Reviews

UDK 66.017/.018:697.514 doi: 10.7251/COMEN1302145P

NANOTECHNOLOGY MATERIALS FOR SOLAR ENERGY CONVERSION

Svetlana Pelemiš^{1,*}, Igor Hut²

¹ University in Istočno Sarajevo, Faculty of Technology Zvornik, Karakaj 34, 75400 Zvornik, Republic of Srpska, B&H
² Innovation Centre of Faculty of Mechanical Engineering, University of Belgrade, Serbia

Abstract: Nanotechnology is a common word these days, although only 15 years ago it was a quite obscure term used almost exclusively in scientific community. It is a fact that nanotechnology is widely present today with numerous applications, especially regarding novel materials. This is a technology that draws a lot of attention not only in the scientific community but also among investors, governments and industry. There is a great deal of expectations connected with it and especially, amongst others, concerning sustainable energy production. This paper briefly explores some of possible implementations of nanotechnology for new and improved energy conversion methods, considering a need for this to be done without doing harm to our environment. Focus is placed on advanced photovoltaic and hydrogen production technology.

Keywords: nanotechnology, materials, solar energy, photovoltaic, solar cells.

1. INTRODUCTION

Modern science is very interested in low dimensional systems, with the dimensions order of even several nanometers, which in practical application show their outstanding properties in all areas (electronics, optoelectronics, high temperature superconductivity...). A need to minimize dimensions is imposed by several mutually dependent and intertwined requirements of modern civilization, probably crucial for its further survival and sustainable development, which can be reduced to energetic and ecological requirement.

Use of fossil fuel-based technologies is probably one of the main causes for continuous increase in pollution and concentration of greenhouse gases. Renewable sources must have a higher contribution in the energetic matrix when it comes to providing more energy available for humanity in a short period, as it has low environmental impact. [1]

An interest in the conversion of environmentally-friendly energy sources led to the development of several devices that benefited from continuous evolution in several fields of research, which can result in new materials for already developed devices. For instance, the performance of direct methanol fuel cells, a well-known technology was improved due to the development of nanomaterials especially designed for the energy conversion process; their evolution allows the use of light to boost the process through a synergic arrangement. The use of sunlight has been gaining much attention due to its abundance. For instance, it is possible to supply human energy needs until 2050 by covering only 0.16 % of the earth surface with 10 % efficiency solar devices [1].

This article provides an insight in how nanoscience and nanotechnology may contribute to the development of more efficient and sustainable energy systems. Nanotechnology is a broad term typically used to describe materials and phenomena at nanoscale, i.e., at the scale of 1 billionth to several tens of billionths of a meter (Fig.1). However, it specificallz implies not only miniaturization but also precise manipulation of atoms and molecules to design and control the properties of nanomaterials/ nanosystems. Nanomaterials exhibit distinct sizedependent properties in the 1-100 nm range where quantum phenomena are involved. This is one of the main reasons why nanotechnology has a significant impact on energy conversion and storage. These properties are completely different from the properties of bulk materials, producing custom-made devices with capabilities not found in bulk materials or in nature [2].

^{*} Corresponding author: alannica@gmail.com

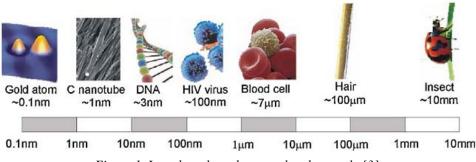


Figure 1. Length scale and some related example.[3].

2. NANOTECHNOLOGY FOR SOLAR ENERGY SYSTEMS

In near future nanotechnology may contribute toward efficient and low-cost systems for generating, storing, and transporting energy. Materials and structures that are designed and fabricated at a nanoscale level as well as thin films can offer a potential to produce new devices and processes that may enhance efficiencies and reduce costs in many areas, such as solar photovoltaic systems, hydrogen production, fuel cells, solar thermal systems and energy saving technologies like low e-coatings and electrochromic devices for smart windows. It is often overlooked that a portion of contribution of renewable energy sources in the total energy budget will come from all possible forms of applications and sources and to be effective it must be combined with energy saving technological breakthroughs [4].

