Review

UDK 620.91:66.017-022.53 doi: 10.7251/COMEN1402172T

SOLAR ENERGY MATERIALS AND SYSTEMS FOR AN AESTHETIC AND SUSTAINABLE FUTURE

Yiannis Tripanagnostopoulos¹, George Leftheriotis¹, Alexandros Vradis¹, Dimitrios Anastasopoulos¹, Nikolaos Spiliopoulos¹, Panagiotis Priftis¹, Ioannis Manariotis², Panagiotis Lianos³, Elias Stathatos⁴

 ¹ University of Patras, Physics Department, 26504 Patra, Greece
 ² University of Patras, Civil Eng. Department, 26504 Patra, Greece
 ³ University of Patras, Chem. Eng. Department, 26504 Patra, Greece
 ⁴ Technological-Educational Institute of Western Greece, Electr. Eng. Department, Patra 26334, Greece

Summary: Renewable energy sources have an important role in global energy demand in the 21st century. New investigations in solar energy materials and solar energy systems offer new opportunities for a sustainable future, adapting local energy needs, environmental protection and aesthetics. Solar energy can be used almost everywhere, with visible materials and systems. In this paper, an overview of new solar energy materials and systems is presented, focused on the work that is performed in the Laboratories of the University of Patras and of the Technical Educational Institute. The research activities of these Laboratories are on nanotechnology, biotechnology, microalgae hydrogen production, photovoltaics, smart glazings and materials for solar energy systems. A brief description of the achieved improvements on these solar energy materials is included, where energy performance and system cost play an important role together with aesthetics, considering their wide application in the future.

Keywords: Solar Energy materials, Photovoltaics, Electrochromics, Nanomaterials, Nanometals, Microalgae, Colored Solar Collectors, Fresnel lenses, PV/T collectors.

1. INTRODUCTION

In the 21st century, there are three main global problems: potable water quality and availability, higher energy demand and degradation of the environment with climatic changes. Regarding energy, the increase of human population with the higher quantities of industrial and agricultural products reduce conventional energy sources and degrade the environment due to CO₂ emission and greenhouse heating effect. Today, the world energy consumption is about 150.000 TWh, with the new Renewable Energy Sources (RES) covering only 2%. Considering 12% of hydro, it is estimated to be at about 30% in 2013, with 7% for RES and 13% for the hydro. The energy consumption by energy sector is: 40% in buildings, 30% in industry and agriculture and 30% in transportation, with solar energy that provides electric power by PV parks and installed PVs on building roofs and facades and heat, mainly for hot water and space heating, by solar thermal collectors.

In order to adjust to the energy demand in the next years, solar energy is going to fill the gap and new technologies will be applied. In this frame, the energy targets for 2020 are critical requirements to achieve the energy saving and CO₂ reduction. A change in the energy mix that is planned for the next decade, aims to prepare for the exit from the "kingdom" of hydrocarbons and the entrance to the new "landscape" of renewables. This transition is not easy and several difficulties should be overcome, although energy production by RES is promoted by support policies. In addition to energy saving and adjusting energy demand, aesthetics and water waste recycling could also be considered as new challenges for the next decade and to this end, solar energy contemporary materials and systems play an important role.

Buildings are the promising sector for a wide application of solar energy while the combination with passive systems of improved technologies are ideal to achieve the energy targets, functionality,

aesthetics and environmental as well as economical issues. The use of technologies and materials with suitable design and management for the building needs of heating, cooling and lighting, energy consumption of buildings can be decreased by about 50%. In this way, the required amount of photovoltaics for the electricity for a building could be reduced, and therefore resulting in lower system cost. Novel solar applications as Building Integrated Solar Thermal Systems (BISTS), Building Integrated PhotoVoltaics (BIPV), Smart Windows, "cold" materials, electrochromic, photochromic and thermochromic sheets, selective coatings, photocatalytic coatings, Phase Change Materials (PCM), new modes for hydrogen production, microalgae bioreactors, etc., are expected to be widely applied, contributing to the reduction of conventional energy sources.

Due to their visibility, solar energy materials and systems need specific architectural requirements for their integration in the buildings, to ensure that they are accepted for application. Several types and forms of solar thermal collectors and photovoltaics comprise new and interesting energy systems, easily integrated into buildings and creating new shapes, symbolizing a new ecological concept. These solar energy systems also appear as a new material in the architect's hands, ready to be shaped and create alternative building forms. Regarding the research and development issues, they focus on new designs and materials, for the conversion of solar energy, solar control of buildings, storage of heat and electricity and aesthetic aspects, constituting therefore the parameters and the requirements for a sustainable future.

Considering the new materials and systems for the collection of solar energy, one can notice the flat and curved Fresnel reflectors and Fresnel lenses for medium and high concentration ratios, the polymeric absorbers for low cost plastic solar thermal collectors and the luminescence solar concentrators. As for the materials and systems of solar energy conversion, we can refer to the polymeric photovoltaics, the Thermophotovoltaics (TPV), the Dyesensitized solar cells, the Thermoelectric (Seebeck) generators (TEG), the Microalgae for biofuel production and the Bacteriorhodopsin films for solar electricity. Some new materials for energy storage of heat and electricity include the PCMs for low, medium and high temperatures, the Thermochemical storage, several types of Capacitors, the Li-ion Batteries, the Superconducting magnetic energy storage (SMES), the Pressured air, the H₂/Fuel Cells, etc. Regarding the materials for the solar control of buildings in temperature and lighting, building Walls+PCM, BIPV+PCM, PV/T collectors, Evacuated Windows, Photo-Electrochromic Windows, Thermochromic paints to adjust solar energy absorption, Infrared Reflectors for roofs/facades, skylights/tunnels, Fresnel lenses for lighting and temperature control, etc have been studied. Finally, for the aesthetic aspects of solar energy materials and systems, solar thermal collectors with colored absorbers, Integrated Collector-Storage Solar Energy Systems, Transpired solar thermal collector facades, colored silicon based PV panels, colored Thin-Film Photovoltaics, Polymeric Photovoltaics, Luminescent solar concentrators, etc. have been developed.

