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Hybrid Nanomaterials

Advances in Energy, Environment and Polymer Nanocomposites

Edited by
Suneel Kumar Srivastava
and Vikas Mittal

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A hybrid material is defined as a material composed of an intimate mixture of inorganic components, organic components, or both types of components. In this regard, 3D hybrid materials have been receiving continuous attention. They can be prepared by hybridizing 1D (MWCNTs, CNF, etc.) and 2D (molybdenum disulfide, titanium disulfide, tungsten disulfide, Na-montmorillonite, layered double hydroxide, graphene, etc.) materials. In addition, formation of hybrid materials has also been reported considering other combinations. These different types of hybrid materials have currently been garnering tremendous attention for their possible use in developing materials for efficient energy harvesting. Nanostructured hybrid materials have also seen many significant advances in providing pollutant-free drinking water, sensing of environmental pollutants, energy storage and conversion. In addition, they have also been used in shielding material to interfere with electromagnetic waves originating from different electronic instruments and appliances, which deteriorate their performance and adversely affect human health. Ever since it was first reported that the work done by a group of researchers at Toyota dramatically improved the properties of polyamide 6 by incorporating modified low content of montmorillonite, immense interest has been generated in developing such high performing polymer nanocomposites for applications in the automotive, aerospace and construction sectors, among others. However, the aggregation of many types of fillers, such as clay, LDH, CNT, graphene, etc., remains a major barrier to their development. Recently, this problem has been overcome by the fabrication and application of 3D hybrid nanomaterials as nanofillers in a variety of polymers. More importantly, these 3D hybrid-filled polymer nanocomposites exhibit synergistic properties, unlike individual phases or their microcomposites alone. Therefore, the development of simple, convenient and efficient methods for the fabrication of hybrid nanomaterials and the realization of their applications in energy, environment and polymer nanocomposites remain a challenging task.
In view of this, the chapters of this book entitled *Hybrid Nanomaterials: Advances in Energy, Environment and Polymer Nanocomposites*, introduce readers to the following emerging research topics:

- Chapter 1: Hybrid nanostructured materials for development of advanced lithium batteries
- Chapter 2: High performing hybrid nanomaterials for super-capacitor applications
- Chapter 3: Nanohybrid materials in the development of solar energy applications
- Chapter 4: Application of hybrid nanomaterials in water purification
- Chapter 5: Advanced nanostructured materials in electromagnetic interference shielding
- Chapter 6: Preparation, properties and application of hybrid nanomaterials in sensing of environmental pollutants
- Chapter 7: Development of hybrid fillers/polymer nanocomposites for electronic applications
- Chapter 8: High performance hybrid filler reinforced epoxy nanocomposites
- Chapter 9: Recent developments in elastomer/hybrid filler nanocomposites

It is expected that these simple, attractive, versatile, technological developments in hybrid materials and their applications will provide a better understanding of the currently ongoing research in related fields.

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Suneel Kumar Srivastava and Vikas Mittal
March 2017
Hybrid Nanostructured Materials for Advanced Lithium Batteries

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Abstract

Efficient energy storage devices are progressively gaining importance due to the limited reserve of fossil fuels and advancement of alternative energy sources. Lithium-based battery systems have acquired a leading position in electrochemical energy storage and have become an important element in the replacement of conventional gasoline-driven vehicles with electrically driven ones. State-of-the-art lithium-ion batteries still cannot fulfill capacity requirements, and lithium-sulfur and lithium-air batteries might be promising for the high-energy-density batteries of the future. In this chapter, a brief overview of common lithium-ion batteries as well as of advanced battery systems is provided, including principles of operation, methods of fabrication utilizing nanohybrids for improved performance, and some aspects for further improvements.

