

Nanotechnology for sustainable energy

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ABSTRACT

Nanotechnology is generating a lot of attention these days and therefore building great expectations not only in the academic community but also among investors, the governments, and industry. Its unique capability to fabricate new structures at atomic scale has already produced novel materials and devices with great potential applications in a wide number of fields. Among them, significant breakthroughs are especially required in the energy sector that will allow us to maintain our increasing appetite for energy, which increases both with the number of people that join the developed economies and with our demand per capita. This needs to be done in a way that includes the environment in the wealth production equation as we gather more evidences of the human impact on the climate, biodiversity and quality of the air, water and soil. This review article does not cover in detail all the specific contributions from nanotechnology to the various sustainable energies, but in a broader way, it collects the most recent advances of nanotechnology to sustainable energy production, storage and use. For this review paper, solar, hydrogen and new generation batteries and supercapacitors are described as the most significant examples of the contributions of nanotechnology in the energy sector. The aim of this review article is to present some significant contributions from many research groups who are mainly unconnected and are working from different viewpoints, to find solutions to one of the great challenges of our time, i.e., the production and use of energy, without compromising our environment, from one of the most exciting and multidisciplinary fields, nanotechnology.

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1. Introduction

Nowadays, our main energy sources for human activity are fossil and mineral fuels, nuclear and hydroelectric sources. They are very harmful to environment because they cause global warming, ozone layer depletion, biosphere and geosphere destruction, and

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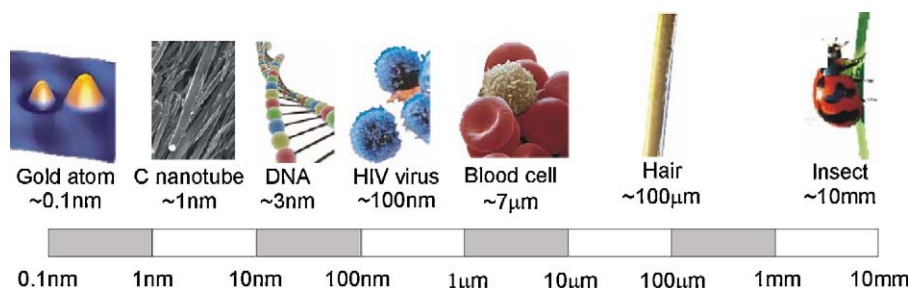


Fig. 1. Length scale and some examples related.

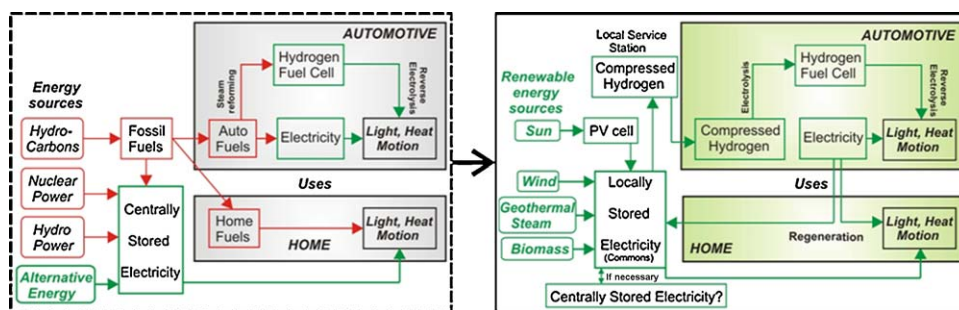


Fig. 2. Evolution of energy state for home and car applications by 21st century (right part) in comparison with current state (left part).

ecological devastation. Consequently, the actual energy production can be considered a harmful industry both in terms of pollution production and environmental impact since the industrial revolution in the 18th century [1–3]. Around 80 wt% of CO₂ emissions in the world are originated by the energy sector.

Contrarily, clean power generation processes are suitable from renewable energy sources such as solar, wind, geothermal, ocean thermal and tidal. Nevertheless, the energy production alternatives are still limited because combining their high cost (manufacturing cost versus efficiency) and the implications on the environment (wildlife cost, hazardous wastes, cooling water, etc.) makes these processes unsuitable [4–7]. As an example, only 7% of the energy employed in the USA in 2005 comes from renewable energy sources (mainly from biomass and hydroelectric sources) versus 8% of nuclear energy and 85% from fossil fuels. Similar data can be found for Germany in 2006, where fossil fuels and nuclear energy cover 56% and 27%, respectively, of the energy for production of electricity, and only 12% corresponds to renewable sources, where both biomass and wind energies have gained special place in the last decade.

Nanotechnology offers, for the first time, tools to develop new industries based on cost-effective and cost-efficient economies, thus seriously contributing to a sustainable economic growth. Nanotechnology is a broad term typically used to describe materials and phenomena at nanoscale, i.e., on the scale of 1 billionth to several tens of billionths of a meter (see Fig. 1). However, it specifically implies not only the miniaturization but also the precise manipulation of atoms and molecules to design and control the properties of the nanomaterials/nanosystems. These properties are completely different than those possessed by the bulk materials, producing custom-made devices with capabilities not found in bulk materials or in nature, or even to replicate some natural processes that have not been currently achieved through synthetic materials.

Focusing on the energy domain, nanotechnology has the potential to significantly reduce the impact of energy production, storage and use. Even if we are still far away from a truly

sustainable energy system, the scientific community is looking at a further development of energy nanotechnologies. In fact, one of the 10 top-level themes of the VII Framework Program of the European Union (FP7) is energy. Accordingly, the research will be focussed on accelerating the development of cost-effective technologies for a more sustainable energy economy. As an example, the qualitative evolution of energy state for home and car applications by 21st century is shown in Fig. 2.

According to the “Roadmap Report Concerning the Use of Nanomaterials in the Energy Sector” from the 6th Framework Program, the most promising application fields for the energy conversion domain will be mainly focused on solar energy (mostly photovoltaic technology for local supply), hydrogen conversion and thermoelectric devices. This review provides an overview of the contribution of nanotechnology to the solar and the hydrogen economies and to sustainable ways to store energy as a step forward a more sustainable use of energy.

2. Solar economy

This section deals with the use of nanotechnology in all the energy-related processes that involve the use of solar radiation as an energy source. Solar energy is free and rather available in many parts around the world. In just 1 year, the sun can provide the earth with 15,000 times more energy than the atomic and fuel energy actually needed during the year. This energy source can be used in different ways: photovoltaic (PV) technology – which directly converts light into electrical current, solar-thermal systems – used in solar collectors, artificial photosynthesis – which produces either carbohydrates or hydrogen via water splitting, the so-called ‘passive solar’ technologies, where building design maximises solar lighting and heating, and even biomass technology – where plants use the solar radiation to drive chemical transformations and create complex carbohydrates, which are used to produce electricity, steam or biofuels. All these energy-related processes and their applications are enclosed in the so-called solar economy (see Fig. 3).