In this paper, we present, in summarized form, the research activities on novel solar energy materials and systems that are performed at the University of Patras and the Technological-Educational Institute of Western Greece (also in Patras). The University of Patras, which was established in 1964, is the 3rd in Greece regarding Schools and students, and includes 6 Schools, 27 Departments and 900 Professors, teaching 25.000 undergraduate and 3.000 postgraduate students. The research works that are presented in this paper are from the Solid State Physics and Polymer Physics Research Lab, the Renewable Energy Group Lab and the Solar Energy Laboratory, all in Physics Department, the Environmental Engineering Lab in the Department of Civil Engineering, the Lab for Photo-fuel-cells for electricity and solar fuel production, in the Deptartment of Chemical Engineering and Nanotechnology and from the Advanced Materials Lab, in the Technological-Educational Institute of Western Greece at Patras. These Laboratories are very active in the field of contemporary solar energy materials and have many publications in international journals and conference proceedings.

2. SOLID STATE PHYSICS AND POLY-MER PHYSICS RESEARCH LABORA-TORY

The main research activity of Solid State Physics and Polymer Physics Lab is on the synthesis of metallic nanowires with application to transparent electrodes. One-dimensional metallic nanostructures, like nanowires (NWs) and nanotubes, have attracted the attention of scientific community due to their unique properties and a wide range of applications, as they can be used as parts of nanoscale electronic, optical, plasmonic, and information storage devices. In particular Cu, Co and Zn nanowires have been extensively studied due to their properties and potential use in many technological applications [1]. An easy and effective way to synthesize a large number of NWs with high aspect ratio (length to diameter ratio) is the so called "template synthesis". In this process, a metal is electrochemically deposited inside a porous material, which acts as a template. A widely used material for this purpose is the porous alumina membrane (PAM), due to its high mechanical and chemical strength and durability at high temperatures. The geometrical characteristics of PAM can be easily controlled during their synthesis process. PAMs with pore diameter between 10 and 250 nm and interpore distance between 25 and 500 nm can be easily synthesized, while the thickness of PAMs can be several hundreds of micrometers [2].

Nanowires can be used in a variety of applications and one of the most interesting is their use as a substrate in LEDs, OLEDs and solar cells. So far ITO glass is the commonly used material for the substrate in the above devices. Nevertheless, the use of ITO glass has some disadvantages such as the relatively small conductivity and a very high cost of indium. Transparent electrodes fabricated from Cu nanowires have better conductivity and are much cheaper to build, because of very low price of Cu. One of the purposes of this work is to explore how the conditions and, more specifically, temperature and voltage, affect the growth and morphology of nanowires. Also in this work the Cu nanowires are collected by dissolving the alumina template and are used to produce a transparent electrode. The conductivity and transparency of produced electrodes is also assessed.

The fabrication process for the nanowires and PAMs is described in more details below. Copper, Zinc and Cobalt nanowires are synthesized by DC electrodeposition, using porous alumina membrane as a template. Electrodeposition is accomplished in an electrochemical cell bearing two electrodes and filled with suitable electrolyte. In case of Cu nanowires, a high purity copper wire serves as anode, while the electrical contact in the porous alumina, which serves as cathode, is achieved by a 350nm Ag film, deposited by PVD on the PAM. The growth of nanowires is achieved under potentiostatic conditions for applied voltages in the range of 0,3V up to 0,8V. In the case of Zn and Co nanowires, a high purity Zn and graphite rod, served as a counter electrode, respectively. The samples were characterized by SEM (Figure 1) and XRD in order to assess the morphology and the size of nanowires.

In the second step the alumina template is dissolved, the nanowires are collected by centrifugation, purified and then placed in a 3% w/v PS and toluene solution. This solution was used to fabricate the transparent electrode, dispersing it by spin coating on glass (Figure 2).

Several samples of PAMs were prepared in a hydrate solution of 0.3 M oxalic acid, under applied voltages of 40 V and 50 V with varying solution temperatures in a purpose-built electrochemical cell. The thickness of the PAMs produced under these conditions was measured using cross section images taken by scanning electron microscopy (SEM). From these measurements, a linear expression between the growth rate of PAMs and the current density during the anodization is deduced, giving an efficiency value of 53% and 65% for applied voltages of 40 V and 50 V, respectively. In steady state conditions, i.e., after the stabilization of the anodization current, this linear dependence is very conveniently transformed into linear dependence of thickness versus total anodization time, thus providing a simple method for controlling the thickness of the produced membranes.

New technologies for achieving cost effective and efficient renewable energy are becoming very important in our years because of high energy prices and global climate change. Flexible solar cells constitute an interesting alternative to inorganic solar cells, mainly due to their low cost and easy fabrication. Furthermore, they are compatible with flexible substrates over large areas. In particular, flexible transparent electrodes based on metal nanowires are aiming in this direction replacing gradually electrodes based on metallic oxides [3, 4].

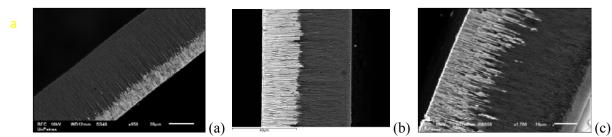


Figure 1. SEM cross section of nanowires into porous alumina membranes (a)copper (b)cobalt and (c) zinc

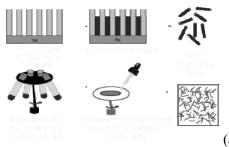
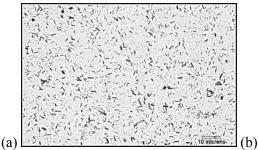


