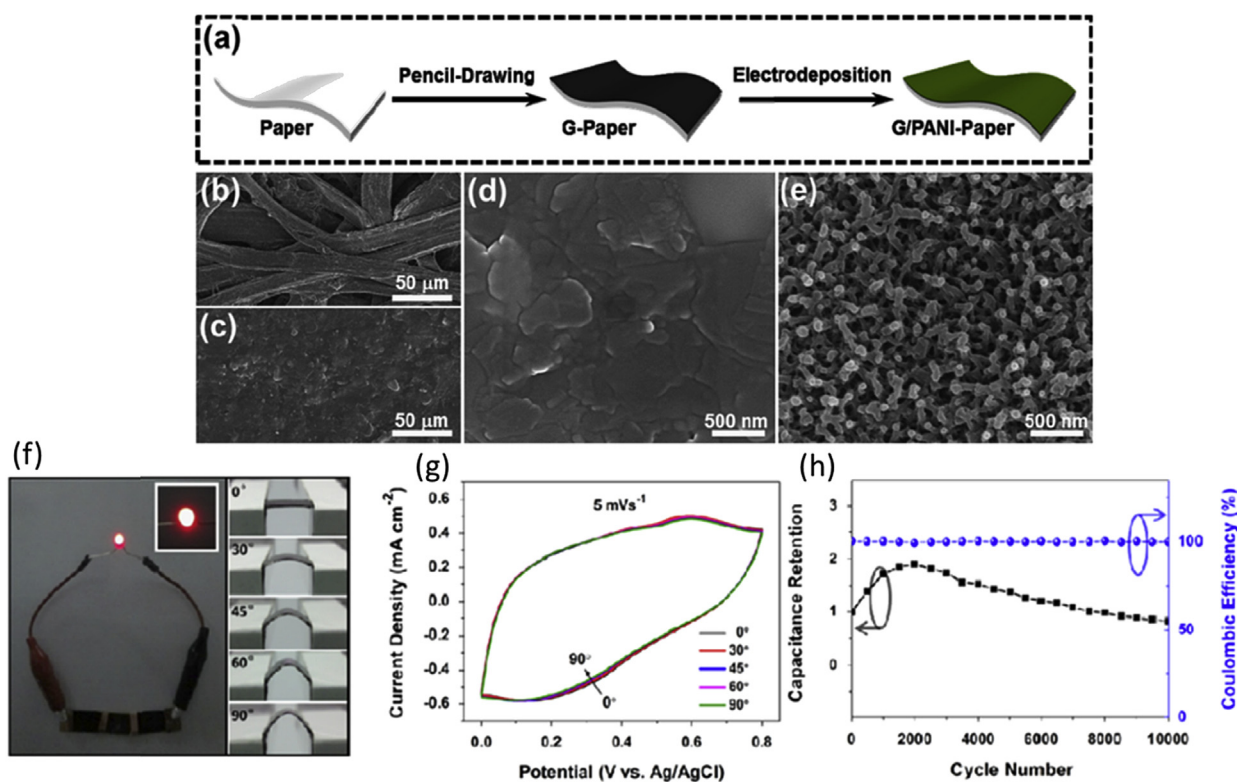


Fig. 9. (a) The schematic of the synthesis of G/PANi paper. SEM images of (b) A4 printing paper, (c, d) graphite paper and (e) G/PANi paper with deposition time of 120 min. (f) Optical picture of a red LED lighted by the G/PANi-Paper based solid-state supercapacitors and five bending states of G/PANi-Paper electrodes. (g) CV curves of the supercapacitors at different bending states. (h) Cycling stability and coulombic efficiency test [55]. Reproduced with permission.

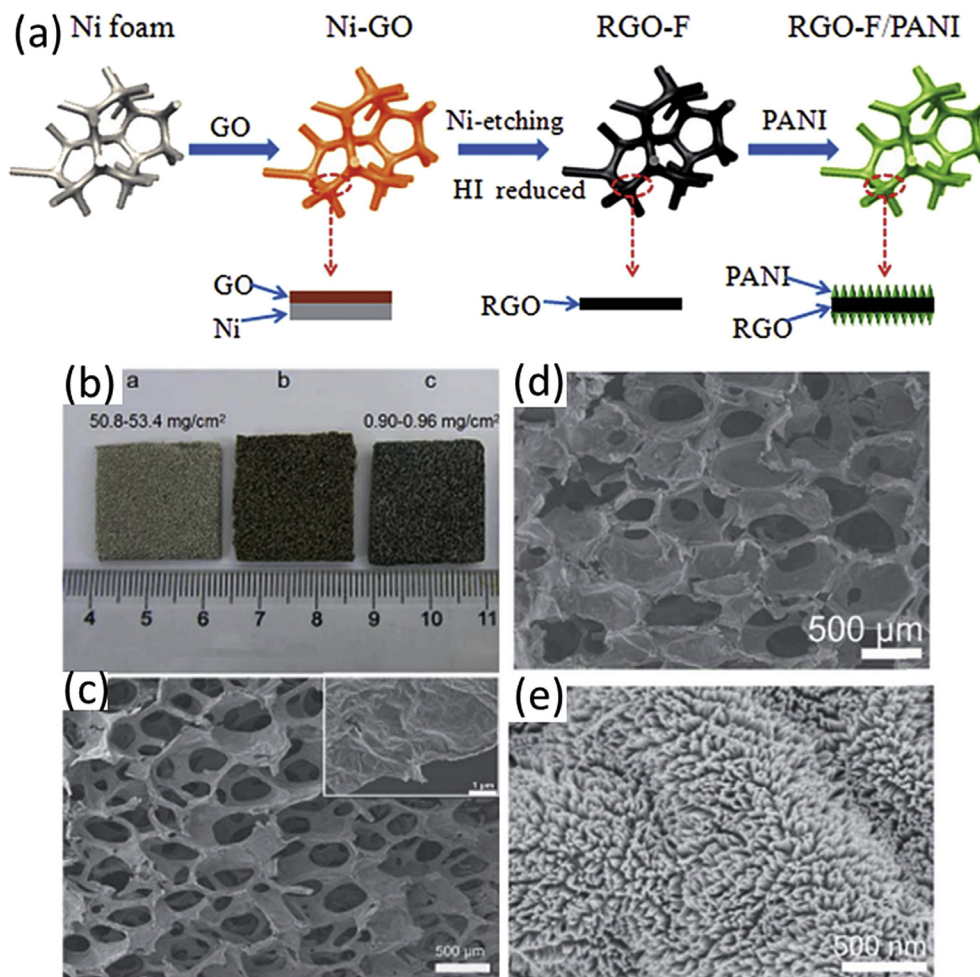


Fig. 10. (a) The schematic of rGO-F/PANI preparation. (b) Digital picture of Ni foam, GO foam and rGO foam. SEM images of (c) rGO foam and (d, e) rGO-F/PANI composites [56]. Reproduced with permission.

carbon for the composite. These kinds of 3D graphene/PANI films are attractive to fabricate flexible free-standing electrodes with superior electronic properties and excellent mechanical stability.

2.1.3. PANi/CNTs composites

Besides graphene, carbon nanotubes (CNTs) have been also the top-rated materials used in energy storage in the last decade due to their excellent intrinsic mechanical, electronic and structural properties [57]. As shown in Fig. 11, there is a side-selective interaction between PANi and single-walled carbon nanotube (SWNT). The function groups on the surface of SWNT could have certain bonding with the active sites ($-\text{NH}-/\text{N}=\text{N}=\text{N}$) of PANi. Moreover, PANi and SWNT could also have $\pi-\pi$ interactions. However, CNT may suffer from the polarization when CNT electrode is in contact with electrolyte and show low capacitance of about $<100 \text{ F g}^{-1}$. The lower capacitance is partially attributed to poor wettability of CNT electrode, which leads to a lower usable specific surface area for charge accumulation of the electrolyte ions on the double-layer. For this reason, reducing the polarization of CNT by introducing pseudocapacitive transition metal oxides or conducting polymers on the CNT surface can greatly enhance the electrochemical performance. Zhang and co-workers have reported the use of a carbon nanotube array directly connected to the current collector (Ta foil) as the support to make PANi/CNT composite electrode with hierarchical porous structures [58].

PANi and CNTs (SWCNTs and MWCNTs) composites were usually fabricated through chemical or electrochemical method with PANi coated on the surface of CNT, forming a core-shell structure [59,60]. These electrodes show excellent electrochemical performance due to pseudocapacitive behaviors of PANi at the surface and high conductivity and mechanical stability of backbone CNTs. The interconnected CNTs can also help to improve the ions diffusion. PANi could be nanofibers or nanowires that surround the CNTs, resulting in caterpillar-like hybrids. However, the chemical polymerization route usually requires previous chemical treatment on the CNTs in order to enhance the stable CNT dispersion during the polymerization step. Y. Yang et al. demonstrated an in situ chemical polymerization of PANi on a single CNT using a grafted poly(4-vinylpyridine) (P4VP) as dopant. The P4VP was grafted onto the CNT surface via covalent bonding in the neutral aqueous solution. The CNT modification can prevent the self-aggregation of CNTs without affecting the intrinsic conductivity and structure of CNTs, resulting in high specific capacitance (1065 F g^{-1}) and long cycling stability (92.2% after 1000 cycles) [59].

A simple and scalable method was introduced by Hongxia Yang et al. for fabricating hybrids graphenepyrrole/CNT-PANi (GPCP), using graphene foam as the supporting template [61]. Graphenepyrrole (G-Py) aerogels were prepared via a hydrothermal process from graphene sheets and pyrrole, while CNT/PANi dispersion was obtained via in situ polymerization (Fig. 12). GPCP was

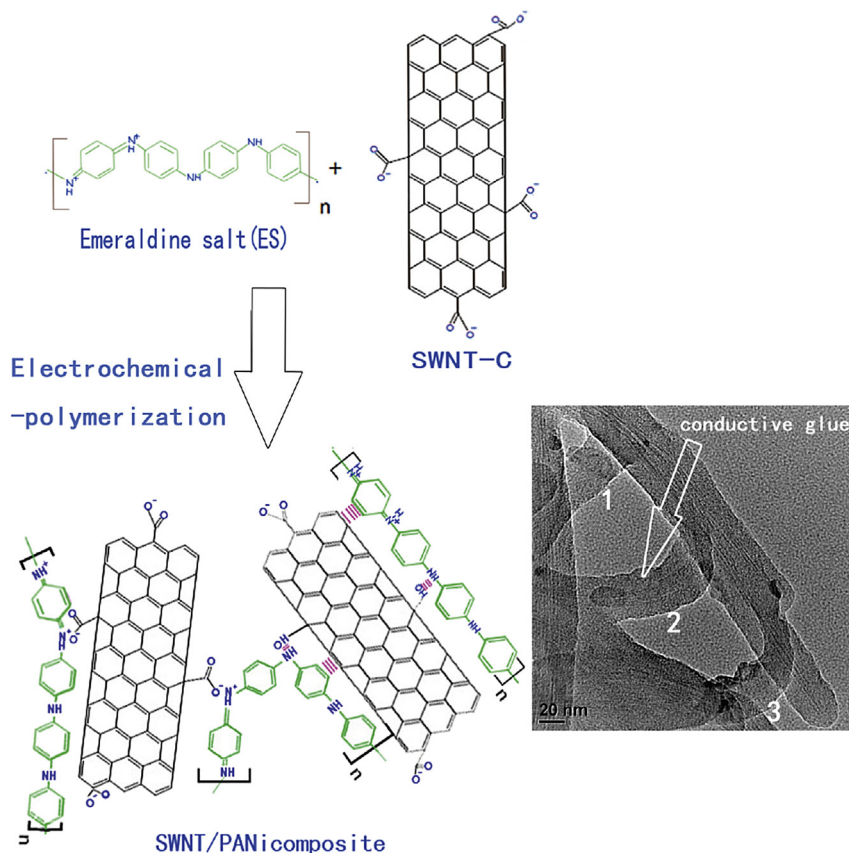


Fig. 11. Schematic illustration of the in-situ electrochemical polymerization of the SWNT-PANI composites (inset is the TEM image of SWNT-PANI composites) [57]. Reproduced with permission.

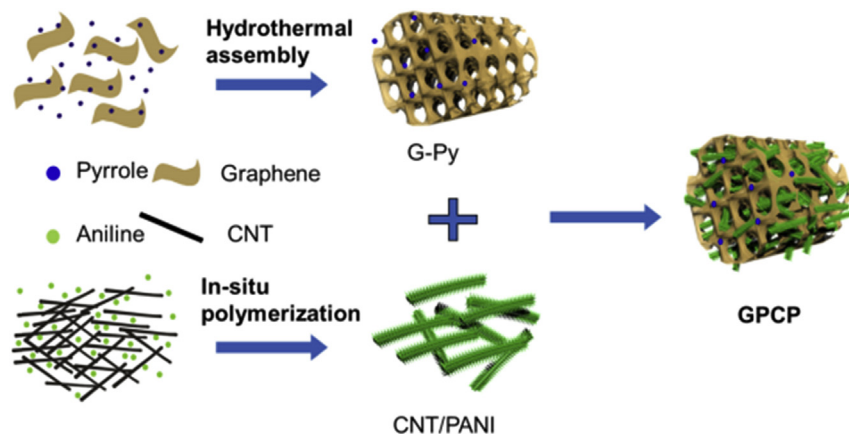


Fig. 12. Schematic illustration of 3D graphene-pyrrole/carbon nanotube/polyaniline architectures fabrication [61]. Reproduced with permission.

obtained by simply dipping the prepared G-py aerogels into the CNT/PANI dispersion. The as-synthesized GPCP maintained its original three-dimensional hierarchical porous architecture, which favors the diffusion of the electrolyte ions into the inner region of the active materials. The GPCP material exhibited significant specific capacitance of up to 350 F g^{-1} , 5 times that of G-Pyaerogel electrode (69.8 F g^{-1}) and 2.2 times that of CNT/PANI electrodes (162 F g^{-1}). A good cycle stability of 84% retention was attained even after 2000 cycles. Usually, the degradation of PANI in capacitance is ascribed to swelling and shrinkage of PANI during charge/discharge, which induces gradually deterioration of the conductivity and the PANI chain structure. As a result, the good stability of

GPCP comes from the synergistic effect between aligned PANI nanorods on CNT and scaffold G-Py aerogel. The 1-D conductive CNT/PANI not only prevent the aggregation and restacking of graphene sheets but also locally improve the conductivity of the aerogels by providing conductive pathways through defects of graphene and bridging the neighboring graphene sheets. Highly porous G-Py scaffold ensures sufficient contact of CNT/PANI with electrolyte and the enhanced electrolyte ions diffusion.

PANI-graphene-CNTs composites have aroused high attention in supercapacitor electrodes fabrication [62,63]. Graphene with high specific capacitance can enlarge the interfacial contact area of electrolyte and electrode, thus increasing the utilization of PANI.

CNTs can act as active wires connecting graphene nanosheets together to enhance the conductivity. PANi contributes most to the capacitance due to its good pseudocapacitive properties. As shown in one paper, PANi could be coated on the surface of graphene nanosheets and the surface of CNTs during the in-situ chemical polymerization of polyaniline (Fig. 13a–c), which means that the utilization of CNTs, graphene could be maximized for thin layer PANi coating.

Porous carbon nanofibers (CNFs) could be alternative materials of CNTs owing to the excellent conductivity, remarkable flexibility, good mechanical/chemical stability and attractive 3D structures. They can serve as free standing current collectors for chemical and electrochemical polymerization of PANi [64–66]. The PANi nanoparticles are uniformly coated on the surface of 3-D interconnected CNFs during the chemical polymerization of PANi. The resulting electrode is very flexible that it can maintain original shape with large angle bending [65]. Qian Cheng and co-workers chose the electrochemical etched commercial carbon fiber cloths as the substrates for the electrochemical polymerization of PANi [64]. After etching, the carbon fibers could have enlarged surface area and facilitated electrolyte diffusion. As show in Fig. 14a, PANi nanofibers were uniformly coated on the carbon fibers and the electrochemical etching of carbon fibers is vital with greatly enhanced electrochemical performance compared with un-etched carbon fibers (Fig. 14b). The electrochemical stability is also good as shown in Fig. 14c. There are also investigations on the fabrication of CNFs with certain organic precursors. One paper illustrated that the carbonized filter paper could be the freestanding substrates to fabricate PANi/CNFs composites and the polyacrylonitrile dissolved in dimethyl formamide (DMF) can be used as CNFs current collectors after one-step carbonization methodology [66].

2.1.4. Carbonization/activation of PANi

PANi has one advantage over metal compounds that it can serve as carbon precursor for the fabrication of nitrogen doped carbon materials for EDLCs. The resulting porous carbon materials are obtained with the same morphologies before and the carbonization and activation, like nanotubes, nanofibers, nanowires and nanorods [67–71]. Activated carbon synthesized by carbonization of PANi and subsequent activation with KOH possesses extremely high specific surface area ($1976 \text{ m}^2 \text{ g}^{-1}$) with narrow pore size distribution ($<3 \text{ nm}$). It exhibits excellent electrochemical performance with specific capacitance of 455 F mg^{-1} in 6 M KOH solution. When graphene is introduced into PANi, the specific capacitance retention ratio of obtained activated carbon is improved from 88.7% to 94.6% after 2000 cycles. It is thus believed that the activated carbon derived from PANi may be highly promising in applications of electrochemical capacitors [67]. The activation process can increase the specific surface area of the carbon matrix by opening the existing close pores and producing new pores with the gas release. Kim et al. adopted NH_3 as the activation gas in the high temperature ($750\text{--}1000 \text{ }^\circ\text{C}$) activation of PANi. The surface area increased from $46.6 \text{ m}^2 \text{ g}^{-1}$ for PANi up to $1719.8 \text{ m}^2 \text{ g}^{-1}$ while large amounts of surface nitrogen functional groups were maintained in pyrrolic and pyridinic states, even after the heat treatment, which is favorable for pseudocapacitance [70]. Besides NH_3 and KOH, ZnCl_2 and H_3PO_4 are also common chemical activation additives used for the activation of carbon materials [72].

2.2. PANi and other conducting polymer blends

PANi can form copolymer blends with other conducting polymers. These copolymers may show better electrochemical

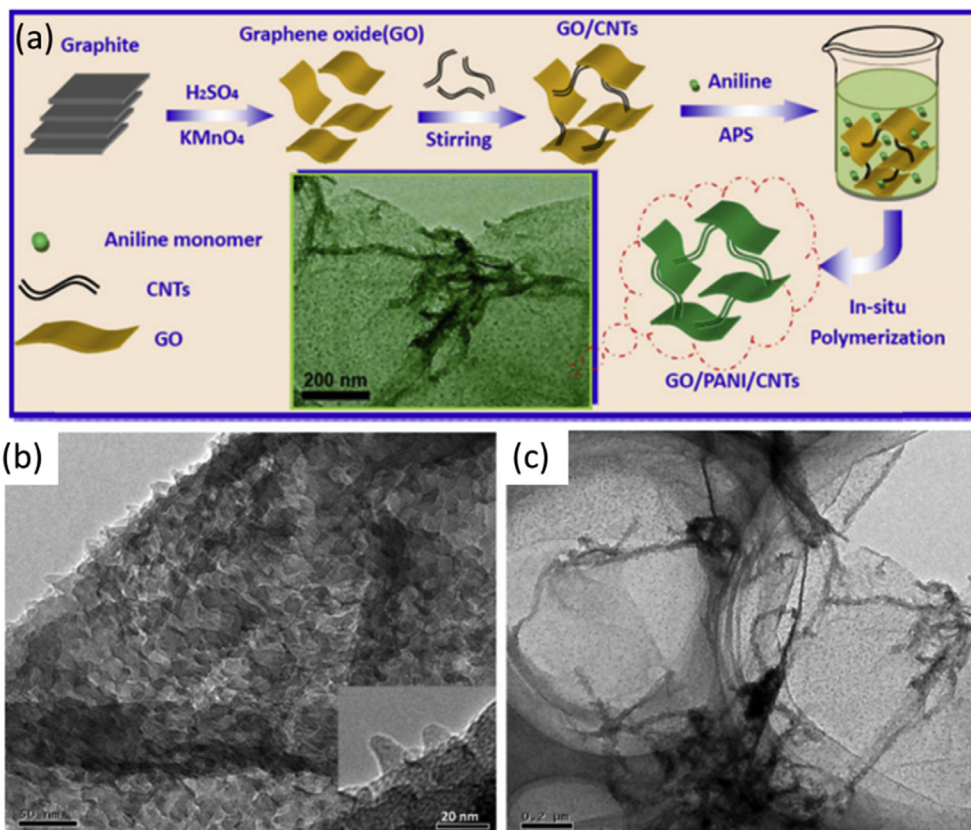


Fig. 13. (a) Schematic diagram of the preparation of PANi-GO-CNT (PGC) composites. (b, c) SEM images of PGC [63]. Reproduced with permission.