Keywords: Nanostructured materials, hybrid materials, lithium-ion batteries, lithium-sulfur batteries, lithium-air batteries

1.1 Introduction

In our society, the worldwide demand for electric energy consumption is progressively increasing day by day, and energy is being exploited in everything from mobile electronics to portable electronic gadgets and, ultimately, electrically driven vehicles. This increasing demand has caused a rapid rise of both primary and secondary batteries. In the 21st century, the steep growth of energy demand and environmental concerns associated

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with global warming, and a limited reserve of fossil fuels, has brought a serious note to the work of politicians and researchers in finding alternatives to the sole dependency on fossil fuels. Energy resources, such as hydroelectric, nuclear, and renewable resources like sun, wind, biological and tidal powers, are competing candidates as alternatives to fossil fuels. Hydroelectric power is a clean source of energy that requires storage of the potential energy of water in dams in suitable regions which are not available everywhere. Nuclear power, although used in different countries at large scale, causes radioactive hazards associated with long-term storage of radioactive wastes, and safety aspects are primary hindrances to be taken care of, especially in the wake of the Fukushima disaster. Although renewable sources offer clean energy, the intermittent nature of sources like the sun, wind or tidal waves practically restricts the continuous production of energy from these sources [1]. In that case, the renewable energies have to be stored when they are available and supplied on demand. These systems can only be operated reasonably with powerful energy storage units, like thermal or chemical storage units including high-energy batteries, to strategically balance source variability and power requirement.

The accumulators (or secondary or rechargeable batteries) can be exploited as a component of energy storage system for giant electric grids, but mostly for local energy storage for smart grids in localized communities; in addition, they are used in consumer electronics to a large extent and are essential for the progress of e-mobility. Nowadays, the rechargeable batteries find applications in laptops, cell phones, medical implants, power tools, toys and many different portable electronic gadgets. In recent years, there has been a strong drive towards research and development to replace gasoline-driven cars with e-cars with rechargeable batteries. So, secondary batteries are now being exploited in high-end applications; for example, in transportation sectors, defense, or aerospace applications as well. State-of-the-art lithium-ion battery technology suffices for batteries for electronic gadgets, but to broaden the prospects of batteries in transportation sectors, a dramatic boost in the current battery technology has to be executed [2].

In particular, to bring the global electrified transportation venture to reality, development of cheap, environmentally friendly, safe, and high-energy-density batteries is the challenge for the near future. However, the state-of-the-art Li-ion batteries presently existing in the market are limited to the energy density of 150 Wh/kg which is, taking weight limitations into account, below the performance of the gasoline-driven vehicles (Figure 1.1). Most advanced e-cars like Tesla Model S have now extended the range with a big battery pack to 500 km. Significant uplift of energy densities by a factor of 2–5 are required to reach the desired performance of
Figure 1.1  (a) Practical driving ranges of a present typical electrically driven vehicle (the values for driving ranges are based on the minimum specific energy for each technology and scaled on the specific energy of the Li-ion cells (140 Wh/kg) and a driving range (160 km) of the Nissan Leaf). The specific energies are given for some rechargeable batteries, along with estimated driving distances and pack prices. For future technologies, a range of anticipated specific energies are shown by the lighter shaded region on the bars in the chart for rechargeable batteries under development and for R&D. (Reprinted with permission from [3]; Copyright © 2012 Macmillan Publishers Ltd). (b) Drive range of all electrically driven cars as per U.S. Environmental Protection Agency (EPA) rating. (Source: Wikimedia Commons, “Electric Car,” 12/2016).
plugged in hybrid-electric vehicles (PHEVs) with approx. 100 km all-electric range and all-electric vehicles (EVs) with a range exceeding 600 km at reasonable weight and price, respectively [2, 3]. The recent advancements of next-generation lithium-ion batteries start to approach the performance requirements of PHEVs, but new electrochemical systems such as lithium-sulfur (Li-S) or lithium-air (oxygen) (or Li-air) can have the potential to meet the performance and cost requirements for EVs. In principle, Li-S and Li-air batteries offer at least five times the practical specific energy of present day lithium-ion batteries, use better available and cheaper constituents, and promise to be more environmentally friendly. This chapter covers the rise of lithium battery technology, and it provides some concepts for this technology to overcome the technological challenges to meet the performance matrices of electrically powered transportation sectors. Efficient electrical energy storage systems such as batteries have now become a key issue of national and strategic importance in a highly competitive international platform [4, 5]. The progress of electrical energy storage in that respect constitutes a challenging scientific and technological task that directly addresses critical economic, social and environmental needs. More specifically, revolutionary development of safe operating, pocket friendly, high-energy-density batteries at reasonable cost could bring the global electrified transportation industry to the market. Those challenges and future opportunities are outlined in several books, reviews and reports [6–15].