Figure 2. (a) Fabrication of transparent electrode



(b) Image of the dispersed NWs on glass surface

3. ENVIRONMENTAL ENGINEERING LAB, DEPARTMENT OF CIVIL EN-GINEERING

The use of wastewater in algal cultivation could have a double role, i.e. the reduction of the wastewater pollution load, and the utilization of microalgae for biomass and energy production. Batch experiments were conducted to evaluate their potential contribution to nutrient removal and biofuel production. The growth rate of microalgae was inversely analogous to their initial concentration. Three freshwater strains were selected, based on their growth rate, and their behavior with synthetic wastewater was further investigated (Figure 3). The strains studied were the *Scenedesmus rubescens* (SAG 5.95), the *Neochloris vigensis* (SAG 80.80), and the *Chlorococcum spec*. (SAG 22.83), and higher growth rate was observed with *S. rubescens*. Total phosphorus removal at an initial phosphate concentration of 6-7 mg P/L in the synthetic wastewater, was 53%, 25% and 11% for *N. vigensis, Chlorococcum spec.*, and *S. rubescens* (Figure 4), respectively. Finally, the higher lipid content of the algae was observed on the 20th day of cultivation [5].

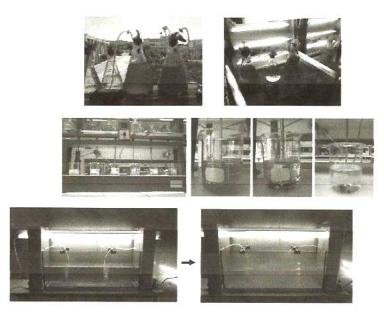


Figure 3. Microalgae cultures

The second activity is the heating of anaerobic reactors treating wastewater by solar energy [6,7]. The solar system consisted of a flat plate solar collector, a heat exchanger and a storage tank for warm water (Figure 5a). The reactor was a cylindrical tank heated with warm water. The water temperature at the reactor inlet was regulated so as to never exceed 35°C. The solar heating energy was transferred to

the reactor, which raised the temperature of the reactant up to 35°C. The warm water at the reactor inlet is kept at the desired limit of 35°C through most of the year. The part of the year during which the warm water with temperature greater than 20°C is delivered to the reactor, increases with the solar collector area and the storage tank volume. Model simulations for different reactor volumes provide practical information for the application of the solar system in areas with similar meteorological conditions of Patras, Greece.

A third work is on dewatering of sewage sludge assisted by solar energy [8]. A pilot scale unit was employed to accelerate dewatering of secondary sludge. A tank made of steel (LxWxH 1x0.5x2 m) was constructed. The tank was covered by Plexiglas to capture the solar energy and electric resistance was used to supply additional thermal energy. The unit was subjected to three operational cycles from March to June 2011. Secondary sewage sludge with 2% dry solids (DS) was obtained from the wastewater treatment plant of the Patras campus. The average evaporation rate was 5.2, 8.1 and 10.3 kg/m² depending on climate conditions and the initial solids concentration. During the summer the sludge dried over two weeks, when filtration was applied, while greenhouse resulted in enhanced dewatering of sludge (Figure 5b).

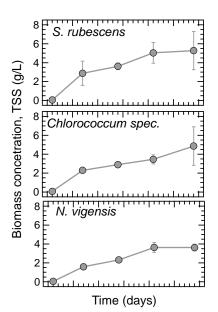


Figure 4. Biomass concentration of microalgae strains.

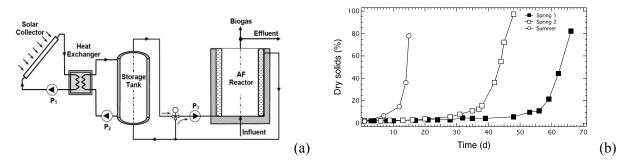


Figure 5. Solar energy for (a) heating anaerobic reactors and (b) sludge dewatering.

4. NANOTECHNOLOGY AND AD-VANCED MATERIALS LAB, TECH-NOLOGICAL EDUCATIONAL INSTI-TUTE OF WESTERN GREECE

Since the first report on dye-sensitized solar cells (DSSCs) introduced by M. Grätzel in 1990, too much attention has been attracted to the development of new and ever better performing materials as this technology fulfils many requirements concerning the cost of the materials and cells, low energy

expenditure and ease of preparation [9, 10]. A large volume of the recent works on DSSCs is devoted to the morphology of TiO₂ semiconductor as negative electrode and also to studies of the physicochemical state of the electrolyte. As it concerns the TiO₂, the mesoscopic nature of TiO₂ films makes it possible to manufacture transparent cells which can be used as photovoltaic windows. Photovoltaic windows can be integrated in building facades operating by frontface light incidence, but also by diffuse light and even by back face light incidence. As it also concerns the nature of electrolyte, this is dictated by some concern that was expressed as to the long-term photochemical stability of the devices as the leakage of the electrolyte caused sealing problems as well as stability and durability of liquid electrolytes. This is of great importance and a challenging topic for research in our labs. However, one more critical factor for better cell performance is an optimization of dye sensitizer in terms of increasing light-harvesting capability, improving charge transport and reducing recombination of excited electrons. In general, after the irradiation of a solar cell, light is absorbed by the dyes' molecules that are anchored on the TiO₂ surface and the electrons are injected from the excite state of dye into the conduction band of the semiconductor film.

Besides the use of TiO_2 as a standard semiconductor in DSSCs, ZnO is also a wide band gap semiconductor with energy band structure and phys-

ical properties similar to TiO2. However, it has higher electronic mobility (155 cm² v⁻¹ s⁻¹ vs. to 10⁻⁵ cm² $v^{-1} s^{-1}$ of TiO₂) favorable for electron transport, it is easily crystallized and anisotropically grows in a variety of morphologies. One of the main factors that limit the efficiency of the DSSCs and increase their cost is the dye used for inorganic semiconductors sensitization in the visible and near IR region of the solar spectrum. Ruthenium-based dyes are usually costly, while their extinction coefficients and absorption spectra cannot effectively cover the requirements for high efficient solar cells. Recent developments in the field showed that semiconductor quantum dots (ODs) could effectively sensitize wide band gap metal oxides instead of organic dyes. Semiconductor QDs in the form of very small crystals can be very stable, and present an advantage to match solar spectrum better, because their absorption spectrum can be tailored by size quantization.