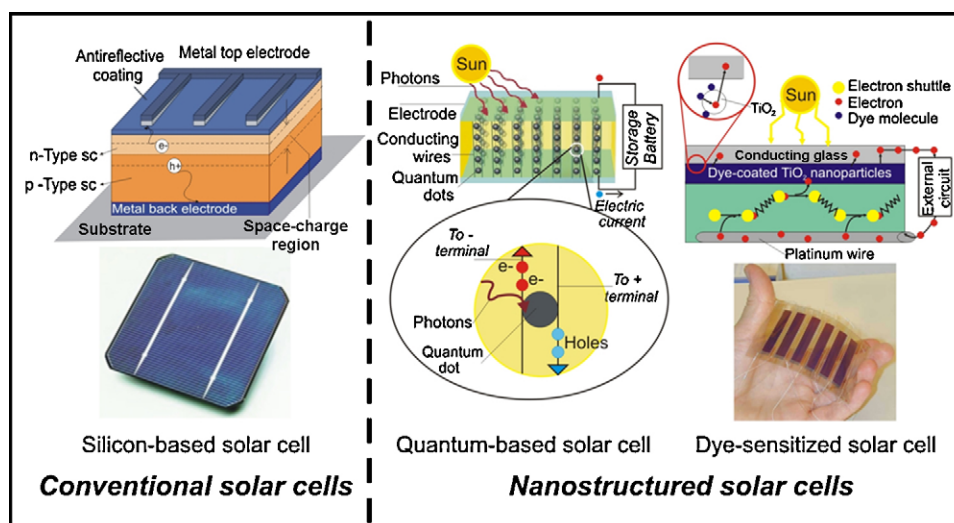


Fig. 3. Evolution of photovoltaic technology: from conventional (silicon-based solar cells) to nanostructured solar cells (quantum-based and dye-sensitized solar cells). Adapted from Refs. [11–14].

Biomass technologies are mostly based on the production of biofuels from agricultural and forest feedstocks specifically grown crops or organic wastes. These biofuels can be further used in fuel cells to obtain electricity. In general, it can be described as the production of energy from the plants. Biomass currently holds a large share (9–13 wt%) of the world's primary energy, probably accounting for around 12,600 TWh a year. In comparison with solar PV, biomass shares a low energy density and relatively low conversion efficiency, but in contrast, biomass has the advantage of being able to store solar energy for use on demand. Current research is focused on the development of new photoactive materials that can be used to directly convert sunlight (or artificial light) into electricity [8]. Also, solar thermal systems find interesting applications in self-cleaning devices, like using heat from solar radiation and storing it in a thermal store ready for use in heating and hot water applications.

2.1. Solar energy for electricity production: photovoltaic technology

Even if solar energy is free and abundant, still, photovoltaic technology represents only around 0.04% of the fuel share of world's total primary energy supply [9]. Continuous advances in PV has produced that its price has fallen down to a tenth in the last 20 years (from 2.00 \$/kWh in 1980 to 0.20–0.30 \$/kWh in 2003). Independent studies suggest that the costs will continue to fall and that it is plausible to envisage costs of around 0.06 \$/kWh by 2020.

PV solar cells are devices which produce electricity from the sun radiation by means of the photoelectric effect, i.e., the photons from light are converted into electrical current. Currently, PV market is based on silicon wafer-based solar cells (thick cells of around 150–300 nm made of crystalline silicon). This technology, classified as the first-generation of photovoltaic cells, accounts for more than 86% of the global solar cell market. The second-generation of photovoltaic materials is based on the introduction of thin film layers (1–2 nm) of semiconductor materials. More specifically, they use thin epitaxial deposits of semiconductors on lattice-matched wafers (see Fig. 3). These cells comprise around 90% of the market space but only a small segment of the global PV market. Unfortunately, although a lower manufacturing cost is achieved, it also involves low conversion efficiencies.

The inclusion of nanoscale components in PV cells is a way to reduce some limitations. First, the ability to control the energy bandgap provides flexibility and inter-changeability. Second,

nanostructured materials enhance the effective optical path and significantly decrease the probability of charge recombination. Fig. 4 shows the evolution of PV technology.

The use of nanocrystal quantum dots [10], which are nanoparticles usually made of direct bandgap semiconductors, lead to thin film solar cells based on a silicon or conductive transparent oxide (CTO), like indium-tin-oxide (ITO), substrate with a coating of nanocrystals. Quantum dots are efficient light emitters because they emit multiple electrons per solar photon, with different absorption and emission spectra depending on the particle size, thus notably raising the theoretical efficiency limit by adapting to the incoming light spectrum.

Arthur J. Nozik reported in 1982 that “a single-threshold quantum-using device in which the excited carriers thermally equilibrate among themselves, but not with the environment, converts solar energy with an efficiency approaching that of an infinite-threshold device” [10]. Quantum well devices such as quantum dots, and quantum wires, as well as devices incorporating carbon nanotubes, are being studied for space applications with a potential efficiency up to 45%. Nowadays, conventional solar cells are mostly built on silicon. Because the cost of silicon keeps growing,

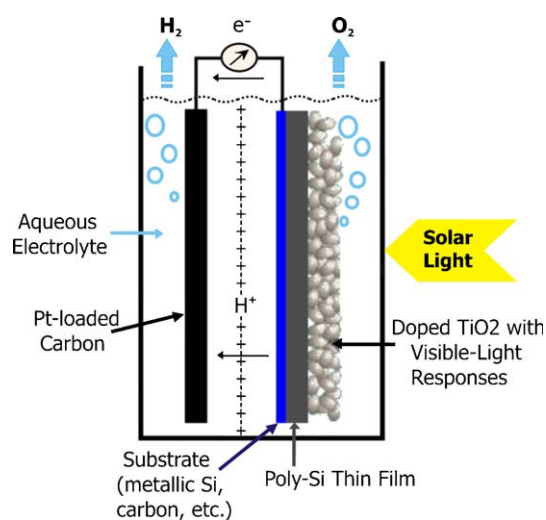


Fig. 4. Schema of solar water splitting system a composite polycrystalline-Si/doped TiO₂ semiconductor thin-film electrode. Adapted from Ref. [76].

this technology will not be the one to bring down the cost of solar generated electricity below 1 \$(/kWh). In contrast, as an example of their attractive future as more efficient solar cells, analogous nanocrystalline quantum dots have close to 40% efficiency.