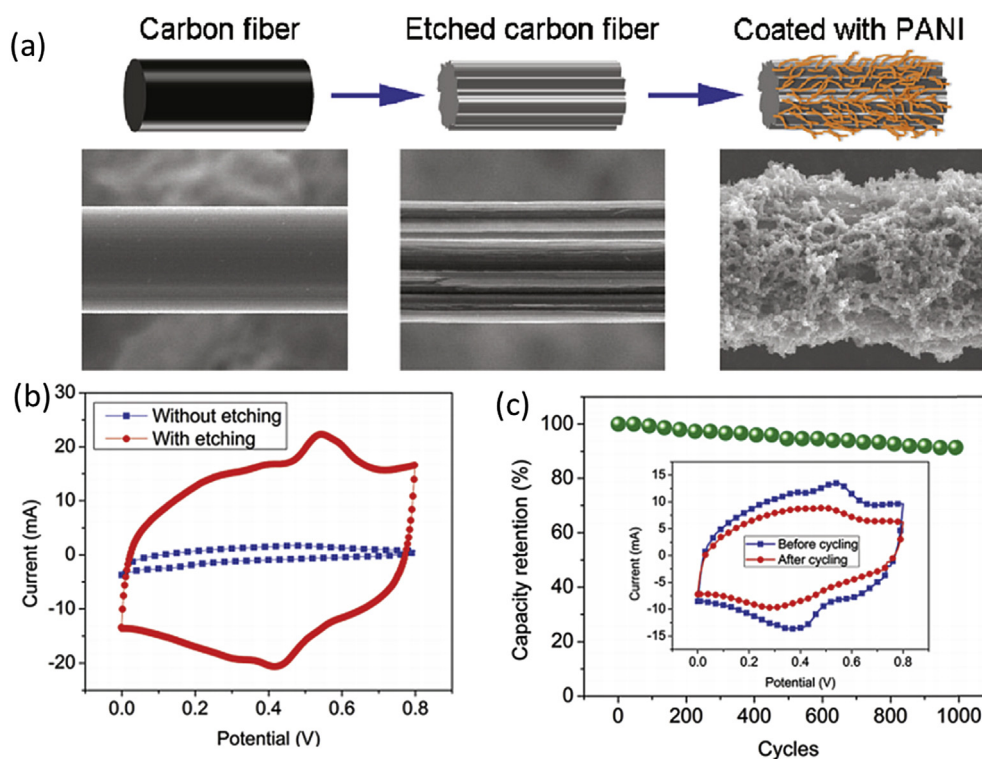


Fig. 14. (a) Schematic diagram of the preparation of PANi-coated electro-etched carbon fiber cloth electrodes and the corresponding SEM images of every step. (b) CV curves of PANi coating carbon fibers with and without etching. (c) Cycling stability test of PANi coated electrode [64]. Reproduced with permission.

performance than that of each component, particularly the cycle stability. Though the values may not be comparable to the PANi/graphene or PANi/CNTs composites, these copolymers are attractive due to their ease of synthesis, high yields and low cost [73–76].

Citric acid (CA), camphor sulfonic acid (CSA), paraphenylenediamine (PPD), melamine and etc. have been used as the organic dopants for the synthesis of PANi based copolymer blends. PPD could improve the morphology and electrochemical performance of PANi based electrodes [74]. PANi nanofibers were longer with less entangled structures in PANi-PPD compared with pure PANi (Fig. 15a, b). The PANi-PPD copolymer electrode showed higher specific capacitance (548 F g^{-1}) and better rate capability compared with pure PANi (Fig. 15c, d). Melamine-PANi copolymers show enhanced cycling stability compared with un-doped PANi. Moreover, when the melamine content is higher, the specific capacitance would be higher (720 F g^{-1}) and enhanced cycling stability compared with un-doped PANi (83% capacitance retention after 1500 cycles vs. 30% after 1250 cycles) [76]. The electrochemical performance of these copolymers may be not comparable to those compositions of PANi/graphene or PANi/CNTs, but such copolymers are attractive due to their easily synthesized methods, high yields and low cost.

2.3. PANi and transition metal oxides/metal chalcogenide hybrids

PANi based organic-inorganic composites have aroused great interests owing to their synergistic effect. Except for carbon materials, metal oxides are also popular to fabricate PANi based organic-inorganic hybrid electrodes. PANi as a kind of flexible conducting polymers has been used to fabricate a conductive coating layer on the surface of metal oxides to enhance the conductivity and stability. Ruthenium oxide with high conductivity shows excellent performance in supercapacitor. However, its low abundance and high cost limit the commercial application.

In the recent years, non-precious transition metal oxides, such as manganese, nickel, cobalt, iron, molybdenum, vanadium, tungsten and titanium oxides have been attempted as supercapacitor electrodes [77]. But their conductivity is usually low, and needs the assistance of conductive polymer coating. In the field of PANi/metal compound composites, manganese oxides and dioxides are most used.

2.3.1. Metal oxides/PANi core-shell structures

Transition metal oxides (TMOs) hold great promise owing to their high specific capacitance and good chemical stability. However, their electronic properties are quite poor, resulting in slowly charge transfer and inferior rate capability. Conducting polymers like PANi can act as the conductive, connective and protective coating layer for TMOs, resulting in improved conductivity/rate capability, enhanced stability and increased specific capacitance. The PANi coating layer is a porous structure without hindering the electrolyte ions from diffusing to the inner TMOs and reacting with the TMOs to induce high capacitance.

The core-shell structural TMO/PANi was usually synthesized through a two-step process. Metal oxides are obtained through a chemical or electrochemical method, following with an annealing process, while chemical or electrochemical PANi coating was carried out as the second step, resulting in metal oxides/PANi core-shell nanostructures. In Fig. 16a, the synthesis of core-shell $\alpha\text{-Fe}_2\text{O}_3$ /PANi nanowire arrays is schematically illustrated. The $\alpha\text{-Fe}_2\text{O}_3$ nanowire arrays were first grown on carbon cloth at 500°C for 2 h after the galvanostatic deposition in the electrolyte containing ferric salt and ammonium oxalate. Then, the galvanostatic polymerization of PANi were conducted, with a porous layer of PANi were uniformly coated on the surface of the $\alpha\text{-Fe}_2\text{O}_3$ nanowire arrays. The resultant $\alpha\text{-Fe}_2\text{O}_3$ /PANi composite could achieve high stability, fast ion/electron transport and large reaction area [78]. The synthesis of metal oxides can also be realized through the

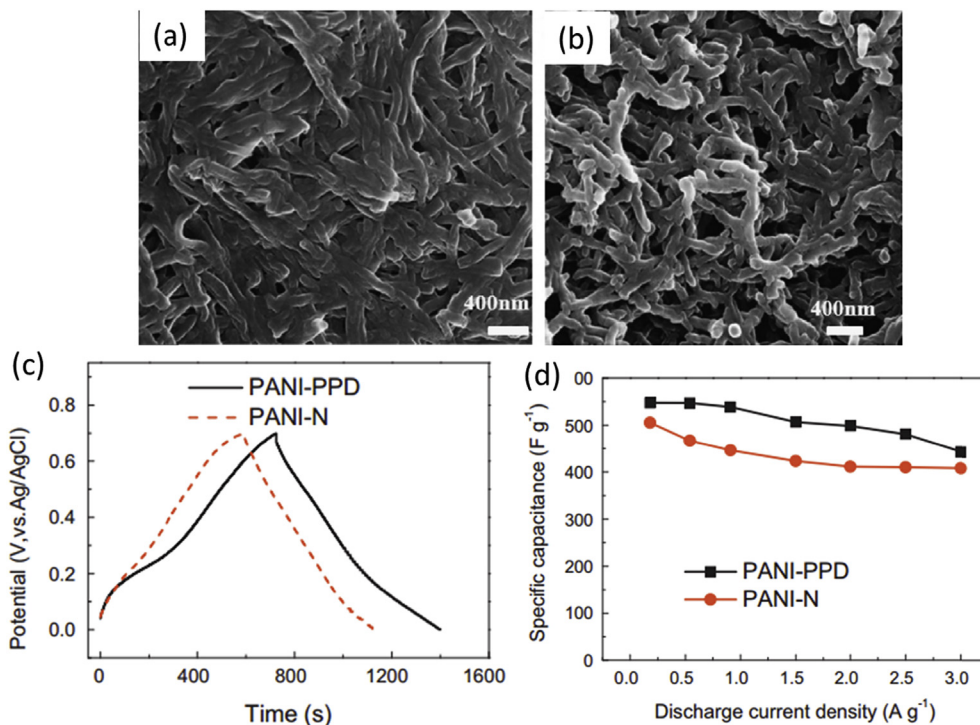


Fig. 15. (a, b) SEM images of PANi with and without PPD doping. (c) Charge–discharge curves of PANi with and without PPD doping. (d) Specific capacitance as a functional of discharge current density of PANi with and without PPD doping [74]. Reproduced with permission.

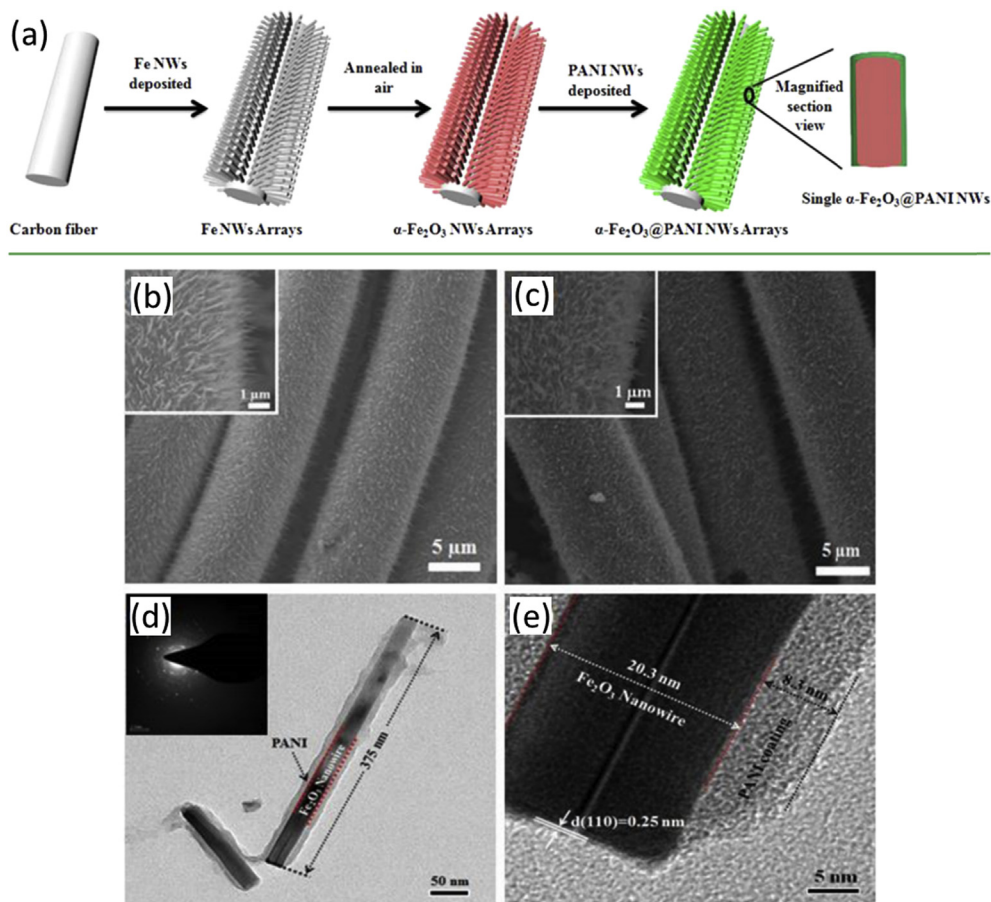


Fig. 16. (a) The schematic of core–shell α -Fe₂O₃/PANI nanowire arrays fabrication. (b, c) SEM images of α -Fe₂O₃ and α -Fe₂O₃/PANI nanowire arrays. (d, e) TEM image and HRTEM of α -Fe₂O₃/PANI nanowire arrays [78]. Reproduced with permission.

chemical routes, like NiO nanoparticles [79]. The PANi coating was conducted by an in-situ chemical polymerization.

There are quite a few studies on the core–shell PANi/TiO₂ or PANi/TiN nanowire arrays used as supercapacitor electrodes [80,81]. TiO₂ and TiN nanomaterials could be a good pseudocapacitive materials for supercapacitors due to the high specific surface area and good electronic properties. However, they are faced with the instability due to irreversible redox reactions in aqueous solutions. The carbon or conducting polymer coating can deal with this problem and the cycling stability could be greatly improved [81]. Interestingly TiO₂ has barely specific capacitance when combining with PANi, which was grown as nanowires encapsulated in an anodized titania nanotube array (see Fig. 17) [80]. The specific capacitance of TiO₂/PANi nanocomposites is around 750 F g⁻¹, with quite good cycling stability, around 85% after thousands of cycles. This result is much better than most of the electrode made by PANi nanowire array or PANi-inorganic (such as Au, CNT, graphene, porous carbon etc) composites. Such an excellent cycle stability is attributed to the novel microstructure of the composite electrode. The volume of TiO₂ nanotubes is large enough to buffer the big volume change of PANi during doping/de-doping processes and hence maintain a good electrical and mechanical stability.

When the nitridation was conducted by the ammonia gas in the furnace tube, TiO₂ could convert into TiN and the electrochemical performance is also enhanced due to the enhanced conductivity of TiN vs TiO₂. As shown in Fig. 18a, a core/shell/shell nanowire arrays, PANi/C/TiN-NWA can be formed through sequentially coating carbon and PANi on the surface of TiN-NWA [81], which achieves a high capacitance of 1093 F g⁻¹ and excellent stability of 98% even after 2000 cycles. PANi contributes most to the pseudocapacitance

due to the fast faradic doping and de-doping reactions. TiN nanowire arrays provide the charge transfer routes. Without the middle carbon shell, the PANi/TiN NWAs also show good performance. However, the existence of carbon shell further enhances the cycling stability due to the protection of TiN from electrolyte corrosion.

Recently, mixed metal oxide systems have shown improvements in pseudo-capacitive performance. Among them spinel ferrites (MFe₂O₄, M = Mn, Co, or Ni) are of great interest for their remarkable properties, such as different redox states and electrochemical stability. Nevertheless, pure ferrites cannot be satisfactory due to poor conductivity. To overcome this problem carbon and conducting polymer coatings are usually employed. Several ternary cobalt, nickel and manganese ferrites/carbon/PANi hybrids based electrodes were reported for high performance supercapacitors [82–84]. These spinel ferrites have remarkable properties, like multiple redox states, excellent pseudocapacitive properties and superior electrochemical stability. However, the pure spinel ferrites have poor conductivity which is unable to satisfy the performance of supercapacitors. The design of spinel ferrite based hybrid electrodes is a good choice to improve the electrochemical performance. The binary PANi and spinel ferrite composites should have good conductivity and high specific capacitance, but limited cycling stability. As a result, the combination of spinel ferrite, PANi and carbon composites are expected to have enhanced electrochemical performance due to the synergistic effect of every component. The graphene oxide and cobalt ferrite composites were obtained through a hydrothermal method (Fig. 19a), following a chemical polymerization of PANi layer on the surface of cobalt ferrite [84]. Fig. 18b shows that the same hydrothermal method and chemical in-situ polymerization of PANi are applicable for the synthesis of

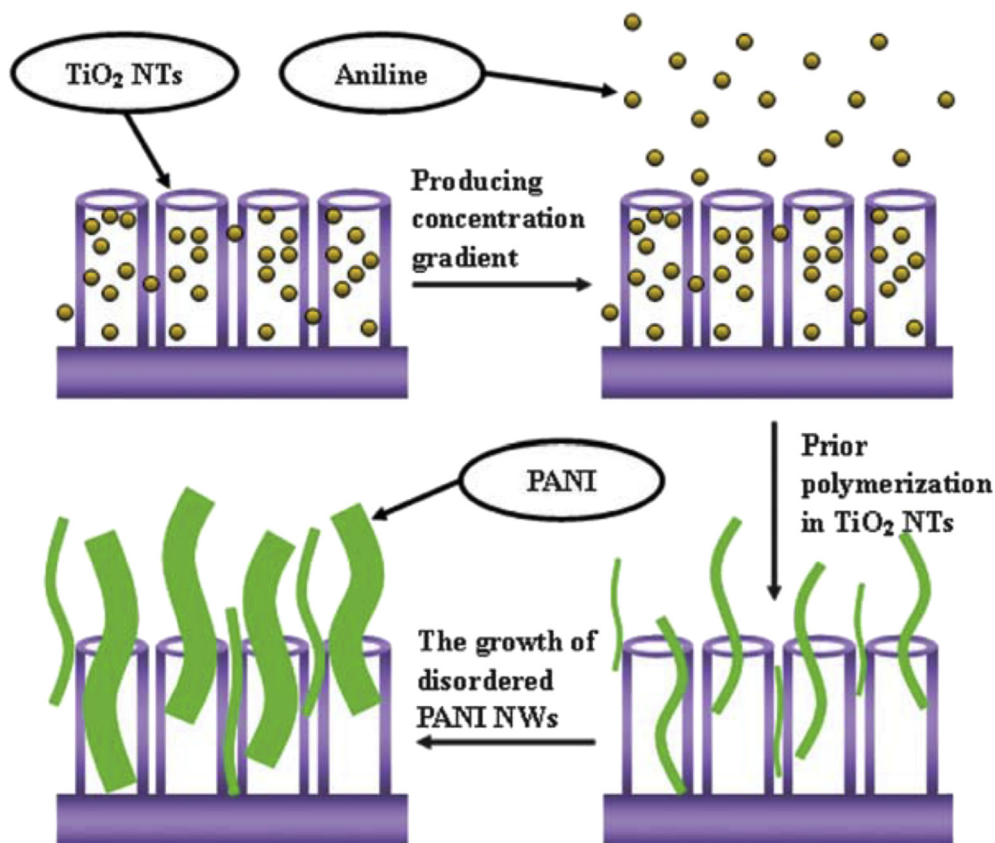


Fig. 17. Schematic illustration of the preparation process of disordered PANI nanowire array on the TiO₂/Ti substrate [80]. Reproduced with permission.

