

Conducting polymers and composites nanowires for energy devices: A brief review

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ABSTRACT

Supercapacitors and batteries have been widely used in portable electronic devices and electric vehicles requiring safety and reliable devices. The improvement in the supercapacitors and battery performance can be achieved by the tuning of the electroactive material architecture used in the construction of such devices. A broad range of different kind of material has been investigated such as conducting polymers, transition metals oxides, graphene and carbon nanotubes, all of them presented in a different morphology, as nanosheets, nanorods, nanowires, nanotubes, nanoflowers, nanofibers, etc. This short review brings out the main approaches about the conducting polymers and composites nanowires for energy devices application. Methods of synthesis, combination of materials and applications are discussed in terms of supercapacitors and Lithium-ion batteries.

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1. Introduction

The quests and challenges towards an energetically sustainable world are one of the main goals outlined in the 21st century, where the substitution of based fossil fuels to clean, renewable and green sources is highly required [1,2]. To meet this current energy demand, the research in solar cells, batteries, fuel cells, supercapacitors, among others devices, has gained a lot of attention in the last years [3–5]. Nowadays, in order to attain more efficient devices, the synthesis of new materials based on tailored multi-functional nanoarchitectures could lead to improved electronic and ionic conductivities, diffusional and electron transfer process [6,7]. Such statement is not only from the confined dimensions played by these materials but also the influence of the bulk and

surface properties, resulting in unusual electrochemical, mechanical and optical properties [8–10].

It is well known that the morphology of the electroactive material play an important role in electrochemical systems, once the intimate contact at the electrode/electrolyte interface is crucial to guarantee the charge transfer process [11,12]. In this sense, nanostructured electroactive materials such as nanorods [13], nanofiber [14], nanoflowers [15,16], nanowires [17,18], among others [19,20], are being widely used to obtain improved electrochemical properties such as higher charge/discharge rate and improved task to accommodate stress due to volume changes occasioned by intercalation process.

Nanowires are one-dimensional, anisotropic structures, small in diameter, and large in surface-to-volume ratio. These characteristics confer to the nanowires special physical properties than those of traditional scale and dimensionality materials, such as electrical, optical thermal and mechanical properties. However, this make this kind of materials to have properties deeply dependent on their surface condition and geometrical configuration [21]. The transport properties in the 1D nanostructures like the nanowires are affected by wire diameter, surface conditions, crystal quality, crystallographic orientation and material composition, thus the synthesis conditions are a crucial factor to obtain reproducible and high-quality nanowires for different application [21].

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Nanostructured materials are particularly good for supercapacitor applications, providing high surface area, which leads to a high specific capacitance [22]. Compared to 3D and 2D materials, 1D nanostructures have smaller dimension and higher aspect ratio, improving the transport of electrical carriers in one controllable direction and also can be exploited as elements in different kinds of nanodevices [23]. In this way, nanowires have been satisfactorily used in supercapacitor electrodes due to their reduced ion diffusion path in comparison with 2D and 3D nanostructures, leading in higher charge/discharge rates [22,24].

Amongst the innumerable materials used to obtain 1D nanostructures, such as, carbon, silicon, transition metal oxides, the 1D nanostructured conductive polymers are a important group to fabricate energy storage devices, due their attractive characteristic, such as, mechanical properties, electrical conductivity, low cost, easy processing, high surface area and unique electroactive behavior, including high voltage window and high-doping rate during charge-discharge process [25]. During the charge/discharge process in the conducting polymer occur the insertion/desertion ions from the electrolyte in the polymer backbone that could result in swelling and shrinkage of the polymer chain, leading to mechanical degradation of the electrodes and fading the electrochemical performance [26]. An alternative to diminish this drawback of the conductive polymers is fabricate composites that could improve the stability and conductivity of the electrodes [27].

In this way, composites based on conducting polymers and carbon or metal oxides materials in a nanowire architecture are a good strategy to develop high-performance devices due to the combination of the electrochemical properties of the polymer and/or composites with the morphological advantages of the nanowires. These combination results in large interface between electrode/electrolyte, effective electronic transport pathway, short ion diffusion distance and easy relaxation strain, which could improve both capacity/capacitance and rate performance of battery and supercapacitors devices, respectively [28]. Furthermore, the mechanical properties of nanowires allow the development of flexible devices, that require materials with versatile functionalities including high flexibility and foldability without losing its high power and energy density and long lifetime [29].

After this brief introduction on the importance of the morphology in the active material of energy devices, in the following two sections we are focusing on the synthesis of conducting polymer and composites for nanowire-structured materials and their application in lithium batteries and supercapacitors systems.

2. Nanowires synthesis

Numerous methods to prepare nanowires, which include template-assisted synthesis [30], vapor–liquid–solid (VLS) [31], electrodeposition [32], electrospinning [33], hydrothermal [34], also hierarchical arrangement techniques [35–37] to organize the nanowires have been studies in the last ten years. Nanowires based on organic, inorganic or hybrid materials have been applied in order to get single or composites nanomaterials for innumerable purposes, such as chemical and biochemical sensing devices, thermoelectric, optical, magnetic and electrical application. In this section, we are focusing on the synthesis of conducting polymer (Section 2.1) and composites (Section 2.2) to develop materials in nanowires architectures.

2.1. Synthesis of conducting polymer nanowires

Several strategies have been used to synthesize conducting polymer nanowires. Template-based methods are powerful techniques to produce these 1D structures and can be divided into

two main groups: hard-template and soft template methodologies [38]. Conventional hard template methods include anodic aluminum oxide (AAO) [39,40], porous silicates [41] and solid aggregates [42,43]. Furthermore, solid materials with specific morphologies can guide the polymerization in the nanowire structure, acting as a hard template and might be present in the final material as a composite [44,45]. In the soft template method, soft-materials are used to produce the nanowires, as surfactants [46–48], liquid crystals, organic acids [38,49], etc.

The hard template approach has been used to produce nanowires for different conducting polymers, as polypyrrole (PPy) [49,50], poly(3,4-ethylenedioxythiophene) (PEDOT) [51], polyaniline (PANI) and poly(3-hexylthiophene) (P3HT) [39]. The AAO is one of the most used hard templates to produce nanowires. This template contains pores with diameters ranging from 15 to 400 nm in a close-hexagonal arrangement [39]. The syntheses using AAO can occur by the infiltration of the polymeric fluid (melt or solution) in AAO cavity, followed by the solidification or by *in-situ* polymerization of the monomer in the template. PEDOT nanowires were already synthesized by electrochemical polymerization of the monomer 3,4-ethylenedioxythiophene (EDOT) using AAO template, as shown in Fig. 1(a–b) [51]. The resulting material showed a 3D arrangement, forming a nanowire network. The diameter of the z-direction was around 40 ± 2 nm (the same size than the alumina template) and the height of the network was about 25–30 μm . PPy nanowires were also produced using AAO template, in this case, by the chemical polymerization. A homemade two-compartment reaction chamber was used and the polymerization occurs by diffusion of the monomer and oxidizing agent within the nanopores of the template [52]. The nanowires presented perpendicular arrays and uniform diameters, also have high flexibility and foldable (Fig. 1(c–d)).