Another alternative offered by nanotechnology to conventional silicon-based solar cells is the use of dye-sensitized solar cells. O'Regan and Grätzel introduced in 1991 the first nanostructured solar cell [14] namely Grätzel cell or dye-sensitized solar cell, based on dye-sensitized colloidal titanium dioxide films. These films were sandwiched between a transparent electrode acting as anode, which is based on a conducting glass, and a platinum electrode, which acts as a catalytic conductor. An electrolyte is placed between the film and the platinum electrode for transportation of the electrons (see Fig. 3). In these cells, most of the light absorption takes place in dye molecules, the electrons produced are injected on the conduction band of the semiconductor and then, charge separation takes place at the interface between titania and dye molecules thus leading to an increase of light harvesting due to the high surface area of the nanoparticles. Since then, dye-sensitized nanocrystalline solar cells have been fabricated from nanoparticles of several semiconductors [15–22] and different architectures such as nanotubes, photonic crystals or photonic sponges instead of nanoparticles [23,24], which considerably increase their efficiency.

The market of these dye-based nanostructured solar cells, still in research stage, is focused on terrestrial applications, where devices such as photoelectrochemical cells, polymer solar cells and nanocrystal solar cells are being tested. These cells, together with quantum dot technologies, represent the third-generation of photovoltaics.

The newest technologies, commonly named composite photovoltaic technology, mixes conductive polymers or mesoporous metal oxides with high surface areas to increase internal reflections with nanoparticles and, consequently, to make a single multispectrum layer. Several of these layers can be stacked for lower expenses and theoretical efficiency up to 86.5%, unfortunately not achieved in practice. As an example, the substitution of liquid electrolyte in classical dye solar cells by a polymer-based electrolyte or a hole-transporting polymer leads to flexible solar cells with lower costs and longer lifetime. In this sense, the production of organic or hybrid organic/inorganic solar cells has notably increased the potential of solar energy conversion, opening a new approach in this area with a broad range of innovative technologies. Actually, there are some companies working on fourth-generation photovoltaics (i.e., Nanosolar, Nanosys, Konarka Technologies, Inc., etc.) and a great amount of scientific effort is focused on the same approach. However, not enough efficiencies have been achieved yet.

In summary, the goal is to notably increase the efficiency/cost ratio, which can be achieved by using materials with different bandgaps, i.e., multilayers of ultra-thin nanocrystalline materials, new dyes or quantum dots, among others. In fact, one of the priorities proposed by the Royal Society of Chemistry (RSC) in their recent review "Chemical science priorities for sustainable energy solutions" is the development of a new generation of photovoltaic materials based on molecular, polymeric and nano-phase materials [8]. Accordingly, the actual cumulative installed capacity of solar PV is just above 2000 MW. Nevertheless, the growing use of photovoltaic devices and the considerable improvements in both efficiency and price keeps generating a market that grows 25% per year.

2.2. Solar energy for hydrogen production: artificial photosynthesis

PV energy can be used to break water molecules into hydrogen and oxygen via the so-called photocatalytic water electrolysis. It

means that solar energy can be directly stored in the form of hydrogen. Consequently, although the next section deals with the hydrogen economy, we decided to include artificial photosynthesis in this section (solar economy) because of the use of solar radiation as source of energy for hydrogen production.

Water splitting is a broad term used to refer any chemical process in which water is converted into oxygen and hydrogen. Active research in this field includes thermochemical splitting of water with the sulphur-iodine cycle, high temperature electrolysis and thermolysis on defective carbon substrates, thus making hydrogen production possible at temperatures just under 1000 °C, and water splitting by photocatalysis (artificial photosynthesis). The latter also produces electrons to power the electron transport chain in the photophosphorylation step of the photosynthesis. In fact, researchers at National Research Energy Laboratory in US proved that on concentrating sunlight, high temperature and solar flux are achieved, thus, obtaining hydrogen in a cheap and environmentally friendly way, i.e., to split methane into hydrogen and carbon.

Water splitting by photocatalysis, also known as artificial photosynthesis, is being actively researched, motivated by a demand for cheap hydrogen which is expected to rise with the new hydrogen economy. Nanotechnology is the tool that can make possible the production of hydrogen from solar energy in a clean, environmentally friendly and low-cost way using photocatalytic water splitting. For this purpose, a variety of semiconductor nanoparticulated catalyst systems based on CdS, SiC, CuInSe₂, or TiO₂ can be used [25–28], the last one being the most promising candidate since it fulfils the above-mentioned requirements. However, this technology is still in the research stage due to the cost associated with its low conversion efficiency. When nanostructured titania is used as catalyst, recombination of hydrogen and oxygen to produce water takes place. Moreover, the bandgap of TiO₂ is around 3.2 eV, which means that only UV light can be used for this purpose. Finally, a rapid recombination of photo-generated electron/hole pairs has also been reported in the literature [28].

Consequently, a lot of work is being carried out to reduce these drawbacks shown by TiO₂ nanoparticles. Leung and co-workers [28], in their comprehensive article "A review and recent development in photocatalytic water splitting using TiO₂ for hydrogen production", summarizes the different approaches for making solar photocatalytic hydrogen production feasible. These approaches can be classified in two broad categories, the addition of chemical additives and the modification of photocatalyst. The addition of chemical additives covers, on one hand, electron donors, which are sacrificial reagents or hole scavengers that react irreversibly with the valence band holes avoiding the recombination and thus increasing the quantum efficiency of the electron/hole separation. Although inorganic ions such as S²⁻/SO₃²⁻ [29] Ce⁴⁺/Ce³⁺ [30] or IO₃⁻/I⁻ have been used [31–33], the most common electron donors are hydrocarbons. The hydrogen production enhancing capability of those has been ranked by Nada et al. [34] in the following order: EDTA, methanol, ethanol and, finally, lactic acid. At the same time, the use of carbonate salts as chemical additives suppresses the backward reaction, because the carbonate species consume the photo-generated holes in adequate quantities, thus significantly increasing both hydrogen and oxygen production [35–40]. The second group, based on photocatalyst modification techniques, wraps the modification of TiO₂ by means of: (i) *noble metal loading*, which can inhibit charge recombination. Platinum is the most common metal but is expensive, other efficient and lower cost metals are Ni, Cu, Ag, Au, Pd and Rh [41–49]. Recently, platinum ion-exchanged titania nanotubes have been synthesized by Khan et al. [50] showing their high catalytic activity on

the stoichiometric hydrogen production in both water and aqueous methanol. (ii) *Ion doping*, including transition metal and rare earth metal ions [51–55] as well as anions like nitrogen and sulphur [56–62] that can expand the photo-response to visible region, (iii) *sensitization*, including dye sensitization [63–67] and coupling of semiconductors, and (iv) *metal-ion implantation*. From these modification techniques, the most effective methods are metal-ion implantation [68–73] and dye sensitization. Moreover, in dye sensitization techniques, described in the previous section, the additional use of sacrificial agents allows to regenerate the dyes, which, in some cases, can enhance the hydrogen production rate even more [62,74,75].