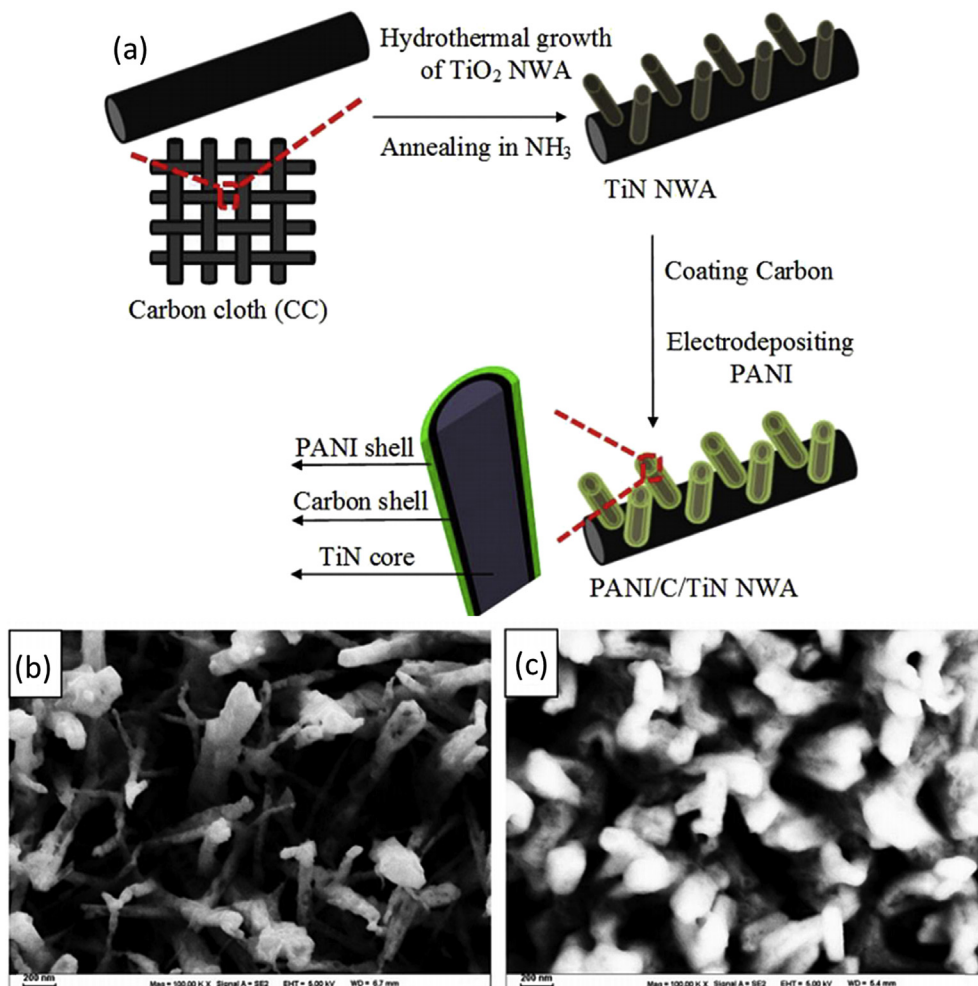


Fig. 18. (a) The schematic of core-shell PANi/C/TiN nanowire arrays fabrication. (b, c) SEM images of TiN nanowire arrays and PANi/C/TiN nanowire arrays [81]. Reproduced with permission.

nickel ferrite/graphene oxide/PANi and manganese ferrite/graphene oxide/PANi nanocomposites.

Besides metal oxides and spinel ferrite, there are also some metal sulfides and metal compounds with unique crystal structures, desiring for a conducting polymer coating layer due to inferior conductivity [85–87]. Among them, Metal-organic frameworks (MOFs), like Co MOF (ZIF-67) and Zn MOF, have received increasing attention as a new class of porous materials for energy storage and conversion applications due to their high specific surface area, exceptional porosities and well-defined tailored pore structure to facilitate the ion diffusion. However, the major problem of MOFs is their poor conductivity, which could be tackled by the conducting polymers, like PANi. Electrochemical studies showed that the PANi-ZIF-67-CC, which was synthesized by depositing PANi on a Co-containing MOF on carbon cloth (denoted as ZIF-67-CC), exhibits an extraordinary areal capacitance of 2146 mF cm^{-2} at 10 mV s^{-1} . This value is thought to be the highest among all MOF-based supercapacitors reported to date and surpasses many other types of supercapacitive materials [87]. Unlike the hot topic of PANi layer coated on metal oxides, there have been reported only few papers talked about the growth of metal oxides on the surface of PANi nanomaterials through hydrothermal method or electrochemical deposition method due to the hydrophobic properties of the surface of PANi materials [88,89].

2.3.2. Electrochemical co-deposition of PANi and metal oxides

As talked about before, PANi and carbon materials can be fabricated as composites through a one step in-situ chemical oxidation process or a facile electrochemical co-polymerization method. However, there are very few in-situ chemical method used for the combination of PANi and metal oxides [90]. This could be attributed to the fact that the syntheses of metal oxides/hydroxides usually need mild alkaline medium containing metal salts precursor whereas the polymerization of PANi usually is conducted in acidic medium for high quality products. Fortunately, the one step co-deposition can still be conducted for PANi and certain metal oxides by electrochemical methods as long as the potential ranges for the deposition of PANi is in agreement with metal oxides and the resulting composites are not soluble in the electrolytes.

A successful example is the electrochemical co-deposition of PANi and manganese oxides/dioxides. There are quite a few papers studying the electrochemical deposition of PANi/MnO_x due to their aligned deposition potential window and similar electrochemical deposition characteristics [91,92]. With manganese salts dissolved and aniline dispersed in the electrolyte, the as obtained PANi/MnO₂ composites show fibroid structure with particles at the surface, indicating a good combination of PANi and MnO₂. The nanofiber structure is beneficial to the conductivity and capacitance, obtaining 1292 F g^{-1} in an organic acetonitrile electrolyte [91]. The energy

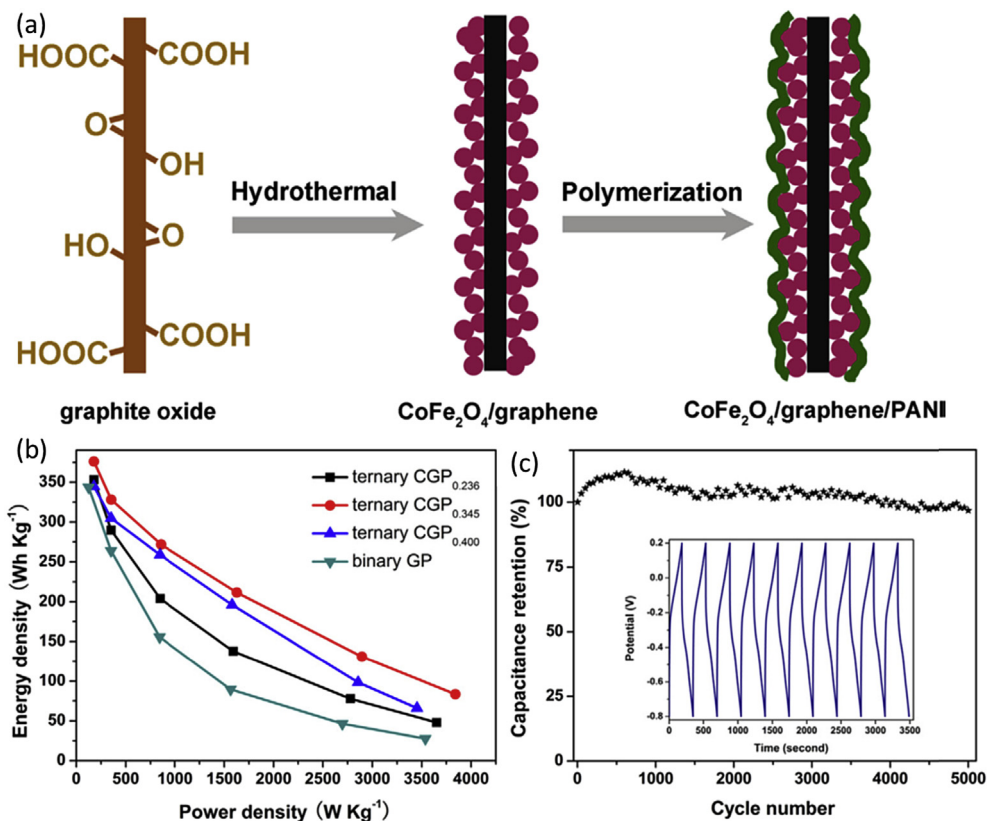


Fig. 19. (a) The schematic of the preparation of the ternary spinel ferrite/PANI/carbon materials. (b) The energy density as a function of power density of binary and ternary electrode materials. (c) The high cycling stability of the ternary nanocomposite: CGP_{0.345} [84]. Reproduced with permission.

density is also high due to large potential range (2 V) and the high specific capacitance, according to the equation of $E = \frac{1}{2} CV^2$. There are also investigations on the electrochemical co-deposition of PANi/WO₃, PANi/V₂O₅ and PANi/NiO composites owing to the matched deposition window of such metal oxides and PANi [93–95]. Tungsten oxides and vanadium oxides are attractive in supercapacitors because of their excellent pseudocapacitive behaviors in negative potential range. Nickel oxides have high theoretical and measured specific capacitance. The electrochemical co-deposition is quite a facile method containing one step. The composites show good stability and high conductivity that the metal oxides are embedded in interconnected PANi matrix.

3. Lithium-ion batteries and beyond

As one of the most promising rechargeable batteries, lithium ion battery (LIB) has been actively developed since 1970s [96]. In this section, we mainly talk about the PANi based electrodes used in lithium-ion batteries (LIBs), as well as the application in beyond batteries, like Lithium-sulfur batteries (LSBs) and sodium-ion batteries (SIBs). The significant merits of PANi used for the fabrication of battery electrodes will be emphatically discussed. The cathode and anode materials' design for LIBs, the fabrication of cathode materials for LSBs and the anode preparation for SIBs related with PANi will also be discussed in detail.

3.1. Lithium-ion batteries (LIBs)

Among secondary cells, LIBs are promising candidates used in portable electronic devices owing to their high energy density, good security and long cycling life. LIB has much higher energy

density than supercapacitors, making it the technology of choice for portable electronics, electric vehicles and power grid applications. In a LIB, Li⁺ ions as the charge carrier move from the negative electrode (anode) via an electrolyte which allows for ionic movement to the positive electrode (cathode) during discharge and back when discharging.

Commercial LIB uses LiCoO₂, LiFePO₄, LiMn₂O₄ and Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ based materials as the cathodes for LIBs. However, these cathode materials may suffer from poor conductivity, inferior rate capability, short cycling life and voltage decay [97]. Conducting polyaniline is an excellent material to make surface modification of these Li-rich cathode materials, resulting in improved conductivity and stability [98]. Actually even without metal compounds, PANi or PANi-derived microporous carbon could be an efficient cathode and anode for LIBs. Fig. 20 shows the spray synthesis of conducting HClO₄-doped PANi nanotubes [99]. Charge–discharge measurements demonstrate the good capacity and cycling capability of the Li/PANi rechargeable cells constructed with the nano-structured doped PANi as the cathode. The PANi electrode might have undergone an induction process from unstable state to stable state, after which, the charge–discharge curves became steady and showed good reversibility with a discharge-plateau voltage of 3.0 V and a charge-plateau voltage of 3.4 V. The reaction of Li/PANi batteries can be written as: emeraldine base + 2LiClO₄ ↔ 2Li + emeraldine salt [99].

The most commercially popular anode electrode is graphite owing to its excellent features, such as flat and low working potential, low cost and good cycle life. It has a capacity of 372 mAhg⁻¹. However, graphite allows the intercalation of only one Li-ion with six carbon atoms. Additionally, the diffusion rate of lithium into carbon materials is limited, resulting in low power density which

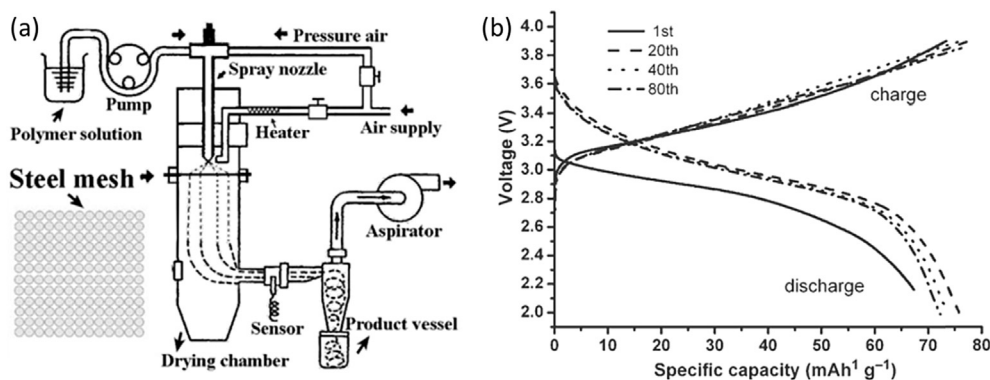


Fig. 20. (a) Schematic depiction of the large-scale synthesis of HClO₄-PANI nanofibers through a spray technique, and (b) charge-discharge cycling performances of Li/PANI cells made with doped PANi nanotubes at the constant charge/discharge current density of 20 mA g⁻¹ and the temperature of 25 °C for Li ions in electrodes [99]. Reproduced with permission.

could not meet the increasing demands of energy. Hence, three new types of anode materials have been being developed, including: (i) Intercalation layer-structured materials, such as graphite and Li₄Ti₅O₁₂; (ii) Alloy materials such as Si, Sn and SnO₂; (iii) Conversion materials like transition metal oxides (Mn_xO_y, Fe_xO_y), metal sulphides (MoS₂) and so on [100]. However, the transition metals chalcogenides usually suffer from large volume expansion during lithiation/de-lithiation and poor conductivity [98]. These disadvantages could result in poor cycling stability and inferior rate capability. The conductivity and stability can be enhanced when transition metal chalcogenides combine with the conducting polymers, like PANi.

3.1.1. PANi modified cathode materials

Li-rich cathode materials like LiCoO₂, LiFePO₄, LiV₃O₈, Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ and Li(Ni_{1/3}Mn_{1/3}Fe_{1/3})O₂ have been used to fabricate PANi modification electrodes for LIBs [97,101–104]. Karima Ferchichi et al. recently showed that the PANi/LiCoO₂ composite improved the specific capacity from 136 mAhg⁻¹ of the pristine LiCoO₂ cathode to 167 mAhg⁻¹ by increasing the reaction reversibility and electronic conductivity with increasing the mass ratio of LiCoO₂ to 4:1 in the composite [102]. LiFePO₄ (LFP) as a cathode material possesses excellent cycle stability and thermal stability, but with poor electron and ion conductivities. Conductive PANi coating on carbon-coated LiFePO₄ could further enhance the capacity and rate capability of LFP via improving the electrical conductivity of the C-LFP composite, mediate the polarity difference between the cathode and the electrolyte, and reduce the charge transfer impedance. The electronic conductivity of the polymer is dependent on the type of inorganic acid dopants. The C-LFP/PANi composite cathodes doped with HCl and H₃PO₄ gives a ca. 15% capacity enhancement at 0.2 C and 40% enhancement at 5 C compared to the parent C-LFP, whereas H₂SO₄ is not a good dopant [104]. Chunli Gong et al. have recently reported the use of PANi and poly (ethylene glycol) (PEG) copolymer were used to modify the performance of LiFePO₄ [105]. LiFePO₄ cathode has two big limitations, poor electric conductivity and low Li ion diffusion. PANi as a conducting polymer with good electronic properties and high flexibility is superior to enhance the conductivity of LiFePO₄ cathode while PEG is a very good solvent for lithium salts and becomes the best known polymer ionic conductor. Therefore, PANi/PEG copolymers have both high electric and ionic conductivity when used for coating of LiFePO₄ as illustrated in their work. Excellent high specific capacity (125.3 mAhg⁻¹ at 5 C) and long cycling stability (95.7% retention after 100 cycles at 0.1 C) are achieved.

Vanadium oxides are third generation of promising cathode materials. Layered LiV₃O₈ has drawn high interests as cathode

material in LIBs owing to its high discharge capacity/specific energy density, high working voltage, good chemical stability and low cost. It exhibited high initial discharge capacity of more than 300 mAhg⁻¹ at current densities of 20 mA g⁻¹, but suffered from low high-rate capacity and fast capacity fading due to phase transformation and electrode dissolution. Conducting PANi coating on LiV₃O₈ nanorods could reduce the charge transfer resistance by connecting LiV₃O₈ nanorods together (Fig. 21d). Moreover, LiV₃O₈ dissolution could be reduced (Fig. 21e, f), achieving high discharge capacity of 204 mAhg⁻¹ after 100 cycles [101].

In addition to the monometallic cathode materials, the trimetallic materials, like Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ and Li(Ni_{1/3}Mn_{1/3}Fe_{1/3})O₂ have also been studied to use PANi coating for improved the electrochemical performance [97,103]. No matter for monometallic, bimetallic or trimetallic materials, the coating layer of conducting polymers is used to enhance the conductivity, improve the stability and as a buffer shell for cathode materials from dissolving in organic electrolytes. In particular, the Li-rich composite cathode materials, which can be written as xLi₂MO₃(1 - x) LiMO₂ (M = Ni, Co, Mn, Fe, Cr, or combination), have attracted increasing attention due to their high reversible capacities (>250 mAhg⁻¹) and high operating voltages (>4.6 V vs. Li/Li+). However, these Li-rich cathode materials still suffer from intrinsic poor rate capability, severe capacity fade, and voltage decay due to the rearrangement of surface structure caused by the activation of Li₂MnO₃ component above 4.5 V, the erosion from the electrolytes, and the structural transformation during cycling. Very recently, Di Wang and co-workers successfully synthesized a spherical lithium-rich cathode material with a layered-spinel hybrid structure and coated a PANi layer of the average 6.3 nm thickness on the surface of each particle of ~1 μm in size. The electrochemical performance of the PANi-coated spherical lithium-rich cathode material was remarkably improved. PANi coating brings an obvious improvement on coulombic efficiency and cyclic stability via the depressed formation of the solid-electrolyte-interface (SEI) layer, the enhanced electron conductivity and improved ion diffusion in the electrode. A high initial coulombic efficiency (which is critically important for practical application of the material) of 83.5% was measured. The capacity retention was as high as 92.4% after 200 cycles at a rate of 0.5 C. The discharge capacities at 0.1 C and 10 C were 302.9 mAhg⁻¹ and 146.2 mAhg⁻¹, respectively [97].

3.1.2. PANi modified anode materials

The coating of conductive PANi layer has been widely employed in fabricating anode for LIB, with transition metal oxides (NiO, TiO₂, SnO₂ and Fe₂O₃) and metal sulfides (SnS₂, MoS₂) [13,98,106–109]. Transition-metal oxides and sulfides usually demonstrate

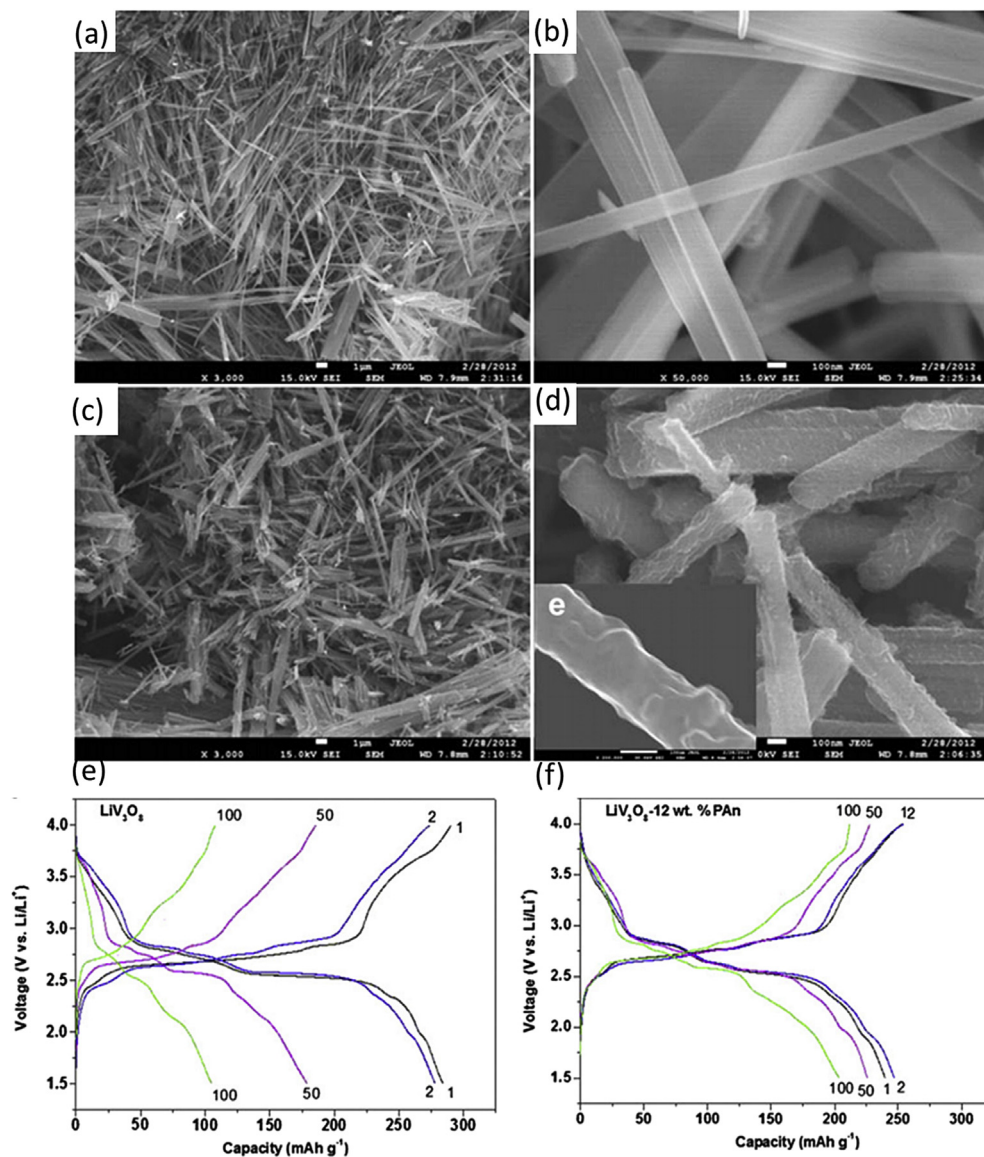


Fig. 21. (a, b) SEM images of bare LiV_3O_8 and (c, d) LiV_3O_8 -12%PANi composite. (e) Charge-discharge curves of LiV_3O_8 and (f) LiV_3O_8 -12%PANi composite (selected cycles) [101]. Reproduced with permission.

capacities over 700 mAhg^{-1} , but for most of the unmodified anodes, the cycling performance is poor, which is related to various factors, such as the poor conductivity, the structural instability, and the aggregation of the Li-active nanoparticles. These types of materials are mostly semiconductors of low conductivity. They are either converted (in the initial discharge reaction) to inactive Li_2O for metal oxide (MO): $\text{MO} + (x + 2) \text{Li}^+ + (x + 2) \text{e}^- \leftrightarrow \text{MLi}_x + \text{Li}_2\text{O}$, or converted to inactive M for metal sulfides (MS): $\text{MS} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{M} + \text{Li}_2\text{S}$. Though M or Li_2S can reversibly store charge in the subsequent charge/discharge cycles, the capacitance may rapidly reduce due to poor electrical contact between the Li-active nanoparticles and the substrate. Furthermore, the aggregation of Li-active nanoparticles may take place, leading to gradual activity loss and thus poor cycling performances of the MO or MS anode. The PANi coating can overcome these problems.