Solar energy is free and readily available. It is also a truly renewable energy source (at least from human perspective). The total solar energy absorbed by Earth's atmosphere, oceans and land masses is approximately 3,850 zettajoules (ZJ) per vear. In 2002, this was more energy in one hour than that used by the world in one year [5,6]. Photosynthesis captures approximately 3,000 exajoules (EJ) per year in biomass [6]. The amount of solar energy reaching the surface of the planet is so large that in one year it is about twice as much as will ever be obtained from all of the Earth's non-renewable resources of coal, oil, natural gas, and mined uranium combined [7]. 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 maximizes solar lighting and heating, and even biomass technology – where the solar radiation is used by plants for driving chemical transformations and creation of complex carbohydrates, used to produce electricity, steam or biofuels. All these energy-related processes and their applications are a part of the so-called solar economy [3].

Intensive research is currently carried out in the domain of light harvesting. A (solar) light harvesting sequence generally involves several steps, namely light absorption, charge separation, and energy extraction in the form of electricity or by inducing a chemical reaction, for instance to produce chemical fuel such as hydrogen. The chemical reaction pathway is essentially what happens in photosynthesis of green plants, where one of the produced energy-rich "fuels" is ATP, used in a number of bimolecular and cellular reactions. Nanotechnology is expected to have a profound impact on new or improved schemes for light harvesting [8], exemplified e.g., by a strong interest in nanoscience for solar photovoltaics.

2.1. Nanotechnology for photovoltaic

PV solar cells enable production of electricity by means of photoelectric effect. 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 introduction of thin film layers (1–2 nm) of semiconductor materials. More specifically, thin epitaxial deposits of semiconductors on lattice-matched wafers are used. Unfortunately, although a lower manufacturing cost is achieved, it also involves low conversion efficiencies.

One of the possible ways to reduce or avoid the mentioned limitations is to include nanoscale components in PV cells. An ability to control the energy bandgap provides flexibility and interchangeability, while the introduction of nanostructured materials enhances the effective optical path and significantly decreases the probability of charge recombination. Evolution of PV technology is illustrated in Fig.2.

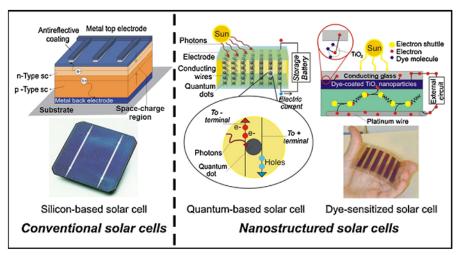


Figure 2. Evolution of photovoltaic technology: from conventional (silicon-based solar cells) to nanostructured solar cells (quantum-based and dye-sensitized solar cells) [3].

The use of nanocrystal quantum dots [9], i.e. nanoparticles usually made of direct bandgap semiconductors, leads 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. Conventional PV solar cells are mostly built on silicon and have low efficiency. Since the cost of silicon keeps growing, silicon-based technology will not be the one to bring down the cost of solar generated electricity below 1\$/kWh. With PV system based on nanocrystalline quantum dots, the efficiency close to 40% can be theoretically reached. It is easy to imagine a bright future for cost-effective PV electricity generation.

There is a lot of interest in photocatalyzed decomposition of pollutants at various titanium surfaces. Electron transfer reactions are at the base of these photoinduced processes and were also the subject of one of theoretical contributions. Water purification, pollutant degradation, and hydrogen production were the most targeted applications. The principle of photocatalysis is to use the energy of photons in the visible to near-UV range (ca. 1.5–5 eV) to generate active chemical species driving a surface chemical reaction on a photocatalyst. The typical scheme of photocatalysis involves harvesting of light photons in a semiconductor (most commonly

 TiO_2), and subsequent conversion of these photons to electronic excitations, which then induce the desired chemical reaction on a semiconductor surface [10].

