Branched nanowires: Synthesis and energy applications

Chuanwei Chenga, Hong Jin Fanb,

a Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, Department of Physics, Tongji University, Shanghai 200092, PR China
b Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore, Singapore

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Summary Branched nanowires (or referred as nanotrees, nanoﬁrests) with tunable 3D morphology, homo or heterogeneous junction, and interface electronic alignment represent a unique system for applications in energy conversion and storage devices. Compared with 0D nanoparticles and 1D nanowires, 3D branched nanowires possess advantages including structural hierarchy, high surface areas and direct electron transport pathways. Therefore, branched nanowires are under the focus of recent research on energy materials. In this Review, the synthesis of a wide variety of branched nanostructures is summarized. The methods cover vapour phase, solution phase, and their combinations. As the main part of this Review, the latest results on the energy applications of branched nanowires in photovoltaics, photocatalysis, photoelectrochemical water splitting, supercapacitors and Li ion batteries are highlighted, and the beneﬁts of the 3D branch structure is discussed.

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Introduction

Energy and environment are the two greatest challenges for 21st century to keep our modern life and earth sustainable. With global awareness of the crisis of conventional fossil fuels and their detrimental impact on environment, the search for clean and renewable alternative energy solutions has stimulated worldwide attention [1—3]. Solar energy, as the clean and unlimited energy source holds the great potential to meet our future energy demand. In this regard, photovoltaics and photocatalysis water splitting are two promising ways towards efﬁcient solar energy utilization [4—12]. The former converts the sunlight into electricity and the later captures solar energy and stores into H2 fuel. In addition to energy generation, with the increasing power consumption, development of advanced energy storage devices such as supercapacitors and batteries are becoming equally important in popular mobile devices and for storing the intermittent alternative energy from the sun, tide or wind [13—15]. Furthermore, increasing the energy utilization efﬁciency is also crucial to lowering the demand for energy. For example, replacement of the conventional ﬂuorescent or high-pressure discharge lamps with solid-state
light emitting diodes (LEDs) will greatly push the external efficiency from 13% to 50%.

To drive the alternative energy technologies to practical application on a large scale, highly efficient energy conversion and high-density power storage technologies, together with cost-effective production process, are needed. However, nearly all the alternative energy technologies are limited by the properties of materials. In the past two decades, nanostructured materials have sparked a worldwide interest due to their fascinating mechanical, electrical and optical properties endowed by confining the dimensions of such materials and because of the combination of bulk and surface properties to the overall behaviour [16—23]. In particular, a smart design of the nanostructured materials and devices will shed light to address the performance/cost tradeoff [24—27]. Recently, the importance of nanostructured materials in energy harvesting, conversion and storage technologies have been highlighted in several review articles [28—32]. In particular, 3D branched nanowire structures with high surface area and direct transport pathway for charge carriers are especially attractive in energy applications [33,34]. For example, the 3D branched nanowires improve the light absorption due to the increased optical path as well as additional light trapping through reduced reflection and multi-scattering in comparison to 1D nanowire arrays, which are beneficial to solar energy harvesting applications. The high surface area can also increase surface activity and electrolyte infiltration in supercapacitors and batteries. The direct charge carrier transport pathway in both the trunks and branches boosts the charge collection efficiency. These fascinating properties of 3D branched nanowire structures have therefore stimulated widespread interests in fabricating them. The bottom-up approaches including vapour phase and solution-based routes allow for fabrication of a wide variety of 3D branched nanowires with diverse functions.

In this Review, we provide a summary of the state-of-the-art research in the synthesis of 3D branched nanowire structures and their emerging applications in various energy devices. In 'Preparation of branched nanowires' section, we will first introduce various methodologies and mechanisms developed for the synthesis of branched structures, ranging from sequential catalyst-assisted vapour—liquid—solid (VLS) or solution—liquid—solid (SLS) growth, vapour—solution combination growth, to phase induced branch growth. In 'Energy applications of branched nanostructures' section, the energy conversion and storage applications using the branched nanowires are highlighted in the key areas in photovoltaics, photocatalysis, photoelectrochemical water splitting, supercapacitors and Li ion batteries. The article will end with an overall conclusion and our outlook to the future direction in the 3D branched nanostructures.

**Preparation of branched nanowires**

Many methods are reported for the realization of branched nanowires. They are generalized and illustrated in Fig. 1. Typical methods that will be elaborated below include sequential catalyst-assisted VLS or SLS, solution growth on pre-formed nanowires, one-step self-catalytic growth, and screw-dislocation in combination with VLS. Importantly, the pros and cons of each method will also be discussed and compared at the end of this section.