A nickel foam-supported NiO/PANi composite exhibited enhanced the conductivity and stability by connecting NiO flakes together and isolating NiO from electrolyte corrosion. Hence better reversibility due to weaker polarization, better cycling performance

and enhanced discharge capacitance were observed. The specific capacity for the NiO/PANi electrode after 50 cycles is 520 mAhg^{-1} , higher than the NiO electrode (440 mAhg^{-1}) [106].

SnO_2 is a promising LIB anode due to its high theoretical specific capacity of 891 mAhg^{-1} , abundance, low cost, chemical stability and environmental friendliness. Its biggest problem is still the large volume expansion during lithiation and de-lithiation. Intensive research has been conducted to tackle this problem by preparing PANi/ SnO_2 - Fe_2O_3 composites [108]. The SnO_2 - Fe_2O_3 composite was prepared through the hydrolysis of corresponding metal salts in a citric acid solution. When aniline was added to the solution, Fe^{3+} ions on the outer surface of SnO_2 - Fe_2O_3 colloidal particles led to the oxidation polymerization of aniline, forming unique SnO_2 - Fe_2O_3 @C structure, in which the SnO_2 - Fe_2O_3 colloidal particles were completely coated with PANi and their aggregation was restricted by the outer PANi shell, resulting in nanosized particles. PANi here played role as carbon-containing precursor and restriction of the particle growth. Finally, thermal treatment of the obtained products at 400°C in air led to the carbon-coated

SnO₂-Fe₂O₃ nano-composite. The introduction of carbon layer can enhance the electronic conductivity of the nanocomposite and facilitate enhanced Li⁺ transport kinetics. In addition, carbon layer may act as the buffer for the huge volume changes in Li insertion/extraction process. The unique structure of SnO₂-Fe₂O₃@C nano-composite effectively improved its electrochemical properties (as compared to pristine SnO₂-Fe₂O₃), achieving the fully reversible reaction and alloy reaction of SnO₂. Excellent rate performance of 611 mAhg⁻¹ at 1600 mA g⁻¹ and 1000 mAhg⁻¹ at 400 mA g⁻¹ after 380 cycles were reported (see Fig. 22).

As a low cost, earth-abundant and high-capacity metal oxide, Fe₂O₃ has become a popular as energy-storage electrode material. One paper introduced a very facile method to prepare Fe₂O₃@PANI with unique structure and excellent performance [107]. As shown in Fig. 23a, large quantity of urchin like FeO_x spheres were obtained through a simple sonication method with iron salts in propylene alcohol as the precursor. Then the hollow structured Fe₂O₃@PANI nanospheres were prepared by the chemical polymerization. Another skillful strategy they used is that the hydrochloric acid not only acts as dopant for PANi, but also etching agent for iron oxides. Therefore, the hollow structure could be achieved at certain reaction time (Fig. 23b–f). These hollow structured Fe₂O₃@PANI nanospheres show highest specific capacity, best cycling stability and rate capability compared with other samples (Fig. 23h–k). Good cycling performance (893 mAh g⁻¹ even after 100 cycles of charge/discharge) was reported, compared with a rapid decay of capacity of the non-hollow Fe₂O₃ electrode (680 mAh g⁻¹ after only a few cycles).

MoS₂ has unique 2D layered structure that is superior for lithium insertion and extraction. However, the electronic properties are not so good between S-Mo-S sheets, which limit commercial application. When hybrid with conducting polyaniline, the conductivity and stability could be greatly improved with MoS₂ embedded in PANi matrix [13,110]. The hierarchical MoS₂/PANI

nanowires were obtained through three steps, firstly the Mo₃O₁₀(C₆H₅NH₃)₂·2H₂O nanowires were synthesized by a chemical method. Then MoO_x/PANI nanowires were prepared using an in-situ chemical polymerization of PANi. Thirdly, the sulfuration was realized by a hydrothermal method. The highest specific capacitance and best cycling stability were obtained with 33.1% percentage of PANi, which indicates that the best performance can only be achieved with the optimum PANi weight ratio. The MoS₂/PANI nanoflowers were prepared through a hydrothermal method with molybdc oxide, potassium thiocyanate in PANi particles suspension (Fig. 24a) [110]. The nanoflowers become larger and denser after annealing, but still hierarchical structures with sufficient void space. Electrochemical performances were enhanced after annealing because of larger specific surface area, better contact and higher conductivity, indicating the significance of heat treatment process.

Similar to MoS₂, SnS₂ also has layered structure that facilitates lithium ion intercalation. The SnS₂@PANI nanoplates with a lamellar sandwich nanostructure can provide a good conductive network between neighboring nanoplates, shorten the path for ion transport in the active material, and alleviate the expansion and contraction of the electrode material during charge–discharge processes, leading to improved electrochemical performance. As an anode material for lithium-ion batteries, SnS₂@PANI nanoplates have a high initial reversible capacity (968.7 mAhg⁻¹), excellent cyclability (75.4% capacity retention after 80 cycles), and an extraordinary rate capability (356.1 mAhg⁻¹ at 5 A g⁻¹) [109].

PANI itself can be used to prepare N-containing porous carbon as anode materials of LIBs. It can be a carbonaceous alternative of graphite, but the charge and discharge capacity are much higher compared with graphite, 624 and 1108 mAhg⁻¹, respectively. Based on the discussion of PANi used in LIB anodes, we could draw a brief conclusion that the conducting polyaniline serves as a conductive, protective and connective layer when combined with metal

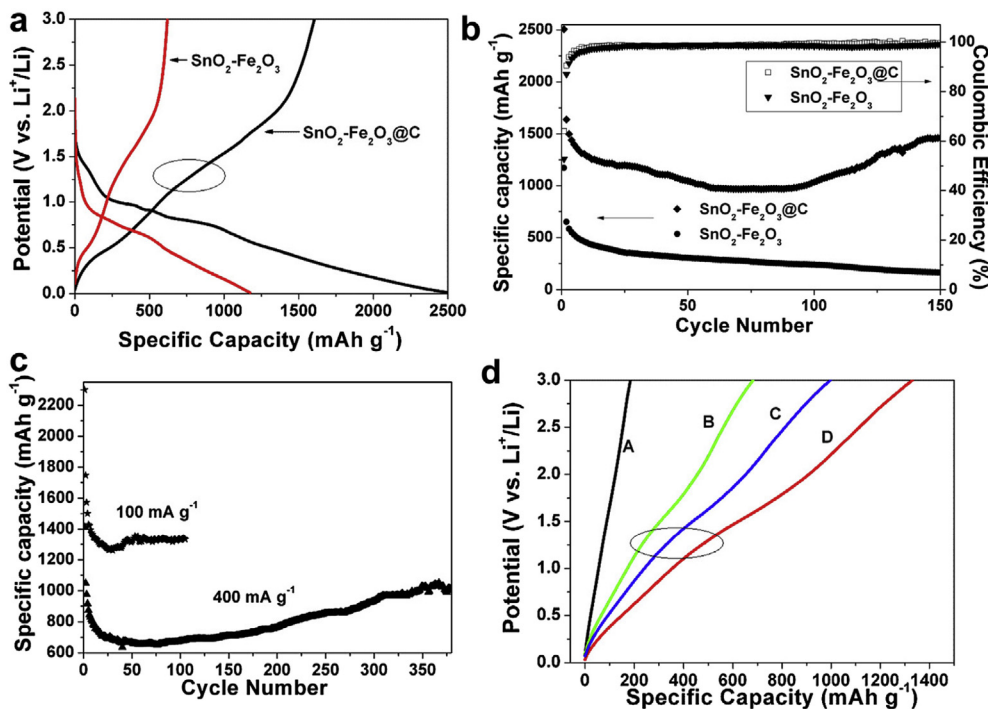


Fig. 22. (a) First cycle of galvanostatic charge–discharge curves of SnO₂-Fe₂O₃ and SnO₂-Fe₂O₃@C. (b) Cycling stability test of SnO₂-Fe₂O₃ and SnO₂-Fe₂O₃@C at 200 mA g⁻¹. (c) Cycling stability test of SnO₂-Fe₂O₃ at 100 mA g⁻¹ and at 400 mA g⁻¹. (d) Galvanostatic charge curves: A, B, C and D are the 130th cycle of SnO₂-Fe₂O₃ at 200 mA g⁻¹, 130th cycle of SnO₂-Fe₂O₃@C at 400 mA g⁻¹, 346th cycle of SnO₂-Fe₂O₃@C at 400 mA g⁻¹ and 130th cycle of SnO₂-Fe₂O₃@C at 200 mA g⁻¹ [108]. Reproduced with permission.

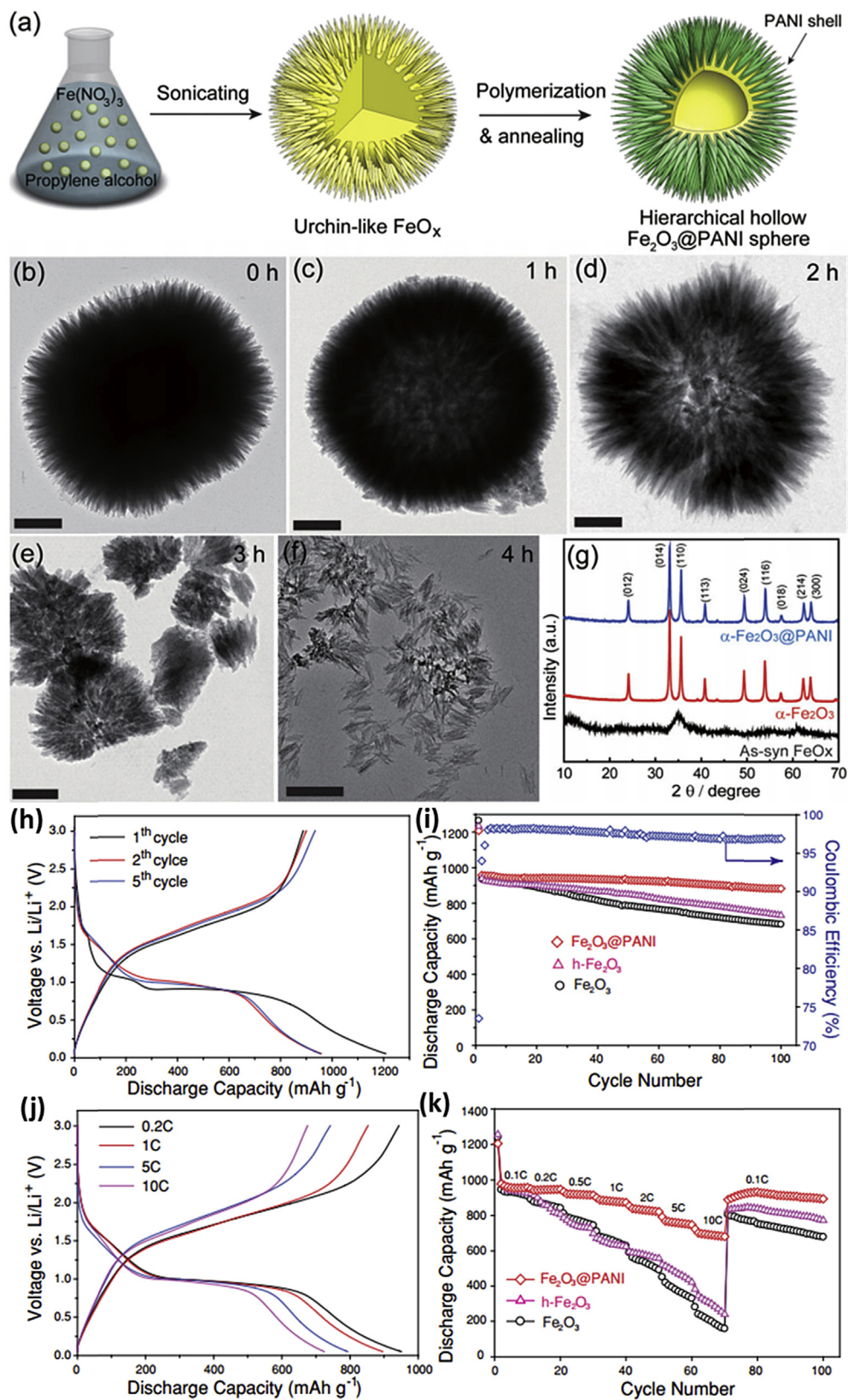


Fig. 23. (a) Schematic diagram of the preparation of hierarchical $\text{Fe}_2\text{O}_3@PANI$. (b–f) TEM images of samples obtained at different PANi polymerization time. (g) XRD patterns of obtained samples with different components. (h) Galvanostatic charge–discharge curves of $\text{Fe}_2\text{O}_3@PANI$ electrode with the potential range of 0.05–3 V (vs. Li^+/Li) at 0.1 C rate. (b) Cyclic performance of every electrode at a 0.1 C rate. (c) Galvanostatic charge–discharge curves of $\text{Fe}_2\text{O}_3@PANI$ electrode at different cycling rates. (d) Rate capability of every electrode at different rates [107]. Reproduced with permission.

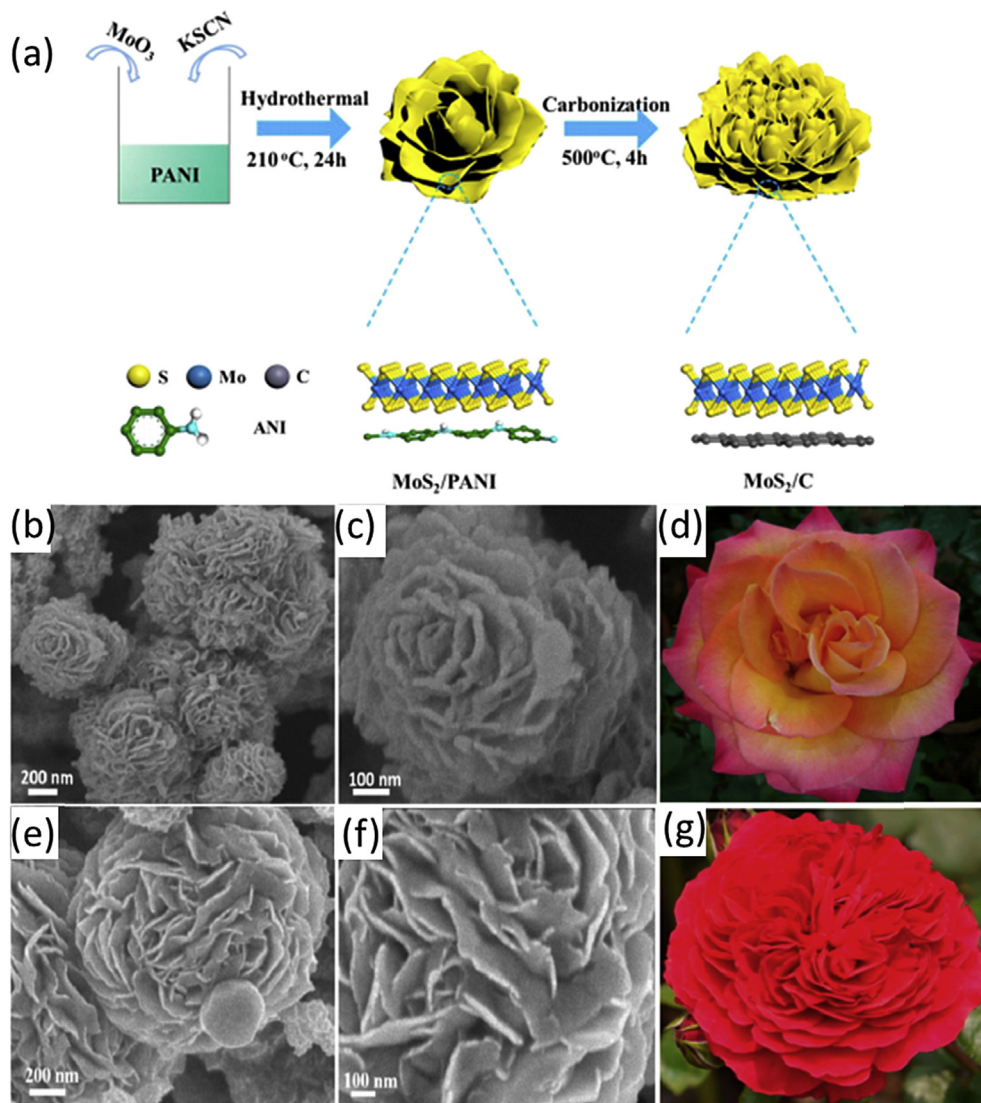


Fig. 24. (a) The schematic of preparation of MoS_2/PANI and MoS_2/C nanoflowers. (b, c) Low and high magnification SEM images of MoS_2/PANI nanoflowers. (e, f) Low and high magnification SEM images of MoS_2/C nanoflowers. (d, g) Photographs of two kinds of Chinese roses [110]. Reproduced with permission.

chalcogenides [111]. It requires lower temperature for the carbonization (700°C vs. $>1000^\circ\text{C}$ for graphitized carbons). In particular, when K_2CO_3 was used as activation agent, the specific surface area of PANi-derived carbon was increased from 8.9 to $917\text{ m}^2\text{ g}^{-1}$ due to the presence of large amount of micropores ($<2\text{ nm}$). The charge and discharge capacity of PANi-derived microporous carbon are much higher, compared with graphite (603 mAhg^{-1} after 20 cycles vs. $\sim 300\text{ mAhg}^{-1}$ of graphite).

3.2. Lithium-sulfur batteries (LSBs)

LSBs with lithium metal as anode and sulfur as cathode are rechargeable batteries with advantages including high specific capacitance ($C_{\text{th}} = 1672\text{ mAhg}^{-1}$), high specific energy (2600 Wh kg^{-1}), light weight, high abundance and low cost. However, they have been suffering from certain problems, like low conductivity, low stability due to high solubility of intermediates (polysulfides Li_2S_x) in organic electrolyte and the large volume change during charge/discharge [112–114]. In order to reduce the negative effects, many efforts have been made, like adding Li-protecting electrolyte additives, developing Li-protecting

separators and encapsulating sulfur in carbon scaffold or conducting polymer matrix. PANi is an ideal coating material with porous structure, low solubility in organic electrolyte and high flexibility to encapsulate sulfur in PANi matrix.