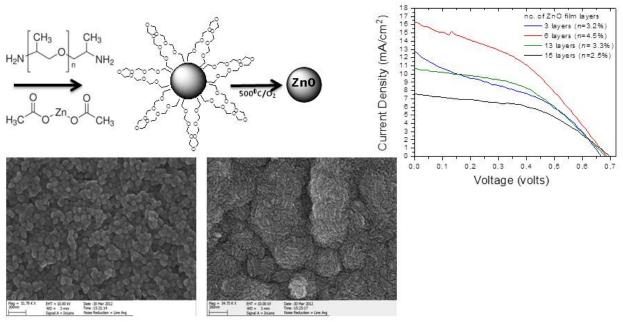


Figure 6. Preparation method for ZnO nanoparticles with two polymorphisms depending the quantity of organic template Solar cell J-V curves for QDSSCs.

Moreover, the possibility of generation of multiple electron-hole pairs from one photon can lead to very high theoretical efficiencies exceeding 66%. To date a wide range of QDs has been used for fabrication of QD sensitized solar cells (QDSSCs) in combination with wide band gap inorganic semiconductors (TiO₂, ZnO) and a redox electrolyte. Among QDs, CdSe, CdS, CdTe, PbS, PbSe and some combinations of them are more often referred to the construction of efficient QDSSCs while a maximum 4.2% efficiency is recorded for a TiO₂/CdS/CdSe composite system [11]. In present paper a novel facile method for the formation of ZnO nanostructured films is described. According to this method, zinc acetate readily reacts with low molecular weight poly(propylene glycol) ended by amine groups at both edges. Co-sensitization of the zinc oxide films with CdS/CdSe QDs is discussed, while a quasi solid state electrolyte employing polysulfide (S^{2-}/S_x^2) redox couple is used for the first time in the QDSSC completion.

Besides research achieved on DSSCs or QDSSCs, people at Nanotechnology and Advanced Materials Lab. at TEI of Western Greece have succeeded to enhance the efficiency of conventional silicon- based photovoltaics after using luminescent solar concentrators (LSC) [12]. In our lab we explored the case of lanthanide (Ln) organometallic complexes as a new prospective in the field of LSC for solar cells. In this paper we synthesized and studied several europium complexes with intense luminescence as possible LSC for the increase in silicon photovoltaic cells performance.

Besides the use of wide band gap nanostructured semiconductors in third generation photovoltaic cells, there is also another challenging application of them. Wastewater treatment is considered one of the main environmental problems, which receives special care in industrial society. Disposition of colored effluents by textile, paper pulp and other related industries represents a technological issue affecting several countries around the world.

Advanced Oxidation Technologies (AOTs) are considered as alternative methods to the decontamination of polluted water. Basically, AOTs are highly efficient treatments to remove recalcitrant dyes from water based on the oxidative power of radical species created during these processes. Photocatalysis, which as a method belongs to AOTs, is one of the strategies that can be successfully applied to the oxidation and final removal of pollutants to the formation of carbon dioxide as a later product. Various organic pollutants can be photodegradated by using wide band gap semiconductors under UV or solar light. Among them, TiO_2 is a relatively inexpensive semiconductor, which exhibits high photocatalytic activity, non-toxicity and stability in aqueous solutions and it is our choice. Furthermore, the synthesis of mesoporous nanocrystalline anatase TiO_2 particles, films or membranes has extended their use in environmental remediation. Ultra fine TiO_2 powders with high particle surface area have a good photocatalytic activity since reactions take place on the surface of the nanocatalyst.

On the other hand, powders can easily agglomerate in larger particles and as a consequence adverse phenomena to their photocatalytic activity are observed. However, TiO₂ can also be used as mobilized catalyst for its high catalytic surface area and activity. Nevertheless, TiO₂ powders cannot easily be recovered from aquatic systems when they are used for water treatment. Highly dispersed TiO₂ particles in suspension are difficult to handle and remove after their application in water and wastewater treatment [13]. The specific surface area, particle morphology and possible aggregation, phase composition and the number of -OH surface groups are among the most critical parameters for high photocatalytic activity of as-prepared films. Another approach to enhance the photocatalytic properties of the catalysts is the promotion of their porous structures which are the subject of our studies.

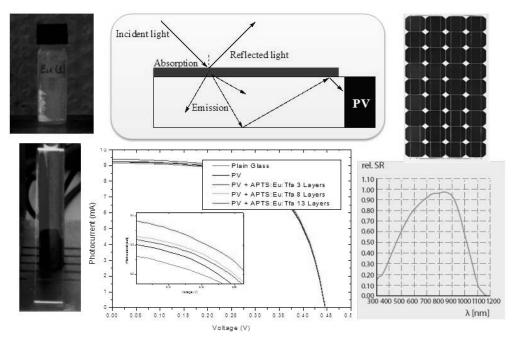


Figure 7. Luminescent Solar concentrators based on Rare Earth complexes for enhanced performance of Si-based solar cells.

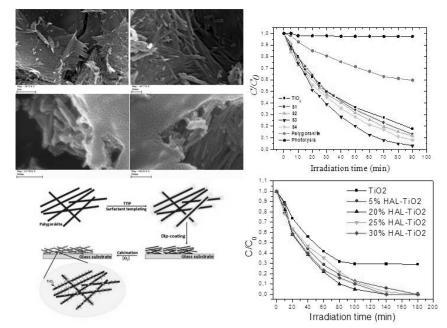


Figure 8. Highly porous nanoscructured TiO_2 films and clay minerals composites for the discoloration of dyestuff in water.