As an example, Nakato and co-workers [76] have synthesized a thin film electrode made of a polycrystalline-Si/doped TiO₂ semiconductor. The system consists on a particulate doped TiO₂ thin film supported on the surface on inexpensive polycrystalline Si thus allowing to the absorption of short- and long-wavelength parts of the solar light, respectively. Consequently, this combination can yield a high solar-to-chemical conversion efficiency of more than 10%, which results in a very promising approach to efficient and low-cost solar energy conversion.

3. Hydrogen economy

Hydrogen itself is a way of transporting and storing energy from the source to the end user. The main renewable sources of energy available in nature, such as solar, wind, geothermal or tidal, need to be transformed, mainly as electricity, to be efficiently transported; unlike hydrogen that needs to be produced. As aforementioned, hydrogen can be produced from renewable energies and conveniently converted into electricity mainly using fuel cell technology. For these reasons, hydrogen, like biofuel, can be considered as an energetic vector, and therefore the core of an energy economy on its own (Fig. 5).

One of the most attractive features of hydrogen is that the only product of its combustion is water. Consequently, by combining both the production of hydrogen from renewable energies with its use in fuel cells, a new pathway emerges leading to a fully environment friendly energy system, with the subsequent reduction in carbon emissions and the dependency on fossil fuels.

3.1. Hydrogen production

Although hydrogen production, storage and transformation into electricity are not new, we are still lacking efficient methods to use this light gas in a way that makes the future hydrogen economy viable.

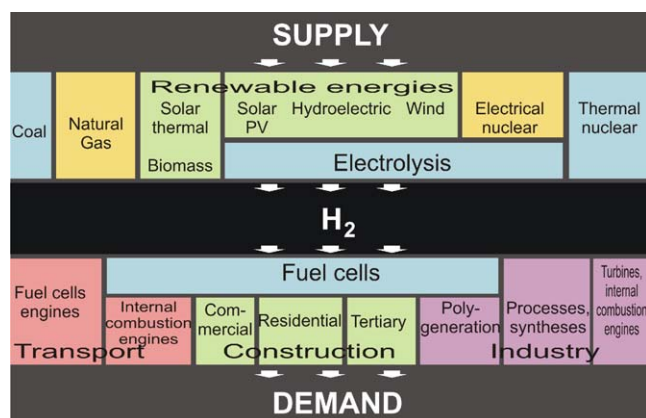


Fig. 5. Summary of hydrogen economy. Upper part: production. Lower part: uses. Adapted from Ref. [77].

Since hydrogen is rather a vector than a source, it is as clean as the way used to produce it. At present, most of the global production of hydrogen is done by steam reforming of natural gas. This method has a 70–80% efficiency with the additional drawback that it also produces CO₂. Because of its low cost, it is likely that this process will provide the bulk of hydrogen over the next 30–50 years until more cost effective sustainable solutions are developed [78].

Renewable energy sources such as photovoltaic, wind, biomass, hydro-, and geothermal can provide clean and sustainable electricity. However, only around 5% of the commercial hydrogen production comes from renewable sources of energy, mostly through water electrolysis [28]. The production of hydrogen through the electrolysis of water and the use of that hydrogen in a fuel cell to produce electricity during times of low power production or peak demand, or the use of hydrogen in fuel cell vehicles are clean alternatives with efficiency higher than 70%. The problem is that it consumes a significant amount of electricity, which considerably increases its costs, thus avoiding its commercialization.

Consequently, the future of hydrogen production is envisioned towards its direct production from renewable sources thus avoiding all, electrical, heat and mechanical losses. These include solar, thermal, wind energy, thermochemical cycles or biomass gasification. Besides these, water splitting by nanophotocatalysis [28–75], which has been described in the previous section, is one of the most promising and attractive methods for direct hydrogen generation from a primary renewable energy source both economically and technically [8,87]. Unfortunately, according to the Royal Society of Chemistry report aforementioned, the replacement of hydrocarbon-based hydrogen production processes by new, clean and sustainable new pathways is not expected before year 2035.

3.2. Hydrogen transport and storage

Most available hydrogen storage systems are quite inefficient. For example, pressure vessels for its storage as pressurized gas are bulky and heavy, hydrogen storage as liquid fuel requires very low temperatures, the gravimetric storage density is low, etc. Consequently, a great part of the energy produced is lost due to these shortcomings. According to the Department of Energy of the United State of America, a gravimetric storage density of 6.5 wt% and 62 kg H₂/m³ is the threshold for a sustainable hydrogen storage system [79].

For these reasons, a great effort is being carried out on increasing the capacity of existing hydrogen storage systems as well as to develop in parallel good hydrogen transport devices. Currently, hydrogen adsorption, either chemisorption or physisorption, is considered to be one of the most efficient ways to store this light gas.

Chemisorption techniques have the drawback of binding hydrogen too tightly, and, in addition, the storage system must operate above ambient temperatures (>400 K) for discharge, while recharge is highly exothermic. In contrast, most physisorption techniques suffer from the opposite problem, appreciable adsorption can only be achieved at very low temperatures (<100 K).

Carpets and Peschka [80,81] suggested the use of activated carbon materials for hydrogen storage testing several carbon structures at cryogenic temperatures. Since then, these materials have been widely studied in the past decades. Its main drawback is their wide pore size distribution and their inadequate pore size, which allows only small efficiency storage as most of the pores present higher sizes than those corresponding to hydrogen atoms or molecules [82,83]. Values of around 48 g H₂ per kg of carbon at –186 °C under a pressure of 6 MPa have been reported [84]. That

was a consequence of the synthesis procedure, i.e., thermochemical processing. In both cases, hydrogen adsorption kinetics can be improved by reducing the size of the adsorbing material to the nanosize range [84–86].

Mesoporous materials exhibit controlled pore size, shape and architecture and large surface areas, in many cases, in excess of 1000 m²/g. In this way, high hydrogen adsorption capacities can be obtained by using nanomaterials that meet the requirements of high surface area, optimized pore size and shape, high storage capacity, controlled desorption and safety.

Novel alternatives to efficiently store hydrogen include the physisorption of it on activated carbon with a controlled pore size distribution and the right surface chemistry. Other porous alternatives to activate carbon include various nanostructures [87,88] such as carbon nanotubes, graphite nanofibers and zeolites, just to cite a few. Carbon nanotubes – both multi-wall (MWCNT) [89–91] and single-wall (SWCNT) carbon nanotubes [92–95] – have been suggested as suitable candidates for hydrogen storage [87,88,96,97].