One strategy is to encapsulate sulfur in PANi matrix [112,113]. Here PANi acts as a conductive shell. In one paper, PANi nanotubes (PANi-NT) were prepared through a self-assembled method for sulfuration [112]. Then the polymer nanotubes and sulfur were heated at 280°C to form a 3-D cross-linked sulfur-PANi (SPANi-NT) structure with sulfur encapsulated in PANi-NT. This structure can tackle the dissolution of polysulfide, accommodate the volume change, resulting in good rate capability cycling stability. Another paper introduced the design and fabrication of PANi coated sulfur yolk-shell structure used for LSBs. This composite shows a high and stable capacity of 765 mAhg^{-1} at 0.2 C after 200 cycles [113]. As shown in Fig. 25a, the in-situ chemical polymerization was conducted firstly to prepare uniform nanospheres, and then, the heat treatment was conducted, resulting in yolk-shell structure. The excellent performances are owing to the heating process that provides high capacity retention and a yolk-shell structure to accommodate the volume expansion and reduce polysulfide dissolution.

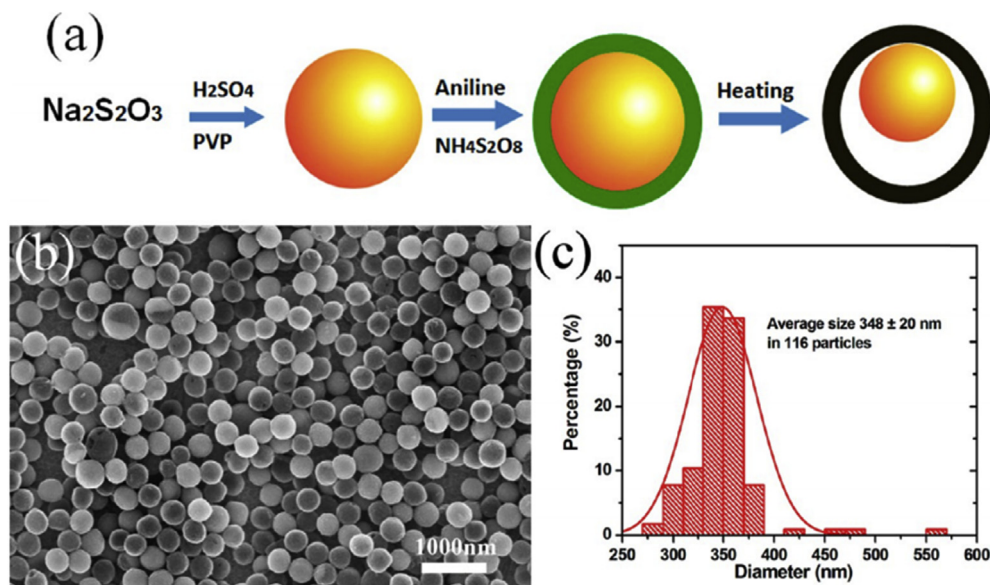


Fig. 25. (a) Schematic diagram of a two-step preparation of S-PANI yolk-shell structure. (b) SEM images of core-shell S-PANI composite. (c) Particle size distribution [113]. Reproduced with permission.

Considering the advantages of both PANi and carbon materials, ternary PANi@C/S composite could be a good choice for the fabrication of LSBs with excellent electrochemical performance. Carbon nanotubes (CNTs) are widely used as a supporting material with high conductivity, good chemical and mechanical stability. However, the surface areas and pore volumes are limited, leading to poor accommodation of sulfur active sites. PANi as a shell of sulfur coating of CNTs (SCNTs) could accommodate high capacity of sulfur. SCNTs could be prepared by a heat treatment in inert gas with sulfur and CNTs [114], or a solution-ultrasound-stirring method with sulfur amine/sodium thiosulfate pentahydrate in CNT suspension [115,116]. The PANi shell was then synthesized through an in-situ chemical oxidation to encase SCNTs, resulting in high capacity, superior rate capability and cycling properties. Graphene oxide (GO) or functional graphene with two dimensional structure and high specific surface area could also be used to wrap PANi and S with outstanding performance. The functional groups on the graphene surface could absorb polysulfides to enhance the stability [117]. Very recently, bipyramidal structured sulfur particles was first coated with a PANi layer to enhance the conductivity, which was then wrapped by GO sheets to improve the stability [118]. Besides CNTs and graphene, other porous carbon materials, like active carbon, have been adopted to fabricate PANi@C/S cathodes [119]. The carbon black could enhance the conductivity by connecting S particles together, while the PANi shell could be an excellent sulfur host for high capacity (Fig. 26a). With coating of PANi shell, the specific capacity has been greatly increased.

3.3. Sodium-ion batteries (SIBs)

SIB has been developed as an alternative rechargeable battery to LIB owing to the low cost and abundant of Na salts. Sodium ions show similar behaviors in energy storage to Li ions. However, the larger size and weaker alloying capability (with certain anode materials such as graphite and Si) of Na ion compared with Li ion make it difficult for wide applications because the development of suitable anode materials to host bigger Na ions becomes a big challenge. Recently, several groups have developed suitable anodes

based on PANi with excellent electrochemical performance [120–123].

PANi can be used as a precursor for the preparation of advanced carbon anode for SIB. The design of novel structures is important when prepare the SIB anode materials because anode materials with suitable structure can facilitate Na ions insertion-extraction. Liu Jun et al. reported a kind of hollow carbon nanowires (HCNWs) derived from the hollow PANi nanowire precursor through a direct pyrolyzation process [120]. This novel structured carbon is attractive as SIB anode for its high conductivity and good chemical/mechanical stability. The PANi derived HCNWs show good electrochemical performance, with a high reversibility of 251 mAhg^{-1} at $50 \text{ mA}g^{-1}$ and good cycling stability over 400 cycles. Besides the novel nanostructure, the doping of heteroatoms in carbon based anodes is still vital to improve the performance. Nitrogen and sulfur doping in carbon matrix can improve the conductivity and enhance the sodium storage capacity by enlarging the interlayer distance of carbon. Zhang Lina and coworkers prepared a N,S-co-doped carbon anode derived from cellulose and PANi microspheres [123]. Cellulose is the most abundant resource on earth and it has been used as a good carbon precursor for the fabrication of electrode materials used in energy storage. PANi is a flexible and low-cost conducting polymer with nitrogen species, which could be excellent for the fabrication of N-doped carbon materials with unique structures. In their work, a green and low-cost method was employed to prepare the N/S-codoped carbon microsphere (NSC-SP) electrode (Fig. 27a). The cellulose/PANi microspheres were obtained by adding oil component into the cellulose/PANi suspension. After adding of S dopant, the as obtained composites were heated to achieve the NSC-SP electrode. In Fig. 27b the N/S codoped carbon anode (NSC-SP) shows higher capacitance and stability at every current density than those without N or S doping.

PANi was also studied as the SIB anode in a nanostructured PS-PANi/rGO hybrid system, where the polystyrene (PS) nanoparticle was used as a substrate or basic frame for the deposition of PANi, while the resulting core-shell PS-PANi was further modified with the coating of rGO to fabricate the PS-PANi@rGO as anode materials [121]. The PS spheres with high surface area can help to improve the dispersion of PANi and the rGO coating could enhance

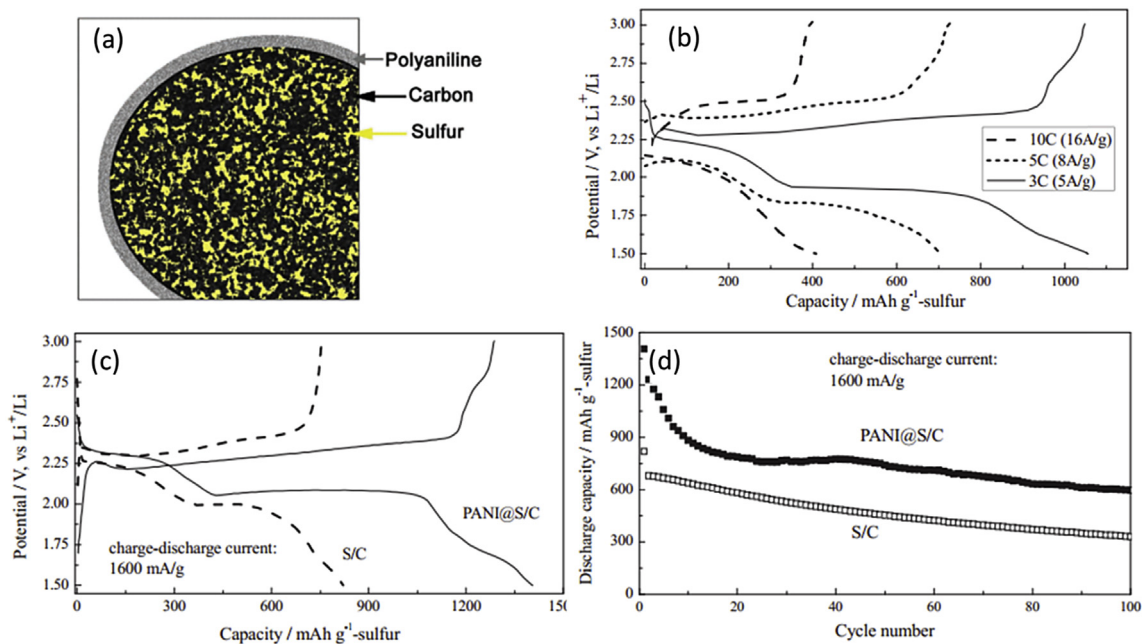


Fig. 26. (a) Schematic diagram of PANi@C/S structure. (b) Charge and discharge potential profiles of PANi@C/S. (c) Charge and discharge potential profiles of C/S and PANi@C/S. (d) Cycling stability of C/S and PANi@C/S [119]. Reproduced with permission.

the stability to deliver a high capacity of 155 mAhg^{-1} and long lifetime of 150 charge–discharge cycles.

Besides direct acting as the active material for SIB, PANi has been widely used as a coating layer material in many hybrid anode systems, including PANi/transition-metal-oxides. Zhan Xingxing and co-workers prepared a SnO_2 @PANi anode which exhibits long cycle life and excellent rate performance. SnO_2 hollow sphere (SnO_2 -HS) was synthesized using carbon sphere as template [122]. After the pyrolysis of carbon core, the SnO_2 hollow spheres were ready for coating with a layer PANi. The SnO_2 @PANi composite was able to deliver a relatively high reversible capacity of 213.5 mAh g^{-1} (after 400 cycles at 300 mA g^{-1}), vs. 14.4 mAh g^{-1} for a bare SnO_2 particle anode. The unique hollow structure and the PANi buffer layer were found to be beneficial in decreasing the likelihood of the pulverization of SnO_2 and agglomeration of the generated Sn particles during the discharge and charge process.

4. Electrocatalysts for fuel cell and water hydrolysis

Fuel cell has been used as one kind of sustainable, clean and efficient energy storage devices in recent years owing to its high energy density and efficiency, low environmental impact. Unlike supercapacitors and batteries, fuel cell could realize the direct conversion of chemical energy to electric energy. Fuel cells like proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), Zn-Air cell, polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC) and microbial fuel cell (MFC) have drawn much attention among scientists, and tremendous progresses have been made in the last decade. Similarly, water electrolysis for converting electricity to hydrogen energy has attracted increasing attention from scientists worldwide. Conducting polymers with good conductivity, high flexibility and variable morphologies have been widely used as supporting matrix or conductive coating layer for metal catalysts used in fuel cells and water electrolysis. These conducting polymer supported and conducting polymer derived catalysts usually show high catalytic activity and good stability. Among them PANi based electrocatalysts

are promising for hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR).

4.1. PANi as support for metal electrocatalysts

Most metal electrocatalysts are supported onto porous carbon materials or conducting polymers to improve the utilization, enhance the conductivity, activity and stability [2]. PANi as supports for metal catalysts has several advantages, including the high flexibility and a variety of controllable morphologies. The conductive polyaniline is favorable for HER and HOR due to its sufficient protonated sites. Platinum(Pt) is a precious metal with excellent HER and ORR activity [124]. In order to increase the utilization of Pt catalysts, PANi was used as a supporting matrix for Pt dispersion. Various non-precious metal catalysts, like molybdenum(Mo), nickel(Ni), cobalt(Co), iron(Fe), manganese(Mn) and their compounds, were discovered as alternatives to replace Pt because of its high cost and low abundance. Among these low-cost non-noble metal catalysts, MoS_2 shows outstanding catalytic performance for HER. One article illustrated the PANi supported MoS_2 hybrid with edge-rich construction and high HER activity [125]. As shown in Fig. 28, MoS_2 nanosheets uniformly and vertically grow on PANi branches with high edge exposure, indicating that PANi can greatly decrease the agglomeration of MoS_2 . All these would result in high utilization of MoS_2 . Except for MoS_2 , Ni and Ni-Mo in PANi matrix composites were also studied as surpassingly stable and catalytic systems [126,127].

Besides Pt, iron is a superior metal catalyst toward ORR. Yong Yuan et al. have shown an efficient iron phthalocyanine (FePc) catalyst, using polyaniline/carbon black (PANi/C) as an electrocatalyst support for ORR of FePc in an air–cathode single-chamber DMFC. The PANi/C/FePc catalyst showed better activity than PANi/C, C/FePc, and Pt, indicating PANi/C (20 wt% of H_2SO_4 -doped PANi in carbon) was a better catalyst support than C in this reaction [128]. Meanwhile, the power per cost of PANi/C/FePc was 7.5 times higher

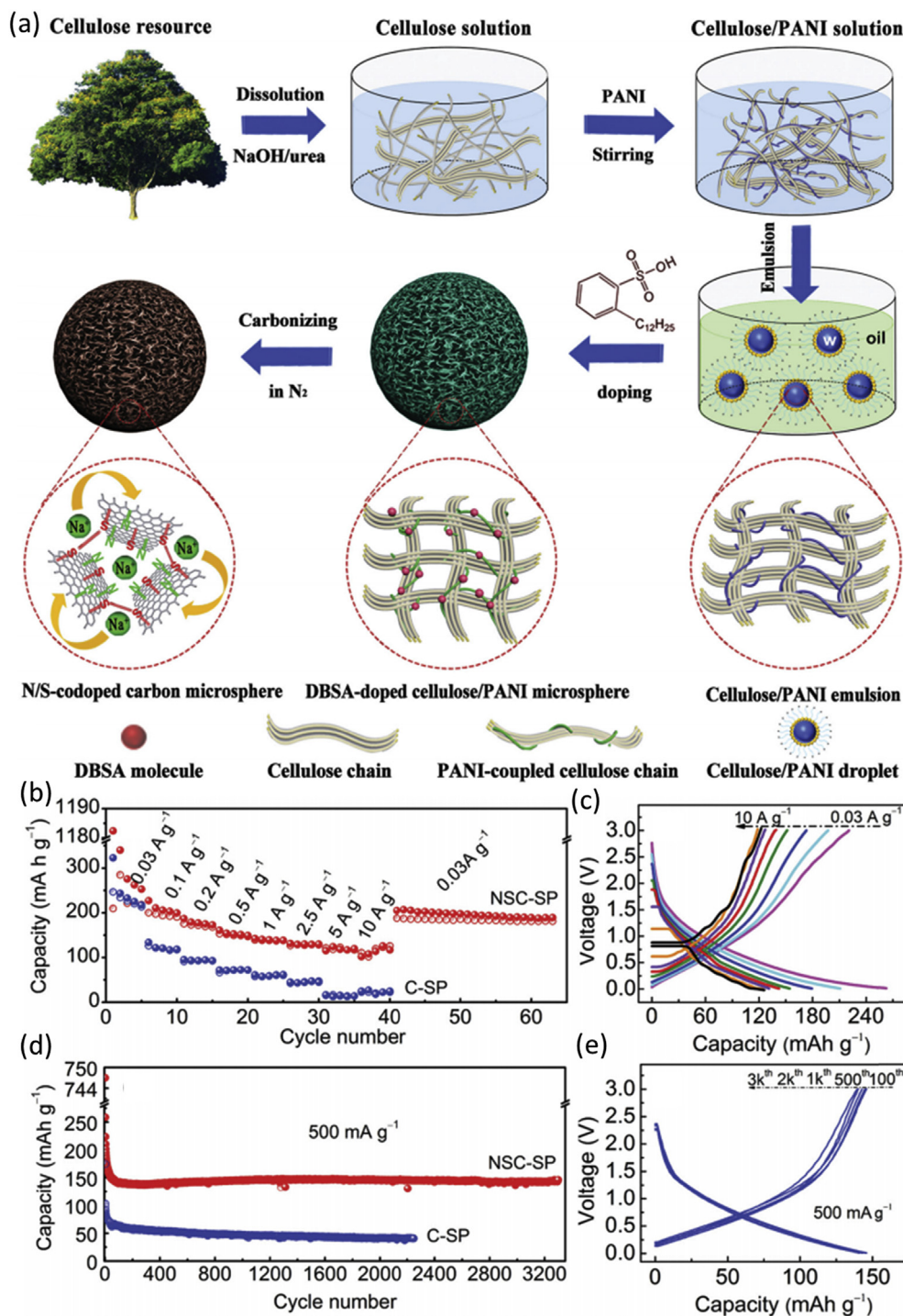


Fig. 27. (a) Schematic diagram of NSC-SP preparation. (b) Rate performances of electrochemical sodium storage, (d) cycling stability test, (c) charge–discharge curves and (e) charge–discharge curves from selected cycles for C-SP and NSC-SP electrodes [123]. Reproduced with permission.

than that of Pt, demonstrating that the PANi/C was an ideal supporting material for FePc and the PANi/C/FePc offered a good alternative to Pt in MFC practical applications.

Very recently, Yang Liu and coworkers developed a novel in situ synthetic method to prepare CoFe₂O₄ ORR catalyst, using PANi–MWCNT as the support [129]. The PANi layer on the MWCNT surface could provide more active sites, leading to the close contact of CoFe₂O₄ nanoparticles with the substrate and homogeneous distribution. Furthermore, PANi could improve the synergistic effect

between the CoFe₂O₄ nanoparticles and MWCNT, promoting the electrical conductivity and stability of the catalyst. The CoFe₂O₄/PANi-MWCNT hybrid exhibited excellent OER activities and remarkably good durability, much better than the CoFe₂O₄/MWCNT hybrid (without PANi) and pure CoFe₂O₄ NPs, indicating that the reaction sites of the electrode increased in the presence of PANi.