In another contribution using alumina membranes, PEDOT nanowires were synthesized, confirming the nanowire size-dependent enhancement of their conductivity and carrier mobility [53]. EDX and XPS was used for investigated the doping levels that was alter the electrical properties of polymers. The estimated doping levels were unrelated to the nanowire diameter and remained almost constant at around 3% up to 5%. Conjugation length enhancement in the smaller diameter nanowires was revealed by Raman analysis nanowires, due the conductivity augmentation. Similarly, the PEDOT nanowires smaller than 50 nm in diameter can reach carrier mobility around $2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The results of this study show that polymers synthesized in alumina templates can improvement a longer conjugation length and so succeed higher carrier mobility for PEDOT nanowires. PANI was also deposited using alumina templates, it was produced compact nanowires filling the pore volume. Aniline electropolymerization in the insulating membrane template under a lateral potential gradient has generated a thickness gradient of the PANI deposit. The potential-dependent length of the PANI nanowires followed the PANI conductivity pattern, reaching a maximum in the region of stability of the conducting emeraldine phase [54].

Different hard templates can also be used, as porous silica, that guided the formation of PEDOT nanowires by electrodeposition on a porous silica film modified electrode, resulting in nanowires with diameters ranging from 3 to 7 nm [41], TiO_2 nanotube array, that was used as working electrode for the electrodeposition of PANI nanowires, producing a composite of PANI nanowire/ TiO_2 nanotube [45] and ZnO nanowires, that were produced by hydrothermal process and acted as a template for chemical polymerization of PEDOT nanowires, resulting in a core-shell system [44]. These composites will be discussed in the next section.

Another hard template widely used is the methyl orange (MO). In this case, MO is added directly in the synthesis solution and to perform the polymerization. Zhao et al. [42] employed MO and a

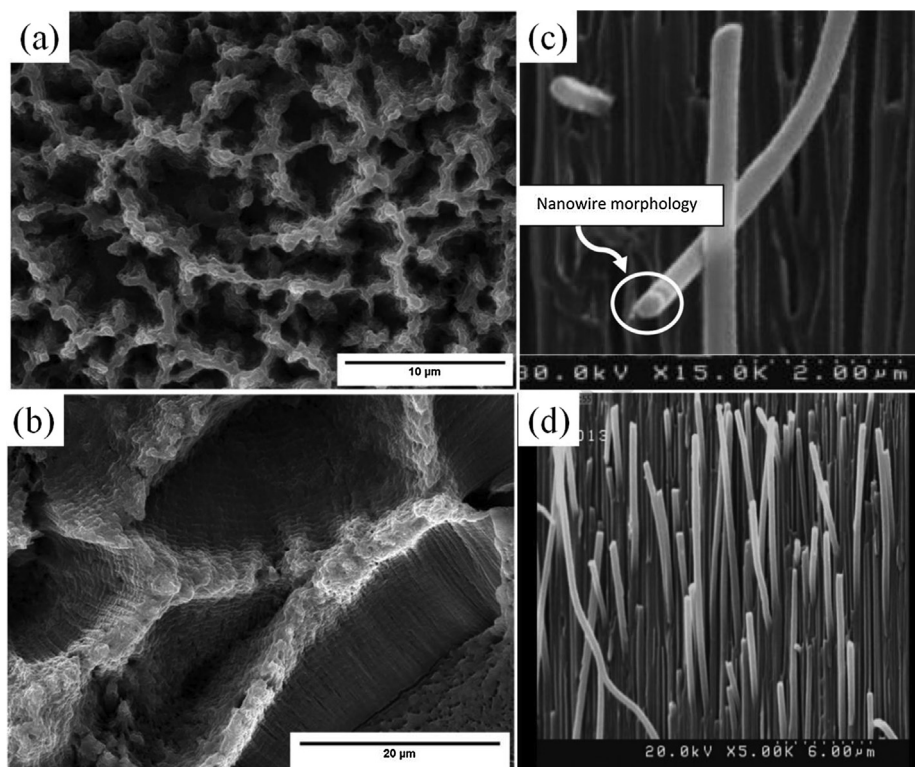


Fig. 1. (a–b) SEM image of 3D arrangement of PEDOT nanowire network synthesized using AAO template by electrochemical polymerization. The 3D network is keeping even after template removal [51]. (c–d) SEM images of PPy nanowires produced using AAO template, showing that the nanowires are flexible and can bend, also have a smooth surface [52]. Modified reference from [51,52].

hard template to polymerize PPy nanowires by chemical oxidation; the width of as-prepared PPy nanowires was around 120 nm, which presented an expressive enhancement on specific capacitance. PPy nanowires were also synthesized in the presence of MO and cetyltrimethylammonium bromide (CTAB) by chemical polymerization using FeCl_3 as the oxidizing agent. When the ratio of $\text{Py}:\text{MO}:\text{FeCl}_3$ was 1:1:2, nanowires with diameters about 120–150 nm and length of 1–2 μm were obtained [43].

Another alternative to obtain conducting polymers nanostructured is using molecules to assemblies as soft templates. In many cases soft templates act not only as structure-directing agents but also as dopants during the nanostructure formation, avoiding further template removal step [48,55–57]. Surfactants are the most common molecules used as soft templates, due to the formation of surfactants micelles which confine the polymerization of conducting polymers into low dimensional nanomaterials [46,48,58,59]. Furthermore, several molecules can be used as soft-template, like long-chain polymer as gelatin [60] and starch [61], among others [49,56].

PPy nanowires were electrochemically synthesized employing gelatin as a soft-template. As reported by Ge et al. [60], the gelatin acts not only as a dopant but also as biotemplate and the diameter of the PPy nanowires is directly influenced by gelatin concentration. Additionally, Tuan et al. [62] describe that the gelatin oriented the PPy nanowires uniformly growth all over the electrode surface even using different substrate. The PPy nanowires obtained by using gelatin as a template were employed mainly as sensor and biosensor.

Another biopolymer used as soft-template is starch [61]. PANI nanowires were electrodeposited onto Ti plate electrode in the presence of 0.05% wt. soluble starch. The aniline monomers interact with the starch structure and, when the electrochemical reaction is initiated, the starch chain act as a template resulting in PANI nanowires randomly distributed. This nano-architecture

was used as electrodes for supercapacitors with high specific capacitance (882F g^{-1}) and stability.

Anthraquinone-2-sulfonic acid sodium (AQS) was used as a soft-template to obtain a 3D PPy nanowires onto textile composites [49]. The synthesized PPy nanowires show an average diameter of 500 nm and were employed on solid-state PPy nanowires/nanofibrous textile supercapacitor display, presenting high flexibility and long-term cycle stability.

p-Toluenesulfonyl sodium is another salt used as soft-template, as described by Xia et al. (2014) [63]. The presence of this salt in the medium, during the nucleation process, promotes the interaction between the salt anions and monomers and/or oligomers molecules induces the polarization of PPy in electropolymerization. Also, the authors reported the influence on PPy nanowires diameter and length, depending on the polymerization potential and temperature (Fig. 2).