The first publication on hydrogen adsorption by using SWCNT dates back to 1998 and it was reported by Ye et al. [92]. The authors analysed the effect of the synthesis procedure by comparing laser-generated with those purified. Different mechanisms of both physisorption and chemisorption of hydrogen on nanotubes have been suggested to describe these processes [98–101]. Interestingly, Nilsson and co-workers [95] have recently reported the hydrogenation of single-walled carbon nanotubes (SWCNTs) using atomic hydrogen as the hydrogenation agent. These authors have proved that the maximal degree of nanotube hydrogenation depends on the nanotube diameter, and for the diameter values around 2.0 nm, nanotube–hydrogen complexes with close to 100% hydrogenation exist and are stable at room temperature. This corresponds to 7 wt% of hydrogen storage capacity, which is higher than the one proposed as the goal for 2010 by the U.S. DOE [79]. Other carbon materials, like graphite particles, have also been proposed as materials with great potential for hydrogen storage in the short-term (6–10 years) [8].

Both zeolites and mesoporous materials with various nanostructures, have been tried as adsorbents for hydrogen storage both at room temperature and cryogenic conditions and at different pressures. Although their storage capacities are still too low (1.6 wt% at 77 K at 36 bar in MCM-41) the addition of metal oxide dopants and incorporation of organic groups in the silica walls (organosilicas) are good leads to increase the hydrogen storage capacity of these materials [102–104].

New mesoporous materials with hierarchical structures and controlled pore size are needed as more efficient hydrogen adsorbents. One of the most promising alternatives is the use of biomolecules to produce bio-inspired porous silica. For example, the addition of lecithin to a conventional synthesis of MCM-41 produces a radically new hierarchical nanostructure with concentrically arranged pores assembled in a hexagonal array [105].

Noteworthy, Danilov et al. [106] have recently synthesized porous carbon nanofibers proving its ability to efficiently store hydrogen and, consequently, making it an alternative to hydride metals for its use in batteries. After activation with KOH, nanofibers showed a surface area of 1700 m²/g. Further modification of the activated nanofibers improves the discharge characteristics of the negative electrode. Moreover, nanomaterials with high hydrogen storage capacities were obtained by Kim and Park [107] through the modification of highly porous carbon nanofibers (surface area of 2000 m²/g) with Ni nanoparticles.

Currently, other hybrid materials based on coordination polymers, known as metal–organic frameworks (MOF) and used as scaffolds for metals, are receiving a lot of attention and being proposed as highly efficient hydrogen storage materials [108].

Taking into account both safety and cost, metal/alloy hydrides are good candidates between the more conventional methods for hydrogen storage (cryogenic liquid, compressed gas, and metal hydrides). In these systems, hydrogen atoms are located in the lattice of the metals or the alloys thus achieving a storage capacity similar to that corresponding to liquid hydrogen or pressurized hydrogen, depending on metal/alloy mass. Some examples of alloys employed for the storage are ZrV₂, Mg₂Ni, FeTi or LaNi₅, while for metal hydrides, MgH₂ is known as a high temperature hydride with a gravimetric storage of 0.07 kg of H₂/kg of metal [109].

The three important factors in the storage of hydrogen in metal/alloy hydrides are: their hydrogen storage capacity, the number of times the storage can be done reversibly, and the kinetics of hydrogen absorption/desorption. All three are intimately related to the alloy microstructure. In this sense, powder particles with nanostructured features have some clear advantages. Magnesium, aluminium or Mg–Al alloys in the form of bulk materials with nanograins, or Mg–Ni alloys (nanocrystalline powders) are envisaged as some of the potential optimal materials for hydrogen storage in 6–10 years time [8]. For example, Mg–Ni alloys have conventional sizes but their nanostructured interior confers efficient hydrogen absorption without requiring a long activation treatment. It is also lightweight and a relatively low-cost material. Another feasible pathway is the doping of metal hydrides with titanium nanoparticles. For example, sodium aluminium hydrides (NaAlH₄) doped with titanium nanoparticles does not show disadvantages for a sustainable and low-cost hydrogen transport and storage. The only problem is that the market of Ti production is small and the technology for storage system is not yet developed.

A widely used technique to maintain the small size of nanoparticles is the use of porous supports. Conventionally, the metal is loaded on the surface of porous materials once the latter has been prepared. Recently, we have described a novel method to incorporate metal nanoparticles in high quality mesoporous materials by functionalization of Pd nanoparticles with trialkoxysilane terminal groups [110]. These modified nanoparticles are incorporated into the porous structure of the silica by copolymerization with tetraalkoxysilanes in the presence of a surfactant. In this way, highly dispersed nanoparticles are obtained, enhancing the hydrogen adsorption performance of silica supported palladium.

Other chemical hydrogen storage materials tested are based on boranes. The formation of hydrides like LiBH₄ or metal hydrides such as LaNi₅H_{6.5} suffers from binding hydrogen too tightly. Nevertheless, the combination of boron and nitrogen seems to be potential solid state hydrogen storage materials for on-board applications. Brown et al. [111] used scaffold having 6–7 nm wide channels to hold ammonia borane (NH₃BH₃) in the nano-phase of silica mesoporous. After adding a saturated solution of ammonia borane, the hydrogen release kinetics at lower temperature was enhanced when embedded in a scaffold.

3.3. Hydrogen conversion: fuel cells

Different technologies have already been developed for hydrogen conversion. For example, hydrogen can be used both in engines and in fuel cells. Engines can burn hydrogen in the same manner as gasoline or natural gas, while fuel cells are electrochemical devices that transform the chemical energy of hydrogen into electricity. Since electrochemical reactions are more controlled and efficient than combustion at generating energy, fuel cells are among the most attractive and promising green technologies [109]. In a hydrogen fuel cell, hydrogen combines with oxygen without combustion in an electrochemical reaction (reverse of electrolysis) and produces direct current electricity. The

Table 1
Operating principle of the different types of fuel cells.

Fuel cell (FC) type	Anode reaction	Cathode reaction	Operating temperatures
Alkaline FC (AFC)	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$	75 °C
Polymer Electrolyte Membrane FC (PEMFC)	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	80 °C
Phosphoric Acid FC (PAFC)	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	200 °C
Molten Carbonate FC (MCFC)	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	650 °C
Solid Oxide FC (SOFC)	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$1/2O_2 + 2e^- \rightarrow O^{2-}$	500–1000 °C

different types of hydrogen fuel cells are classified depending on the electrolyte as: *Polymer Electrolyte Membrane Fuel Cell* (PEMFC), *Phosphoric Acid Fuel Cell* (PAFC), *Alkaline Fuel Cell* (AFC), *Molten Carbonate Fuel Cell* (MCFC) and *Solid Oxide Fuel Cell* (SOFC). The operating principle and temperature operation range for each one is illustrated in Table 1.

The main barriers to overcome are the high manufacturing costs due to the expensive materials used for the fabrication of electrodes (bipolar plates), electrolytes, membranes and catalysts (especially because of the platinum price). In this regard, the contribution of nanotechnology can be summarized as to considerably reduce the cost by improving the efficiency. More than 300 papers focused on nanotechnology applied to fuel cells have been published in 2008 in scientific journals, which points out the extraordinary impact of this subject [112].