**Sequential catalyst-assisted growth**

Similar to the growth of unidirectional semiconductor nanowires that needs a metal nanocluster as catalyst, the growth of secondary nanowire branches or even hyper-branches can be induced by introducing new metal catalyst onto the primary nanowire surfaces. Therefore, the methods used in early reports on branched nanowires usually involve sequential depositions of metal catalyst, followed by a VLS or SLS growth [35—38]. Typically, this process involves three steps, as shown in Fig. 1(a): standard VLS growth of the primary nanowires as the backbone, followed by the deposition of metal catalyst onto the nanowires, and finally second VLS growth of the branched nanowires onto the nanowire backbones. This method allows good control of the density of the branches by adjusting the amount of the Au particles deposited on the primary nanowires, and length of the branches by the growth time. It also allows the use of different type or different-sized metal catalyst for alternate generations of branches, providing an additional control. For example, branched and hyperbranched Si and GaN nanowires have been prepared via a multistep Au nanocluster-catalysed VLS approach [35] (see Fig. 2a). The widely known ordered arrays of GaP nanotrees were reported by Samuelson group (Fig. 2b) [36,37]. Au aerosol particles were deposited onto the primary vertical-aligned GaP nanowire stems for the subsequent VLS growth of GaP branches. Homojunction GaSb nanotrees were grown epitaxially on InAs substrates based on VLS, in which the Ga droplets served as the catalyst for both stem and branches [39]. Similar approaches were adopted to fabricate various hetero-branched structures with diverse materials combination, such as In2O3 and SnO2 branched nanowires [40,41].

Compared with the above homobranchied nanowires, there are much less reports on heteroepitaxial growth of branches based on sequential catalyst-assisted method. The heterobranch growth is more challenging, as the solubility of dissimilar materials in the same metal catalyst are generally different, which requires different growth temperature and partial pressure. Not to mention the possible crystal phase change and lattice mismatching. The reported successful growths are as follows; CdS nanobranches on pre-formed ZnS backbone nanowires have been realized based on VLS [42,43], GaAs, GaP and Ge nanobranches on Si nanowires [44], and CdSe branches on ZnSe nanowires based on a sequential SLS growth [45]. The SLS method provides more flexibility than VLS.

**Solution growth on preformed nanowires**

Solution methods, including hydrothermal, solvothermal, chemical bath deposition, electrodeposition, have been widely employed for growth of nanowires on nonplanar substrates. With slight modification, it can be straightforwardly applied to produce hierarchical branched nanowires using pre-formed nanowires as the growth substrate. Recently, various types of 3D branched metal oxide nanowire heterostructures have been realized in our group by a
Figure 1  Schematics of typical fabrication processes for branched nanowires. (a) Sequential catalyst-assisted vapour liquid solid (VLS) growth. (b) Solution growth on pre-formed nanowires. CVD, chemical vapour deposition; HT, hydrothermal; PVD, physical vapour deposition; CBD, chemical bath deposition; ED, electrodeposition. (c) Screw dislocation in combination with VLS. Reprinted with permission from Ref. [65]. (d) General self-catalysed growth, including laser ablation, vapour transport and deposition, vapour oxidation, and phase separation.

Figure 2  Sequential epitaxial VLS growth of nanobranches or trees. (a) Hyperbranched Si nanowires. Reprinted with permission from Ref. [35] (Copyright 2008, ACS). (b) Ordered array of GaP nanotrees. Reprinted with permission from Ref. [36] (Copyright 2008, NPG). (c) GaSb nanotrees. Reprinted with permission from Ref. [39] (Copyright 2012, ACS).
combination of VLS growth for the backbone nanowires and the subsequent solution growth of branches [46–49]. Fig. 3 shows some examples of branched nanowires realized by the powerful solution growth. VLS-grown SnO$_2$ nanowires are very stable and are an ideal candidate for this purpose. Our group has achieved SnO$_2$/ZnO, SnO$_2$/Fe$_2$O$_3$, SnO$_2$/MnO$_2$ and SnO$_2$/TiO$_2$ branched nanowires (Fig. 3a–d). In fact, the pre-formed nanowires are not limited to VLS ones, instead, they can be in principle any type of 1D, 2D or even 3D nanostructures, so long as they are holey and accessible by liquid precursors. For example, this method has been extended to fabricate Si/ZnO forest-like arrays by hydrothermal growth of ZnO nanorods on lithographic-prepared Si nanopillars (Fig. 3e) [50]. Similar to this methodology, various other branched structures like TiO$_2$/ZnO [51], CuO/ZnO [52] were also demonstrated by others. Furthermore, different solution methods can be rationally combined leading to a wide variety of branched nanowires. Fig. 3f gives an example of Co$_3$O$_4$/NiO core/shell nanowires, where the Co$_3$O$_4$ core was obtained by hydrothermal while NiO shell by chemical bath deposition [53].

