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"Hierarchical Nanostructures for Energy Devices"

Edited by Seung Hwan Ko (Seoul National University, Korea) and Costas P. Grigoropoulos (University of California, Berkeley, USA), RSC Nanoscience & Nanotechnology Series, No. 35, Royal Society of Chemistry, Cambridge, UK, 2015, 308 pages, ISBN: 978-1-84973-628-2, £165.00, US$270.00, €206.25

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Introduction

"Hierarchical Nanostructures for Energy Devices" is part of the Royal Society of Chemistry Nanoscience & Nanotechnology Series. The editors Seung Hwan Ko and Costas P. Grigoropoulos have published more than 60 articles together with a strong focus on laser processing of nanomaterials and hierarchical surface coatings.

This book highlights the advantages of hierarchical arrangements for energy conversion, and particular attention is paid to nanowire-based materials and their manufacturing techniques. Inspiration is found in nature, where hierarchical structures are present whenever energy transfer processes have to be optimised. Divided into 13 chapters, the book shows relevant applications as well as physical fundamentals and the unique characteristics of nanostructured materials.

Developing and commercialising sustainable energy conversion systems are among the major issues of today's society. In the past decade, research associated with energy devices has concentrated on developing new materials for these applications. As progress has become sluggish, there is a stronger focus on the three-dimensional arrangement of nanostructures.

Hierarchical nanostructure designs in various applications are introduced, together with their advantages compared to zero-dimensional (0D), one-dimensional (1D) or two-dimensional (2D) nanostructures. Typical improvements are the increased surface-to-volume ratio and diffusion optimisation for chemical species. In general, hierarchical structures strongly increase the efficiency of many physical and chemical devices.

Chapters 1 and 2 introduce the topic with fundamental considerations and the physics of nanomaterials. Chapter 3, 'Nanotechnology's Wonder Material' describes carbon nanotubes and their growth process. Chapters 4 to 11 are each dedicated to one application of hierarchical structures: solar cells, fuel cells, thermoelectric devices, piezoelectric energy harvesting, photoelectrochemical cells (PEC), supercapacitors, field electron emission devices and sensors. Chapter 12 shows other applications like hierarchical adhesives, superhydrophobic surfaces and metal nanowire percolation networks. The final chapter summarises the book and gives an outlook on the great potential of hierarchical designs in future applications.

This review focuses on the applications of hierarchical nanostructures rather than the fundamentals of nanotechnology and quantum effects, which however should always be considered when developing nanomaterials. **Figure 1** shows the change in melting temperature of gold nanoparticles compared to bulk material, exemplary for changing properties of nanostructures.

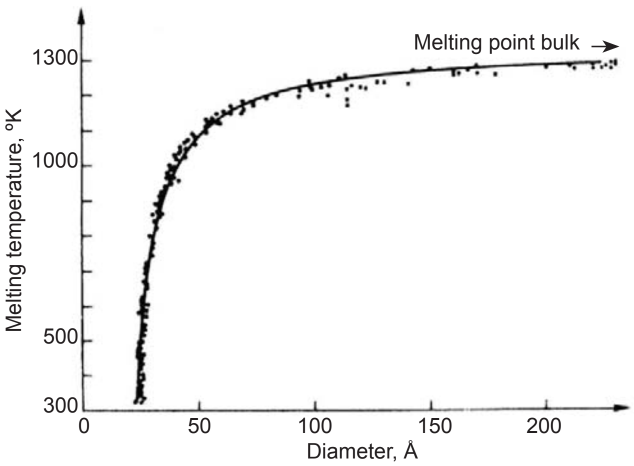

Fig. 1. The graph shows the melting temperature as a function of the gold particle size. The melting point strongly decreases when the particle size falls below 5 nm (Reprinted with permission from (1). Copyright (1976) by the American Physical Society)

Solar Cells

Chapter 4, 'Hierarchical Nanostructures for Solar Cells' examines dye-sensitised solar cells (DSSC, Grätzel cell). Solar cells are typically divided into three generations. The first generation is the widely used crystalline silicon solar cell (mono- or multi-crystalline), which account for more than 90% of the worldwide market. Thin-film solar cells are referred to as the second generation; their market share is around 8%.