2.2 Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSCs) invented by Michael Grätzel became a very popular alternative to silicon-based solar cells because of their great potential to convert solar energy into electric energy at low cost. This cell can be made from cheap materials such as inorganic and organic dyes which do not need to be highly pure as required for silicon wafer. The operating principle of a solar cell is presented in Figure 3. Here we can see that inorganic dye is anchored to a wide bandgap mesoscopic semiconductor. The popular dyes used for DSC are ruthenium bipyridine and zinc porphyrin complexes. For a mesoscopic semiconductor, TiO₂ (anatase) is widely used in the solar cells; however, other alternative metal oxides such as ZnO, SnO₂ and Nb ₂O₅ can be used [11]. After excitation of dye by light, the dye releases its electron from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital). This photoelectron then swiftly transfers from the LUMO of the dye to the conduction band of semiconductor TiO2. The semiconductor carries the electron to photoanode which passes the electron to the platinized counter electrode [11].

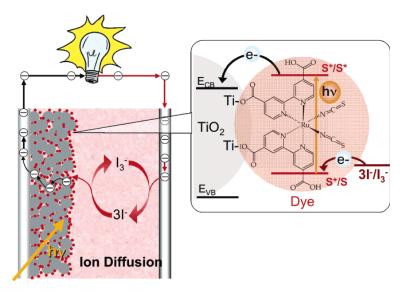


Figure 3. The dye sensitized solar cell [11].

2.3. Organic Solar Cells

The seminal work of Heeger, Shirakawa and MacDiarmid (winners of 2000 Nobel Prize in Chemistry) opened a new window to use organic conducting polymer for a wide range of semiconductor devices such as light emitting diodes, solar cells, and thin film transistors [12,14]. The motivation behind developing organic materials for solar cell is to reduce the cost related to raw materials and manufacturing. Solarmer and Konarka Power Plastic, two US based companies, to produce flexible polymer solar cells for many applications including portable electronics, smart fabrics, and integrated solar cells. The power conversion efficiency of 8.6% for the polymer-based single solar cells , has been reached in laboratory conditions, as reported by several groups [11]. Two well-known challenges associated with donor-acceptor based polymer solar cell are that these polymers cannot cover the sun's broad spectrum due to their comparatively high bandgap (1.6 - 2.0 eV) and that they have lower carrier mobility [11].

2.4. Solar water splitting (artificial photosynthesis)

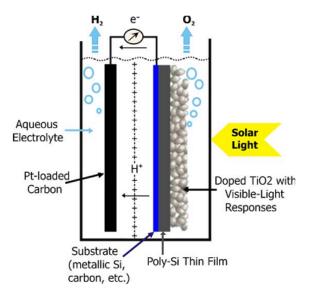
Solar energy can be used to break water molecules into hydrogen and oxygen via the so-called photocatalytic water electrolysis (see Fig.4). This means that the solar energy can be directly stored in form of hydrogen. Water splitting the by photocatalysis, also as artificial known photosynthesis, is being actively researched, motivated by a demand for cheap hydrogen which is expected to give rise to new hydrogen economy [15,16].

Visible light at wavelengths shorter than 500 nm has enough energy to split H_2O into hydrogen and oxygen. However, water is transparent in this visible range and does not absorb energy. The combination of a light harvesting system and a water splitting system is therefore necessary to implement the use of sunlight to split water. Wide-band gap semiconductor nanoparticulated catalyst systems with limited light absorption in the visible spectrum (e.g. TiO₂) have been used for this purpose [17].

Nanotechnology approaches to improved light harvesting, described in the photovoltaics section above, are applicable also to water-splitting case and other opportunities to circumvent this limitation. Basically, photovoltaics and photoinduced water splitting differ in how the excited electrons (e–h pairs) are used – to drive a current or to drive a chemical redox reaction.

Apart from limited light absorption in the visible range, current systems for photoelectrochemical water decomposition also suffer from fast electron–hole recombination and concurrent low efficiencies. Deposition of small noble metal islands (<5 nm) has for a long time been known to enhance the photocatalytic activity for titania-assisted water splitting due to charge separation across the metal–semiconductor interface. More recent approaches to improving visible-light harvesting processes and/or increasing the probability of excited charge carriers reaching the surface (where the actual water splitting reaction takes place) include carbon-doped titania nanotube arrays, single-walled carbon nanotubes, and nanostructured hematite films, which all have been

shown to be capable of water splitting [2].