Phase transition induced branching

Another interesting approach towards semiconductor branched nanostructures is through phase transition during the growth without the addition of intentional branching catalyst [54,55]. Generally, these materials are limited to those that can crystalize in either wurtzite (WZ) or zinc blende close-pack crystal structure or even mixed polytype under specific conditions. For example, CdTe [55] has cubic-close-packed zinc blende polymorph with very similar thermodynamic stability to its hexagonal-close-packed wurtzite form. They also have a relatively small stacking fault energy to switch between the zinc-blende ⟨111⟩ or wurtzite ⟨0001⟩ epitaxial interface. Fig. 4 shows one example of such crystallographic phase change-induced CdTe nanotetrapod. A zinc blende structure is more favoured at smaller nanoscale size whereas wurtzite is the more stable in bulk phase. Therefore, in a homogeneous solution, the initial CdTe first nucleate with a tetrahedral zinc-blende core; when the core reaches a certain critical size, branched nanowires with two, three, or up to four equivalent ⟨111⟩ directions form resulting in a tetrapod geometry. The variation of crystal phase could also be mediated by chemical solvents during solution growth. Chu et al.
Table 1  A comparison of different growth techniques for branched nanowires.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Typical materials (see Refs. in the text)</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Application priority</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequential catalyst assisted growth</td>
<td>Si, GaN, Ge, GeSe, InOx/SnO2</td>
<td>High quality, good control</td>
<td>Metal catalyst needed, high temperature</td>
<td>Metal catalyst, sensors</td>
</tr>
<tr>
<td>Solution growth on pre-formed nanowires</td>
<td>SnO2/ZnO, SnO2/Fe2O3, Si/ZnO, Co3O4/NiO</td>
<td>High yield, large-scale homogeneity, low cost</td>
<td>Limited materials with polytype phase</td>
<td>Batteries, supercapacitors</td>
</tr>
<tr>
<td>Phase transition induced branching</td>
<td>CdTe, CdS</td>
<td>Metal catalyst-free, high quality</td>
<td>High temperature CVD</td>
<td>High temperature CVD, relative low yield</td>
</tr>
<tr>
<td>One-step self-catalysed growth</td>
<td>ZnO, TiO2, ZnO/In2O3, PbS, PbSe, PbS, PbSe, FeS, FeSi, TiS</td>
<td>Screw dislocation driven, and others in vapour transport and deposition</td>
<td>High quality</td>
<td>Batteries, photocatalysts, supercapacitors</td>
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Figure 4  TEM of CdTe tetrapods. Wurtzite-phase branches grow out of the (111) faces of the tetrahedral zinc-blende core. Reprinted with permission from Ref. [55] (Copyright 2003, NPG).

reported the synthesis of different branched CdS products by adjusting the ratio of two solvents, ethylenediamine and ethylene glycol, under the solvothermal condition [56].

One step self-catalysed growth

In contrast to the multi-step sequential catalyst-assisted growth, the general self-catalysed growth including vapour transport and deposition, vapour oxidation, and laser ablation, as well as their combinations, allows the fabrication of 3D branched and even hyperbranched nanowires in a single step. Wurtzite crystals like ZnO and ZnS often exhibit a branched nanostructure, even by a simple oxidation of metal Zn [57]. It is recently discovered that highly oriented and hierarchically structured rutile TiO2 nanotrees can be formed by an acid vapour oxidation method (see Fig. 5a—d) [58]. The side branches form a 4-fold symmetry with the trunk, indicating a homoeptaxial interface (Fig. 5e). In this mechanism, the HCl acid played a crucial role that it served not only as catalyst for the generation of rutile phase but also the corrosive agent to introduce defects on the trunk surface. The titanium source was provided directly from the titanium substrate and oxygen was from vapour with the assistance of HCl.

Vapour transport and deposition which usually involves in a "self-catalytic" process is another common route towards branched nanostructures. Numerous reports are available in literature. Typical examples include cubic chalcogenides and wurtzite crystals [59—61]. The classical example is the ZnO/In2O3 hierarchical structures reported in 2002 based on a vapour transport and condensation technique [62]. It was found that the primary core is In2O3 nanowire and secondary branches are ZnO nanorods, with a variety of 6-, 4- and 2-fold symmetries. Using the same method, lead chalcogenide hyperbranched nanowires
Figure 5  TiO$_2$ nanoforests formed directly on Ti substrate via HCl acid vapour etching and oxidation. (a–d) Schematics of the proposed growth process. The HCl vapour etching introduces defects and thus provides nucleation for both the trunk and successive growth of branches. (e) SEM image of one TiO$_2$ nanotree. Reprinted with permission from Ref. [58] (Copyright 2009, ACS).

Figure 6  SEM images of (a) PbS and (b) PbTe branched nanowires. Reprinted with permission from Ref. [61] (Copyright 2007, Wiley). (c and d) Chiral branched nanowires whose stem is formed by screw dislocation or Eshelby twist, while the branches are due to catalyst-assisted VLS growth. (c) PbS pine trees. Reprinted with permission from Ref. [65] (Copyright 2008, Science) (d) PbSe nanowires. Reprinted with permission from Ref. [66] (Copyright 2008, NPG).
were also realized using PbCl₂ as the source material and reducing H₂ as the carrier gas [61]. As shown in Fig. 6a and b, the nanowire array is consisted of a central cube with nanowires growing perpendicularly from each of the six faces. Finally, branched nanostructures have also been realized using laser ablation, such as Zn₃P₂ nanowires [63] and TiO₂ nanotrees [64], which also most likely involves the self-catalytic process as the growth mechanism.