PEMFC fuel cells have traditionally attracted the attention of the automobile industry for zero-emission vehicles, and power generation industries for both home and electronic applications. They are envisioned as clean and efficient energy systems, but there are two main components that prevent its commercialization, the high cost of Pt/support electrodes and the low performance of the membrane, mainly at high temperatures.

The cost of the electrodes could be considerably reduced by significantly decreasing both the amount and the durability of Pt catalyst needed for the application. This cost is also directly related with the support and its influence on catalytic activity. Several examples of the contribution of nanotechnology to this point can be found elsewhere. Wang et al. [113] have synthesized carbon nanotubes-based electrodes for PEMFC fuel cells. The authors found that MWNT can be used as catalyst support instead of carbon powder thus allowing for the reduction of the Pt used in a 2/3 times in comparison with the traditional PEMFC fuel cells. Rajalakshmi et al. [114] compared both catalytic activity and membrane performance of Pt/nanotitania electrodes with traditional Pt/C electrodes. A higher performance and durability was observed for membrane electrode assemblies, while the electrodes showed higher thermal stability and higher catalytic activity. Shao et al. [115] in his recent review "Novel catalyst support materials for PEM fuel cells: current status and future prospects" summarized the most promising candidates for catalyst support in nanotechnology. Tungsten carbides are presented as the anode alternative while diamond materials, both conductive doped and nanodiamonds, are preferred for its use as cathode. At the same time, carbon nanotubes and carbon nanofibers, mesoporous carbon and conductive oxides such as SnO_x/ITO , Ti_xO_y , TiO_2/ITO or WO_x are envisioned to be used in commercial electrodes, both cathode and anode. For most of them, doping is the main strategy to further improve these nanomaterials for its application as supports of catalyst for membrane fuel cells.

Other approaches are based on the preparation of metallic nanostructured electrocatalysts using different self-assembled templates as structure-directing agents, which are later removed. Choi et al. [116] employed a silica-based template containing nanosized holes and bimetallic Pt–Ru nanowire networks to be grown inside the holes, for its further use as anodes of Direct

Methanol Fuel Cells (DMFC). Later, a new family of nanocatalysts based on three-dimensional Pt and Pt–Ru nano-structures with interconnected holes has been developed by Chien and Jeng [117] by using the same concept. The nanocatalysts have been synthesized by growing the metal networks in the voids of the layers formed by the self-assembly of polymer nanospheres. Thus, although they have been tested as cathode (Pt) and anode (Pt–Ru) of DMFC, these electrodes have potential applications on membrane fuel cells in general, i.e., DMFC and PEMFC. Recently, mesoporous Pt nanowire array has been prepared by using hexagonal self-assembled Ti/Si template showing potential applications for portable fuel cells [118].

Finally, concerning the membrane performance, the use of nanoscale hydrophilic inorganic materials in electrolytes inorganic lithium salts to improve hydrogen ion conductivity of the membrane at high temperatures (the inorganic materials present high affinity to water and the salts work in the right temperature range) is one of the contributions of nanotechnology. Other approaches are based on the use of capillary fuel cells instead of flat cell membranes, which are considerably cheaper than the latter ones and, consequently, their more compact construction leads to three to six times higher power density and permits the saving of the bipolar plates of the electrodes. In addition, the capillary fuel cells production is fully automated and its miniaturization is readily possible for portable applications. Additionally, some examples are pointed out. Mecerreyes et al. [119] reported the synthesis of nanoporous films of polybenzimidazole's (PBI) doped with phosphoric acid. PBI doped with phosphoric acid has already been used as electrolyte for methanol fuel cells [120], nevertheless, the introduction of nanoporosity in PBI improves the membrane performance by enhancing its conductivity. Abbaraju et al. [121] have recently modified a conventional Nafion membrane with titania and tin dioxide nanoparticles obtaining an enhanced performance, mainly at high temperatures. Nanostructured membranes have been constructed by deposition of silica nanoparticles on sulfonated poly(aryl ether sulfone) for proton and ethanol fuel cells [122].

On the other hand, some advances in SOFC are also being done thanks to nanotechnology. Recently, nanostructured SOFC have been fabricated by Ignatiev et al. [123] as ultra-thin films supported on metallic foils dramatically decreasing the operating temperature in comparison with traditional SOFC. These nanostructured fuel cells showed efficiencies higher than 50% and maximum power density of 140 mW/cm² at 575 °C.

4. Sustainable electricity storage

Many of the sustainable energy alternatives herein described produce (e.g. PV solar cells) or require (e.g. water splitting) electricity. Therefore novel more efficient ways to store electricity are very much needed in the way to a more sustainable production, transformation and use of energy. Some of the most important energy storage systems are batteries and capacitors. The contribution of nanotechnology to hydrogen storage has been explored in the previous section devoted to the new hydrogen storage.

4.1. Rechargeable batteries

Most of the active research in this field is currently focused on rechargeable lithium batteries. This market actually accounts for around 10 billion dollars per year. As compared with the aqueous batteries, the Li-ion chemistry leads to an increase of 100–150% on storage capability of energy per unit weight and volume. Nevertheless, some disadvantages arise, related to low energy and power density, large volume change on reaction, safety and costs. The aforesaid shortcomings can be reduced (or are being reduced) by the application of nanotechnology to the field of rechargeable batteries. Actively research in nanobatteries points out the use of nanomaterials for both the electrodes and the non-aqueous electrolyte.

Recently, Sony Corporation has commercialized a tin-based anode nanobattery, trade named Nexelion. It is the first time that a nanoalloy replaces the graphite electrode [124,125]. In the same line, Toshiba Corporation has announced a breakthrough in lithium-ion batteries that makes long recharge times a thing of the past. The company's new nanobattery can recharge 80% of a battery's energy capacity in only 1 min, approximately 60 times faster than the typical lithium-ion batteries in wide use today, and combines this fast recharge time with performance-boosting improvements in energy density (see Fig. 6).

Noteworthy, several recently published reviews are focused on the use of nanotechnology for rechargeable lithium ion batteries [126–129]. There is a general consensus on the key role that nanotechnology plays for future battery applications and its market adoption. The main achievements pointed out by the authors are listed below.