Fig. 2 showed the different PPy nanowire morphology due potential applied to electropolymerization. It is also possible to notice that, at low potential, the PPy tends to form vertically aligned nanorods (Fig. 2(a–b)). As the potential increases, the polymer grows from nanorods to aligned nanowires (Fig. 2(c–d)) and randomly distributed nanowires at higher potential (Fig. 2(e–f)). Furthermore, the wetting behavior of PPy nanowires is also dependent on the morphology. The higher electropolymerization potential, the greater is the contact angle in water, it means that the wettability is higher in the nanowires than in nanorods or well-aligned nanowires (Fig. 2(g–h)), that could improve the contact area between electrode/electrolyte interface [63].

Ru et al. [56] developed a PPy nanowires network by electrochemical method, using adenosine triphosphate (ATP) as a soft-template to polymerization. The oxygen atoms of the phosphate groups in the ATP structure can form hydrogen bond with the N-H group of the pyrrole molecules which contribute the self-alignment of the pyrrole oligomers resulting in the formation of

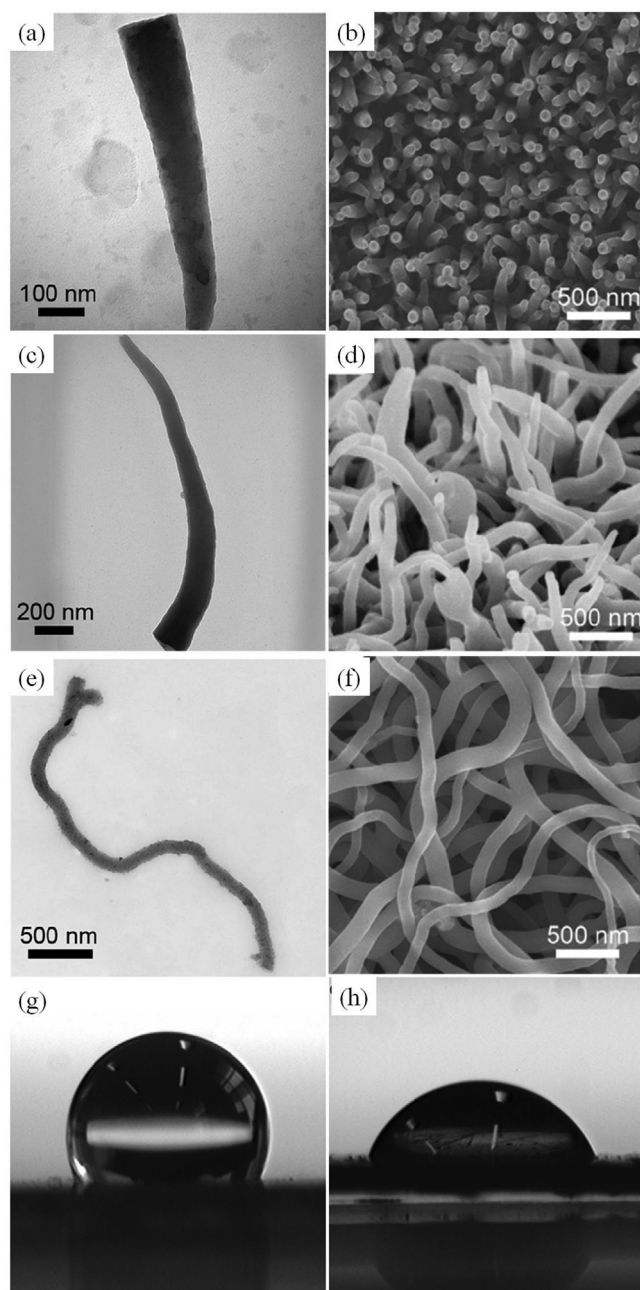


Fig. 2. Morphologies of PPy nanowires electropolymerized at different potentials and wetting behaviors of water on the nanostructure surfaces, modified reference from [63]. (a, c, d) TEM and (b, d, f) SEM images of the PPy nanowires obtained at: (a–b) 0.65 V, (c–d) 0.75 V and (e–f) 0.85 V. Digital photos of wetting behaviors of water for samples of PPy nanowires obtained at 0.7 V (g) and 0.85 V (h).

the nanowire network with numerous interconnected micro- or nano-pores. Moreover, ATP serves both as morphology-directing agent and model drug.

Among the surfactants, sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS) are usually used. Tan et al. [48] investigated the influence of dopant on the morphologies of polypyrrole-polydopamine (PPy-PDA) by electrochemical synthesis. According to the authors, among the dopants studied, nanowire structures could be observed only in the presence of SDBS. Moreover, it was observed superhydrophobic surface properties when SDBS was used as dopant on PPy-PDA electrosynthesis.

It is even possible to combine and use a soft- and hard-template in the same synthesis, as reported by Wang et al. [58]. In this work,

carbon nanotubes (CNTs) were employed as a hard-template to PEDOT polymerization, but also SDS was added as a soft template. In this case, the presence of surfactant improves the CNTs dispersion and promote the PEDOT polymerization onto the CNTs surface, ordering the polymerization and enhancing the interfacial interaction between PEDOT and CNTs. The nanowires showed 30–60 nm diameter. Tian et al. [46], Zhang et al. [59] and Ni et al. [47] also used SDS as a soft-template to produce PEDOT nanowires by chemical synthesis and apply it on thermoelectric materials. According to Tian et al., PEDOT nanowires show diameter around 100 nm and several micrometers as length [46]. Zhang et al. reported the polymerization of longer PEDOT nanowires when used FeCl_3 than iron(III)4-methylbenzenesulfonate ($\text{Fe}(\text{Tos})_3$) as an oxidizing agent. The average width in both cases was the same, around 12 nm, but the use of FeCl_3 results in PEDOT nanowires length of 0.5–5 μm , on the other hand, $\text{Fe}(\text{Tos})_3$ result in nanowires length of 0.2–0.7 μm [59].

The template-based method is certainly the more explored way to produce the nanowires, anyway, removing the templates sometimes is a difficult procedure and can damage the nanomaterial [64]. In this way, template-free methodologies have been attracted attention in the scientific community. Different template-free approaches are related in the literature, as PPy nanowires electrochemically deposited on biomedical titanium by simultaneous polymerization of dopamine and pyrrole [65], vertically aligned PANI nanowires deposited by galvanostatic method in a one-step procedure [22] and PANI nanowires synthesized by interfacial polymerization [66].

A successful example of template-free method was exploited by Debieume-Chouvy et al. [67], where PPy nanowire array was electrodeposited in the presence of jointly non-acidic and weak-acidic anions. This method is based on the variation of the interfacial concentration of anions, once protons are released in the Py oxidation process, being collected by the weak-acid anions. This results in a decrease (or elimination) of anions in the electrode/electrolyte interface and Py oxidation requires the presence of anions, so the reaction cannot occur. In this case, it occurs the water oxidation forming hydroxyl radicals, that can react with PPy already deposited, resulting in overoxidation and the formation of H_2O_2 . These molecules are oxidized to O_2 , forming nanobubbles inside the polymer and preserving some conductive zones of PPy. After the evolution of the bubbles, the monomers are oxidized in these zones, forming the nanowires [67]. These steps are present in Fig. 3(a).