Other branching mechanism induced growth

Apart from the above mentioned growth techniques, there are some other branching mechanisms worthy of mentioning. Prominent examples are pine tree like PbS nanowires [65] and chiral branched PbSe nanowires [66] reported nearly at the same time. SEM images of such unique nanotrees are given in Fig. 6c and d. In this growth methodology, the authors proposed a screw dislocation driven growth mechanism for the trunk and VLS mechanism for the branches; both processes occurred simultaneously but the latter is slower than the former, accounting for true resemblance of a pine tree. In addition, several branched metal silicide nanowires such as FeSi [67] and TiSi₂ [68] were obtained from a chemical vapour transport route, but the branching mechanism was not well understood yet. It was suggested that the surface energy difference might be accounted for the two-dimensional TiSi₂ nanotree structures [68]. Our group has also obtained a striking structure of rutile TiO₂ nanonets using a slightly modified method, and study of growth mechanism is still underway.

To conclude this part, we have provided a brief summary and comparison of the different fabrication strategies for branched nanowires as shown in Table 1. Overall, vapour-phase and solution-phase are the two competitive methods but both have their advantages and drawbacks. In a nutshell, the former provides subtle control of the branches and ordering but requires high temperatures and sophisticated growth facilities. The obtained branched structures are useful in electronic and photonic applications, for which a high crystalline quality and a well-defined interface is generally required. The latter solution-phase method can take place at low temperatures with high yield and low cost. It enables the production of branched nanostructures with a rich variety of morphologies easily by adjusting the precursor solution and preparation conditions, and the process could be readily chunked to different stages. However, the branched nanostructures obtained by solution method in most cases have no alignment but are random oriented, and also they may suffer from poor crystal quality. Nonetheless, this is not a problem for energy applications (and probably also gas sensors).

Energy applications of branched nanostructures

Photovoltaic devices

A photovoltaic device, or solar cell, that harvests and converts the sunlight directly into electricity is one of the effective approaches for clean and sustainable energy supply. Although the state-of-art commercial solar cells are still dominated by crystalline Si, the high production cost motivates research on lower-cost whereas good efficiency solar cells. To decrease the cost per watt installed, various competitive photovoltaic materials are developed such as CdTe, CuInGaSe alloy and amorphous silicon, each having pros and cons of their own. Exciton solar cells in which small molecules, polymers, or quantum dots are used as light absorbing materials represent a promising candidate for future photovoltaic technology due to its cost-effective fabrication and relative high efficiency. Of essence is the choice of right materials and design of electrode. The 3D branched nanostructures having large surface areas and additional light trapping effect by light multi-scattering as well as reduced carrier diffusion paths are believed beneficial to photovoltaic devices. However, the drawback of 3D structured electrode is that it may increase the recombination rate of carriers, which is negative to the charge collection. So the final performance will be a delicate gain-loss balance. In this section, the recent advance in the application of branched nanostructures in exciton solar cells are highlighted, including dye sensitized solar cells (DSSC), polymer/inorganic hybrid devices and quantum dots (QDs) sensitized solar cells.

Dye sensitized solar cells

Dye sensitized solar cells in which dye molecular absorbed onto nanostructured semiconductors like TiO₂ or ZnO for light harvesting is the type of most investigated exciton cells [69]. The current record efficiency of ∼12% was from TiO₂ nanoporous electrode with porphyrin-sensitizer [70]. However, the electron transports in the percolation network of nanoparticles via the "hopping" mode. This means if one wants to further increase the film thickness to maximize the optical path and surface area for loading more dye molecules, some charges will be lost due to the increased transport path. As such, efforts have been paid to 1D semiconductor nanowires, which provide a direct electron transportation path. In the past few years, much progress has been made in ZnO and TiO₂ nanowires-based DSSCs [71–74]. Albeit demonstrated the improvement in carrier transportation and collection in 1D nanowires, the efficiencies are still behind the nanoparticle electrode due to the lower surface area. In this regard, 3D branched nanostructures with larger surface areas in comparison to 1D nanowires have attracted increasing attention [75–79]. For example, Cheng et al. fabricated branched ZnO nanowires with a two-step hydrothermal route for DSSCs application [75]. It was demonstrated the short-circuit current density (Jsc) and the energy conversion efficiency of branched ZnO nanowires DSSCs were 4.27 mA/cm² and 1.51%, respectively, which were twice those of bare ZnO nanowire ones. In a later work, the hydrothermal growth condition was improved to construct a ZnO nanoforest hierarchical structure photoelectrode (Fig. 7a) with a higher density and longer branch length [76]. The optimized Jsc and efficiency were 8.78 mA/cm² and 2.63%, respectively, nearly five times higher than that of free upstanding ZnO nanowires. The increased surface area enabling for more dye loading, and light harvesting as well as reduced electron–hole recombination through direct conduction path along the ZnO
branches are believed to account for the efficiency improvement. In the follow-up work, the ZnO branch length effect on the solar cells efficiency was investigated [80]. It is found that, while the efficiency was evidently increased by introducing the branches, the increase slowed down with further increasing the branch length. This is not surprising as the bundling of the long branches reduces the effective surface areas and thus the dye loading.