This chapter briefly outlines the current development strategies adopted for lithium-based batteries, different chemistries behind the operation of lithium-based batteries and electrode nanostructures, challenges associated with the nanostructure design and their remedies. It includes an overview of the importance of nanostructured materials over bulk battery materials and their advancements so far as well as important aspects on lithium-based batteries. So we briefly introduce the working principles of lithium-based batteries (Li-ion, Li-air, and Li-S) and cover the various challenges associated with lithium-based batteries. In this chapter, the importance of controlled synthesis strategies will be outlined, thus providing an ideal platform to study synergistic effects of various hybrid structures for enhanced performance.

1.2 Battery Requirements

Before continuing the discussion about batteries, one must recall why we need batteries and what the requirements for the batteries are. It is obvious that we need batteries for mobile energy supply and storage but batteries
have been classified as per their cell voltage, capacity, energy density, and whether they are rechargeable or for single use. In a battery the electrical energy is generated from the chemical reaction of two components, often referred to as Faradaic reactions. On the contrary, supercapacitors are operated mostly by ion electroosorption [16, 17]. So there is no change of oxidation state of the acting ions. In a battery, one electrode is referred to as the anode, which releases electrons and thereby generates ions, and another is referred to as the cathode, which accepts electrons [18]. The flow of electrons is possible due to the change of oxidation state of the reactants. This produces current and hence capacity. The anode and cathode are separated by a separator which is soaked with electrolyte and also acts as electrolyte reservoir [18]. Principally, all batteries are of two types: primary and secondary.

1.2.1 Primary and Secondary Batteries

Primary batteries are those which can be used only once and which are discarded after a single use. The reason behind this is that the chemical reactions which are responsible for the production of electrical energy cannot be easily reversed. Still, their ease of fabrication, low cost, simple design, and high energy output for a short period of time make them the most popular batteries on the market. Primary batteries are normally used in low-drain applications [19].

The primary battery systems currently used are carbon/Zn, Mg/MnO₂, Zn/alkali/MnO₂, Zn/HgO, Cd/HgO, Zn/Ag₂O, Zn/air, which have operating potential in the range of 1.0–1.6 V and can offer energy densities in the range of 50–120 Wh/kg, excepting Zn/air system, which can deliver 290 Wh/kg at 1.5 V [20, 21]. There are also Li-based primary batteries which are preferred due to their much higher cell voltage of ca. 3 V and much higher specific energies of ca. 200–300 Wh/kg. Such systems are Li/SOCl₂, Li/SO₄, Li/MnO₂, etc. However, they do not fit high-drain operations due to their short life span and one-time usage. Primary batteries typically provide only 2% of the energy used during the manufacturing process and therefore are energetically inefficient and have poor sustainability, but their easy handling still makes them attractive in various applications such as flashlights, radios, electronic toys, wristwatches, cameras, camcorders and many more portable electronic gadgets. Although primary batteries currently occupy a big fraction of the overall energy storage market, in some cases the use of primary batteries cannot be avoided (pacemakers, military applications, etc.) [22, 23], an urgent move towards rechargeable batteries is essential for environmental reasons. Therefore, in
this chapter more emphasis will be given to hybrid nanostructured materials for rechargeable batteries.

1.2.2 Battery Market

The battery market is still dominated by primary batteries but battery technology is strongly moving towards rechargeable batteries, especially in the industrial, consumer, automotive and energy storage sectors (Figure 1.2). The data in Figure 1.2 is presented from the fractions of market acquired by different applications based on revenue break down. It is clearly seen from Figure 1.2a that the automotive and renewable energy storage applications for grids are expected to rise dramatically by 2020 in comparison to 2013. That means there is a significant movement towards replacement of gasoline-driven vehicles to electrically driven ones. This tendency towards

Figure 1.2 (a) Global battery market for Li-based batteries. (Source: Vishal Sapru, Frost & Sullivan). (b) Hybrid electric vehicle (HEV) market evaluation. (Reproduced with permission from [24]; Copyright © 2009 Elsevier B.V.). (c) cost for lithium-ion battery packs and yearly demand for EV battery power. (Source: Bloomberg New Energy Finance).
hybrid electric vehicles (HEVs) is even clearer from Figure 1.2b, although the optimistic scenario is far from the real number of HEVs sold worldwide. The same is applicable for grid-level storage (Figure 1.2a). All these data indicate a tendency to minimize the sole dependency on fossil fuels in the near future. In addition, if we look at Figure 1.2c, we can clearly see that the price of battery packs is inversely proportional to the demand for EVs. Continuous research and development efforts on cost-effective batteries largely benefit the true commercialization of EVs in modern society.