Electrolyte conductivity increases up to six times by introducing nanoparticles of alumina, silicon or zirconium to non-aqueous liquid electrolytes. Most efforts have been focused on solid state electrolytes, solid polymer electrolytes (SPE). Poly(ethylene oxide)-based (PEO-based) SPE received most attention since PEO is safe, green and lead to flexible films. Nevertheless, polymers usually have low conductivity at room temperature and, depending on SPE compositions, their interfacial activity and mechanical stability are not high enough. In this sense, nanocomposite polymer electrolytes could help in the fabrication of highly efficient, safe and green batteries. For example, the introduction of ceramic nanomaterials as separators in polymer electrolytes increases the electrical conductivity of these materials at room

temperature from 10 to 100 times compared with the corresponding undispersed SPE system. TiO_2 , Al_2O_3 and SiO_2 and S-ZrO₂ (sulphate-promoted superacid zirconia) have been used for this purpose, founding that the introduction of S-ZrO₂ led to the best performance [127]. Another example is the formation of a crystalline complex by dissolution of lithium salts (LiXF_6 , being X phosphorus, tin or antimony) in low molecular mass and high polydispersity PEO. The crystalline structure of PEO makes the ionic conductivity. Moreover, the short chains and polydispersity of PEO cause a high defect concentration that considerably enhances this conductivity [127].

Some effective approaches regarding the nanostructuring of the anode for rechargeable lithium batteries involved the substitution of LiC_6 electrode, with storage capacities of 340 mAh/g, by graphite nanoparticles and carbon nanotubes. These had been further replaced by nanosized metal oxides (i.e., titanium, aluminium, vanadium, cobalt, tin as well as silicon oxides) mostly in the form of nanotubes and nanowires thus avoiding both the lithium deposition and some safety problems. In this way, a similar storage capacity to the traditional graphite electrodes has been achieved [130–132]. For instance, the synthesis of silicon nanowires further anchored to the substrate acting as current collector led to Chan et al. [133] to obtain a charge capacity of ca. 3000 mAh/g during 10 cycles after the first one, losing around one third of capacity in the first cycle.

Other approaches include the use of nanoscaled metal alloy composites to increase the life cycle of nanocomposites through the reduction of volume change caused during the formation of the alloy. As an example, Li_4Si has the highest gravimetric energy density, 4200 mAh/g, of all lithium alloys, volume changes during alloy formation are around 400%. In this sense, the most promising results are: (i) the construction of a nanoarchitected anode in a variety of nanoforms (i.e., silicon nanopillars done by etching of bulk materials); (ii) the fabrication of intermetallic electrodes as nanoparticles through displacement reactions by deposition of nanoparticles on nanostructured copper rods (i.e., Ni_3Sn_4 for $\text{Li}_{4.4}\text{Sn}$); or (iii) the use of amorphous nanostructured alloys (titanium, vanadium, chrome or cobalt in amorphous tin phase) [134–137].

Finally, the nanostructuring of the cathode has been satisfactory explored with transition-metal dioxides, LiFePO_4 , LiMn_2O_4 and vanadium oxide (V_2O_5). Manganese oxides are suitable candidates for both environmental and economical reasons. In bulk, LiMn_2O_4 shows the best performance. Different nanostructures have been tested for this purpose. Nanoparticles are less preferred since they should be coated to avoid sinterization and increasing conductivity. Nanotubes and nanowires of vanadium oxide or lithium intercalation host including manganese oxides have shown a good performance. Wang et al. [138] proved that storage and rate capability of V_2O_5 depends on the morphology finding that core-shell nanocable showed better performance than nanotubes or nanorods. Other architectures involve the use of mesoporous silica templates as well as liquid crystalline electrolytes to synthesize ordered mesoporous cathodes, which could arrange the electrolyte inside the pores thus notably increasing the battery performance. Some examples are mesoporous LiMn_2O_4 , LiCoO_2 or NiOOH .

4.2. Supercapacitors

Electrochemical capacitors (ECs), also named supercapacitors and ultracapacitors, store electrical energy, like batteries, but using a different mechanism. While batteries do it chemically, ultracapacitors store electricity physically, by separating the positive and negative charges. Since the discovery of ECs [139], these devices have attracted considerably less attention than batteries as energy storage devices. Nevertheless, thanks to both the con-

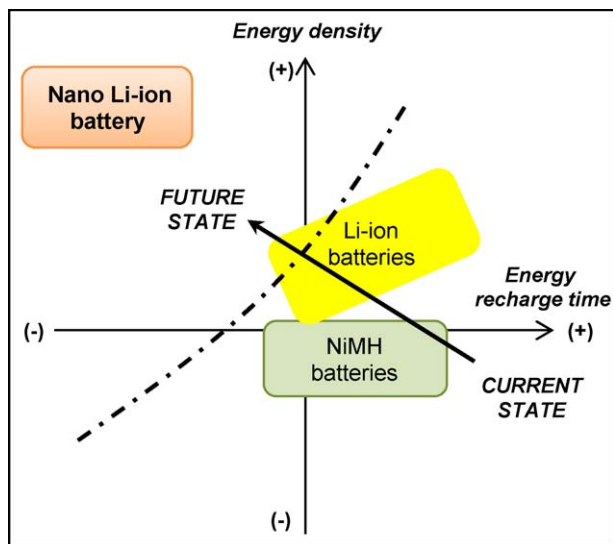


Fig. 6. Comparison in terms of energy density and recharge between conventional and new batteries, pointing out the excellent performance of Toshiba's new rechargeable lithium-ion battery.

tribution of nanotechnology and the better understanding of charge storage mechanisms (ion behaviour in small pores) the interest on ECs has noticeably increased recently. The number of publications in scientific journals during the last 3 years has been multiplied by a factor of 6 as compared with year 1998 [112].

The drawbacks of classical capacitors can be summarized in three main points: (i) the high cost of premium performance electrodes due to the miniaturization, (ii) the large requirements for long cycle life (around 10^5 cycles) and (iii) their low efficiency—materials that combines both high surface area with a low resistivity are required. The main determining factor for power density and maximum power output is the surface area of each electrode that makes up the capacitor. The use of nanostructured materials dramatically increases this surface area (e.g. up to $1000 \text{ m}^2/\text{g}$ of carbon). Moreover, in contrast to capacitors, supercapacitors utilize a small volume of electrolyte, which interacts with the surface of each electrode to store charge. Consequently, they offer a unique combination of high power and high energy performance parameters.

There are three types of ECs: pseudocapacitors, also named redox supercapacitors, electrochemical double layer capacitors (EDLCs) and hybrid capacitors. The nanomaterials typically used are metal-based nanocomposites and conductive polymers, carbon-based nanostructures and hybrid inorganic/organic nanocomposites, respectively.

EDLCs are the most common devices currently. Current technologies are mainly based on blending porous materials (like activated carbon) with a conductive additive (like graphite or metals). A transition from activated carbon electrodes to carbon-based nanostructures is being done in order to improve the performance of these devices. Carbon nanotubes (CNTs) form an open mesoporous network which allow the solvated ions to easily access to the interface of the double layer. Similar results have been observed for carbon nanofibers. Several examples have been reported for example by Obreja in his recent review [140]. In summary, the capacitance of CNT exceeds that corresponding to traditional activated carbons only if these are functionalized, e.g. controlled oxidation of their surface, or addition of some impurities [140–144]. Higher specific power, higher specific capacitance and higher conductivity can be achieved by the blending of activated carbon with small quantities of CNTs, which can be further improved by doping with metal oxides or conductive polymers, but currently, the cost is too high as to be economically feasible for the industry. Another approach includes the use of carbon aerogels, which could lead to an improvement in both capacitance and cyclability due to their low electronic charging and ionic resistance [141,145]. Similar characteristics have been proved for fullerene-like carbon nanoparticles [145].