Similar TiO2 branched nanotrees were also demonstrated for DSSC with improved performance [64,77,81]. Fig. 7c and d shows the DSSC photoanode constructed from solution-grown TiO2 nanowires with short branches (i.e. nanotrees). Based on comparison of two sets of data, the nanotree devices exhibit consistently higher \( J_{sc} \) than the nanorod ones, which can be ascribed to the enhanced light absorption in the nanotree sample due to increased dye adsorption and light scattering. The trend of the \( J-V \) curves is found very consistent with their IPCE spectra [81].

Improved light harvesting effect has also been demonstrated using optical fibres. The Wang group designed a novel 3D photoanodes with optical fibre as backbone to guide and confine the light, and ZnO nanowire branches as the photoactive component for dye loading [78]. This smart design allows remote input of sunlight and more efficient light absorption in the working region. The two light illumination conditions resulted in a substantial difference in the DSSC performance. In the parallel illumination case, an efficiency of up to 3.3% was demonstrated. In their more recent follow-up work, the ZnO nanowires were replaced with TiO2 nanotubes by a liquid phase deposition method and the counter electrode was re-designed into a cylindrical shape. This resulted in an even higher efficiency of around 6% [79].

Polymer—inorganic hybrid solar cells
Another type of exciton cells is polymer—inorganic hybrid solar cells, in which inorganic crystals serve as the electron acceptor and conjugate polymer as electron donor, and both components contribute to light absorption. For this device, 3D branched nanostructures are proven superior to both nanorods and quantum dots when blended with polymers [82,83], as the former provides high organic—inorganic contact interface area, short diffusion distance for exciton dissociation and direct conduction pathway for charge transportation and collection. Photovoltaic devices prepared from blends of branched CdSe tetrapods and a conjugate polymer have been fabricated (see Fig. 8) [82,83]. The CdSe tetrapods showed an improved electron extraction in
photovoltaic devices compared with that of nanorods. When a lower bandgap (~1.4 eV) conjugated polymer is used, a certified solar-to-power conversion efficiency of 3.2% under AM 1.5 illumination has been demonstrated [83].

Semiconductor sensitized solar cells
Semiconductor quantum dot (QDs) sensitized solar cells in which QDs replace the dye molecular for light harvesting has also attracted intensive attention due to some unique physical processes (such as the quantum confinements, multiple exciton generations), and the general higher efficiency than DSSCs. The bandgap of QDs can be easily tuned by their sizes, enabling wavelength-selective light absorption. Furthermore, semiconductor QDs have higher extinction coefficient than dye molecules. An example of Si/ZnO branched hierarchical nanowires as the host material for QDs sensitized solar cell electrode [84] is given in Fig. 9. By sensitization with CdS/CdSe QDs, the devices yielded an overall efficiency of ~3%, which was higher than that of ZnO nanowire arrays due to increased QDs loading and enhanced light scattering by the 3D geometry. It was also noted that the doping in the Si backbone nanowire played an important role in the performance: the nanowires with intrinsic-Si (i-Si) had a $J_{sc}$ of 2.71 mA/cm$^2$ and efficiency of 0.37%, whereas the n-doped Si sample resulted in $J_{sc}$ of 11.00 mA/cm$^2$ and efficiency of 3.00%. It is indicated, through detailed electrochemical impedance analysis, that the doping of Si nanowires not only improves the transport properties of the electrode due to increased conductivity, but also reduces the recombination process. As shown in Fig. 9d, the i-Si/ZnO photoanode gives the lowest performance due to the poor conductivity.

Compared to the widely applied QDs, nanorod-shaped photosensitizers are believed more interesting for sensitized solar cells [85]. The length variation in one-dimensional rods brings in advantages in solar cell performance as compared to just diameter control in zero-dimensional QDs. These advantages include a higher loading of sensitizers due to increased surface area, easier electron—hole charge separation due to more favourable energy band alignment between nanorod/TiO$_2$ and thus efficient electron injections, and lastly, a larger optical absorption cross section. Research on this particular direction just is started but will most likely progress fast.

Photocatalysis and photoelectrochemical water splitting

Photocatalysis
Another important research direction on sunlight utilization is photocatalysis. Upon light illumination, the photogenerated electrons and holes in a semiconductor can participate in chemical reduction and/or oxidation reactions, so that the photoactive semiconductors act as the reaction catalyst. Typical applications on photocatalysis are found in photo-decomposition of organic pollutants [86,87], and photocatalytic splitting of water to yield hydrogen fuels [10]. The merits of 3D branched nanostructures in these applications are essentially the same as those in solar cells. A study on the photocatalytic properties of 3D radial ZnO nanowires/Si microrods [88] is presented in Fig. 10. It is demonstrated that the branched structures showed improved light harvesting ability due to an increased optical path by multi-scattering (as shown in Fig. 10b). As a result, together with its enlarged contact area with the sample solution, the catalytic effect in degradation of methyl red of the 3D ZnO nanowire/Si microrod structures, with a medium ZnO nanowire length, are evidently superior to ZnO nanowires on flat Si substrates (see Fig. 10c).