A third generation of solar cells is currently on the rise due to its low manufacturing costs and higher flexibility compared to conventional silicon solar cells, namely DSSC or organic photovoltaic (OPV). These solar cells usually involve a platinum catalyst at the counter electrode to utilise a redox reaction, where the yield can be improved by nanostructures (2). The anode is typically made from titanium dioxide (TiO_2) or zinc oxide (ZnO), both of which are wide band-gap semiconductors. The electrons emerging from the reaction of the photosensitive dye with sunlight are transferred into the conduction band of the semiconductor. By using hierarchical TiO_2 or ZnO nanostructures (**Figure 2**) on the anode, the performance can be boosted: higher carrier mobility (nanowire structures lead to less recombination), large surface area to adsorb more dye molecules and capture more sunlight (compare the principle of a tree) and light scattering layers to efficiently capture more sunlight by multiple scattering.

Fuel Cells

In November 2014, Toyota presented the world's first commercially available fuel cell car at the Los Angeles Auto show (4). Fuel cells are seen as one of the most promising future technologies to replace combustion engines due to their much higher efficiency. Besides transportation, fuel cells can also be used in combined heat and power (CHP) or power-to-gas systems to convert and store energy efficiently.

Chapter 5, 'Hierarchical Nanostructures for Fuel Cells and Fuel Reforming', explains the two most common types of fuel cells: polymer electrolyte membrane fuel cells (PEMFC) and solid oxide fuel cells (SOFC). The main advantages of SOFC are their high conversion efficiency and direct conversion of hydrocarbons instead of hydrogen. Furthermore, these systems do not require expensive precious metals on the electrodes. SOFC are mainly used for stationary power generation due to their high operating temperature and the related lengthy heat-up process.

PEMFC is mostly used for automotive applications due to its low operating temperature. These fuel cells usually use hydrogen (anode reaction) and oxygen from air (cathode reaction) to run the system, Equation (i):

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \text{(i)}$$

Another approach is to directly convert alcohols, which leads to potentially higher efficiencies and increased energy densities compared to hydrogen fuel cells. The conversion of a primary fuel into H_2 can be avoided. These types of fuel cells are a sub-category of PEMFC and are usually referred to as direct alcohol fuel cell (DAFC); typically the fuel is methanol or ethanol. However, the complete dissociation from ethanol to CO_2 remains challenging. The complete reaction of methanol to CO_2 is shown in Equation (ii):

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad \text{(ii)}$$

In simple terms, the efficiency of fuel cells can be improved by increasing the catalytic activity of the