### 1.3 Survey of Rechargeable Batteries

Figure 1.3 schematically illustrates the basic principles behind a rechargeable battery. It consists of one cathode (here LiCoO$_2$) coated on a current collector (e.g., Al), an anode (here graphite) and a porous separator soaked with organic electrolyte (e.g., LiPF$_6$ in EC/DEC). The function of the separator is to store the electrolyte as well as to separate the two electrodes to avoid short circuiting. The Li$^+$ ions intercalate among the layers of graphite and the cell being charged. The opposite reaction happens during discharging where Li$^+$ ions migrate back to the crystals of the cathode [25]. The redox reactions are given below:

$$\text{LiCoO}_2 + x\text{C}_6 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{LiC}_6$$

Table 1.1 lists some of the commonly used battery systems, their cell constructions, the available voltage extracted, available specific energies and their current status.

![Figure 1.3](image_url) Operating principle of lithium ion battery taking LiCoO$_2$ as representative cathode material and graphite as anode.
Table 1.1 Commonly used rechargeable battery systems. (Adapted from with kind permission from [26]; Copyright © 2012 Royal Society of Chemistry)

<table>
<thead>
<tr>
<th>Battery system</th>
<th>(-ve) Electrode</th>
<th>(+ve) Electrode</th>
<th>Av. OCV (V)</th>
<th>Theoretical Sp. Cap (mAh/g)</th>
<th>Theoretical Sp. energy (Wh/kg)</th>
<th>Practical Sp. energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-acid</td>
<td>Pb</td>
<td>PbO₂</td>
<td>2.1</td>
<td>83</td>
<td>171</td>
<td>20–40</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>Cd</td>
<td>NiOOH</td>
<td>1.35</td>
<td>162</td>
<td>219</td>
<td>20–40</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>MH alloy</td>
<td>NiOOH</td>
<td>1.35</td>
<td>ca. 178</td>
<td>ca. 240</td>
<td>50–70</td>
</tr>
<tr>
<td>Na-S (350 °C)</td>
<td>Na</td>
<td>S</td>
<td>2.0</td>
<td>377</td>
<td>754</td>
<td>ca. 120</td>
</tr>
<tr>
<td>Li-ion</td>
<td>Graphite</td>
<td>LiCoO₂ (layered)</td>
<td>2.58</td>
<td>305</td>
<td>787</td>
<td>ca. 90</td>
</tr>
<tr>
<td>Li-ion</td>
<td>Graphite</td>
<td>LiMn₂O₄ (spinel)</td>
<td>4.0</td>
<td>104</td>
<td>424</td>
<td>80–100</td>
</tr>
<tr>
<td>Li-ion</td>
<td>Graphite</td>
<td>LiFePO₄ (olivine)</td>
<td>3.4</td>
<td>117</td>
<td>398</td>
<td>80–100</td>
</tr>
<tr>
<td>Li-ion</td>
<td>Li₄Ti₅O₁₂</td>
<td>LiMn₂O₄ (spinel)</td>
<td>2.5</td>
<td>80</td>
<td>200</td>
<td>50–70</td>
</tr>
<tr>
<td>Li-ion</td>
<td>Graphite</td>
<td>LiMn₁₅Ni₆₅O₄ (Advanced spinel)</td>
<td>4.7</td>
<td>105</td>
<td>493</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Li-ion</td>
<td>Graphite</td>
<td>LiMn₉₆Ni₃₃O₄ (Advanced layered)</td>
<td>3.7</td>
<td>160</td>
<td>592</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Li-polymer</td>
<td>Li</td>
<td>LiV₃O₈</td>
<td>2.6</td>
<td>340</td>
<td>884</td>
<td>ca. 150 (abandoned)</td>
</tr>
<tr>
<td>Li-S</td>
<td>Li</td>
<td>S</td>
<td>ca. 2.1</td>
<td>584</td>
<td>ca. 1168</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Li-O₂</td>
<td>Li</td>
<td>O₂</td>
<td>ca. 3.0</td>
<td>584 (Li₂O₂), 897 (Li₂O)</td>
<td>ca. 1752–2691</td>
<td>R&amp;D</td>
</tr>
</tbody>
</table>
1.4 Advanced Materials for Electrodes