As the photocatalysis involves charge separation and transport, a heterojunction with proper band alignment will exhibit a positive effect. Sun et al. also reported the photocatalysis property of 3D ZnO@ZnTe hetero-branched nanowires [89]. The significant improvement of the photocatalytic ability compared to both pure ZnO and ZnTe nanowires were attributed to the enhanced electron—hole separation at ZnTe/ZnO interfaces, in addition to the increased surface area. When the stem is prepared to be a metal or metallic nanowire, it can act as the electric cable for transferring photoelectrons from the semiconductor branches and helpful to facilitate the electron—hole separation [90]. Additional performance improvement in photocatalytic ability can be achieved by...
hybridization semiconductor nanostructures with plasmonic metal nanoparticles.

**Photoelectrochemical water splitting**

Solar light driven water splitting by photoelectrochemical (PEC) cells offers an ideal route for H₂ generation due to the sustainable solar energy and abundant water resources. In the past few years, a number of demonstrations on the application of 3D branched nanostructures for PEC water splitting have been made [91–98]. A branched TiO₂ nanowire array is expected to be superior to 1D nanowires in terms of higher light absorption ability due to stronger anti-reflection effect. This is demonstrated by Cho et al., who showed that the branched nanorods exhibit the best PEC performance compared to the nanoparticle and 1D nanorod counterparts (see Fig. 11a–c) [97]. The branched nanorod photoanodes yielded a photocurrent density of 0.83 mA/cm² (at 0.8 V versus reversible hydrogen electrode). The incident photon-to-current conversion efficiency (IPCE) reached 67%.
at 380 nm, nearly two times higher than that of the bare nanorods without branches. The high IPCE value is a result of a combination of effective carrier transport and collection in the branched nanorods.

In addition to the above values rendered by branched nanowires, a heterojunction will give additional merit by facilitating the electron—hole separation. Fig. 12 shows a 3D branched Si/TiO2 electrode design for efficient PEC water splitting [91]. The 3D Si/TiO2 nanostructures were prepared by growing TiO2 nanorods onto Si nanowire backbones via the surface-reaction-limited pulse chemical deposition technique. To fully isolate the Si from the electrolyte, an additional thin film of anatase TiO2 was coated on TiO2 nanorods by atomic layer deposition (Fig. 12a and b). The n-doped Si nanowire core provided a direct conducting channel for fast electron—hole separation and charge transportation as well as long optical path for light harvesting (Fig. 12c). As a result, the 3D branched nanowire electrode gave a maximum photo-to-hydrogen conversion efficiency of 2.1% corresponding to the sample with 20 μm long wet-etched Si nanowires and 250 cycles ALD overcoating. Too much TiO2 overcoating gave negative effect as it reduced the overall porosity. Similarly, the Si/ZnO branched nanowire PEC electrodes also demonstrate a strong structure dependent performance [92]; the largest photocurrent was 8 mA/cm2, about 80 times that of ZnO thin film coated Si nanowire electrode.

While a semiconductor heterojunction is generally beneficial to charge separation, it would be more desirable to have a metallic backbone nanowire core as the direct current collector, such as metal, FTO or silicide nanowires. Indeed, 3D network TiSi2/TiO2 [96] and TiSi2/Fe2O3 [95] electrodes for water splitting application have been achieved. The network structures of metallic TiSi2 silicide nanowires serve as not only a high-surface-area scaffold to improve the photon absorption of TiO2, but also a highway for electrons. This combined advantages led to the high performance in PEC measurements. When the TiO2 is replaced with electrochemical active materials (transition metal oxides), this structure should also be an ideal battery electrode.

**Energy storage devices**

Development of advanced electrical energy storage technology is the key to meet the daily increasing demand of portable power and the widespread use of intermittent alternative energy, such as solar and wind energy. There are two main techniques for charge storage: one is supercapacitor, also called electrochemical capacitor (EC) which stores energy primarily as charge (a pseudocapacitor stores energy via Faradic redox reaction); the other is battery, such as Li-ion battery that stores energy in chemical reactants capable of generating external charge flow. In both types of charge storage devices, 3D branched nanowire structures and materials are being extensively investigated.