*Figure 4. Graphic presentation of solar water splitting system composite polycrystalline-Si/doped TiO*₂ *semiconductor thin-film electrode.* [16]

3. SOME MATERIALS FOR PHOTOVOL-TAIC SOLAR SYSTEMS

Many materials have been tested, such as Ge, Si, GaAs, InP, GaP, ZnS, BN as well as contemporary photovoltaic material TiO₂, with which the efficiency of approximately 12% was determined. After laying an ultrathin coating of TiO₂ on the upper surface, the efficiency of about 18% was determined. After the analysis of different collector materials with ultrathin (nanometer) coatings of 10^{-7} m order, it was shown that TiO₂ was by 50% more efficient compared to the same material but without ultrathin coatings [18].

Silicon is most commonly used for solar cell manufacture. Depending on the structure of silicon, solar cells can be divided into solar cells of monocrystalline, polycrystalline and amorphous silicon.

Solar cells from monocrystalline silicon consist of p-type semiconductor, about 300 μ m thick, pn junction and the n-type semiconductor, about 0.2 μ m thick, metal contacts (electrodes) and antireflection layer. Commercial solar cells of monocrystalline silicon have the efficiency 15% while the laboratory solar cells have the efficiency of 24%.

Solar cells from polycrystalline silicon consist of polycrystalline p-n junction, antireflection layer and electrodes. Commercial solar cells from polycrystalline silicon have the efficiency of 14% while the laboratory solar cells have the efficiency of 18%.

In addition to silicon, other materials are used to produce solar cells such as gallium arsenide (GaAs), cadmium telluride (CdTe), copper-indiumdiselenide (CuInS₂ or CIS) copper-sulfide/cadmiumsulfide (Cu₂S/CdS), etc. [19].

4. CONCLUSION

Solar energy is being explored as an alternative and sustainable route to fill the gap for the rising demand for energy. The given examples illustrate only a fraction of actual and potential use of nanotechnologies in advanced solar energy production. Novel multifunctional materials produced trough utilization of nanotechnology offer great improvements in all domains of total energy system, such as transportation and storage of energy. To predict where and how nanotechnology will have the largest impact is not possible. In a short term it will probably have a more visible influence on the existing energy system through introduction of materials with better performances and higher energy efficiency, on fuel conversion schemes etc. In future nanotechnology will most likely play a major role in the development of truly sustainable solutions like advanced PV systems. For sustainable energy production, nanotechnology is one of the fastest growing research fields today. Hopefully it

will help the development of sustainable energy economy leading to a future in which energy, environmental, and security problems created by the consumption of fossil fuels will be solved once and for all.

5. REFERENCES

[1] F. L. de Souza and E. R. Leite (eds.), *Nanoenergy*, DOI: 10.1007/978-3-642-31736-1_2, _ Springer-Verlag Berlin Heidelberg 2013

[2] I. Hut, D. Ninković, Nanotechnology implementations for sustainable energy production – current trends and future developments, IEEP'11, Proceedings (CD-ROM, VII Energetska efikasnost – oblasti / Energy efficiency – different areas), Kopaonik, Serbia2011.

[3] E. Serrano, G. Rus, and J. García-Martínez, *Nanotechnology for sustainable energy*, Renewable and Sustainable Energy Reviews, Vol. 13–9 (2009) 2373–2384.

[4] P. Yianoulis, M. Giannouli, *Thin Solid Films and Nanomaterials for Solar Energy Conversion and Energy Saving Applications*, Journal of Nano Research Vol. 2 (2008) 49–60. Online available since 2008/Aug/07 at www.scientific.net © (2008) Trans Tech Publications, Switzerland, doi:10.4028/www.scientific.net/JNanoR.2.49

[5] O. Morton, *Solar energy: Silicon Valley sunrise*. Nature, Vol. 443 (7107) (2006) 19–22.