1.4.1 Benefits and Limitations of Nanostructured Battery Materials

In recent years, there has been a significant rise of nanoscience and nanotechnology because of interesting properties of nanomaterials, which can be superior over properties of the bulk materials [27]. By downsizing to nanoscales, these materials may possess specific properties determined by nanoscopic size (quantum states) and surface, and thereby may demonstrate extraordinary mechanical, electrical, magnetic, optical, biological and chemical properties, among others. The applications are widespread to microelectronics, chemical and biological sensors, catalysis, drug delivery, superconductivity and magnetism, photonic devices, etc. [28–34]. Similarly, the electrochemical performance of battery materials is largely influenced by several factors such as crystal structure [35], composition, particle size [36], etc. Nanostructured materials have progressively gained significance for electrochemical energy storage in Li-ion battery systems despite having several limitations associated with nanomaterials in addition to their benefits [25, 37–39].

The benefits of nanostructured hybrid materials are [25, 40, 41]: (i) They enable (or enhance) electrode reactions to occur that essentially do not occur for materials composed of micrometer-sized particles. (ii) Their reduced dimensions significantly increase the rate of lithium ingress/egress because of the reduced Li\(^+\) transference within the particles. The characteristic time constant for diffusion is expressed as \(\tau = L^2/D\), where \(L\) is the diffusion distance and \(D\) the diffusion coefficient. It is very clear that the time for intercalation decreases with the square of the particle diameter when one changes from micrometer to nanometer. (iii) Electron transport within the particles is also significantly improved by sizing down to nanometer scale, similarly the lithium ion transport. (iv) Higher contact area with the electrolyte can be achieved with the material having higher surface area. The higher surface area of nanomaterials results in high Li\(^+\) ion flux across the interface. This may lead to higher active mass utilization per cycle. (v) For very small particles, the thermodynamics of the electrode reaction significantly tune the electrode potentials for lithium ions and electrons. (vi) The range of composition over which solid solutions exist is often more extensive for nanoparticles. (vii) A better accommodation of strain associated with Li\(^+\) intercalation process and volume expansion can be achieved.

Despite several advantages, the use of nanostructured electrodes also has some demerits which limits the real exploitation of nanostructuration
of the electrode materials on an industrial scale such as (i) the difficulties in synthesis and poor control of dimensions of the nanostructures; (ii) side reactions with electrode/electrolyte are enhanced by the increase in surface area because the electrodes have higher contact area to the electrolyte; and (iii) higher volume is needed. Mostly, the density of the nanomaterials is lower than the density of the same materials in bulk. As a result, the volume increases for a given amount of bulk material. This issue basically affects the volumetric energy density.

1.4.2 Hybrid Materials as Anodes

While talking about anode material for lithium-based battery systems, one automatically takes into account metallic lithium which is known to have high specific capacity (3860 mAh/g). But the use of lithium metal as an anode material automatically raises safety aspects due to the low melting point of lithium, possibility of lithium dendrite growth causing a short circuit, and high reactivity of lithium towards organic electrolytes and water. All these factors are a strong barrier against the practical implication of lithium metal anode [42]. To counter such problems, lithium insertion compounds are proposed as a replacement of pure metallic lithium. Carbonaceous materials, more specifically graphite, can reversibly store lithium ions in the layer spacing [43]. These types of batteries, often called “rocking chair” or “lithium ion” batteries, were first commercialized by Sony in 1991. In such batteries, lithium containing metal oxides are used as a source of lithium ions. Although graphite has maximum capacity of ca. 370 mAh/g, it is still used in many batteries. Since then, there has been intense research to find suitable insertion compounds to gain energy density and rate capability at an affordable cost [44].