PANI nanowires were also synthesized by template-free method, by a mechanochemical polymerization using ammonium peroxydisulphate (APS) as the oxidizing agent and citric acid as dopant [68] (Fig. 3(b)). During the synthesis using citric acid, the two carboxyl groups attached to two $-\text{CH}_2-$ groups show affinity with two adjacent positively charged PANI. The combination of these repeat units leads to linearity and the formation of some branching, as can be observed in Fig. 3(c).

Arter et al. [69] reported the synthesis of virus-PEDOT nanowires using lithographically patterned nanowire electrodeposition (LPNE). In this method, a nickel film is deposited on glass and after coating the film with a photoresist, a photolithographic pattern is defined for the nanowires. The key step of the procedure is the oxidative degradation to remove the exposed nickel and etch in the exposed sides of the pattern. The nickel nanotrench was used as working electrode for electrodeposition of PEDOT nanowires and virus-PEDOT nanowires [69].

2.2. Synthesis of conducting polymer composites nanowires

The advance in nanotechnology allows to produce various nanoscales objects with higher precision and enhanced performance, in this context composites are widely studied. Composites

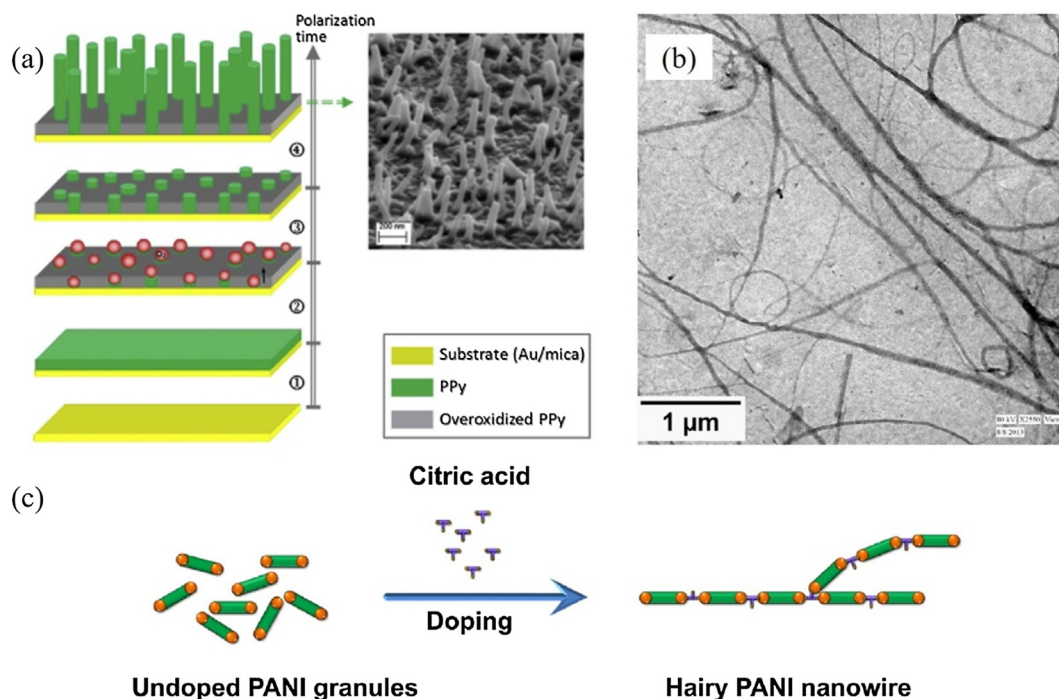


Fig. 3. (a) Mechanism of PPy nanowire generation in the presence of jointly non-acidic and weak-acidic anions, modified from reference [67]. (b) TEM image of PANI nanowires synthesized by a template-free methodology using citric acid and (c) scheme representing the formation of PANI nanowires with citric acid, modified reference from [68].

can be obtained in different forms, but core-shell structures are certainly one of the most explored [1–8]. In core-shell structure it is possible to combine inorganic materials with conducting polymers, to obtain distinct characteristics from the starting materials, as the stability, composition, optical and magnetic properties and enhanced surface area [9]. In this section, some methodologies to obtain nanowires core-shell structures containing conducting polymers will be described. In the synthesis, the conducting polymer can act as a core, where the nanowire of the conducting polymer is formed in the first place, or as a shell, where the polymer recovers different nanowires structures previously formed.

Wang et al. [44] describe a scalable route to prepare core-shell structured ZnO@PEDOT nanowires. The ZnO nanowires were used as a core and template, while PEDOT nanowires were chemically polymerized onto its surface, acting as a shell. As reported, the obtained material showed an improvement in the specific capacitance due to distinct structures in the composite. Similarly, Wang et al. [58] synthesized a core-shell structure containing carbon nanotubes and PEDOT (PEDOT/CNT), which exhibits a high thermoelectric power factor. Furthermore, the characterization analysis confirms a strong interfacial interaction between PEDOT and the CNTs, which facilitates the charger transfer in the core-shell composites, improving and developing its properties. In the same way, Pt-TiO₂@PANI core-shell nanowire arrays were prepared and applied to membrane electrode assembly of proton exchange membrane fuel cell [70]. Compared to the conventional Pt-C cathode catalyst layer, the Pt-TiO₂@PANI core-shell nanowire arrays showed an improvement in the durability and in the performance (polarization curve, power density curve, electrochemical active surface area, and charge transfer impedance).

Javed et al. [66] purposed the association of graphene oxide (GO), mesoporous silica nanoparticles (MSNs) and PANI (synthesized by interfacial polymerization). The obtained material presented a unique nanostructure, like core/shell and porous structure, moreover, the presence of MSNs with GO facilitates electron transmission, which increases the conductivity of PANI

nanocomposite. As result, a significantly enhanced specific capacitance, rapid charge-discharge rates, and good cycling stability of the device were reported [66]. Likewise, Yang et al. [71] describe the synthesis of a hollow shell coated on PPy nanowires. PPy was electrochemical polymerization onto carbon cloth surface, and then a thin layer of ZnO and a thin shell of TiO₂ were deposited uniformly on the surface of the PPy nanowires. The ZnO layer was removed, resulting in a nanogap (hollow) between PPy and TiO₂ (PPy-TiO₂). The presence of the hollow in the structure enhanced the specific capacitance and better cycling stability when compared to the bare PPy nanowires, suggesting an electrochemical performance improvement [71].