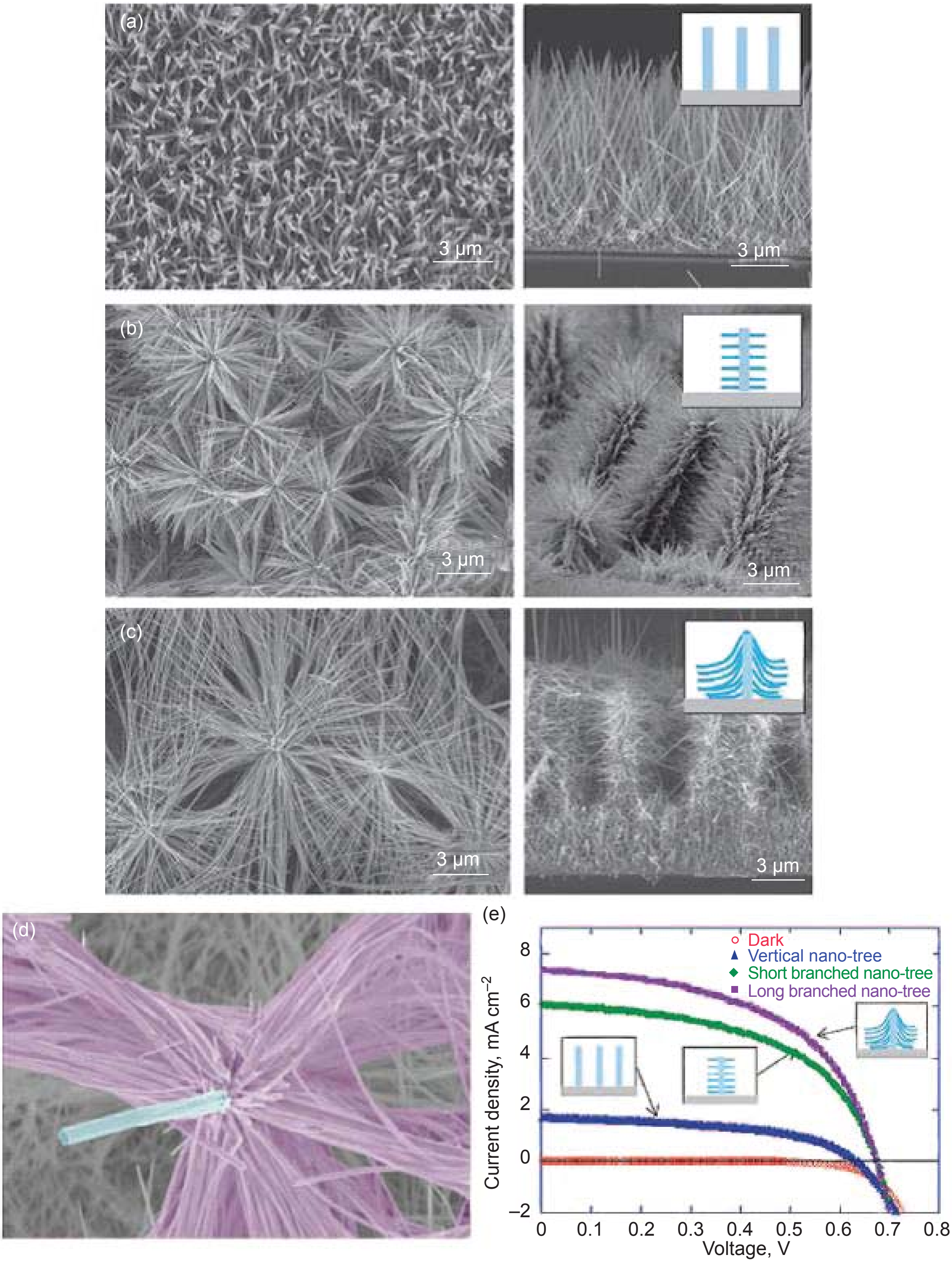

Fig. 2. Scanning electron microscopy pictures of the ZnO nanowire hierarchical nanostructures for DSSC: (a) vertically aligned nanowire carpet; (b) short branched nano weeping willow tree; (c) long branched nano weeping willow tree; (d) pseudo-coloured SEM picture of the long branched nano weeping willow tree. Magenta coloured nanowire represents backbone nanowire after first growth and purple coloured nanowires represent branch nanowires after second growth; (e) current-voltage curve of DSSC made from the long branched nano weeping willow trees of ZnO nanowires (3) (© IOP Publishing. Reproduced with permission. All rights reserved)

electrodes. Hierarchical structures strongly increase the active surface area and hence the number of catalytically active sites. They also enhance the diffusion of the fuel to the electrode site and raise the mass activity since only the top layer consists of the catalytically active material (core-shell principle).

Thermoelectric Materials and Devices

Chapter 6, 'Thermoelectric Materials and Devices', introduces the materials, their applications and explains the benefits of nanostructures in thermoelectric devices.

Thermoelectric devices convert thermal energy into electrical energy and *vice versa*. The effect is based on differences in the Fermi levels at the point of contact of two metals or semiconductors. The Fermi level is a measure of the affinity of the electrons to leave a material: the electrons flow from the material with a higher Fermi level to the material with the lower Fermi level. When a temperature gradient between the two materials creates an electrical potential, it is referred to as the Seebeck effect. The reverse effect, where an electrical potential is applied to create a temperature difference, is called the Peltier effect.

Practical applications are found in power generation, energy harvesting, cooling and heating. Typical materials used in thermoelectric devices are bismuth telluride (Bi_2Te_3), lead telluride (PbTe) and silicon-germanium (SiGe). All these materials are semiconductor alloys, which were found to be more efficient than insulators or metals. The ideal thermoelectric material has a high electrical and a low thermal conductivity.

Besides the pioneering work from the US National Aeronautics and Space Administration (NASA) in the 1950s to power their spacecraft with thermoelectric energy, the biggest commercial success to date is the thermoelectric refrigerator. These are mainly used in small solid state devices in order to cool down the hot spots in a central processing unit (CPU).

The possibility of generating energy from waste heat is another hot topic and is often referred to as energy harvesting. However, the low energy conversion efficiency, which is typically in the range 3% to 10%, is often too low for the required energy.

Nanostructures are being widely investigated to increase the conversion efficiency. The mean free pathway of an electron is in the range of 10 nm, whereas a phonon has a mean free pathway of around 100 nm. When using structures smaller than 100 nm the thermal conductivity is reduced but the electrical conductivity is unaffected thus leading to a more efficient thermoelectric device (5).