The surface of an electrode material plays an important role in achieving good electrochemical properties. At low voltages, organic electrolytes decompose to form a solid electrolyte interphase (SEI) through which lithium ions can migrate in and out. So a uniform, stable and compact SEI layer is essential to achieve high efficiency during cycling. Too weak SEI consumes charge and can affect the electrode performance significantly. Therefore, many research groups have tried to modify the electrode surface to have better charge and mass transfer across the interface. Pan et al. studied the surface modification of natural graphite via diazonium chemistry [45]. By this modification a stable and compact SEI layer was formed. This SEI layer was formed by covalent anchoring of aromatic multilayers of lithium benzoate onto the surface of graphite. The stable SEI so formed on one hand avoids the further degradation of
electrolyte and on the other hand accommodates the volume expansion on repetitive cycling.

In another report by Zhang and coworkers, urchin-like carbon nanostructures were fabricated [46]. These kinds of materials have much higher surface area compared to normal spherical electrode materials. The authors created urchin-like nanostructures by growing carbon nanofibers onto the surface of natural graphite by chemical vapor deposition (CVD) process. The carbon electrodes with urchin-like morphologies are beneficial in terms of better rate capability, stable cycle life and reduced volume expansion in comparison to pristine graphite materials.

The use of lithium cannot be overlooked due to the attractive specific capacity offered by lithium. The dendritic growth issue is still present when graphite is used as anode. A large variety of lithium alloying systems have been reported as a replacement for trivial anodes like graphite and lithium. Si, Ge, Al, Sn, Sb, etc., can store a large amount of lithium in their structure via formation of alloys like Li$_{1.4}$Si, Li$_{4.4}$Ge, LiAl, Li$_{4.4}$Sn, and Li$_3$Sb [39, 47]. The main drawback of such alloying system is their high volume expansion upon lithiation. For instance, Sn and Si can undergo higher than 300% volume expansion on full lithiation. These volume changes result in pulverization of electrode and loss of interparticle contact. As a consequence, the electrochemical performances are significantly hampered after the first few cycles [48–52]. One way of mitigating this problem is to keep some spaces for accommodating large strains caused by volume changes. Rational design of nanostructured electrodes (e.g., nanowires, nanotubes, 3D porous particles, etc.) can solve such problems (see below).

Another approach is to substitute the alloys by lithium containing intermetallics. Some studies are reported to use intermetallic materials by embedding the active lithium alloying element in an inactive matrix. In this way the inactive material can be useful in accommodating huge strains due to volume changes upon lithiation compared to pure metal [53, 54]. Intermetallic electrodes of ternary systems (Li$_x$AB) show good cycle performances. There exists a strong structural relationship between a parent binary intermetallic electrode AB and its lithiated counterpart. For instance, Cu$_6$Sn$_5$, InSb, and Cu$_2$Sb electrode materials have been studied as potential anode materials [55–57]. Due to their relatively low density, these materials possess high energy density on a volumetric basis but they have low gravimetric energy density, and the capacity decay with prolonged cycles is noticeable.

In commercial batteries, the bulk anode materials are limited in terms of specific power performance due to the kinetic inhibition imposed and undergo slow charge/discharge rate. Nanostructured anodes based on Si or
Sn with various morphologies, such as nanowires, porous nanospheres, nanotubes, etc., and nanocomposite anodes, have been formulated to improve the rate capability and durability of lithium-ion batteries. All these efforts are taken in order to shorten lithium ion diffusion distance and to have better control of volume expansion. In some cases surface modification of anode materials by carbon coating have also been implemented to improve electrical conductivity, thereby achieving better electrochemical properties. Various methodologies are implemented to create a carbon coating onto the active materials. These include spray pyrolysis, carbonization of organic precursors, chemical vapor deposition, etc. In some reports, covering of SnO$_2$ nanowires by Sn nanoclusters and conductive coating of TiN onto the surfaces of Li$_4$Ti$_5$O$_{12}$ by ammonia treatment are presented. In some reports the use of stabilizing substances (e.g., SiO$_2$, Al$_2$O$_3$, Nb$_2$O$_5$, or RuO$_2$) onto the surface of TiO$_2$ nanotubes is documented as well. These will be discussed in the following sections.