In electrochromic field, Zhang et al. [72] obtained V₂O₅@PANI composite nanowires. To ensure the colored change and the short ions/electrons transport distance, V₂O₅ nanobelts were used as a core; the PANI nanowires were chemically synthesized on V₂O₅ surface, being the shell at this structure. The interaction between PANI and V₂O₅ preserve the oxide from dissolve or inactive, besides enhancing the electrical conductivity, such as multicolor ranging, long-term stability and fast switching time. Also, Gou et al. [73] purposed a new method to produce a composite of V₂O₅ and PEDOT, the method was described as resembling a cocoon-to-silk fiber reeling process. As reported, V₂O₅/PEDOT has been shown as a promising hole injection layer in light emitting diodes.

In a different study, Chi et al. [74] purposed the use of PANI-MnO₂ hybrid nanowires to act as oxidase mimicking. The composite was synthesized via redox reaction between PANI nanowires and KMnO₄. The imino group in the PANI structure can be used as a reducing agent to reduce KMnO₄ and produce MnO₂, generating the hybrid nanowire in a core-shell structure. The obtained materials presented a diameter ranging from 40 to 80 nm, and a length from several hundred nanometers to several micrometers. The composite exhibited an improvement oxidase-like catalytic activity when compared to the isolated materials (PANI and MnO₂), evidencing the synergistic catalytic effect and the potential to construction functional artificial enzymes [74].

Many composites between conducting polymers and hard structures are related in the literature. Nanotubes structures [75–77], such as titania nanotubes and carbon nanotubes (CNTs) are a good alternative to produce composites since their structure allows the deposition of polymers nanowires onto their surface and/or inside their structure. Xie et al. [75] described a simple method to obtain nanocomposites between PANI nanowires and titania nanotubes by electrochemical route. The nanocomposite exhibited a high energy density, high power density as well as long cycle life showing great potential for supercapacitor applications. Moreover, the authors attributed the good electrochemical performance to the unique microstructure, disordered PANI nanowires arrays (diameter was around 60 nm and the length was about several hundred nanometers) encapsulated inside the TiO_2 nanotubes, provides high surface area, fast diffusion and long-term cycle stability [75].

Carbon-derived materials are good candidates for polymer composites, showing excellent electrical, electrochemical and mechanical properties [78] and with improved specific capacitances when combined with conducting polymers [79–81]. PPy nanowires were electrochemically deposited onto carbon fiber electrodes in a solution containing phosphate buffer, LiClO_4 , soluble starch and pyrrole monomer using constant potential of 0.78–0.90 V for 100–800 s [79]. The PPy nanowires lengths were about 0.5–1.1 μm with diameters about 85–128 nm, while the carbon fibers coated with PPy nanowires have about 7.4 μm of diameter.

Focusing on energy storage devices, carbon nanostructures, such as nanotubes (CNTs) [82], nanohorns (CNHs) [26], graphene [83], graphene oxide (GO) [84], among others, are good options to obtain composites with nanostructured conducting polymers. In this context, Wang et al. [82] synthesized PANI onto CNTs surface by electrochemical polymerization and obtained polymer nanowires exhibiting diameter of 8 ± 2 nm and lengths of a hundred nanometers. The composite showed an interesting electrochemical behavior and the CNTs structure not only enhance the charge transfer, but also, due to its rigid structure, suppress the volumetric change of polymeric chains during GCD process, as consequence increase the materials stability and lifetime [82].

A composite between carbon nanohorn (CNHs) and conductive polymers was proposed by Chang and Imae [26]. Carbon nanohorn were decorated with PPy nanowires (chemical synthesis) which exhibit about 30 nm in diameter, moreover the authors also decorated the nanohorns structure with PANI, but in this case, an irregular shape structure was observed. Although both composites exhibit higher capacitance retention than pristine polymers, the specific capacitance of PANI-series composite, increased by increasing the CNHs ratio, on the other hand, the increment on CNHs content on PPy-series composite, result in a specific capacitance decrease.

Composites with graphene oxide (GO) and conducting polymers have been explored. GO presents negative charge, as carbonyl and carboxyl groups, which can act as an anchor to in situ polymerize the monomer [78,83]. A composite with GO and PPy was prepared by an in situ chemical oxidation polymerization procedure [83]. As reported by the authors [83], GO/PPy composite showed similar structures even at different mass ration and PPy nanowires diameter was around 40 nm. The composite showed high performance as an energy storage device, presenting high specific capacitance values and cycling stability. Similarly, Rajagopalan et al. [78] synthesized a composite of GO and PANI, but in the presence of MnO_2 and surfactant (sodium lauryl sulfate) to prevent GO sheets aggregation. As reported by the authors, a synergistic effect between PANI nanowires and graphene sheets resulted in an excellent electrochemical performance, due to the surfactant-treated graphene allows a faster electrolyte diffusion, and, a good cycle stability was observed.

GO can be considered a noble material, which results in high costs, but low costs materials based on carbon, such as carbon paper showed to be a promising material [84]. In the reported work [84] filter paper derived carbon paper and PANI nanowires were obtained by chemical polymerization (length about 200–300 nm and epitaxial grow); the obtained material presented potential to be used as a supercapacitor, since a high specific capacitance, low resistance and cycle stability were observed.

Hybrid structures can also be formed by conducting polymers nanowires, followed by the addition of metallic nanoparticles or different organic structures at the surface of the previously formed nanowires. One of these examples is the synthesis of polythiophene nanowires and platinum nanoparticles [85]. The nanowires were electrochemically deposited into a mesoporous silica thin film, then the modified electrode was immersed in a PtCl_6^{2-} solution, then it was applied 0.8 V to form positive charges in the polymeric matrix to incorporate the PtCl_6^{2-} anions, followed by the application of -0.5 V for 10 s, to produce the Pt nanoparticles. The nanowires were formed in a brush-like disposition with an average width of ~ 5 nm and the Pt nanoparticles were deposited with different sizes, with about 1300 nanoparticles per μm^2 of the polymer.

Another example is the formation of PEDOT nanowires, followed by the integration of polystyrene sulfonate (PSS)-doped PEDOT and tosylate-doped PEDOT, as reported by Zhang et al. [86]. The nanowires were obtained with a length in the range of 0.5–5 μm and diameters ranging from 6 to 20 nm. The thermoelectric properties of the obtained hybrid composites were evaluated, and a synergistic effect was observed, the power factor was found to be enhanced by 9-fold in comparison to their reference material.

To finish, the synthesis of the nanowires composites or hybrid structures containing conducting polymers can be performed by an *in-situ* strategy. Poly(3-hexylthiophene)/ZnO (P3HT/ZnO) hybrid nanowires were synthesized using this approach, in which the P3HT polymer was dispersed in toluene solution, followed by blending with a Zn^{2+} solution in THF [87]. The nanowire assembly was done by the addition of anisole in the solution, that promotes the transition of the coil-like state to a planar rod-like conformation, leading to the formation of highly ordered nanowires, followed by a thermal oxidation treatment to produce the P3HT/ZnO nanowires. This methodology was further improved by the adoption of a hydrothermal crystallization at an elevate pressure, that both created highly ordered ZnO nanocrystals and enhanced the crystallinity of P3HT films [88].