5. PHOTO-FUEL CELLS FOR ELECTRICI-TY AND SOLAR FUEL PRODUCTION, DEPTARTMENT OF CHEMICAL EN-GINEERING

A PhotoFuelCell (PFC) is a standard photoelectrochemical cell. It consists of a Photoanode electrode, which carries an n-type semiconductor photocatalyst, a Cathode (or Counter) electrode, which carries a reduction electrocatalyst and an electrolyte. It is possible to use an electrocatalytic anode and a photocathode carrying a p-type semiconductor photocatalyst but the most efficient cells prefer a standard photoanode configuration. Typical n-type semiconductor photocatalyst is mesoporous titania, the most studied semiconductor photocatalyst. Its popularity stems from its chemical stability, its efficiency, its low cost and the ease of its synthesis and deposition. Because titania does not absorb visible light, it may be combined with a sensitizer that broadens the range of photon usage. In aqueous environment, the choice of known sensitizers is unfortunately limited to only a few metal sulfide quantum dots [14]. Typical reduction electrocatalyst is a mixture of platinum with carbon nanoparticles, while a great effort is made to substitute Pt by less costly materials [15,16]. Finally, the electrolyte is a simple salt like Na₂SO₄ or an alkaline electrolyte like NaOH. Alkaline electrolytes facilitate oxidation process by the intermediate of OH⁻, which are excellent hole scavengers at the conduction band of titania and facilitate hole consumption by creation of highly oxidative [•]OH radicals (OH⁻⁺ $h^+ \rightarrow ^{\bullet}OH$). Fuel is dissolved in the electrolyte. Electrolyte may involve a redox couple but it is not necessary, since the charges are consumed at the photoanode and the cathode and do not need to be shuttled between electrodes. What matters is to preserve the composition of electrolyte, as it will be discussed below. Figure 9 shows a schematic representation of a PFC.

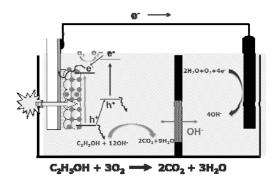


Figure 9. Schematic representation of a Photo Fuel Cell

In this design, ethanol is used as model fuel. Ethanol is indeed studied as model fuel since it is a product of biomass and among the most efficient PFC fuels. However, other small chain alcohols, diols, organic acids and carbohydrates are equally interesting as PFC organic fuels [17]. In absence of oxygen, ethanol is photocatalytically reformed producing H_2 according to the following reaction [18]:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{1}$$

Ethanol is oxidized directly or through hydroxyl radicals and by successive steps [18, 19] it leads to mineralization. During these oxidation steps, a total of 12 holes are scavenged for the mineralization of one ethanol molecule. Hydrogen ions may be formed but they survive only in acidic or moderate pH. If all hydrogen ions were to survive, the oxidation of one ethanol molecule would lead to the formation of 12 hydrogen ions by the simultaneous consumption of 3 water molecules. These hydrogen ions can be reduced at the cathode to give molecular hydrogen. However, in alkaline pH, hydrogen ions cannot survive. In that case, hydrogen is produced by water reduction. In addition to hydrogen production, hydroxyl ions are then also produced, thus preserving the population of hydroxyl ions in the electrolyte. Reaction (1) shows that, no matter what the pH value is, in the absence of oxygen, ethanol is photocatalytically reformed by consuming 3 water molecules and 12 photons (electronhole pairs) to produce 6 hydrogen molecules for each ethanol molecule. Ethanol reforming in a PFC necessitates the flow of electrons from the photoanode to the cathode electrode. A potential difference between the two electrodes under ideal conditions is defined by the level of the titania conduction band and the level of the redox reaction taking place at the cathode electrode, which is about 0.3 V. Due to inevitable losses, such a difference is too low to run the cell so that under real conditions it is necessary to apply an external bias in order to produce hydrogen. In the presence of oxygen, ethanol is photocatalytically mineralized according to the following reaction:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{2}$$

For each ethanol molecule, 12 photons (electron-hole pairs) are consumed to perform the reaction. In an alkaline environment, the reduction reaction at the counter electrode involves consumption of 3 molecules of O_2 per ethanol molecule. This reduction reaction takes place at a potential of +0.46 V at alkaline pH. The potential difference with the titania conduction band is then around 1.5 V, i.e. it is more than enough to spontaneously run the cell and is expected to generate a high open-circuit voltage. When titania is combined with a sensitizer, holes are

accumulated in the valence band of the sensitizer and their oxidative power is decreased, since they jump to a less positive level. Depending on the nature of the sensitizer, this modification may render certain oxidation reactions impossible. CdS sensitizer, for example, is only at the limit capable of creating 'OH radicals. Other sensitizers, as it will be discussed later, are not. Finally, it must be underlined at this point that compounds of the general chemical structure $C_xH_yO_z$ are the best fuels for PFCs. The generalized photocatalytic reforming and mineralization schemes are given by the reactions:

$$C_{x}H_{y}O_{z} + (2x-z)H_{2}O \rightarrow xCO_{2} + (2x+\frac{y}{2}-z)H_{2}$$
(3)

$$C_{x}H_{y}O_{z} + (x + \frac{y}{4} - \frac{z}{2})O_{2} \rightarrow xCO_{2} + \frac{y}{2}H_{2}O$$
 (4)

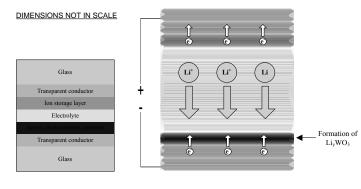
in the absence and in the presence of oxygen, respectively. The reactions at the cathode remain the same independently of the fuel. Differences between fuels are presented by the nature of the oxidation steps that lead to mineralization.

6. RENEWABLE ENERGY GROUP, PHYSICS DEPTARTMENT

The Renewable Energy Group of the Physics Department, University of Patras has more than 15 years of experience in electrochromic (EC) "smart" windows, intended for the dynamic solar control of buildings. Based on WO₃ films prepared by vacuum methods, these devices change their optical properties reversibly upon Li^+ intercalation and deintercalation, in a similar way to Li^+ batteries, as shown in Figure 10.