Piezoelectric Energy Harvesting

Chapter 7, 'Piezoelectric Energy Harvesting Nanofibers' reports key accomplishments in nanofibre generators composed of polyvinylidene fluoride (PVDF) and lead zirconate titanate (PZT). In the last few years, autonomous piezoelectric power generators have gained much attention due to the miniaturisation of electrical devices and medical implants. Independence from a space consuming battery and eliminating the need to recharge or replace these systems are the main driving forces in developing energy harvesting solutions with piezo materials.

Research is devoted to three different kinds of piezoelectric nanogenerators: film-based, nanowire-based and nanofibre-based. Film-based piezoelectric materials, for example aluminium nitride (AlN) or PZT (6, 7) are commonly applied by thin-film deposition or spin-on methods. Nanowire-based piezoelectric materials are typically made of semiconductors like ZnO, zinc sulfide (ZnS), gallium nitride (GaN) or cadmium sulfide (CdS). By coupling their semiconducting and piezoelectric properties, mechanical strains are directly converted into electrical energy.

Ceramic PZT and polymeric PVDF are the two most promising materials in making piezoelectric nanofibres. The key manufacturing techniques to produce these nanofibres are either near-field or far-field electrospinning.

PZT is known for its exceptional piezoelectric properties; however the manufacturing process *via* electrospinning requires solvents, which lower the density and the overall power efficiency. PVDF has lower piezoelectric performance, but has the advantages compared to PZT of flexibility, biocompatibility, fibre length and weight. High-temperature annealing is also not required for PVDF.

Piezoelectric energy harvesting is still in the early stages of research due to its limited power output. Success will depend on low energy systems and advanced microelectronic technologies. Recent studies with multiple layers of nanofibres have the potential to produce enough energy to drive miniaturised electrical devices. New approaches, using real mechanical actuation sources like the human heartbeat also show promising results for practical uses. Another interesting approach is the support of energy storage systems like batteries, where an energy harvester could potentially enhance the overall lifetime of, for example implantable devices. A possible breakthrough in nanofibres is predicted by the chapter's author in the field of wearable electronics (smart watches, displays), where these devices are directly powered by human motions.

Photoelectrochemical Cells

Chapter 8, 'Hierarchical Nanostructures for Photo-Electro-Chemical Cells' is closely related to the previous chapter on solar cells. The most famous PEC is the aforementioned Grätzel cell (DSSC). Besides photovoltaics, PEC are often used for hydrogen generation by splitting of water.

In the beginning of the chapter the importance of hierarchical arrangements for catalysis and photogenerated electrons is emphasised. The cell efficiency was enhanced by a factor of 4 to 5 through hierarchical structures compared to non-hierarchical nanowire structures. Hierarchical structures enable higher light harvesting as well as a longer effective path for photons to be absorbed by improving scattering and trapping. It strongly increases the chemical reactions and the diffusion of species to the electrode sites. Another important fact is that hierarchical structures are usually constructed by hybridising two or more different materials. For example, the integration of a material with different band structures can increase the range of photon absorption. In terms of catalysis, different materials can trigger different reactions at the same potential and, for example, avoid electrode poisoning.

In the following sub-chapters several fabrication strategies for hierarchical structures are introduced. The chapter finishes with theoretical considerations and examples of hierarchical structures for PEC applications.

Supercapacitors

Chapter 9, 'Hierarchical Nanostructures: Application to Supercapacitors' considers two types of supercapacitors (sometimes referred to as ultracapacitors, **Figure 3**): electrical double-layer capacitors (EDLC) and pseudocapacitors, and the different nanomaterials for supercapacitor electrodes such as activated carbon and carbon-based nanomaterials like carbon nanotubes and graphene. Supercapacitors are electrochemical capacitors that bridge the gap between electrolytic capacitors and batteries. The power density of supercapacitors is significantly higher than that of lithium-ion batteries and the time needed to charge such a device is much shorter. Supercapacitors also allow a large amount of charge and discharge cycles. The main disadvantage, however, is the much lower energy density in supercapacitors.