3. Energy applications

The portable electronic devices and electric vehicles industry continues to face technological and economic challenges as the device feature must have high power and energy density, long cycle life, safety and reliability. In order to meet all these mentioned qualities in the lithium-ion batteries and supercapacitors performance, it is mandatory to understand the role of the active material [89–91]. An insight into the general working principle of such devices presents a structure comprised of two electrodes (cathode and anode), immersed in an electrolyte and separated by a membrane. During the charge process (polarization), cations such as H^+ , Li^+ and Na^+ , or anions such as OH^- , from electrolyte or one of the electrodes, move across the electrolyte and insert into or adsorb onto the other electrode. In the same line, during the discharge process (depolarization), ions are spontaneously extracted or desorbed from one electrode and transported to the electrolyte or other electrode [92]. The ionic transportation mentioned above must be accompanied by an electronic flux through an external circuit where electricity is produced, as depicted in Fig. 4 for an



Fig. 4. Schematics working principle of (a) carbon based EDLC (Na_2SO_4 electrolyte), (b) MnO_2 active material based pseudocapacitor and (c) graphite anode and LiCoO_2 cathode based Li^+ ion battery (LiPF_6 electrolyte, for instance). Reprinted with permission of [93].

electrochemical double-layer capacitor (EDLC), pseudocapacitor and a Li^+ ion battery.

Electrodes based on the adsorption process must present a superior surface area to promote a maximum number of available adsorption sites. For this reason, it is very common to find carbonaceous materials such as graphite, graphene and carbon nanotubes as active material concerning an improved adsorption process based electrodes [80,94]. Now, considering the electrodes based on the insertion process, the storage capacity is governed by the load of ions that can be reversibly inserted and extracted into the host material. In this way, the search for the right material with improved structural stability is a challenge, once the insertion/extraction of ionic species during the charge/discharge process is accompanied by phase or volumetric changes of the host material, which could lead to a loss of specific capacity after several charge/discharge cycles [95–97].

The electrochemical properties of the host materials are significantly determined by its morphology, crystallinity and electronic structure [98–100]. For instance, it can be found in the literature several papers in the last decade where improved electrochemical properties of the host material are attained by tuning its morphology [101–103]. These studies are based in the synthesis and characterization of various nanostructured materials, where the enhancement of the electrochemical properties is mainly due to the reversibility of the ionic insertion/extraction reaction without destroying the structure of the host material and a superior electroactive material/electrolyte interface area to guarantee a maximum number of available intercalated sites [104,105]. Amongst the various nanostructures, such as, nanoflowers [16], nanotubes [106], nanospheres [107], nanopipes [108], urchins-like [109] and nanosheets [110,111] where 2D and 3D nanostructures can be observed, the nanowires approach might present a way to guarantee some of these features, where the unique characteristic of one-dimensional confinement could improve the electric and ionic transport resulting in higher electrochemical performance [108,112,113]. In this section we discuss the application of nanowires in the development of lithium-ion batteries (Section 3.1) and supercapacitors (Section 3.2) applications.

3.1. Batteries

Considering the combination of high energy and power densities, the lithium-ion batteries appeared commercially in the 90th decade as an excellent alternative to lead-acid and nickel-metal hydride batteries. Nonetheless, with the requirement of portable electronic devices, power tools and hybrid/full electric vehicles, the need to an even higher energy and power densities device is

mandatory. In order to meet such demand, the application of nanostructured electroactive materials was found to be a good way to upgrade the batteries performance [114–116]. In lithium-ion batteries, for instance, the utilization of nanostructured electroactive materials should enhance the charge transfer rate due to an improved lithium ion intercalation/deintercalation and electronic transference into/from the nanostructures processes and, mainly, overcome the capacity fading due to volume change because of lithium intercalation [117,118]. Chan et al. [31] presented a high-performance lithium battery anode based on silicon nanowires despite the very known issue of silicon anode to change its volume in the order of 400% upon the lithium intercalation process. They showed that silicon nanowire anode, synthesized directly onto stainless steel using the vapour-liquid-solid (VLS) template-free growth methods, could accommodate large strain without pulverization (Fig. 5), provided by this way a short lithium

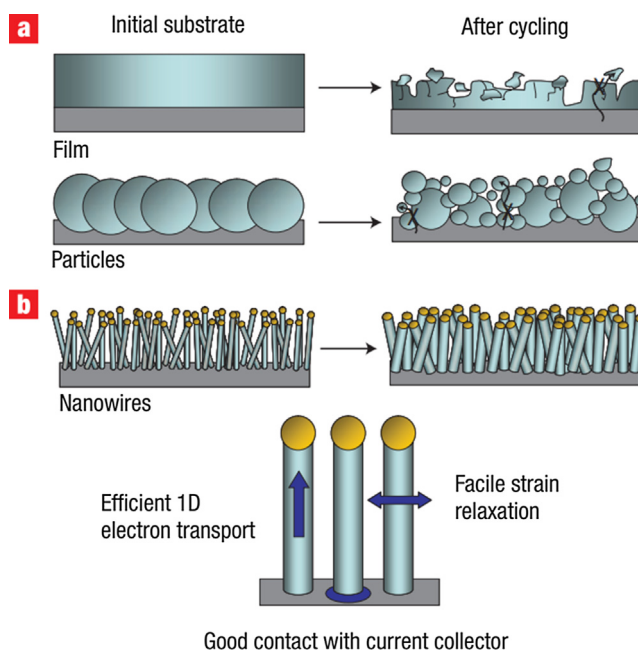


Fig. 5. Scheme of morphological changes that occur in Si during electrochemical cycling. (a) The volume of silicon anodes changes by about 400% during cycling. As a result, Si films and particles tend to pulverize and peel off during cycling. (b) Si nanowires grown directly on the current collector do not pulverize or break into smaller particles after cycling. Rather, facile strain relaxation in the nanowires allows them to increase in diameter and length without breaking. These nanowires anode design has each nanowire connected with the current collector, allowing for efficient 1D electron transport down the length of every nanowire [31].

intercalation distance, efficient 1D electron transport and an effective interface area between the electrode and electrolyte. Such nanostructure design allowed the attainment of the silicon theoretical charge capacity of silicon anodes with a discharge capacity close to 75% of its maximum value.

In the same line, Ge et al. [119] reported both experimental and theoretical studies regarding porous doped silicon nanowires synthesized by direct etching of boron-doped silicon wafers. Superior electrochemical performance and long life-cycle as anode material in lithium ion battery as observed, where even after 250 cycles, the capacity remained stable above 2000, 1600 and 1100 mAh g⁻¹ at an applied density current of 2, 4 and 18 A g⁻¹, respectively, which demonstrated a high structure stability due to the high porosity and electron conductivity of the porous silicon nanowires. In a recent work, the authors reported the formation of high capacity Li-ion battery anodes from Si_(1-x)Ge_x alloy nanowire arrays that were grown in a single step route directly onto a stainless steel substrate. In a full cell configuration, capacities up to 1350 mAh g⁻¹ were retained after 100 cycles, which was attributed to the both high capacity provided by the Si and improved rate performance and capacity retention by the Ge [120]. Considering the given examples, one can see that lithium batteries anodes based on silicon nanowires were very important to the development of the batteries performance, once it can be still finding many papers taking such kind of nanostructures into account [121,122].