Prototypes up to 40 cm x 40 cm have been fabricated with excellent optical properties: transmittance modulation up to 6:1, long term stability up to 5000 coloration-bleaching cycles and more than 5 years in operation [20]. Examples of the fabricated electrochromic window prototypes are shown in Figure 11.

Recently, WO₃/Ag/WO₃ multilayers have been used as a replacement for the typical SnO_2 :F/WO₃ arrangement, enabling both reflectance and absorptance modulation in the colored state. Depending on the direction of the incoming radiation, either high reflectance results, if the Ag film is encountered first or high absorptance in the opposite direction, caused by the Li_xWO₃ film, as shown in Fig 12. These multilayers were designed by home-made optical design software based on the characteristic matrix and effective medium theories and using Monte Carlo optimization routines [21].



ELECTROCHROMIC COLORATION DEVICE PROCESS Figure 10. EC windows: Layout and principle of operation.

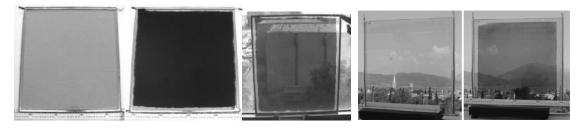


Figure 11. Electrochromic window prototypes 40 cm x 40cm in the bleached and colored states.

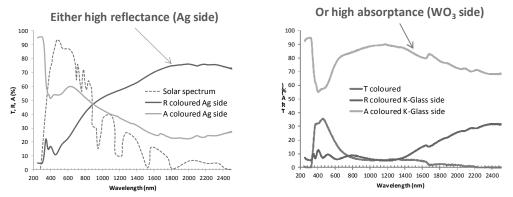


Figure 12. Layout of a modified EC device and the transmittance, reflectance and absorptance spectra in the colored state with high reflectance (left) or high absorptance (right).

The electrochromic devices were combined with dye sensitized solar cells (DSSCs) [22, 23] to develop photoelectrochromic (PEC) windows [24, 25]. They are passive devices that combine solar control and energy production. The electrical power produced by the DSSC element is used for the coloration of electrochromic films. Once the window has achieved the required amount of coloration, the surplus solar electricity can be fed to the external circuit. The coloration of the window is controlled by the external electrical load: full coloration is achieved upon illumination in the open circuit and bleaching is effected by shortening the devices in the dark. PEC devices with promising optical properties and shelf life of more than 9 months have been fabricated. Further development is underway to address reversibility and stability issues.

Of the materials and devices presented herein, electrochromic windows comprise the most mature technology. They are actually on the verge of commercialization, as several companies are in the process of preparing electrochromic window products. On the other hand, DSSCs and photoelectrochromics are still in the materials development stage. However, intense research effort is committed for their development worldwide, and significant breakthroughs are expected in the years to come.

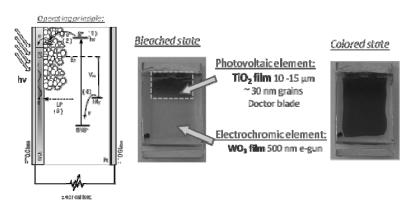


Figure 13. Layout and operating principle of a PEC device (Left.) The fabricated devices (Right).

7. SOLAR ENERGY LABORATORY, PHYSICS DEPTARTMENT

The Solar Energy Laboratory (SEL) is established at the Physics Department of University of Patras and has a 35-year long experience in education and research. The main research activities of SEL include work on solar thermal collectors, photovoltaics, hybrid photovoltaic/thermal collectors, low concentration solar energy systems, small wind turbines, energy saving technologies and solar control of buildings and greenhouses and also energy systems for application in the built construction, industrial and agricultural sectors. Solar thermal collectors are mostly used for hot water in households and tourism sector, while photovoltaics are used to provide electricity to grid, mainly by the PV plants installed on ground and on buildings.

The materials play an important role in the efficiency, cost and appearance of solar energy systems. A more efficient system design and the use of new materials to collectors and photovoltaics can achieve cost effective systems and will expand their application. In SEL research activities, the work on materials includes mainly the study on solar collectors with absorbers of different color than black (Figure 14, left), the solar collectors with colored absorbers, which are suggested as an interesting solution for the architects to avoid the monotony of black color and to contribute to a wider application of solar energy systems [26]. These collectors are of lower thermal efficiency because of the lower absorptance but can be of higher aesthetical performance due to the colored (red, blue, etc) absorber. Some efforts to achieve low emissivity colored absorbers did not have any satisfactory results and thus these collectors are still in the developing stage.

A second work is on the hybrid photovoltaic/thermal (PV/T) systems, which convert solar radiation into electricity and heat, with water and air heat extraction (Figure 14, on the right). In the case of air heat extraction, an increase in the system performance is based on the specific heat properties of the used materials inside the air channel [27]. SEL is on the first international line regarding the research work on PV/T collectors, with studies on water, air and on both water and air heat extraction [28]. In these works SEL has suggested the use of diffuse reflectors to overcome the reduction of electrical output due to the placement of an additional glazing in order to avoid the thermal losses. The study on diffuse reflectors shows that even for white painted surface, the distribution of the reflected radiation on PV module surface is not homogenous.

The third work deals with the optical media for the concentration of solar radiation and the solar control of building atria and greenhouses (Figure15). In these applications, the Fresnel lenses are the suitable optical media and SEL studies relate to the requirements for optimal design and operation [29], where the optical and thermal properties of lenses are critical for higher concentration ratios. The effective use of the system is shown in Figure15, right, with the receiver out of focus (Figure15,R-a) and on focus (Figure15,R-b)



Figure 14. Colored collectors (left) Hybrid PV/T Systems (right) to produce electricity and heat

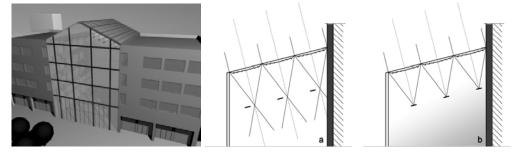


Figure 15. (Left: Fresnel lenses on building atrium (Right):, receiver out of focus(a) and on focus (b)

In addition to these studies, research steps have started on PCM materials as thermal storage in Integrated Collector Storage collectors and PV/T collectors. In roof installation of solar thermal collectors, photovoltaics and PV/T collectors the concept of booster reflectors has been suggested (Figure 16) [30]. The booster reflectors with photovoltaics and PV/T collectors should be diffuse reflectors, in order to avoid high difference in solar radiation density on the receivers (Figure 17, left). Furthermore, photovoltaics can be effectively combined with small wind turbines and the example of the cycladic building gives a good idea about this concept, where sustainability is combined with aesthetics (Figure 17, right).