**Supercapacitors**

Because of the fast charging and discharging, long cycle life, and high energy density, supercapacitors play an important role in next-generation plug-in hybrid electric vehicles and modern consumer electronics devices [99–104]. The supercapacitors are generally classified into two types: electrical double-layer capacitors (EDLC) and pseudocapacitors. In the past few years, the majority types of supercapacitor electrode materials: carbonaceous materials, metal oxides/hydroxides and conducting polymers. To achieve a
high capacitance, the electrode design should satisfy the following merits: First, a high surface area enabling more reaction sites; Second, a highly conductive transport path for fast electron transportation and short ion diffusion path. In this regards, 3D branched nanowire structures are good choices. Recently, our group has presented a series of 3D pseudocapacitor electrode design based on core–shell metal oxide nanostructures [47,53,105,106]. In all these designs, both metal oxides are pseudocapacitive contributing to the charge storage. One example is MnO2 ultrathin nanosheet branches hydrothermal grown on pre-formed Co3O4 nanowires (see Fig. 13a–d) [47]. When using LiOH as the electrolyte, both of two metal oxides undergo simultaneous charge-storage reactions with anions and cations, respectively. The Co3O4 nanowires provide direct electron transport pathway, and importantly their surfaces are still accessible to charged ions because of the rugged MnO2 shell, leading to the fast discharging and regenerating. As shown in Fig. 13d, the Co3O4@MnO2 hybrid nanowire arrays exhibit capacitance of 480 F/g at 2.67 A/g with good cycle performance.

To further increase the electrode surface area, 3D branched and hybrid structures of Co3O4/NiO core shell nanowire arrays [53] and porous CoO nanowire/nickel hydroxidenitrate nanoflakes [105] are prepared directly on nickel foam. The nickel foam provides more material loading per unit area because of its macroporous structure. Meanwhile its high conductivity as well as 3D network structure can reduce the diffusion resistance and provide ideal electron pathway. Fig. 13e shows the typical SEM image of oxide nanowires on a Ni foam substrate. Through a two-step solution method, the nanowires can be core–shell branched structure. Specific capacitances measurement of Co3O4/NiO branched nanowires at different current densities demonstrate that the branched nanowire arrays present much improved performance in the terms of specific capacitance and rate capability than those of single components (see Fig. 13f). The specific capacitance is 853 F/g (at 2 A/g) for the branched nanowire arrays, compared to 642 F/g of the Co3O4 nanowire arrays and 178 F/g for the NiO nanoflake arrays. This composite structure is found also robust. 95.1% of the highest value can be maintained after 6000 charge/discharge cycles.

Lithium-ion batteries
Lithium-ion batteries (LIBs) are being widely used in portable electronics. To meet the demand of high-power and high-energy density requirements in both thin-film microbatteries and conventional batteries, it is necessary to explore novel nanostructured electrode materials with higher figure of merits than the conventional graphite. Compared to traditional anode materials with single components, 3D heterostructured materials with two or more components in suitable combinations may exhibit...
Figure 13  Two examples of branched nanowires as the supercapacitor electrode. (a) SEM image of Co$_3$O$_4$/MnO$_2$ hybrid nanowire arrays. Inset shows an enlarged view. (b) Charge/discharge curves for hybrid nanowire array and pristine Co$_3$O$_4$ array. (c) Schematic of the charge storage mechanism of the hybrid nanowire array, in which both the Co$_3$O$_4$ core and MnO$_2$ shell contribute to the charge storage. (d) Cycling performance of both the hybrid nanowire and pristine Co$_3$O$_4$ arrays. The inset shows the charge–discharge curves of the last 15 cycles (total 5000 cycles) for the hybrid array. Reprinted with permission from Ref. [47] (Copyright 2011, Wiley). (e) SEM image of metal oxides nanowires directly grown on Ni foam substrate. (f) Specific capacitance at different current densities of Co$_3$O$_4$/NiO branched nanowires as compared to individual nanostructures. Reprinted with permission from Ref. [53] (Copyright 2012, ACS).

better performance arising from a possible synergetic effect [107–111]. This concept was demonstrated using α-Fe$_2$O$_3$/SnO$_2$ branched nanoheterostructures as the potential polymer binder-free anode material for LIBs [48]. The lithium storage properties of these α-Fe$_2$O$_3$/SnO$_2$ branched heterostructures are electrochemically evaluated versus Li with a comparison to pure α-Fe$_2$O$_3$ nanorods and SnO$_2$ nanowires under galvanostatic condition at the current rate of 1000 mA/g. The branched nanoheterostructures show an evidently improved initial discharge capacity of 1167 mAh/g, which is almost twice that of SnO$_2$ nanowires and α-Fe$_2$O$_3$ nanorods (see Fig. 14a). Moreover, the composite electrode also exhibits the lowest initial irreversible loss of 30.6%, compared to 43.9% for α-Fe$_2$O$_3$ nanorods, and 56.4% for SnO$_2$ nanowires (see Fig. 14b). This reduced irreversible loss of the branched nanoheterostructure can be attributed to a synergistic effect between SnO$_2$ and α-Fe$_2$O$_3$. A large drop in capacity of second cycle is obviously seen for all the samples due to the initial irreversible loss. Despite the relatively faster capacity fading behaviour, the composite electrode exhibits a consistently higher capacity than the pristine SnO$_2$ nanowires and α-Fe$_2$O$_3$ nanorods arrays.