Conducting polymers were also used to develop electrodes for Li-ion batteries, working as a hybrid device. Gowda et al. [123], reported a Ni-Sn/PANI system, free of Li-based electrodes, using a LiPF₆ electrolyte. The system works on as a hybrid mechanism based on Li⁺ intercalation at the anode and PF₆⁻ doping at the cathode (Fig. 6(a)). The PANI nanowires cathode was produced using alumina template. First the Ni-Sn was electrodeposited on the pores of the AAO, and drop coating of separator, then a PANI solution was dropped onto the surface of the template, allowed to infiltrate in the alumina pores (Fig. 6(b)). The system showed good charge/discharge characteristics with a discharge capacity of 3 μAh cm⁻² at a current rate of 0.03 mA cm⁻² [123].

Hou et al. [117] prepared a composite with ZnFe₂O₄ (ZFO) and PPy combining scalable electrospinning technique and gas-phase polymerization. As described, the pristine ZFO nanowires were uniformly coated by PPy with a thickness of 2 and 4 nm, moreover, the robust structural stability displayed superior Li-storage performance with high initial Coulombic efficiency, large reversible capacities, high-rate capability and long-term cycling performance.

The reader will find other nanowire structured materials, i.e., metal-based materials such as vanadium, titanium, cobalt and iron [124–127], nonetheless, the improved battery performance like high capacity and long cycle life will be strongly influenced by the electrode nanoarchitecture, which provides a superior interfacial area between the active material and the electrolyte and minimization of the volume strain due to the ionic intercalation [128,129].

3.2. Supercapacitors

Supercapacitors are a kind of energy storage devices presenting unique properties like fast charge/discharge process, good cycle-life and high power and energy specific densities [130,131]. Depending on the mechanism of the charge accumulation, supercapacitors can be divided into two categories; (i) Electrochemical Double-Layer Capacitors (EDLC), where the process of the charge accumulation comes from the formation of the electrical double-layer capacitance at the electrode/electrolyte interface as a result of fast ionic adsorption and (ii) Pseudocapacitors, where the mechanism of the charge accumulation is from fast redox reactions occurring at the electrode/electrolyte interface. Typical EDLC mate-

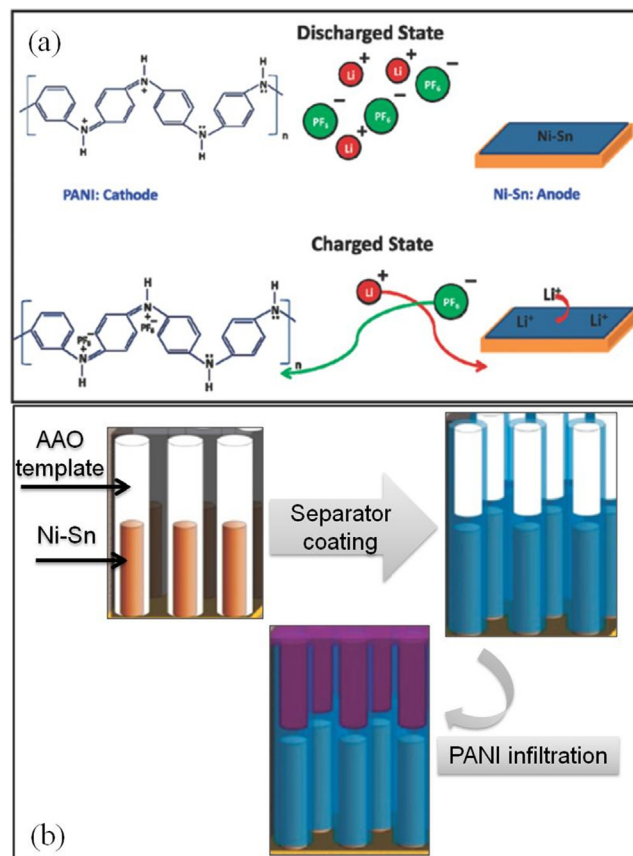


Fig. 6. (a) Scheme of the hybrid mechanism of the energy storage device operation showing Li⁺ ion insertion/deinsertion at the Ni-Sn anode and PF₆⁻ ion doping/undoping at the PANI cathode during charge and discharge processes. (b) Representation of alumina template to fabricate Ni-Sn/PANI nanowires system to energy storage devices. Modified reference from [123].

rials are those presenting high specific surface areas in order to obtain high values of electrical double-layer capacitance such as carbonaceous materials [132,133]. In the same way, typical pseudocapacitive materials must also present high specific surface areas for the same reasons presented by the EDLC materials, in addition providing a high number of available electroactive sites where the fast redox reactions occur, which makes the metallic oxides and conducting polymers good pseudocapacitive materials [134,135].

As discussed above, due to fast redox reactions occurring at the electrode/electrolyte interface of the pseudocapacitive materials, the ionic intercalation process to maintain charge neutrality is mandatory, which refers to the same problem described for lithium batteries, the volumetric variation of the active material upon intercalation process [22]. In this way, nanostructured active materials can overcome some issues presented by pseudocapacitive materials such as stability towards volumetric changes upon intercalation process avoiding the peel off from the current collector of the active material, the increase of the number of electroactive sites, increasing, by this way, the specific capacitance and the shortening of the ionic diffusion pathway [89,135,136]. Considering this methodology, Zhou et al. [137] synthesized a supercapacitor electrode composed of well-aligned CoO nanowire array grown on 3D nickel foam with PPy uniformly deposited onto to each nanowire surface. The resulted specific capacitance was 2223F g⁻¹, approaching the theoretical value, in addition to a good rate capability and cycling stability of 99.8% of retention after 2000 cycles, which was attributed from the authors due to the syner-

gism between the CoO and PPy, providing high electrochemical activity and the short ion diffusion pathway in ordered mesoporous nanowires.

Another composite used for high-performance supercapacitor was three-dimension porous carbon framework coated with one-dimensional nanostructured PANI nanowires [76]. In this composite, the 3D porous structure benefits not only the electrolyte diffusion but also the carbon skeleton surrounded by PANI nanowires, provided more transfer channels for electrons during the charge/discharge process, enhancing the supercapacitive properties. Hui et al. [77] also reported excellent result with a 3D nanostructure between ordered PANI nanowire arrays and CNTs networks, improving the supercapacitor performance and catalytic activity toward inorganic anions electrochemical reduction. Porous tubular carbon (PTC) was also used in the synthesis of PANI nanowires composites [138]. The PTC microtubular structure alleviates PANI accumulation, reinforces its structural stability and improves PANI pseudocapacitance.