Ruthenium (Ru) and iridium (Ir) are the most two promising metal catalysts for OER as they show suitable binding energy with the surface oxygen species [130]. However, the main problem is still

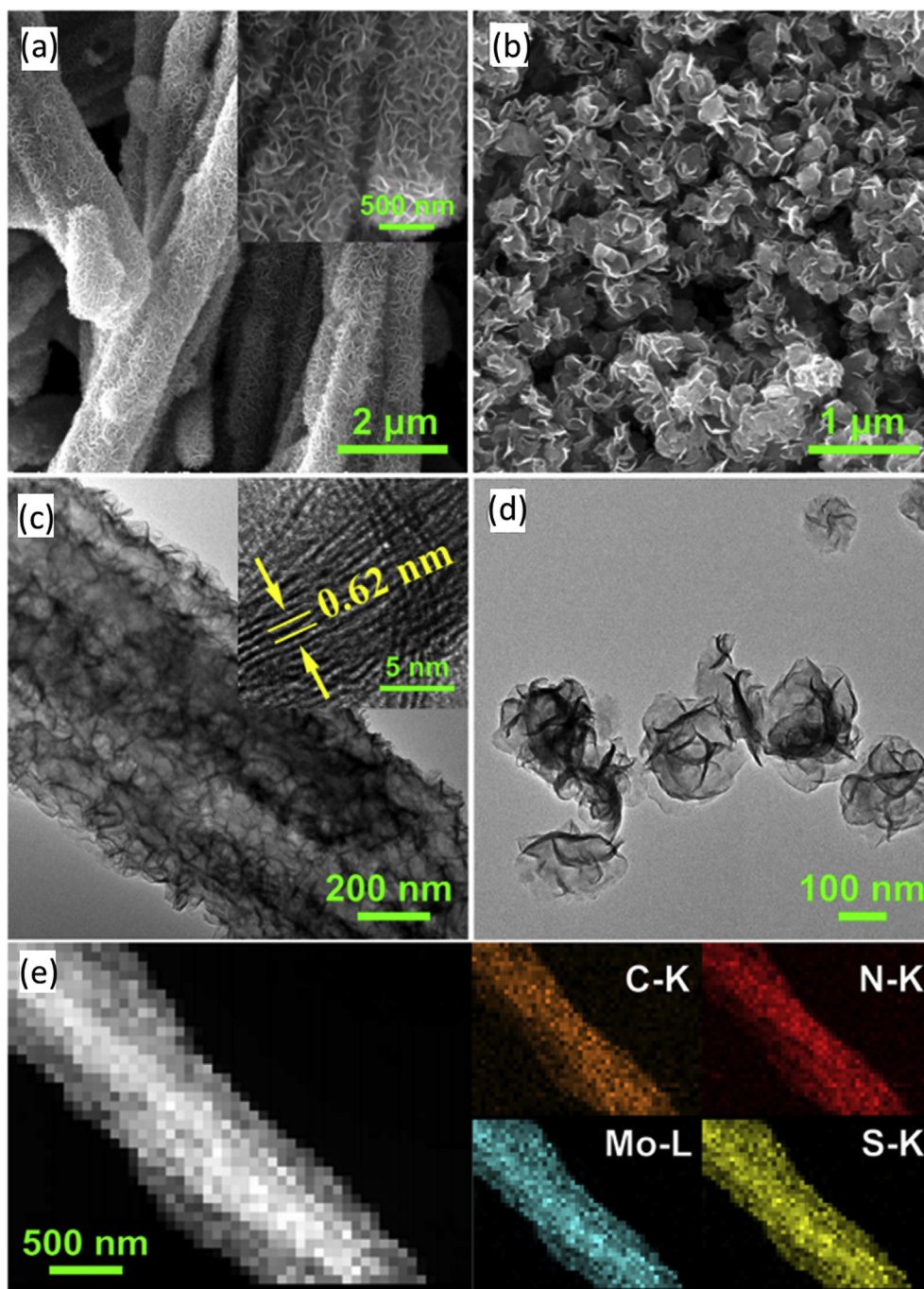


Fig. 28. (a, c) SEM and TEM images of MoS_2/PANI . (b, d) SEM and TEM images of MoS_2 . (e) STEM image of MoS_2/PANI and elemental mapping images [125]. Reproduced with permission.

the high cost. Scientists have been tried to find non-precious metal candidates and most of the common transition metals have been used as the electrode materials for OER. Among them, nickel and cobalt and their compounds show superior performance over others due to high theoretical activity [131,132]. The nickel and cobalt layered double hydroxide (LDH) nanosheets have been achieved for OER with low onset potential (290 mV), high current density and good durability [131]. The binary nickel and iron nanosheets have been obtained through a one-step electrochemical co-deposition on nickel foam and possess excellent performance, a smaller overpotential of 200 mV [132].

Direct methanol fuel cells (DMFCs) are also promising FC devices and they have been investigated in the former years. Besides of HER and ORR, Pt has good catalytic properties in methanol oxidation [133]. However, Pt still has some drawbacks like low electrocatalytic efficiency and high cost. The former one could be fixed by introducing a supporting matrix, like porous carbon materials and conducting polymers, to increase the specific surface area. Then the utilization of Pt is greatly improved. The later one could be tackled by the binary metal catalysts [134]. PANi was proved to be a good support for Pt catalysts in methanol oxidation. Furthermore, there is investigation of PANi/CB/Pt composites acted

as catalyst that CB has great significance to improve the polymeric degree and lower the defect density in the PANi backbone, leading to a higher catalytic activity due to more active sites exposed and a faster charge transfer at the electrode/electrolyte interface due to enhanced conductivity [134].

In conventional fuel cells, carbon black XC-72 is typically employed as Pt support material while nafion is added as both a binder and proton conductor in the electrode fabrication process. However, this fuel cell electrode preparation technique is likely to hinder catalyst accessibility due to carbon particles agglomeration as well as blockage of electron transport by the ionomer. Very recently, a one-step simultaneous electrospinning of PANi/Poly (ethylene oxide) (PEO) and Nafion/PEO was proposed to fabricate nanostructured PANi/Nafion composite architecture as the substrate for fuel cell catalysts [135]. The preparation of such composite is schematically illustrated in Fig. 29a. Both PANi and Nafion solutions are not electrospinnable and PEO is added as carrier

polymer to enhance the spinnability of the mixture solutions. The fabricated dual nanofibers possess a 3D porous, interconnected non-woven network (Fig. 29b–e) of both electron- and proton-conducting nanofibers, providing accessible triple phase boundary for all fuel cell electrode processes. The nanofibers after post-annealing, densification and acid-doping treatments showed excellent electrical and proton conductivity of 0.014 and 0.023 S cm⁻¹, respectively.

Liming Yang et al. used a vertical reduced graphene oxide (VrGO) and PANi composite to support Pd catalyst for DMFCs through a facile one-step electrochemical deposition of PANi layer and Pd onto VrGO nanosheets [136]. The VrGO nanosheets can facilitate the mass transport and electron transfer. On the other hand, the conductive PANi thin layer coated on the surface of VrGO nanosheets can not only enhance the conductivity, protect rGO sheets from restacking and acidic environmental corrosion, but also improve the compatibility between support and metal by providing

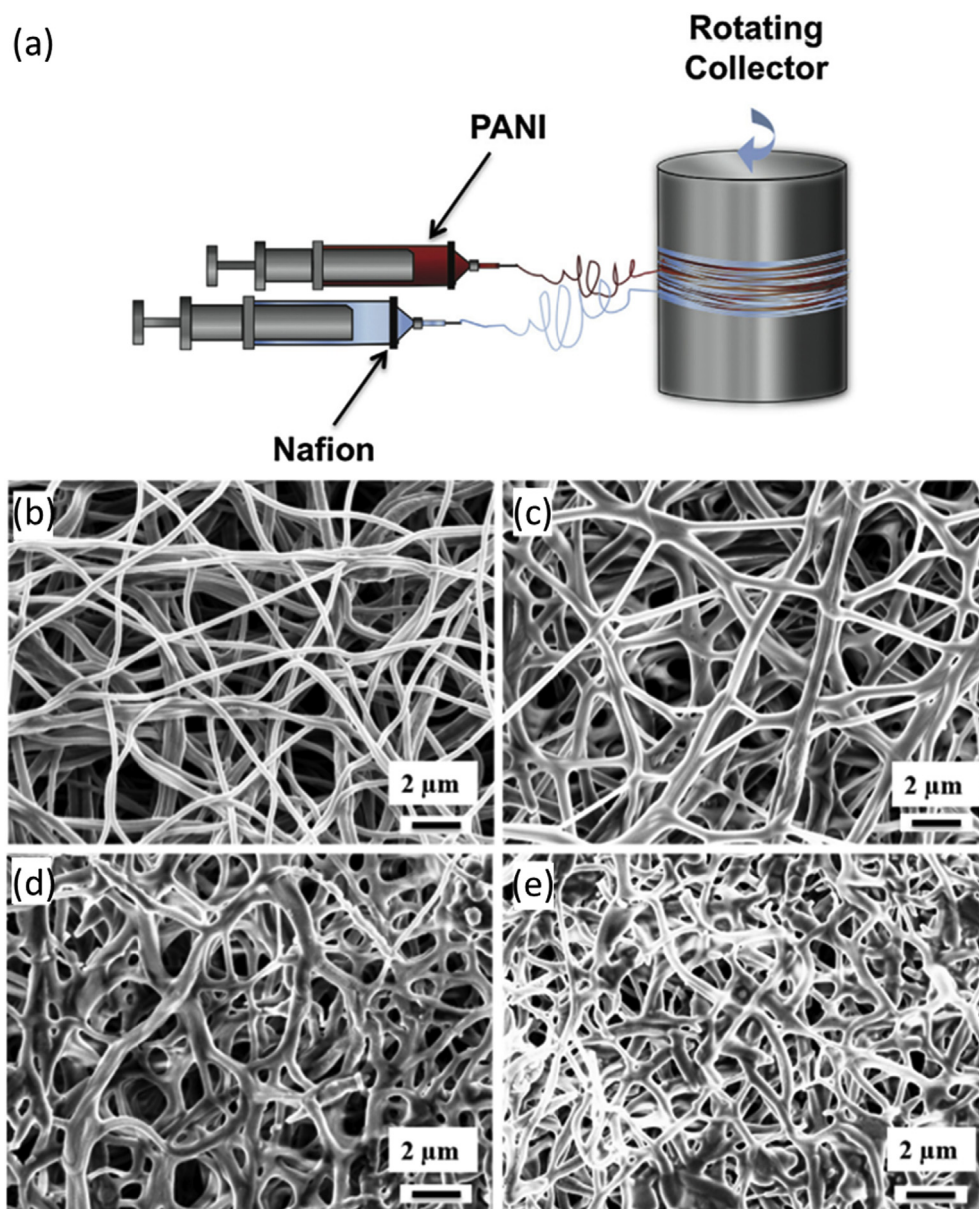


Fig. 29. (a) Schematic illustration of the electrospinning of Nafion/PANi nanofiber mat. (b–e) SEM images of Nafion/PANi based composites [135]. Reproduced with permission.

abundant nitrogen atoms for binding with metal catalysts. The binary supporting matrix for Pd catalyst induced high catalytic activity and long durability.

A unique sandwich Pd/PANI/Pd nanoarray structure was designed for ethanol electrooxidation (Fig. 30e) [137]. This unique hollow structure was prepared using ZnO nanorod arrays (NRAs) as a template, which was electrodeposited on Ti plates. Pd and PANI layers were then deposited on NRA layer-by-layer, using electrodeposition. The ZnO nanorods were removed by chemical etching, leading to the Pd/PANI/Pd sandwich-structured nanotube arrays (SNTAs). The unique SNTA nanotube array structure can highly improve the utilization rate of catalysts and the diffusion of electroactive species while the double thin Pd layers with improved utilization make the fast reactions possible. PANi not only enhances the system conductivity, but also modifies the electronic structure of Pd. The electron delocalization between Pd orbitals and PANi π -conjugated ligands makes it difficult for metallic Pd to be oxidized (or dissolved) and accordingly enhancing the activity and durability of Pd/PANI/Pd SNTAs. All these result in excellent electrochemical performance, higher current density and lower onset potential compared with other samples (Fig. 30g).

4.2. PANi functionalized support for metal electrocatalysts

At present, the most commonly used catalysts in polymer electrolyte membrane fuel cells (PEMFC) are highly dispersed 2–5 nm Pt nanoparticles (NPs) supported on carbon both for cathode and anode. However, Pt NPs suffer from poor durability because of the loss of platinum electrochemical surface area (ECSA) over time due to the corrosion of carbon support, Pt dissolution, Ostwald ripening, and aggregation. PANi has been utilized as a conductive layer to protect the Pt/C catalysts. Their unique π -conjugated structures lead to good environmental stability, high electrical and proton conductivity in acidic environments, high hydrophilic property (vs. carbon materials) and unique redox properties. However, the protect effect of PANi layer is strongly dependent on the catalyst structure and synthesis procedure.

In 2012, a new design and synthesis of a Pt/C@PANI core-shell structured catalyst could address both the activity and durability issues. As shown in Fig. 31a, the aniline monomer was first selectively adsorbed on the carbon surface via preferential π - π conjugation between the aniline and the carbon support and was then polymerized in situ on the carbon surface via ammonium peroxodisulfate (APS) oxidation in acidic solution, without covering Pt

nanoparticles [138]. The electrochemical tests show that Pt/C@PANI (30%) has the best catalytic activity and much better durability compared with Pt/C because the suitable thickness (5 nm) PANi layer can not only protect the carbon core from direct corrosion but also allow the facilitated penetrability of electrolyte (Fig. 31b–e). In addition to Pt, PANi-decorated catalysts, including iron carbide, iron nitride, and manganese-based catalysts are found in literature [139,140].

4.3. PANi-derived porous carbon based electrocatalysts

PANI as a nitrogen-containing carbon precursor has been widely used for the fabrication of porous carbon materials in supercapacitor and battery applications. PANi derived N-doped porous carbon materials as advanced catalyst support or non-precious-metal catalysts for fuel cells have also attracted increasing attention. The investigations of PANi derived carbon materials are mainly focused toward ORR since the demand of Pt for ORR is much higher than HOR in anode electrodes in commercial PEM fuel cells [14,141]. Heteroatom (N, B, S, P)-doped carbon materials have been considered as the most feasible metal-free catalysts alternative to Pt for ORR because they show better fuel cross-over resistance and long-term durability than commercially available Pt/C in an alkaline medium. A high electron affinity atom such as N or a low electron affinity atom such as B can create charged sites in the carbon framework that are favorable for O₂ adsorption. In this respect, B/N co-doped carbon materials have drawn immense attention because of their unique electronic structures [14]. The B/N co-doped porous carbon nanosheets with high heteroatom doping (5%) were synthesized via the oxidation polymerization of aniline, aminophenyl boronic acid, and phenylenediamine with amino-functionalized GO as the template. The GO-based, boronic-acid-functionalized PANi nanosheets were heated at 1000 °C, resulting in typical 2-D carbon nanosheets with a thickness of 20 nm and a high specific surface area of 363 m² g⁻¹. This B/N co-doped porous carbon exhibited excellent electrochemical performance for ORR.

PANI-derived O and N co-doped mesoporous carbons were synthesized by in situ polymerization of PANi within the pores of SBA-15 mesoporous silica, followed by carbonization under an inert atmosphere and the etching away the silica framework, as illustrated in Fig. 32a. The electrochemical catalytic activity of the PANi derived N- and O-doped mesoporous carbons (PDMCs) is even better compare with Pt/C catalyst with high current density and lower onset potential and the PDMCs could realize four electrons

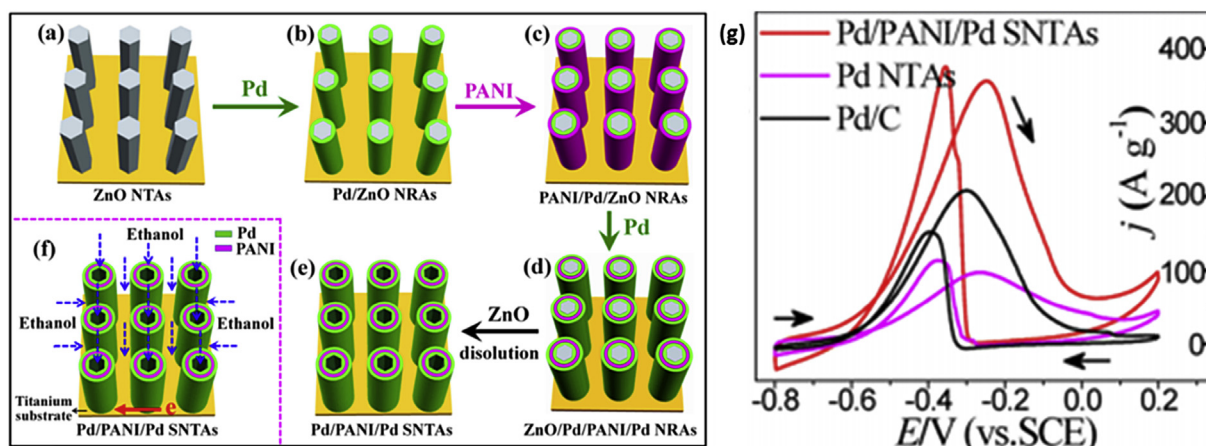


Fig. 30. (a–e) Schematic illustration of the fabrication of Pd/PANI/Pd sandwich-structured nanotube arrays (SNTAs). (f) The schematic description of Pd/PANI/Pd sandwich-structured nanotube arrays (SNTAs) advantages as a catalyst. (g) CV curves of different samples tested in ethanol + NaOH electrolyte [137]. Reproduced with permission.

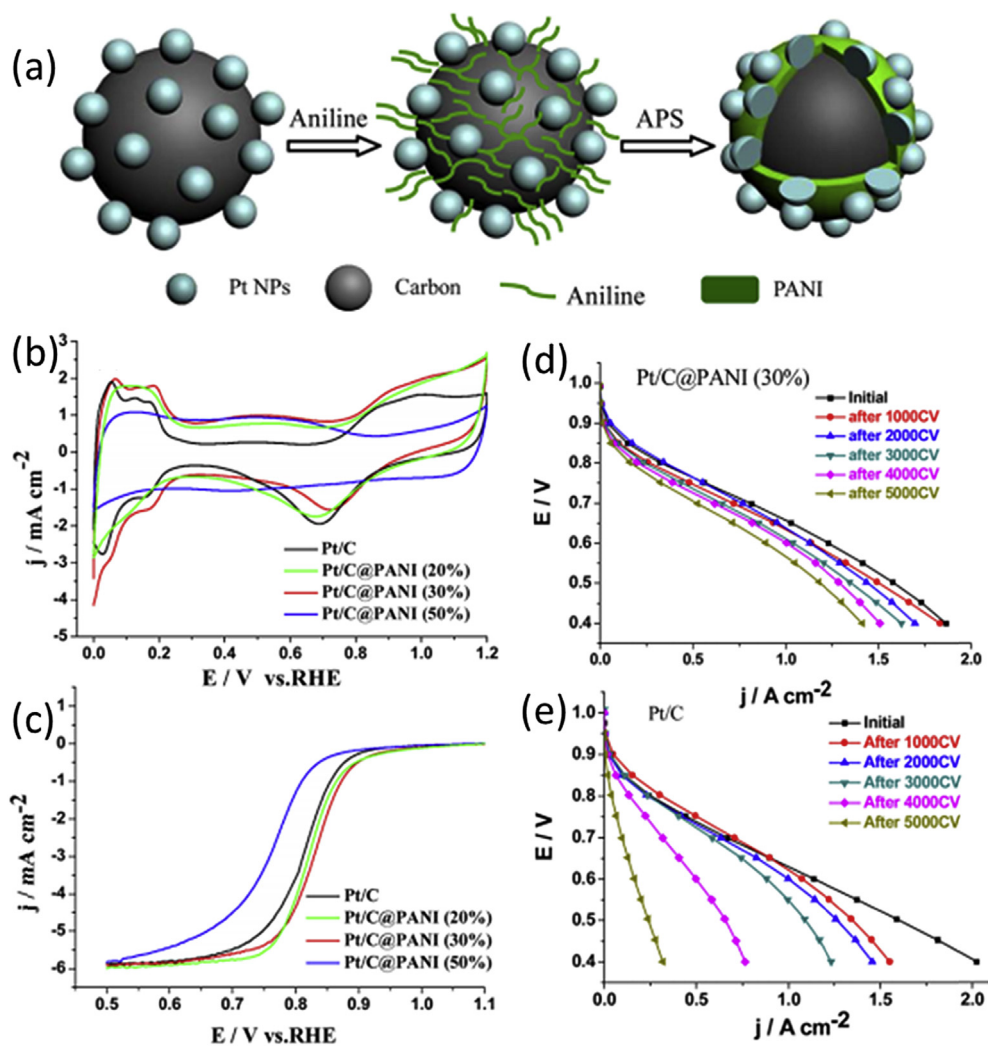


Fig. 31. (a) Schematic illustration of Pt/C@PANI catalyst. (b) CV curves of Pt/C and Pt/C@PANI with different PANi loading mass. (c) LSV curves of Pt/C and Pt/C@PANI with different PANi loading mass. (d, e) Polarization curves of Pt/C@PANI(30%) and Pt/C catalysts [138]. Reproduced with permission.

pathway toward ORR (Fig. 32b, c). This unprecedented activity by the metal-free O/N co-doped carbon toward ORR was attributed to the synergetic activities of nitrogen and oxygen (or hydroxyl) species that were implanted in it. Moreover, the catalytic behaviors could be greatly dependent on the pyrolysis temperature, which is vital for the formation of unique microporous structures.

It is widely recognized that the co-doping of the transition metals would further enhance the performance of the metal-free heteroatom doped carbon catalysts. Many efforts have been undertaken to reveal the role of transition metals for the performance enhancement of the catalysts. However, the issues related to the role of the metals as well as the activation mechanism remain unclear. In a very recent study the addition of various transition metals (Mn, Fe, Co, Ni, Cu) on the structure and performance of the doped carbon catalysts M-PANI/C-Mela was shown to affect structures and performances of the catalysts significantly. Doping with Fe and Mn leads to a catalyst with a graphene-like structure, and doping with Co, Ni, and Cu leads to a disordered or nanosheet structure. The doping of transition metals can enhance the performance of the catalysts, and their ORR activity follows the order of Fe > Co > Cu > Mn > Ni, which is consistent with the order of their active N contents. It was suggested that the various performance enhancements of the transition metals may be the result of

the joint effect of the following three aspects: the active N content, metal residue, and the surface-area/pore-structure of the catalyst. Although the activity enhancement is not the effect of any single factor, PANi plays an important role since it contributes N-sites [142].