Finally, the use of nanotemplates (i.e., mesoporous silica, zeolites, etc.) to synthesize nanostructured carbon has been also explored for carbon electrodes [146–153]. We are exploring a radically innovative approach to fabricate, via supramolecular templating, carbon materials that combine high specific surface area and electrical conductivity without the need of conductive additives or binding materials for mechanical strength. Precise control over complex architectures at both the nano- and the macroscale is achieved with this technique (Fig. 7) [154]. The as-synthesized carbon nanofoam (CNF) exhibits, in addition to high surface area and good electrical conductivity, excellent chemical, mechanical, and thermal stabilities. All these properties make this carbon material an excellent alternative for supercapacitor electrodes. When tested by cyclic voltammetry, CNF exhibits specific capacitances over 120 F A/g or 100 F A/cm^3 , powder densities of 10 kW A/kg and energy densities of 10 Wh A/kg .

On the other hand, similarly to rechargeable Li-ion-based batteries, the nanostructuring of materials for pseudocapacitors

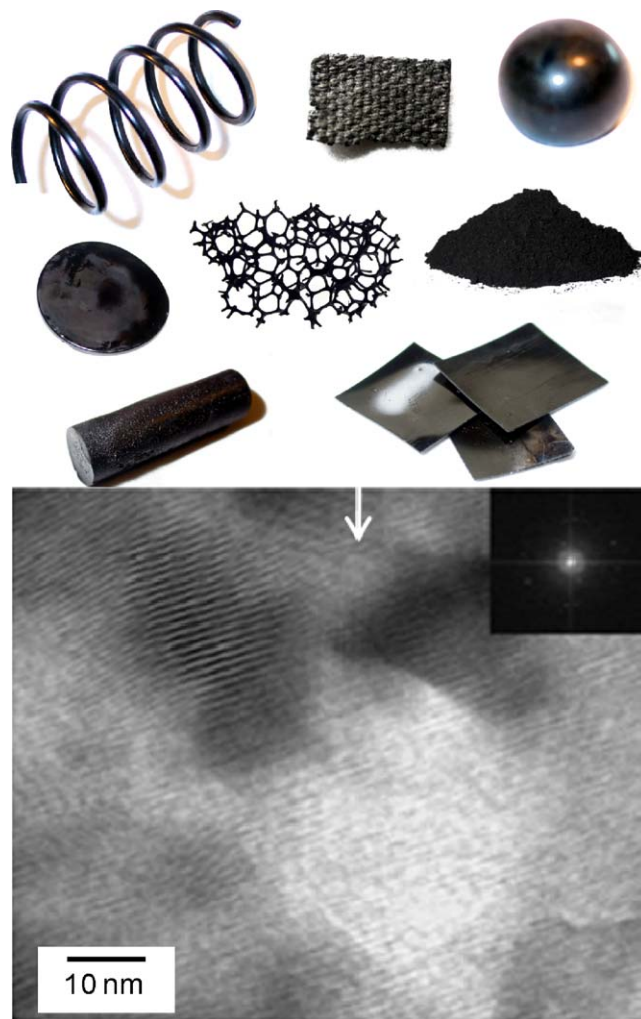


Fig. 7. Some examples of nanostructured carbon materials with different structures prepared via supramolecular templating and TEM image for nanostructured carbon thin films, similar to that described in Ref. [154].

could considerably improve their performance since the stored charge is directly related with the electrode surface [155]. Thus nanomaterials used for the nanostructuring of the cathode in Li-ion batteries are good candidates for redox supercapacitors. In this sense, transition-metal oxides such as V_2O_5 , RuO_2 or MnO_2 and transition-metal nitrides can be used in form of nanoparticles or nanofilms. As aforementioned, the synthesis of nanotubes and nanowires of vanadium oxide could improve the performance since the agglomeration of nanoparticles is avoided with these morphologies.

Finally, hybrid supercapacitors based on nanotechnology combine the advantages of Li-ion batteries with those typically found in EDLCs since they are composed by a negative electrode, which is a battery-like electrode acting as energy source, and a positive electrode made of carbon-based nanostructures, similar to that used in EDLCs, acting as power source. Both electrodes are in the same cell with an electrolyte, which could be either aqueous or organic. For the capacitor electrode, i.e., the positive one, nanomaterials, typically carbon nanotubes, can be used in the development of ultracapacitors that will have important uses for many walks of life – from communication to transportation – since they dramatically increase this surface area (i.e., up to $10^3 \text{ m}^2/\text{g}$ of carbon). Regarding the negative electrode, the contribution of nanotechnology has defined two ways of research: (i) electrodes consisting on an inorganic nanomaterial capable of lithium intercalation in contact with water as electrolyte (i.e., $\text{Li}_4\text{Ti}_5\text{O}_{12}$),

and (ii) pseudocapacitive electrodes based on metal oxides nanomaterials. Consequently, their characteristics and alternatives are the same that already pointed out in batteries and supercapacitors. The main contributions of nanostructured materials in the near future to hybrid supercapacitors should focus on increasing the energy density of these devices.

5. Conclusion

Sustainable energy production, transformation and use are very much needed to maintain the readily and cheap access to energy to the growing and increasingly demanding world population while minimizing the impact on the environment. The novel multifunctional materials produced from the broad and multidisciplinary field that is nowadays called nanotechnology are critical to overcome some of the technological limitations of the various alternatives to the non-renewable energies.

Thanks to better nanomaterials, PV solar cells are increasing their efficiency while reducing their manufacturing and electricity production costs at an unprecedented rate. Hydrogen production, storage and transformation into electricity in fuel cells are being benefited from more efficient catalysts for water splitting, better nanostructured materials for higher hydrogen adsorption capacity and cheaper simpler fuel cells.

To transit from a carbon-based energy economy to others more sustainable, many technological breakthroughs are needed, not only in the energy production (we tend to focus too much on the energy source) but also in the transportation, transformation, storage, and final use of the energy. In all these steps we face significant scientific and engineering challenges. In many cases, the materials we have today are not able to provide the solution at the efficiency required at a feasible cost. Thanks to the unprecedented control over the size, structure, and organization of matter that many nanotechnologists around the World are getting, novel materials with unique properties are already contributing to overcome some of these challenges. This is an excellent example of how better material science can contribute to the well-being of present and future generations.

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