[6] N. S. Lewis, and D.G. Nocera, *Powering the planet: Chemical challenges in solar energy utilization*. Proceedings of the National Academy of Sciences, Vol. 103–43 (2006) 15729–15735.

[7] *Exergy (available energy) Flow Charts.* [cited 2011 02.06.]; Available from: http://gcep.stanford.edu/research/exergycharts.html.

[8] K. R. Catchpole, *Nanostructures in photovoltaics*. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 364–1849 (2006) 3493–3503.

[9] R. T. Ross and A.J. Nozik, *Efficiency of hot-carrier solar energy converters*. Journal of Applied Physics, Vol. 53–5 (1982) 3813–3818.

[10] M. S. A. Abdel-Mottaleb, Frank N⁻uesch, Mohamed M. S. A. Abdel-Mottaleb, *Solar Energy and Nanomaterials for Clean Energy Development*, Hindawi Publishing Corporation International Journal of Photoenergy, Volume 2009, Article ID 525968, 2 pages doi:10.1155/2009/525968

[11] M. A. Halim, *Harnessing Sun's Energy* with Quantum Dots Based Next Generation Solar Cell, Nanomaterials, Vol. 3 (2013) 22–47; doi:10.3390/nano3010022.

[12] D. Braun, A. J. Heeger, *Visible light emission from semiconducting polymer diodes*. Appl. Phys. Lett. Vol. 58 (1991) 1982–1984.

[13] S. E. Shaheen, R. Radspinner, N. Peyghambarian, G. E. Jabbour, *Fabrication of bulk heterojunction plastic solar cells by screen printing*, Appl. Phys. Lett. Vol. 79 (2001) 2996–2998.

[14] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M; Nielsen, K.Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, et al., Two-dimensional charge transport in self-organized, high-mobility conjugated polymers, Nature, Vol. 401 (1999) 685–688.

[15] M. Dresselhaus, M. V. Buchanan, and G. Crabtree, *The Hydrogen Economy*, Physics Today; Vol. 57–12 (2004) p. Medium: X; Size: 39.

[16] S. Takabayashi, R. Nakamura, and Y. Nakato, *A nano-modified Si/TiO2 composite electrode for efficient solar water splitting*. Journal of Photochemistry and Photobiology A Chemistry, Vol. 166(1–3): (2004) 107–113.

[17] M. Ni, et al., A review and recent developments in photocatalytic water-splitting using *TiO2 for hydrogen production*. Renewable and Sustainable Energy Reviews, Vol. 11(3) (2007) 401–425.

[18] D. Lj. Mirjanić, J. P. Setrajčić, *Nanotechnological materials for solar cells*, UNITECH III, Gabrovo 2012, 440–442.

[19] T. M. Pavlović, D.Lj. Mirjanić, D. D. Milosavljević, D. S. Pirsl, *Application of contemporary materials in solar energetics*, UNI-TECH IV, Gabrovo 2013, 371–376.

ନ୍ଧର

НАНОТЕХНОЛОШКИ МАТЕРИЈАЛИ ЗА КОНВЕРЗИЈУ СУНЧЕВЕ ЕНЕРГИЈЕ

Сажетак: Нанотехнологија је ријеч која се у данашње вријеме често користи, иако је само прије 15 година то био доста нејасан појам који се користио готово искључиво у научним круговима. Чињеница је да је нанотехнологија данас свуда присутна са својим бројним примјенама, нарочито у погледу нових материјала. То је технологија која привлачи доста пажње не само у научној заједници већ и међу инвеститорима, владама и индустрији. У њу се полажу велика очекивања, нарочито, између осталог, у погледу производње одрживе енергије. У овом раду укратко се истражују неке могуће примјене нанотехнологије за нове и побољшане методе конверзије енергије, с обзиром да је то потребно учинити не штетећи животној средини. Нагласак је нарочито стављен на напредну технологију производње фотоволтаика и хидрогена.

Кључне ријечи: нанотехнологија, материјали, соларна енергија, фотоволтаици, соларне ћелије.

(38)