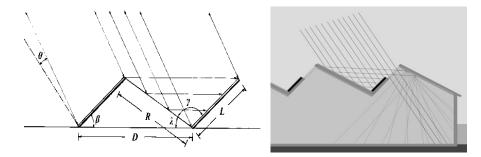


Figure 16. The geometry of booster reflectors (left), Booster reflectors on building roof (right)

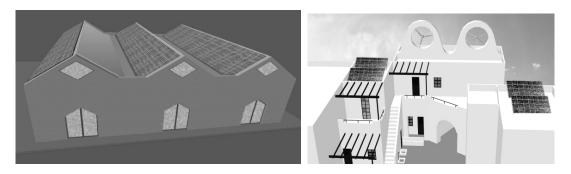


Figure 17. Booster diffuse reflectors with PV modules (left), Photovoltaics with small wind turbines (right)

8. CONCLUSIONS

Solar Energy systems can contribute to the energy demand of buildings, industry and agriculture. The investigation and development of new solar energy materials and systems could adapt energy needs and change the energy profile, contributing to energy saving and environmental protection. A number of Laboratories at the University of Patras are active in the research and development of solar energy materials and systems. The present paper gives a brief overview of the research activities performed in the Labs of the University of Patras and of the Technical Educational Institute of Western Greece (also in Patras). The included material refer to nanotechnology, biotechnology, DSSC, QDs photovoltaics, luminescent solar concentrators, nanocatalysts, hydrogen production, polymer photovoltaics, smart glazings with photo-electrochromics and materials for solar energy systems. A brief description of the achieved improvements on these items is included, where energy performance and system cost play an important role, considering their wide application in the future. Sustainability and aesthetics are additional properties of the built environment and should be considered in all cases for a comfortable and beautiful future.

9. REFERENCES

[1] S. Dellis, A. Christoulaki, N. Spiliopoulos, D.L Anastassopoulos and A. A. Vradis. *Electrochemical synthesis of large diameter monocrystalline nickel nanowires in porous alumina membranes* J. Appl. Phys., Vol. 114 (2013), 164308-1-5.

[2] A. Christoulaki, S. Dellis, N. Spiliopoulos, D.L. Anastassopoulos and A.A. Vradis, *Controlling the thickness of electrochemically produced Porous Alumina Membranes: The role of the current density during the anodization.* J. App. Electrochem., Vol. 44 (2014), 701–707.

[3] M-G. Kang, H. J. Park, S. H Ahn, L. J. Guo, *Transparent Cu nanowire mesh electrode on flexible substrates fabricated by transfer printing and its application in organic solar cells*, Solar Energy Materials and Solar Cells, Vol. 94 (2010) 1179–1184.

[4] M-G. Kang, M-S. Kim, J. Kim and L. J. Guo, *Organic Solar Cells Using Nanoimprinted Transparent Metal Electrodes*, Adv. Mater., Vol. 20 (2008) 4408–4413.

[5] A.F Aravantinou, M. A. Theodorakopoulos and I. D. Manariotis, *Selection of Microalgae for Wastewater Treatment and Potential Lipids Produc-* tion. Bioresource Technology, Vol. 147 (2013) 130–134.

[6] A. C Yiannopoulos, I. D. Manariotis and K. V. Chrysikopoulos, *Design and Analysis of a Solar Reactor for Anaerobic Wastewater Treatment*. Bioresource Technology, Vol. 99–16 (2008) 7742–7749.

[7] A. C Yiannopoulos, I. D. Manariotis and C.V. Chrysikopoulos, *Anaerobic Wastewater Treatment Powered by Solar Energy*, Water Air and Soil Pollution, Vol. 223–4 (2012) 1443–1454. doi 10.1007/s11270-011-0956-9

[8] D. Giannelos and I. D. Manariotis, *Dewatering of sewage sludge assisted by solar energy*, Ecotechnologies for Wastewater Treatment 2012 International Conference, IWA Specialist Conference, June 25-27, (2012), Santiago de Compostela, Spain.

[9] E. Stathatos, *Dye Sensitized Solar Cells: A New Prospective to the Solar to Electrical Energy Conversion. Issues to be Solved for Efficient Energy Harvesting.* Journal of Engineering Science and Technology Review, Vol. 5 (2012) 9–13.

[10] E. Stathatos, P. Lianos, S. M. Zakeeruddin, P. Liska, M. Graetzel, A Quasi-solid state dyesensitized solar cell based on a sol-gel nanocomposite electrolyte containing ionic liquid. Chemistry of Materials, Vol. 15–9 (2003) 1825.

[11] D. Karageorgopoulos, E. Stathatos and E. Vitoratos, *Thin ZnO nanocrystalline films for efficient quasi-solid state electrolyte quantum dot sensitized solar cells.* Journal of Power Sources, Vol. 219 (2012) 9–15.

[12] G. Katsagounos, E. Stathatos, N. B. Arabatzis, A. D. Keramidas and P. Lianos, *Enhanced photon harvesting in Silicon multicrystalline solar cells by new lanthanide complexes as light concentrators.* Journal of Luminescence, Vol. 131 (2011) 1776–1781

[13] E. Stathatos, D. Papoulis, C. A. Aggelopoulos, D. Panagiotaras, A. Nikolopoulou, $TiO_2/palygorskite$, composite nanocrystalline films prepared by surfactant templating route: Synergistic effect to the photocatalytic degradation of an azodye in water. Journal of Hazardous Materials, Vol. 211–212 (2012) 68–76.