As mentioned in previous section, a metallic silicide network would be an ideal current collector for energy storage devices. This has been realized nicely by Zhou et al., who developed a novel 3D Si/TiSi$_2$ branched nanostructures by coating Si onto the surface of TiSi$_2$ nanonets as the anode material for Li ion batteries [109]. In this structure, the highly conductive TiSi$_2$ nanonets serve as inactive component to support Si and facilitate charge transport, while Si is the active component to store and release Li ions.
Figure 14  Application of branched nanostructures as lithium-ion battery anodes. (a) First charge–discharge profiles of Fe$_2$O$_3$/SnO$_2$ branched nanowire anode at a rate of 1000 mA/g in the potential window of 0.005–2.5 V. (b) Cycling performance as a comparison to bare α-Fe$_2$O$_3$ nanorod arrays and pristine SnO$_2$ nanowires. (c) Comparison of the unidirectional nanowires and branched nanostructures for electron collection. Reprinted with permission from Ref. [48] (Copyright 2011, Wiley). (d) Schematic of Si/TiSi$_2$ hyperbranched nanonets. (e) Charge capacity and Coulombic efficiency of the Si/TiSi$_2$ nanonet electrode. Reprinted with permission from Ref. [109] (Copyright 2010, ACS).

(Fig. 14d). At a fast charge/discharge rate of 8400 mA/g, the anodes present outstanding capacity retention of >99% per cycle at the level of 1000 mAh/g over 100 cycles (see Fig. 14e). Within the same concept, carbon coated CNT@Fe$_2$O$_3$ branched nanostructures were also fabricated which was composed of hollow α-Fe$_2$O$_3$ nanohorn branches and CNT backbones [111]. When tested as the LIB electrode, this hybrid structure demonstrated stable capacity retention of 800 mAh/g over 100 cycles at a current density of 500 mA/g and an exceptional high-rate capability.

Conclusion and future outlook

3D branched nanostructures have sparked considerable research interest in recent years. In this Review, we have summarized the common routes to the fabrication of branched nanostructures, including sequential catalyst-assisted VLS or SLS growth, solution growth on pre-formed nanowires, self-catalytic vapour phase growth, and phase change induced branch growth and so on. Applications of the 3D branched nanostructures in the emerging energy conversion and storage areas are highlighted, ranging from solar cells, photocatalysis, photoelectrochemical water splitting to advanced energy storage devices such as Li ion batteries and supercapacitors as well as light emitting diodes. However, the potential energy applications of 3D branched nanostructures are not limited to above; instead, applications in other venues such as fuel cells, thermoelectric devices, piezoelectric devices are also being explored. Furthermore, using 3D branched structures to harvest various type of ambient power like thermal, wind, vibration and electromagnetic energy would also be very promising, which provides a potentially endless source of energy.

In comparison to the fast progress of 1D nanostructures, the fabrication and applications of 3D branched structures
have lingered far behind. Further development in this research field requires improvement in synthetic methods and novel fabrication processes to provide better control of the structural complexity, composition uniformity, surface chemistry and interface electronics, and last but not least, the yield, of branched nanostructures. While the vapour phase epitaxy method results in high-quality nanobranches, it relies on expensive equipment and toxic source materials. Therefore, developing simple and environment-friendly benign growth methods such as multiple solution growth for the fabrication of 3D semiconductor branched structures are of great interest.

The ultimate goal is to push the energy devices towards practical applications, which requires the development of devices with high efficiency, low cost and long lifespan. Thus, the optimization of the branched nanostructures and the improvement of the energy conversion efficiency will remain the future research focus. On the other hand, the 3D branched nanostructure in energy applications also has drawbacks that it brings challenge in quantifying the charge transport and recombination loss in terms of solar devices. Understanding the light absorption property, interface electronic band structure, and photocarrier dissociation and recombination are key issues to the overall performance. For batteries and supercapacitors, it is also a question if the entire branched nanowires maintain their electrical conductivity during repeated cycling. To establish a reliable structure–performance correlation, a wide range of characteristics should be carried out in a self-consistent way. Maybe, in situ measurements would be ideal to provide more insights. Overall, these are very multidisciplinary topics, for which physics and chemistry experimentalists, and theoreticians need sit together and brainstorm innovative ideas.

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References

Dr. Chuanwei Cheng received his PhD degree in Materials Processing and Engineering from Nanjing University of Aeronautics and Astronautics, China in 2009. From 2009 to 2011, he worked in Nanyang Technological University, Singapore, as a postdoctoral fellow. In June 2011, he joined in Tongji University, Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, as an associate professor. His current research interest includes controlled fabrication of novel semiconductor nanostructures, energy conversion devices such as solar cells and PEC water splitting.

Dr. Hong Jin Fan is an assistant professor at Nanyang Technological University since 2008. He received his PhD from National University of Singapore, followed by postdoc at Max-Planck-Institute of Microstructure Physics, Germany and University of Cambridge. He has published 90 journal articles and 4 book chapters. He has co-organized symposia in international conferences including 2008 and 2010 MRS Spring meetings, 2011 MRS Fall meeting, and ICMAT 2011. The research interests of Dr. Fan are nanomaterials and energy applications, including (i) oxide and chalcogenide semiconductor nanowires, (ii) atomic layer deposition (ALD) for nanofabrication and surface engineering and (iii) supercapacitors and solar energy conversion materials and technologies.