Since silicon has a high theoretical capacity (ca. 4,200 mAh/g based on Li$_{4.4}$Si alloy stoichiometry), the use of silicon as a replacement of graphite is still attractive [58]. The first and foremost problem of high degree of volume expansion can be alleviated by building several nanostructures. One of them is to size down to nanoscale in particulate form. For example, Kim et al. reported a facile approach to fabricate 3D porous Si particles by thermal treatment followed by wet etching process [59]. In this approach, initial nanocomposite was prepared by mixing butyl-capped Si gels and silica nanoparticles (70:30 wt ratio). It was further annealed at 900 °C under Ar flow. In the subsequent step, the silica fractions were removed by washing with HF solution. The end product (amorphous C-coated Si) contains ca. 12 wt% of carbon. The resulting hybrid having 40 nm thin carbon walls ensures faster charge transport, better intercalation kinetics, high specific capacity as well as excellent cycle stability with prolonged charge-discharge cycles even at high specific currents (99% and 90% capacity retention after 100 cycles at a rate of 0.2 C and 1 C, respectively). This kind of porous nanostructure helps in mitigating the volume expansion effect by serving as “buffer layers.”

Another interesting geometry of nanostructures is nanowires in which aspect ratio of the nanosized material is high. Cui’s group applied a vapor-liquid-solid (VLS) process to grow silicon nanowires directly on stainless steel collector using gold catalyst [60]. This approach has multiple advantages. First, by growing Si nanowires directly onto the current collector good electrical contact is kept with the substrate, and thus attains maximum active mass utilization. Secondly, the available spaces around the nanowires can lead to facile strain relaxation. Thirdly the quasi-ordered
vertically grown Si nanowires result in shorter Li-ion diffusion length, efficient charge and electron transport, and do not need any binder or ancillary components for electrode preparation. Due to these unique structural features, the Si nanowires accommodate a large amount of volume expansion after electrochemical cycling, as clearly seen from the SEM image (Figure 1.4b,c). These materials showed remarkable electrochemical properties with specific capacity close to theoretical limit (Figure 1.4d). Charge and discharge capacities attain stable values after little decay up to 10 cycles with coulombic efficiency close to 70%.

From the discussion above, it is demonstrated that nanoarchitectures like nanowires and porous particulate silicon provide a good degree of cycle stability as anodes for batteries. One of the disadvantages of these systems is increased polarization at higher current rates and capacity decay during prolonged cycling. This might be caused by the limited accessible surface area of the electrolyte which gradually grows the SEI layer. Cho et al.

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**Figure 1.4** (a) Schematic representations of the morphological changes during cycling: Thin film and particles underwent large volume changes leading to pulverization of the electrodes, whereas the Si nanowires directly grown on the substrate are capable of efficient 1D electron transport as well as free spaces around the wires which can accommodate large strains and volume changes. *(Continued)*
proposed the use of silicon nanotubes to avoid such limitations. They used an alumina template to fabricate silicon nanotube structure by reduction of silicon precursor directly inside the template [61]. In doing so, more surface area of the nanotubes is exposed to the electrolyte, which facilitates the access of Li⁺ ions from both exterior and interior surfaces of the nanotubes. To construct a stable SEI during cycling, the silicon nanotubes were coated with carbon. This design of nanotube electrode exhibits superior electrochemical performance, and reversible capacities of 3200 mAh/g were achieved with ca. 89% of the initial capacity retention after 200 cycles at a rate of 1C.

So far we have seen that Si- or Sn-based materials can be considered two of the replacements of carbonaceous anodes due to their high theoretical specific capacity. Tuning the morphology by several approaches enhances the electrochemical properties significantly. Besides the synthetic approaches to get desired nanostructures, there are some case studies where active materials like Si, Sn, etc., are dispersed in carbon-based matrix and

**Figure 1.4 (Cont.)** (b) SEM images of the silicon nanowires before and (c) after electrochemical cycling and (d) cycle performances of the silicon nanowires (Si NW)s at the C/20 rate in comparison to silicon nanocrystals (Si-NC) and graphite. (Reprinted with permission from [60]; Copyright © 2008 Nature Publishing Group).