In a recent paper, a two-step hydrothermal method was used to synthesize a hierarchical reduced holey graphene oxide (rHGO)-decorated NiCo_2O_4 nanowires onto carbon fibers (rHGO/ NiCo_2O_4 @CF) (Fig. 7). High specific capacitance of 1178 F g^{-1} at 1

A g^{-1} a superior capacitance retention of 93.4% at 10 A g^{-1} was achieved, which was attributed to the abundant nanopores and good conductivity of rHGO, hierarchical porous interpenetrating network architecture and the synergistic effect between rHGO and NiCo_2O_4 nanowires [139].

Conducting polymers presenting nanowire architecture are also well established in supercapacitors devices [22,47,140,141]. In this way, a high-performance yarn electrode material was synthesized by coating primary fiber cores inside cotton yarns with graphene sheets with further growing PANI nanowires array layers through in situ polymerization of aniline by Jin and co-workers [142]. The 3D yarn electrode structure attained an excellent electrochemical performance with a specific capacitance of 246 mF cm^{-2} at 5 mV s^{-1} with a capacitance retention of 98% after 3800 cycles that was attributed to the small diameters of the PANI nanowires, that ensure a high electrochemically active surface area and fast electrolyte ionic diffusion, and to the enhancement of the electronic transportation due to the 3D graphene conductive network on cotton fibers, which further bridges the PANI nanowires.

It can be stated that independent of the nanostructure used in the active electrode for supercapacitors, the reduction to the nanoscale enhances the properties of the energy storage devices,

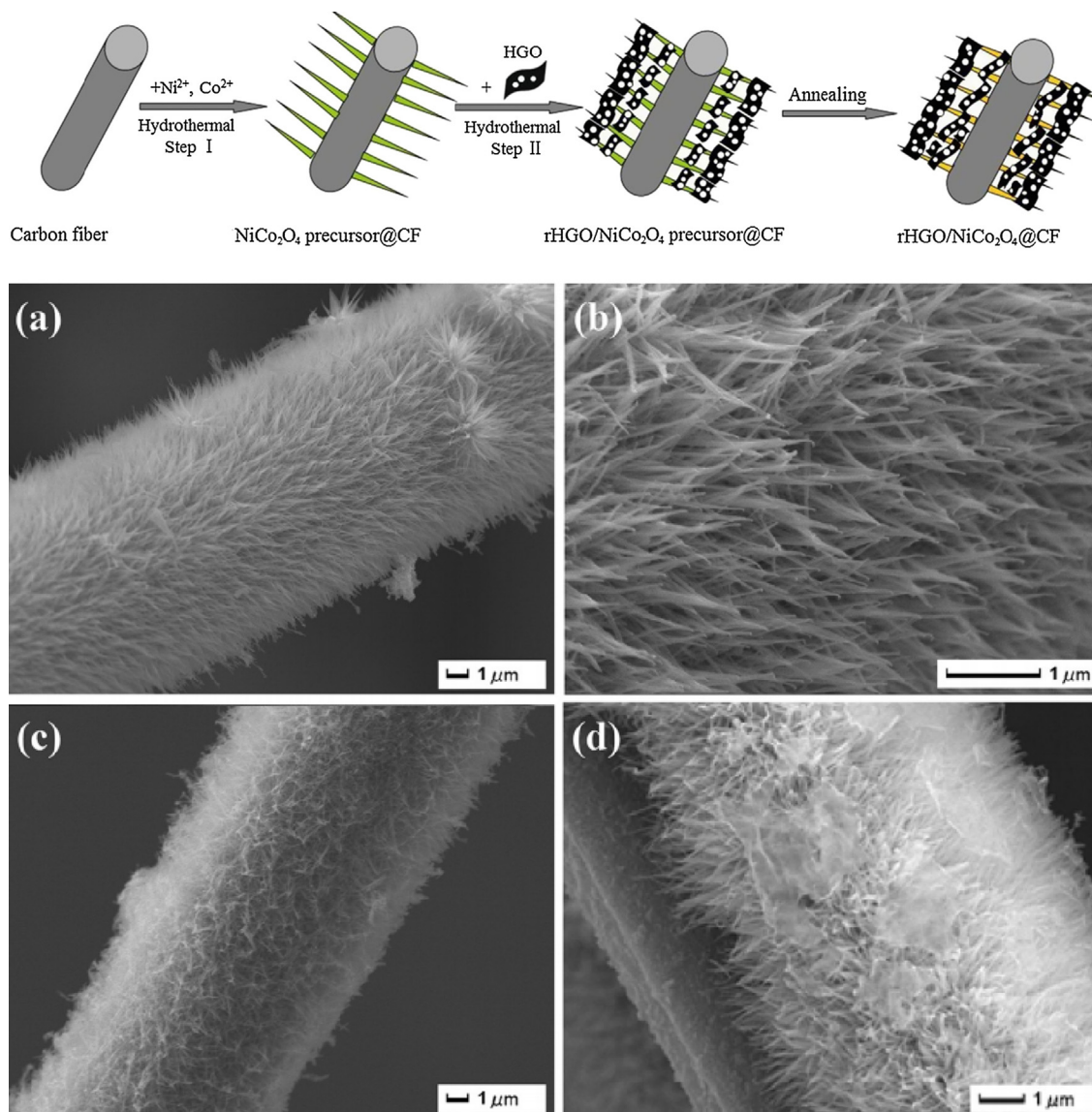


Fig. 7. Scheme of the rHGO/ NiCo_2O_4 @CF fabrication process. SEM images of (a) and (b) NiCo_2O_4 @CF and (c) and (d) rHGO/ NiCo_2O_4 @CF. Modified reference from [139].

because the nanoscale increases the contact of the interface area between the electrode and electrolyte, decreases the transport pathway for both electrons and ions, and increases the number of the electroactive sites favoring the fast redox reactions, which all together will strongly result in a superior specific capacitance and long cycle-life.

4. Concluding remarks

In this brief review, we have shown the main advances of using nanowires based on conducting polymers and composites for energy applications in the last ten years. We have focused on the synthesis of these materials using hard, soft and template-free methods in either pure form or composite nanomaterial and their application in Lithium-ion batteries and supercapacitors. By considering this report, the production of nanowire architecture is clearly a strategy that has been grown very rapidly in past decade, thanks to the great effort of the scientific community by a variety of synthetic procedures, full-characterization and several applications, especially in the energy-field.

The nanowire approach is still growing by materials combination and new synthetic routes to develop high performance electrodes, anyway, some perspectives and challenges must be pointed out. In this sense, new electrolytes represent important progress to obtain more effective devices. Developing electrolytes that can operate over a wide potential window can result in high energy density systems, making possible to explore all the materials characteristics. Furthermore, high compatibility with other cell components is desired, avoiding unwanted reactions and ensuring efficiency.

Also, the nanowires are very promissory for flexible devices manufactures that we expect to see frequently in the future. To do so, new electrode substrates can be exploited, focusing on low-cost flexible and stable materials, with mechanical resistance, affinity to the nanowires (to promote adhesion) and high efficiency, achieving high cyclic and high rate performance, being twisted or not. And finally, environmental-friendly synthetic routes must be chosen to produce the nanowires, reducing the use of solvents and hazardous reagents.

Declaration of Competing Interest

None.

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