[14] M. Antoniadou, D. I. Kondarides, D. D. Dionysiou, P. Lianos, *Quantum dot sensitized titania applicable as photoanode in photoactivated fuel cells: J. Phys. Chem. C*, Vol. 116 (2012) 16901–16909.

[15] S. Sfaelou, M. Antoniadou, G. Trakakis, V. Dracopoulos, D. Tasis, J. Parthenios, C. Galiotis, K. Papagelis, P. Lianos. *Buckypaper as Pt-free ca*- *thode electrode in photoactivated fuel cells*, Electrochim. Acta, Vol. 80 (2012) 399–404.

[16] N. Balis, V. Dracopoulos, M. Antoniadou, P. Lianos, *One-step electrodeposition of polypyrrole applied as oxygen reduction electrocatalyst in Photoactivated Fuel Cells*, Electrochim. Acta, Vol. 70 (2012) 338–343.

[17] M. Antoniadou, P. Lianos, *Near Ultra*violet and Visible light photoelectrochemical degradation of organic substances producing electricity and hydrogen. J. Photoc. Photobio. A, Vol. 204 (2009) 69–74.

[18] F. D. Foglia, G. L. Chiarello, M. V. Dozzi, P. Piseri, L. G. Bettini, S. Vinati, C. Ducati, P. Milani, E. Selli, *Hydrogen production by photocatalytic membranes fabricated by supersonic cluster beam deposition on glass fiber filters*. Int. J. Hydrogen Energ., Vol. 39 (2014) 13098–13104.

[19] P. Panagiotopoulou, M. Antoniadou, D.I. Kondarides, P. Lianos, *Aldol condensation products during photocatalytic oxidation of ethanol in a photoelectrochemical cell*. Appl. Catal. B, Vol. 100 (2010) 124–132.

[20] S. Papaefthimiou, G. Leftheriotis, P. Yianoulis, T. J. Hyde, P. C. Eames, Y. Fang, P. Y. Pennarun, P. Jannasch, *Development of electrochromic evacuated advanced glazing*, Energy and Buildings, Vol. 38 (2006) 1455–1467.

[21] G. Leftheriotis, E. Koubli, P. Yianoulis. Combined electrochromic-transparent conducting coatings consisting of noble metal, dielectric and WO3 multilayers, Solar Energy Materials & Solar Cells, Vol. 116 (2013) 110–119.

[22] G. Syrrokostas, G. Leftheriotis, P. Yianoulis, *Effect of acidic additives on the structure and performance of TiO2 films prepared by a commer-* *cial nanopowder for dye-sensitized solar cells*, Renewable Energy, Vol. 72 (2014) 164–173.

[23] G. Syrrokostas, A. Siokou, G. Leftheriotis and P. Yianoulis. *Degradation mechanisms of Pt counter electrodes for dye sensitized solar cells*, Solar Energy Materials & Solar Cells, Vol. 103 (2012) 119–127.

[24] G. Leftheriotis, G. Syrrokostas, P. Yianoulis, *Development of photoelectrochromic devices for dynamic solar control in buildings*. Solar Energy Materials & Solar Cells, Vol. 94 (2010) 2304–2313.

[25] G. Leftheriotis, G. Syrrokostas, P. Yianoulis. *Partly covered photoelectrochromic devices with enhanced coloration speed and efficiency*. Solar Energy Materials & Solar Cells, Vol. 96 (2012) 86–92.

[26] Y. Tripanagnostopoulos, M. Souliotis and Th. Nousia, *Solar Collectors with Colored Absorbers*, Solar Energy, Vol. 68 (2000) 343–356.

[27] Y. Tripanagnostopoulos, Th. Nousia, M. Souliotis, P. Yianoulis, *Hybrid photovoltaic/thermal solar systems*, Solar Energy, Vol. 72 (2002) 217–234.

[28] Y. Tripanagnostopoulos, *Cost effective designs for building integrated PV/T solar systems*. Conference Proceedings, 21st European PV Solar Energy Conf. Dresden, Germany 4–6 Sep 2006.

[29] Y. Tripanagnostopoulos, Ch. Siabekou, J.K. Tonui, *The Fresnel lens concept for solar control of buildings*. Solar Energy, Vol. 81 (2006) 661–675.

[30] Y. Tripanagnostopoulos and M. Souliotis, *Booster Reflector Contribution to Performance Improvement of Solar Collectors*, Conf. Proc. in CD, Int. Conf. WREC 2005, 63–68, Aberdeen, Scotland, UK, 22–27 May 2005.

ନ୍ଧର୍ୟ

МАТЕРИЈАЛИ И СИСТЕМИ СОЛАРНЕ ЕНЕРГИЈЕ ЗА ЉЕПШУ И ОДРЖИВУ БУДУЋНОСТ

Сажетак: Одрживи извори енергије имају значајну улогу у глобалној потражњи енергије у 21. вијеку. Нова истраживања из материјала за соларну енергију и система соларне енергије пружају нове могућности с тачке гледишта одрживе будућности, прилагођавања локалних енергетских потреба, заштите људске средине и естетике. Соларна енергија може се користити готово свуда, са видљивим материјалима и системима. У овом раду дат је приказ нових материјала за соларну енергију и соларне системе, са освртом на рад који се обавља у лабораторијама Универзитета у Патри и Техничком образовном институту. Истраживачке активности ових лабораторија обухватају нанотехнологију, биотехнологију, производњу водика из микроалги, паметно стакло и материјале за системе соларне енергије. Дат је кратак опис постигнутих побољшања на овим материјалима за соларну енергију, при чему енергетске перформансе и трошкови система играју важну улогу заједно са естетиком, с обзиром на њихову широку примјену у будућности.

Кључне ријечи: материјали за соларну енергију, фотонапонски уређаји, електрохромски производи, наноматеријали, нанометали, миркоалге, обојени соларни колектори, Фрезнелове леће, PV/T колектори.