5. Conclusion and prospect

In this review, we summarize recent advances of PANi in the application as electrode materials for energy storage and conversion. Because of its good environmental stability, ease of preparation, low cost, excellent flexibility, unique redox properties and high electrical and proton conductivity in doped states, PANi itself can be used as active electrode materials for supercapacitor and rechargeable battery. PANi is a typical electrode material for pseudocapacitors with high specific capacitance and cycling stability. It is also an outstanding cathode material for Li ion battery. Porous carbon derived from PANi carbonization and subsequent activation processes possesses high surface area and suitable pore structure, with high nitrogen content, which can be used as superior carbon material in both energy storage and conversion, particularly as the support for electrocatalysts. Nevertheless, the wide application of PANi is more relied on its unique conjugated-

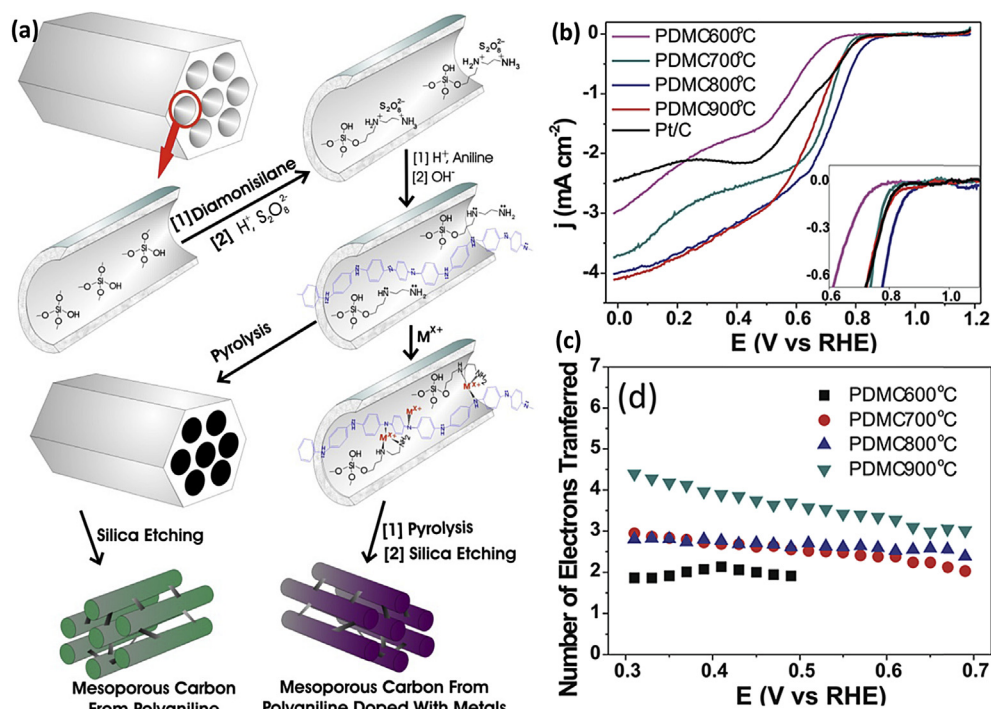


Fig. 32. (a) Schematic illustration of the synthesis of the PANi derived N- and O-doped mesoporous carbons (PDMCs). (b) Polarization curves of PDMCs pyrolysis at different temperature. (c) The number of transferred electrons as a function of voltage for PDMCs pyrolysis at different temperature [141]. Reproduced with permission.

bonding structure as well as the availability of abundant N-active sites, which allows for PANi to easily couple with other electrode materials, like carbonaceous materials, metal compounds or other polymers, resulting in composite materials with superior performance over each component due to synergistic effects. PANi-based composite supercapacitors, rechargeable batteries, and electrocatalysts could have enhanced or improved behaviors, in which PANi usually acts as a porous conductive support, protective network or/and connective matrix on the surface of active electrode materials. Various techniques have been employed in preparing the composites with suitable morphology, size and structure, resulting in great advances in the past decades. In conclusion, PANi is a promising excellent electrode material for energy storage and conversion devices.

Acknowledgments

The authors acknowledge financial support from the CNRS International NTU THALES Research Alliance (CINTRA), NTU, Singapore. We also acknowledge the financial support from the Ministry of Education, Tier 1 (Grant no: M4011424.110) and Tier 2 (Grant no: M4020284.110).

References

- L.L. Zhang, X. Zhao, Carbon-based materials as supercapacitor electrodes, *Chem. Soc. Rev.* 38 (2009) 2520–2531.
- S.L. Candelaria, Y. Shao, W. Zhou, X. Li, J. Xiao, J.-G. Zhang, Y. Wang, J. Liu, J. Li, G. Cao, Nanostructured carbon for energy storage and conversion, *Nano Energy* 1 (2012) 195–220.
- S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, Progress in preparation, processing and applications of polyaniline, *Prog. Polym. Sci.* 34 (2009) 783–810.
- G.A. Snook, P. Kao, A.S. Best, Conducting-polymer-based supercapacitor devices and electrodes, *J. Power Sources* 196 (2011) 1–12.
- J. Liu, L. Zhang, H.B. Wu, J. Lin, Z. Shen, X.W.D. Lou, High-performance flexible asymmetric supercapacitors based on a new graphene foam/carbon nanotube hybrid film, *Energy Environ. Sci.* 7 (2014) 3709–3719.
- C.H. Silva, N.A. Galiote, F. Huguenin, É. Teixeira-Neto, V.R. Constantino, M.L. Temperini, Spectroscopic, morphological and electrochromic characterization of layer-by-layer hybrid films of polyaniline and hexaniobate nanoscrolls, *J. Mater. Chem.* 22 (2012) 14052–14060.
- G. Louarn, M. Lapkowski, S. Quillard, A. Pron, J.P. Buisson, S. Lefrant, Vibrational properties of polyaniline – isotope effects, *J. Phys. Chem.* 100 (1996) 6998–7006.
- D.W. Hatchett, M. Josowicz, J. Janata, Comparison of chemically and electrochemically synthesized polyaniline films, *J. Electrochem. Soc.* 146 (1999) 4535–4538.
- C.A. Amarnath, J. Kim, K. Kim, J. Choi, D. Sohn, Nanoflakes to nanorods and nanospheres transition of selenious acid doped polyaniline, *Polymer* 49 (2008) 432–437.
- H.D. Tran, J.M. D'Arcy, Y. Wang, P.J. Beltramo, V.A. Strong, R.B. Kaner, The oxidation of aniline to produce “polyaniline”: a process yielding many different nanoscale structures, *J. Mater. Chem.* 21 (2011) 3534–3550.
- K. Wang, J. Huang, Z. Wei, Conducting polyaniline nanowire arrays for high performance supercapacitors, *J. Phys. Chem. C* 114 (2010) 8062–8067.
- J. Yan, T. Wei, Z. Fan, W. Qian, M. Zhang, X. Shen, F. Wei, Preparation of graphene nanosheet/carbon nanotube/polyaniline composite as electrode material for supercapacitors, *J. Power Sources* 195 (2010) 3041–3045.
- L. Yang, S. Wang, J. Mao, J. Deng, Q. Gao, Y. Tang, O.G. Schmidt, Hierarchical MoS₂/Polyaniline nanowires with excellent electrochemical performance for lithium-ion batteries, *Adv. Mater.* 25 (2013) 1180–1184.
- Y. Zhang, X. Zhuang, Y. Su, F. Zhang, X. Feng, Polyaniline nanosheet derived B/N co-doped carbon nanosheets as efficient metal-free catalysts for oxygen reduction reaction, *J. Mater. Chem. A* 2 (2014) 7742–7746.
- M. Gotz, J. Lefebvre, F. Mors, A.M. Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable power-to-gas: a technological and economic review, *Renew. Energy* 85 (2016) 1371–1390.
- G. Wu, K.L. More, C.M. Johnston, P. Zelenay, High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt, *Science* 332 (2011) 443–447.
- C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, A review of electrolyte materials and compositions for electrochemical supercapacitors, *Chem. Soc. Rev.* 44 (2015) 7484–7539.
- C. Peng, S. Zhang, D. Jewell, G.Z. Chen, Carbon nanotube and conducting polymer composites for supercapacitors, *Prog. Nat. Sci.* 18 (2008) 777–788.
- M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, Nanostructured carbon–metal oxide composite electrodes for supercapacitors: a review, *Nanoscale* 5 (2013) 72–88.
- G. Lota, K. Fic, E. Frackowiak, Carbon nanotubes and their composites in electrochemical applications, *Energy Environ. Sci.* 4 (2011) 1592–1650.
- H.H. Zhou, H. Chen, S.L. Luo, G.W. Lu, W.Z. Wei, Y.F. Kuang, The effect of the polyaniline morphology on the performance of polyaniline supercapacitors, *J. Solid State Electrochem.* 9 (2005) 574–580.

- [22] H.L. Li, J.X. Wang, Q.X. Chu, Z. Wang, F.B. Zhang, S.C. Wang, Theoretical and experimental specific capacitance of polyaniline in sulfuric acid, *J. Power Sources* 190 (2009) 578–586.
- [23] S. Mondal, K. Barai, N. Munichandraiah, High capacitance properties of polyaniline by electrochemical deposition on a porous carbon substrate, *Electrochim. Acta* 52 (2007) 3258–3264.
- [24] K.S. Ryu, Y.-G. Lee, K.M. Kim, Y.J. Park, Y.-S. Hong, X. Wu, M.G. Kang, N.-G. Park, R.Y. Song, J.M. Ko, Electrochemical capacitor with chemically polymerized conducting polymer based on activated carbon as hybrid electrodes, *Synth. Met.* 153 (2005) 89–92.
- [25] M.J. Bleda-Martínez, E. Morallón, D. Cazorla-Amorós, Polyaniline/porous carbon electrodes by chemical polymerisation: effect of carbon surface chemistry, *Electrochim. Acta* 52 (2007) 4962–4968.
- [26] O. Misoon, K. Seok, Effect of dodecyl benzene sulfonic acid on the preparation of polyaniline/activated carbon composites by in situ emulsion polymerization, *Electrochim. Acta* 59 (2012) 196–201.
- [27] C.-C. Hu, W.-Y. Li, J.-Y. Lin, The capacitive characteristics of supercapacitors consisting of activated carbon fabric–polyaniline composites in NaNO_3 , *J. Power Sources* 137 (2004) 152–157.
- [28] D. Salinas-Torres, J.M. Sieben, D. Lozano-Castelló, D. Cazorla-Amorós, E. Morallón, Asymmetric hybrid capacitors based on activated carbon and activated carbon fibre–PANI electrodes, *Electrochim. Acta* 89 (2013) 326–333.
- [29] H. Liu, B. Xu, M. Jia, M. Zhang, B. Cao, X. Zhao, Y. Wang, Polyaniline nanofiber/large mesoporous carbon composites as electrode materials for supercapacitors, *Appl. Surf. Sci.* 332 (2015) 40–46.
- [30] Y. Yan, Q. Cheng, Z. Zhu, V. Pavlinek, P. Saha, C. Li, Controlled synthesis of hierarchical polyaniline nanowires/ordered bimodal mesoporous carbon nanocomposites with high surface area for supercapacitor electrodes, *J. Power Sources* 240 (2013) 544–550.
- [31] S.-W. Woo, K. Dokko, H. Nakano, K. Kanamura, Incorporation of polyaniline into macropores of three-dimensionally ordered macroporous carbon electrode for electrochemical capacitors, *J. Power Sources* 190 (2009) 596–600.
- [32] Y.G. Wang, H.Q. Li, Y.Y. Xia, Ordered whiskerlike polyaniline grown on the surface of mesoporous carbon and its electrochemical capacitance performance, *Adv. Mater.* 18 (2006) 2619–2623.
- [33] W. Xing, S. Zhuo, H. Cui, Z. Yan, Synthesis of polyaniline-coated ordered mesoporous carbon and its enhanced electrochemical properties, *Mater. Lett.* 61 (2007) 4627–4630.
- [34] Y. Yan, Q. Cheng, G. Wang, C. Li, Growth of polyaniline nanowhiskers on mesoporous carbon for supercapacitor application, *J. Power Sources* 196 (2011) 7835–7840.
- [35] L.L. Zhang, S. Li, J. Zhang, P. Guo, J. Zheng, X. Zhao, Enhancement of electrochemical performance of macroporous carbon by surface coating of polyaniline, *Chem. Mater.* 22 (2009) 1195–1202.
- [36] Z. Lei, Z. Chen, X. Zhao, Growth of polyaniline on hollow carbon spheres for enhancing electrocapitance, *J. Phys. Chem. C* 114 (2010) 19867–19874.
- [37] K. Shen, F. Ran, X. Zhang, C. Liu, N. Wang, X. Niu, Y. Liu, D. Zhang, L. Kong, L. Kang, Supercapacitor electrodes based on nano-polyaniline deposited on hollow carbon spheres derived from cross-linked co-polymers, *Synth. Met.* 209 (2015) 369–376.
- [38] X. Ning, W. Zhong, L. Wan, Ultrahigh specific surface area porous carbon nanospheres and its composite with polyaniline: preparation and application for supercapacitors, *RSC Adv.* 6 (2016) 25519–25524.
- [39] L.Z. Fan, Y.S. Hu, J. Maier, P. Adelhelm, B. Smarsly, M. Antonietti, High electroactivity of polyaniline in supercapacitors by using a hierarchically porous carbon monolith as a support, *Adv. Funct. Mater.* 17 (2007) 3083–3087.
- [40] L. Li, S. Dong, X. Chen, P. Han, H. Xu, J. Yao, C. Shang, Z. Liu, G. Cui, A renewable bamboo carbon/polyaniline composite for a high-performance supercapacitor electrode material, *J. Solid State Electrochem.* 16 (2012) 877–882.
- [41] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, Graphene-based ultracapacitors, *Nano Lett.* 8 (2008) 3498–3502.
- [42] S. Vivekchand, C.S. Rout, K. Subrahmanyam, A. Govindaraj, C. Rao, Graphene-based electrochemical supercapacitors, *J. Chem. Sci.* 120 (2008) 9–13.
- [43] J. Yan, T. Wei, B. Shao, Z. Fan, W. Qian, M. Zhang, F. Wei, Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance, *Carbon* 48 (2010) 487–493.
- [44] N.I. Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva, A.D. Gorchinskiy, Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations, *Chem. Mater.* 11 (1999) 771–778.
- [45] H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, Graphene oxide doped polyaniline for supercapacitors, *Electrochem. Commun.* 11 (2009) 1158–1161.
- [46] J. Xu, K. Wang, S.-Z. Zu, B.-H. Han, Z. Wei, Hierarchical nanocomposites of polyaniline nanowire arrays on graphene oxide sheets with synergistic effect for energy storage, *ACS Nano* 4 (2010) 5019–5026.
- [47] Q. Zhang, Y. Li, Y. Feng, W. Feng, Electropolymerization of graphene oxide/polyaniline composite for high-performance supercapacitor, *Electrochim. Acta* 90 (2013) 95–100.
- [48] K. Zhang, L.L. Zhang, X. Zhao, J. Wu, Graphene/polyaniline nanofiber composites as supercapacitor electrodes, *Chem. Mater.* 22 (2010) 1392–1401.
- [49] H. Mi, J. Zhou, Q. Cui, Z. Zhao, C. Yu, X. Wang, J. Qiu, Chemically patterned polyaniline arrays located on pyrolytic graphene for supercapacitors, *Carbon* 80 (2014) 799–807.
- [50] L. Lai, H. Yang, L. Wang, B.K. Teh, J. Zhong, H. Chou, L. Chen, W. Chen, Z. Shen, R.S. Ruoff, Preparation of supercapacitor electrodes through selection of graphene surface functionalities, *ACS Nano* 6 (2012) 5941–5951.
- [51] L. Wang, Y. Ye, X. Lu, Z. Wen, Z. Li, H. Hou, Y. Song, Hierarchical nanocomposites of polyaniline nanowire arrays on reduced graphene oxide sheets for supercapacitors, *Sci. Rep.* 3 (2013) 1–9.
- [52] K.H.S. Iessa, Y. Zhang, G. Zhang, F. Xiao, S. Wang, Conductive porous sponge-like ionic liquid–graphene assembly decorated with nanosized polyaniline as active electrode material for supercapacitor, *J. Power Sources* 302 (2016) 92–97.
- [53] S. Wang, L. Ma, M. Gan, S. Fu, W. Dai, T. Zhou, X. Sun, H. Wang, H. Wang, Free-standing 3D graphene/polyaniline composite film electrodes for high-performance supercapacitors, *J. Power Sources* 299 (2015) 347–355.
- [54] M. Moussa, M.F. El-Kady, H. Wang, A. Michimore, Q. Zhou, J. Xu, P. Majeswski, J. Ma, High-performance supercapacitors using graphene/polyaniline composites deposited on kitchen sponge, *Nanotechnology* 26 (2015), 075702.
- [55] B. Yao, L. Yuan, X. Xiao, J. Zhang, Y. Qi, J. Zhou, J. Zhou, B. Hu, W. Chen, Paper-based solid-state supercapacitors with pencil-drawing graphite/polyaniline networks hybrid electrodes, *Nano Energy* 2 (2013) 1071–1078.
- [56] P. Yu, X. Zhao, Z. Huang, Y. Li, Q. Zhang, Free-standing three-dimensional graphene and polyaniline nanowire arrays hybrid foams for high-performance flexible and lightweight supercapacitors, *J. Mater. Chem. A* 2 (2014) 14413–14420.
- [57] J.L. Liu, J. Sun, L.A. Gao, A promising way to enhance the electrochemical behavior of flexible single-walled carbon nanotube/polyaniline composite films, *J. Phys. Chem. C* 114 (2010) 19614–19620.
- [58] H. Zhang, G.P. Cao, Z.Y. Wang, Y.S. Yang, Z.J. Shi, Z.N. Gu, Tube-covering-tube nanostructured polyaniline/carbon nanotube array composite electrode with high capacitance and superior rate performance as well as good cycling stability, *Electrochem. Commun.* 10 (2008) 1056–1059.
- [59] Y. Yang, Y. Hao, J. Yuan, L. Niu, F. Xia, In situ preparation of caterpillar-like polyaniline/carbon nanotube hybrids with core shell structure for high performance supercapacitors, *Carbon* 78 (2014) 279–287.
- [60] F. Guo, H. Mi, J. Zhou, Z. Zhao, J. Qiu, Hybrid pseudocapacitor materials from polyaniline@ multi-walled carbon nanotube with ultrafine nanofiber-assembled network shell, *Carbon* 95 (2015) 323–329.
- [61] H.X. Yang, N. Wang, Q. Xu, Z.M. Chen, Y.M. Ren, J.M. Razal, J. Chen, Fabrication of graphene foam supported carbon nanotube/polyaniline hybrids for high-performance supercapacitor applications, *2D Mater.* 1 (2014) 1–14.
- [62] H. Fan, N. Zhao, H. Wang, J. Xu, F. Pan, 3D conductive network-based free-standing PANI–RGO–MWNTs hybrid film for high-performance flexible supercapacitor, *J. Mater. Chem. A* 2 (2014) 12340–12347.
- [63] G. Ning, T. Li, J. Yan, C. Xu, T. Wei, Z. Fan, Three-dimensional hybrid materials of fish scale-like polyaniline nanosheet arrays on graphene oxide and carbon nanotube for high-performance ultracapacitors, *Carbon* 54 (2013) 241–248.
- [64] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya, L.-C. Qin, Polyaniline-coated electro-etched carbon fiber cloth electrodes for supercapacitors, *J. Phys. Chem. C* 115 (2011) 23584–23590.
- [65] X. Yan, Z. Tai, J. Chen, Q. Xue, Fabrication of carbon nanofiber-polyaniline composite flexible paper for supercapacitor, *Nanoscale* 3 (2011) 212–216.
- [66] C. Tran, R. Singhal, D. Lawrence, V. Kalra, Polyaniline-coated freestanding porous carbon nanofibers as efficient hybrid electrodes for supercapacitors, *J. Power Sources* 293 (2015) 373–379.
- [67] J. Yan, T. Wei, W. Qiao, Z. Fan, L. Zhang, T. Li, Q. Zhao, A high-performance carbon derived from polyaniline for supercapacitors, *Electrochem. Commun.* 12 (2010) 1279–1282.
- [68] M. Yang, B. Cheng, H. Song, X. Chen, Preparation and electrochemical performance of polyaniline-based carbon nanotubes as electrode material for supercapacitor, *Electrochim. Acta* 55 (2010) 7021–7027.
- [69] D.-s. Yuan, T.-x. Zhou, S.-l. Zhou, W.-j. Zou, S.-s. Mo, N.-n. Xia, Nitrogen-enriched carbon nanowires from the direct carbonization of polyaniline nanowires and its electrochemical properties, *Electrochem. Commun.* 13 (2011) 242–246.
- [70] N.D. Kim, S.J. Kim, G.-P. Kim, I. Nam, H.J. Yun, P. Kim, J. Yi, NH_3 -activated polyaniline for use as a high performance electrode material in supercapacitors, *Electrochim. Acta* 78 (2012) 340–346.
- [71] M. Dirican, M. Yanilmaz, X. Zhang, Free-standing polyaniline–porous carbon nanofiber electrodes for symmetric and asymmetric supercapacitors, *RSC Adv.* 4 (2014) 59427–59435.
- [72] M. Sevilla, R. Mokaya, Energy storage applications of activated carbons: supercapacitors and hydrogen storage, *Energy Environ. Sci.* 7 (2014) 1250–1280.
- [73] A. Subramania, S.L. Devi, Polyaniline nanofibers by surfactant-assisted dilute polymerization for supercapacitor applications, *Polym. Adv. Technol.* 19 (2008) 725–727.
- [74] H. Guan, L.-Z. Fan, H. Zhang, X. Qu, Polyaniline nanofibers obtained by interfacial polymerization for high-rate supercapacitors, *Electrochim. Acta* 56 (2010) 964–968.
- [75] H. Mi, J. Zhou, Z. Zhao, C. Yu, X. Wang, J. Qiu, Block copolymer-guided fabrication of shuttle-like polyaniline nanoflowers with radiating whiskers for application in supercapacitors, *RSC Adv.* 5 (2015) 1016–1023.
- [76] H. Mahdavi, P.K. Kahriz, H.G. Ranjbar, T. Shahalizade, Enhancing supercapacitive performance of polyaniline by interfacial copolymerization with melamine, *J. Mater. Sci. Mater. Electron.* 27 (2016) 7407–7414.
- [77] L. Hao, X. Li, L. Zhi, Carbonaceous electrode materials for supercapacitors, *Adv. Mater.* 25 (2013) 3899–3904.