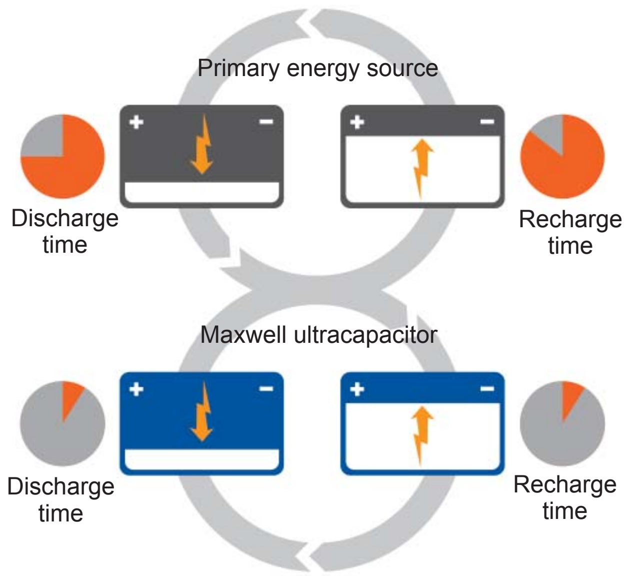

Fig. 3. A comparison between ultracapacitors and primary energy sources like batteries (Courtesy of Maxwell Technologies, Inc)

Supercapacitors usually complement a primary energy source like fuel cells, batteries or combustion engines. Typical applications are power harvesting from regenerative braking systems, power back-up, providing burst power for heavy operations and voltage stabilisation in start/stop systems of automotive vehicles.

Hierarchical nanostructures increase the energy that can be stored by a supercapacitor per geometrical surface area. The hierarchical designs enable these devices to be more compact and efficient.

Sensors

Chapter 11, 'Sensors' introduces three types of sensors: gas sensors, biosensors and optical surface enhanced Raman spectroscopy (SERS) sensors, where hierarchical designs play an important role. Sensors are analytical components that convert physical or chemical input signals into appropriate electronic output signals. In order to increase sensor performance and obtain high surface-to-volume ratios, nanostructures are widely used in chemical sensor applications. Limitations of nanostructures are found in the lower nanometre scale due to degradation and aggregation effects of the structures.

Hierarchical designs increase the surface-to-volume ratio without decreasing the size of the nanostructures. Additionally diffusion and mass transport of chemical species to the surface are improved. This leads to higher sensitivity, better resolution and faster response times of sensor elements. **Figure 4** shows a picture of hierarchical platinum nanostructures, which are applied to increase sensitivity and selectivity of non-enzymatic glucose sensors.

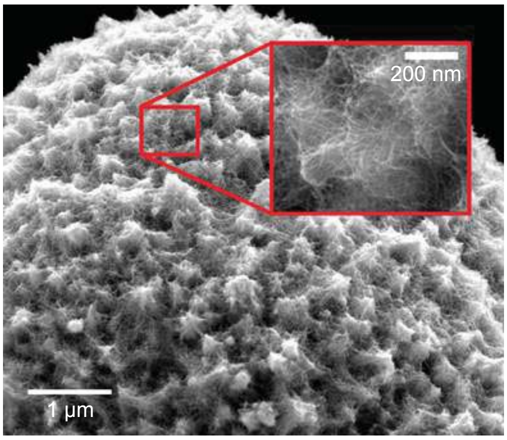

Fig. 4. Hierarchical platinum nanostructures to improve the efficiency of glucose biosensors and other catalytic applications (Image courtesy of the Department of Microsystems Engineering (IMTEK), University of Freiburg, Germany)

Conclusions

The book gives a great introduction into important energy conversion technologies, where the efficiency is increased by using hierarchical nanostructures. Most of the inventions are related to improved electrochemical reactivity, but other areas like piezo and energy harvesting technology are also investigated. In pacemakers or neurostimulators applications, hierarchical (or fractal) structures to increase the energy transfer have been state-of-the-art for more than ten years and the ideas behind this have spread to many other technology areas. The book is ideal for people working in catalysis and/or energy related fields and want to find inspiration for new developments.

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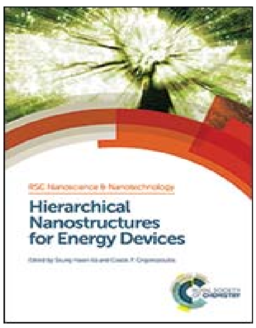

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The Reviewer

Patrick Daubinger works for Johnson Matthey Medical Components in technical sales and business development. He obtained his Masters degree from the University of Freiburg, Germany, in 2013, where he was conducting research on hierarchical platinum nanostructures for biosensor applications. His work on hierarchical nanostructures resulted in various publications and he holds a patent in this field.