- [78] X.-F. Lu, X.-Y. Chen, W. Zhou, Y.-X. Tong, G.-R. Li, α -Fe₂O₃@ PANI core-shell nanowire arrays as negative electrodes for asymmetric supercapacitors, *ACS Appl. Mater. Interfaces* 7 (2015) 14843–14850.
- [79] D. Das, L.J. Borthakur, B.C. Nath, B.J. Saikia, K.J. Mohan, S.K. Dolui, Designing hierarchical NiO/PANI-MWCNT core-shell nanocomposites for high performance super capacitor electrodes, *RSC Adv.* 6 (2016) 44878–44887.
- [80] K. Xie, J. Li, Y. Lai, Z.a. Zhang, Y. Liu, G. Zhang, H. Huang, Polyaniline nanowire array encapsulated in titania nanotubes as a superior electrode for supercapacitors, *Nanoscale* 3 (2011) 2202–2207.
- [81] Y. Xie, C. Xia, H. Du, W. Wang, Enhanced electrochemical performance of polyaniline/carbon/titanium nitride nanowire array for flexible supercapacitor, *J. Power Sources* 286 (2015) 561–570.
- [82] D. Zha, P. Xiong, X. Wang, Strongly coupled manganese ferrite/carbon black/polyaniline hybrid for low-cost supercapacitors with high rate capability, *Electrochim. Acta* 185 (2015) 218–228.
- [83] W. Wang, Q. Hao, W. Lei, X. Xia, X. Wang, Ternary nitrogen-doped graphene/nickel ferrite/polyaniline nanocomposites for high-performance supercapacitors, *J. Power Sources* 269 (2014) 250–259.
- [84] P. Xiong, H. Huang, X. Wang, Design and synthesis of ternary cobalt ferrite/graphene/polyaniline hierarchical nanocomposites for high-performance supercapacitors, *J. Power Sources* 245 (2014) 937–946.
- [85] K.-J. Huang, L. Wang, Y.-J. Liu, H.-B. Wang, Y.-M. Liu, L.-L. Wang, Synthesis of polyaniline/2-dimensional graphene analog MoS₂ composites for high-performance supercapacitor, *Electrochim. Acta* 109 (2013) 587–594.
- [86] S. Guo, Y. Zhu, Y. Yan, Y. Min, J. Fan, Q. Xu, H. Yun, (Metal-Organic Framework)-Polyaniline sandwich structure composites as novel hybrid electrode materials for high-performance supercapacitor, *J. Power Sources* 316 (2016) 176–182.
- [87] L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen, B. Wang, Flexible solid-state supercapacitor based on a metal-organic framework interwoven by electrochemically-deposited PANI, *JACS* 137 (2015) 4920–4923.
- [88] C. Pan, H. Gu, L. Dong, Synthesis and electrochemical performance of polyaniline@ MnO₂/graphene ternary composites for electrochemical supercapacitors, *J. Power Sources* 303 (2016) 175–181.
- [89] D. Zhao, X. Guo, Y. Gao, F. Gao, An electrochemical capacitor electrode based on porous carbon spheres hybridized with polyaniline and nanoscale ruthenium oxide, *ACS Appl. Mater. Interfaces* 4 (2012) 5583–5589.
- [90] Y. Huo, H. Zhang, J. Jiang, Y. Yang, A three-dimensional nanostructured PANI/MnO_x porous microsphere and its capacitive performance, *J. Mater. Sci.* 47 (2012) 7026–7034.
- [91] W.-y. Zou, W. Wang, B.-I. He, M.-I. Sun, Y.-s. Yin, Supercapacitive properties of hybrid films of manganese dioxide and polyaniline based on active carbon in organic electrolyte, *J. Power Sources* 195 (2010) 7489–7493.
- [92] L.-J. Sun, X.-X. Liu, K.K.-T. Lau, L. Chen, W.-M. Gu, Electrodeposited hybrid films of polyaniline and manganese oxide in nanofibrous structures for electrochemical supercapacitor, *Electrochim. Acta* 53 (2008) 3036–3042.
- [93] X.-Y. Peng, X.-X. Liu, P.-J. Hua, D. Diamond, K.-T. Lau, Electrochemical co-deposition of nickel oxide and polyaniline, *J. Solid State Electrochem.* 14 (2010) 1–7.
- [94] B.-X. Zou, Y. Liang, X.-X. Liu, D. Diamond, K.-T. Lau, Electrodeposition and pseudocapacitive properties of tungsten oxide/polyaniline composite, *J. Power Sources* 196 (2011) 4842–4848.
- [95] M.-H. Bai, T.-Y. Liu, F. Luan, Y. Li, X.-X. Liu, Electrodeposition of vanadium oxide-polyaniline composite nanowire electrodes for high energy density supercapacitors, *J. Mater. Chem. A* 2 (2014) 10882–10888.
- [96] M.S. Whittingham, Electrical energy storage and intercalation chemistry, *Science* 192 (1976) 1126–1127.
- [97] D. Wang, X. Wang, X. Yang, R. Yu, L. Ge, H. Shu, Polyaniline modification and performance enhancement of lithium-rich cathode material based on layered-spinel hybrid structure, *J. Power Sources* 293 (2015) 89–94.
- [98] C. Lai, H. Zhang, G. Li, X. Gao, Mesoporous polyaniline/TiO₂ microspheres with core-shell structure as anode materials for lithium ion battery, *J. Power Sources* 196 (2011) 4735–4740.
- [99] F.Y. Cheng, W. Tang, C.S. Li, J. Chen, H.K. Liu, P.W. Shen, S.X. Dou, Conducting poly(aniline) nanotubes and nanofibers: controlled synthesis and application in lithium/poly(aniline) rechargeable batteries, *Chem. Eur. J.* 12 (2006) 3082–3088.
- [100] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R.P. Zaccaria, C. Capiglia, Review on recent progress of nanostructured anode materials for Li-ion batteries, *J. Power Sources* 257 (2014) 421–443.
- [101] X.-W. Gao, J.-Z. Wang, S.-L. Chou, H.-K. Liu, Synthesis and electrochemical performance of LiV₃O₈/polyaniline as cathode material for the lithium battery, *J. Power Sources* 220 (2012) 47–53.
- [102] K. Ferchichi, S. Hbaieb, N. Amdouni, V. Pralong, Y. Chevalier, Pickering emulsion polymerization of polyaniline/LiCoO₂ nanoparticles used as cathode materials for lithium batteries, *Ionics* 20 (2014) 1301–1314.
- [103] K. Karthikeyan, S. Amaresh, V. Aravindan, H. Kim, K. Kang, Y. Lee, Unveiling organic-inorganic hybrids as a cathode material for high performance lithium-ion capacitors, *J. Mater. Chem. A* 1 (2013) 707–714.
- [104] W.M. Chen, Y.H. Huang, L.X. Yuan, Self-assembly LiFePO₄/polyaniline composite cathode materials with inorganic acids as dopants for lithium-ion batteries, *J. Electroanal. Chem.* 660 (2011) 108–113.
- [105] C. Gong, F. Deng, C.-P. Tsui, Z. Xue, Y.S. Ye, C.-Y. Tang, X. Zhou, X. Xie, PANI-PEG copolymer modified LiFePO₄ as a cathode material for high-performance lithium ion batteries, *J. Mater. Chem. A* 2 (2014) 19315–19323.
- [106] X. Huang, J. Tu, X. Xia, X. Wang, J. Xiang, Nickel foam-supported porous NiO/polyaniline film as anode for lithium ion batteries, *Electrochim. Commun.* 10 (2008) 1288–1290.
- [107] J.M. Jeong, B.G. Choi, S.C. Lee, K.G. Lee, S.J. Chang, Y.K. Han, Y.B. Lee, H.U. Lee, S. Kwon, G. Lee, Hierarchical hollow spheres of Fe₂O₃@ polyaniline for lithium ion battery anodes, *Adv. Mater.* 25 (2013) 6250–6255.
- [108] J. Guo, L. Chen, G. Wang, X. Zhang, F. Li, In situ synthesis of SnO₂-Fe₂O₃@ polyaniline and their conversion to SnO₂-Fe₂O₃@ C composite as fully reversible anode material for lithium-ion batteries, *J. Power Sources* 246 (2014) 862–867.
- [109] G. Wang, J. Peng, L. Zhang, J. Zhang, B. Dai, M. Zhu, L. Xia, F. Yu, Two-dimensional SnS₂@ PANI nanoplates with high capacity and excellent stability for lithium-ion batteries, *J. Mater. Chem. A* 3 (2015) 3659–3666.
- [110] L. Hu, Y. Ren, H. Yang, Q. Xu, Fabrication of 3D hierarchical MoS₂/polyaniline and MoS₂/C architectures for lithium-ion battery applications, *ACS Appl. Mater. Interfaces* 6 (2014) 14644–14652.
- [111] X. Xiang, E. Liu, Z. Huang, H. Shen, Y. Tian, C. Xiao, J. Yang, Z. Mao, Microporous carbon derived from polyaniline base as anode material for lithium ion secondary battery, *Mater. Res. Bull.* 46 (2011) 1266–1271.
- [112] L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M.H. Engelhard, L.V. Saraf, Z. Nie, G.J. Exarhos, J. Liu, A soft approach to encapsulate sulfur: polyaniline nanotubes for lithium-sulfur batteries with long cycle life, *Adv. Mater.* 24 (2012) 1176–1181.
- [113] W. Zhou, Y. Yu, H. Chen, F.J. DiSalvo, H.c.d. Abruña, Yolk-shell structure of polyaniline-coated sulfur for lithium-sulfur batteries, *JACS* 135 (2013) 16736–16743.
- [114] F. Wu, J. Chen, L. Li, T. Zhao, R. Chen, Improvement of rate and cycle performance by rapid polyaniline coating of a MWCNT/sulfur cathode, *J. Phys. Chem. C* 115 (2011) 24411–24417.
- [115] C. Wang, H. Chen, W. Dong, J. Ge, W. Lu, X. Wu, L. Guo, L. Chen, Sulfur-amine chemistry-based synthesis of multi-walled carbon nanotube-sulfur composites for high performance Li-S batteries, *Chem. Commun.* 50 (2014) 1202–1204.
- [116] J.L. Chang, Z.Y. Gao, X.R. Wang, D.P. Wu, F. Xu, X. Wang, Y.M. Guo, K. Jiang, Activated porous carbon prepared from paulownia flower for high performance supercapacitor electrodes, *Electrochim. Acta* 157 (2015) 290–298.
- [117] K. Zhang, Y. Xu, Y. Lu, Y. Zhu, Y. Qian, D. Wang, J. Zhou, N. Lin, Y. Qian, A graphene oxide-wrapped bipyramidal sulfur@ polyaniline core-shell structure as a cathode for Li-S batteries with enhanced electrochemical performance, *J. Mater. Chem. A* 4 (2016) 6404–6410.
- [118] K. Ding, Y. Bu, Q. Liu, T. Li, K. Meng, Y. Wang, Ternary-layered nitrogen-doped graphene/sulfur/polyaniline nanoarchitecture for the high-performance of lithium-sulfur batteries, *J. Mater. Chem. A* 3 (2015) 8022–8027.
- [119] G.-C. Li, G.-R. Li, S.-H. Ye, X.-P. Gao, A polyaniline-coated sulfur/carbon composite with an enhanced high-rate capability as a cathode material for lithium/sulfur batteries, *Adv. Energy Mater.* 2 (2012) 1238–1245.
- [120] Y. Cao, L. Xiao, M.L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L.V. Saraf, Z. Yang, J. Liu, Sodium ion insertion in hollow carbon nanowires for battery applications, *Nano Lett.* 12 (2012) 3783–3787.
- [121] J. Chen, Y. Liu, W. Li, C. Wu, L. Xu, H. Yang, Nanostructured polystyrene/polyaniline/graphene hybrid materials for electrochemical supercapacitor and Na-ion battery applications, *J. Mater. Sci.* 50 (2015) 5466–5474.
- [122] X. Zhao, Z. Zhang, F. Yang, Y. Fu, Y. Lai, J. Li, Core-shell structured SnO₂ hollow spheres-polyaniline composite as an anode for sodium-ion batteries, *RSC Adv.* 5 (2015) 31465–31471.
- [123] D. Xu, C. Chen, J. Xie, B. Zhang, L. Miao, J. Cai, Y. Huang, L. Zhang, A hierarchical N/S-codoped carbon anode fabricated facilely from cellulose/polyaniline microspheres for high-performance sodium-ion batteries, *Adv. Energy Mater.* 6 (2016) 1–7.
- [124] M. Grzeszczuk, P. Poks, The HER performance of colloidal Pt nanoparticles incorporated in polyaniline, *Electrochim. Acta* 45 (2000) 4171–4177.
- [125] N. Zhang, W. Ma, T. Wu, H. Wang, D. Han, L. Niu, Edge-rich MoS₂ nanosheets rooting into polyaniline nanofibers as effective catalyst for electrochemical hydrogen evolution, *Electrochim. Acta* 180 (2015) 155–163.
- [126] D.A. Dalla Corte, C. Torres, P. dos Santos Correa, E.S. Rieder, C. de Fraga Malfatti, The hydrogen evolution reaction on nickel-polyaniline composite electrodes, *Int. J. Hydrogen Energy* 37 (2012) 3025–3032.
- [127] A. Damian, S. Omanovic, Ni and Ni Mo hydrogen evolution electrocatalysts electrodeposited in a polyaniline matrix, *J. Power Sources* 158 (2006) 464–476.
- [128] Y. Yuan, J. Ahmed, S. Kim, Polyaniline/carbon black composite-supported iron phthalocyanine as an oxygen reduction catalyst for microbial fuel cells, *J. Power Sources* 196 (2011) 1103–1106.
- [129] Y. Liu, J. Li, F. Li, W. Li, H. Yang, X. Zhang, Y. Liu, J. Ma, A facile preparation of CoFe₂O₄ nanoparticles on polyaniline-functionalised carbon nanotubes as enhanced catalysts for the oxygen evolution reaction, *J. Mater. Chem. A* 4 (2016) 4472–4478.
- [130] T. Reier, M. Oezaslan, P. Strasser, Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials, *ACS Catal.* 2 (2012) 1765–1772.
- [131] J. Jiang, A. Zhang, L. Li, L. Ai, Nickel-cobalt layered double hydroxide nanosheets as high-performance electrocatalyst for oxygen evolution reaction, *J. Power Sources* 278 (2015) 445–451.
- [132] X.Y. Lu, C.A. Zhao, Electrodeposition of hierarchically structured three-dimensional nickel-iron electrodes for efficient oxygen evolution at high current densities, *Nat. Commun.* 6 (2015) 1–7.

- [133] L.-M. Huang, W.-R. Tang, T.-C. Wen, Spatially electrodeposited platinum in polyaniline doped with poly (styrene sulfonic acid) for methanol oxidation, *J. Power Sources* 164 (2007) 519–526.
- [134] G. Wu, L. Li, J.-H. Li, B.-Q. Xu, Polyaniline-carbon composite films as supports of Pt and PtRu particles for methanol electrooxidation, *Carbon* 43 (2005) 2579–2587.
- [135] S.K. Simotwo, V. Kalra, Study of co-electrospun nafion and polyaniline nanofibers as potential catalyst support for fuel cell electrodes, *Electrochim. Acta* 198 (2016) 156–164.
- [136] L. Yang, Y. Tang, D. Yan, T. Liu, C. Liu, S. Luo, Polyaniline-reduced graphene oxide hybrid nanosheets with nearly vertical orientation anchoring palladium nanoparticles for highly active and stable electrocatalysis, *ACS Appl. Mater. Interfaces* 8 (2015) 169–176.
- [137] A.-L. Wang, H. Xu, J.-X. Feng, L.-X. Ding, Y.-X. Tong, G.-R. Li, Design of Pd/PANI/Pd sandwich-structured nanotube array catalysts with special shape effects and synergistic effects for ethanol electrooxidation, *JACS* 135 (2013) 10703–10709.
- [138] S. Chen, Z. Wei, X. Qi, L. Dong, Y.-G. Guo, L. Wan, Z. Shao, L. Li, Nano-structured polyaniline-decorated Pt/C@ PANI core-shell catalyst with enhanced durability and activity, *JACS* 134 (2012) 13252–13255.
- [139] Z.Y. Wu, X.X. Xu, B.C. Hu, H.W. Liang, Y. Lin, L.F. Chen, S.H. Yu, Iron carbide nanoparticles encapsulated in mesoporous Fe-N-doped carbon nanofibers for efficient electrocatalysis, *Angew. Chem. Int. Ed.* 54 (2015) 8179–8183.
- [140] M. Xiao, J. Zhu, L. Feng, C. Liu, W. Xing, Meso/macroporous nitrogen-doped carbon architectures with iron carbide encapsulated in graphitic layers as an efficient and robust catalyst for the oxygen reduction reaction in both acidic and alkaline solutions, *Adv. Mater.* 27 (2015) 2521–2527.
- [141] R. Silva, D. Voiry, M. Chhowalla, T. Asefa, Efficient metal-free electrocatalysts for oxygen reduction: polyaniline-derived N-and O-doped mesoporous carbons, *JACS* 135 (2013) 7823–7826.
- [142] H.L. Peng, F.F. Liu, X.J. Liu, S.J. Liao, C.H. You, X.L. Tian, H.X. Nan, F. Luo, H.Y. Song, Z.Y. Fu, P.Y. Huang, Effect of transition metals on the structure and performance of the doped carbon catalysts derived from polyaniline and melamine for ORR application, *ACS Catal.* 4 (2014) 3797–3805.