

Chimia 52 (1998) 557–560
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 ISSN 0009–4293

Molecular Photovoltaics and Nanocrystalline Junctions

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Abstract. Photosensitization of wide-band-gap semiconductors is a promising low-cost photovoltaic technology. We present herein recent advances in photovoltaic devices and related technologies which have been achieved at the Laboratory for Photonics and Interfaces of the EPFL. New photosensitizing molecules have been developed which exhibit an increased spectral response. Semiconductor oxide nanoparticles used in the formation of thin-film photoelectrodes self-organize in a cubic array. Additionally, prototypes of small devices powered by dye-sensitized photovoltaic devices are now appearing.

1. Introduction

Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions. Junctions of both n- and p-type regions of a single semiconductor material and heterojunctions, between different semiconductor materials or between a semiconductor and a metal (*Schottky* junction), exhibit photovoltaic activity. The semiconductor performs two processes simultaneously: absorption of light and the separation of the electric charges ('electrons' and 'holes') which are formed as a consequence of light absorption. To avoid the premature recombination of electrons and holes, the semiconductors employed must be highly pure and defect-free. In contrast, we have developed solar cells in which the processes of light absorption and charge separation occur in different materials [1]. The junction in this photoelectrochemical cell is a semiconductor-electrolyte interface. Earlier, these interfaces were thought unable to yield competitive photovoltaic devices, as semiconductors with a band gap sufficiently narrow to allow optical absorption of visible-light photons were necessarily unstable against photocorrosion. Wide-band-gap semiconductors, such as titanium dioxide, have an absorption edge towards the ultraviolet spectrum and an insensitivity in the visible spectrum, and are therefore stable

against photocorrosion. The combination of a wide-band-gap semiconductor with a redox-active photosensitizer to produce a photoelectrochemical device represented a major breakthrough when first presented. This patent-protected concept is now well-known in principle and has been licensed for industrial development [2–7].

2. Operating Principles

The solar cell developed at the EPFL operates on the following principles, illustrated in *Fig. 1*. Light absorption is performed by a monolayer of dye (S) adsorbed chemically at the semiconductor surface. A typical photoelectrode consists of a 10 micron thick, highly porous layer of nanocrystalline TiO₂ deposited on a substrate of conducting glass. After having been excited by a photon of light, the dye (S*) – usually a transition-metal complex whose molecular properties are specifically engineered for the task – is able to inject an electron into the conduction band of the oxide semiconductor. The uncharged dye ground state (S⁰) is restored by transferring the positive charge from the dye (S⁺) to a redox mediator R/R⁺ present in the electrolyte with which the cell is filled, and thence to the counterelectrode. *Via* this last electron transfer, in which the mediator is returned to its reduced state, the circuit is closed. The system operates as a regenerative electrochemical cell that converts light into electricity without inducing any permanent chemical transformation. The maximum voltage ΔV that

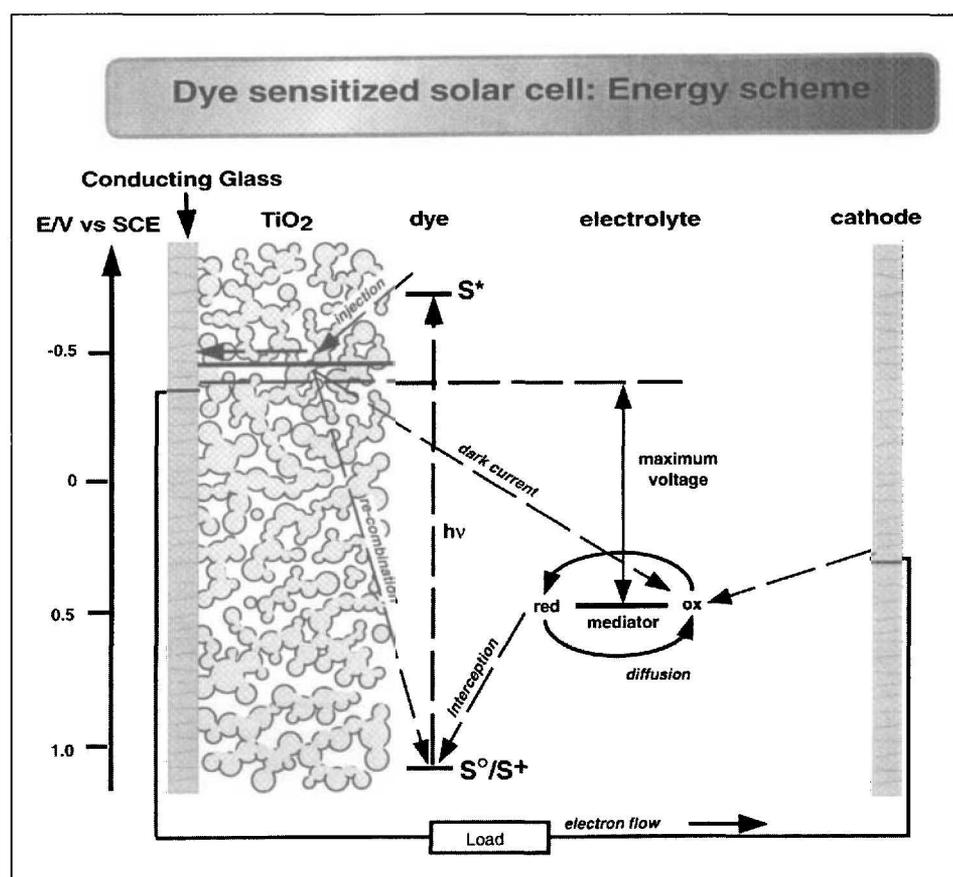


Fig. 1. Charge-transfer mechanisms in the dye-sensitized nanocrystalline photoelectrochemical cell. The sensitizer (S) is excited by the energy of the absorbed photon, then relaxes by electron injection into the semiconductor layer. The charged dye molecule is neutralized by the redox system, which is then regenerated at the counterelectrode by electrons passed through the load. Potentials shown are with reference to the standard calomel electrode (SCE).

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such a device could deliver corresponds to the difference between the redox potential of the mediator and the *Fermi* level of the semiconductor.

In the EPFL laboratory, titanium-dioxide particles and thin films have been widely investigated as substrates for the sensitizing dye [8][9]. This semiconducting material has many advantages: it is a low-cost, widely available, nontoxic and biocompatible material, and used even in health-care products and domestic ap-

plications such as paint pigmentation. Tris(2,2'-bipyridyl-4,4'-carboxylate)ruthenium(II), adsorbed to the oxide surface through the carboxylate groups, was initially used as a photosensitizer. Progress on the sensitized solar cell has been incremental: a synergy of structure, substrate roughness, dye photochemistry, and electrolyte redox chemistry. In 1991, a sensitized electrochemical photovoltaic device with a conversion efficiency of 7.1% under solar illumination was announced [1].

Advancements have continued progressively since then, with certified efficiency now over 10% (Fig. 2). In the remainder of this short review, we will discuss some of the developments which have led to this increase and highlight other interesting developments.

3. Dye Chemistry

Tris(2,2'-bipyridyl-4,4'-carboxylate)ruthenium(II) used initially as a dye suffers from decreased photoactivity at wavelengths longer than 650 nm (Fig. 3). Scandola and coworkers attempted to increase the absorption spectrum and spectral intensity by chemically linking a carboxylated central ruthenium complex to two pendant ruthenium complexes. The central ruthenium complex absorbs light at a wavelength of 525 nm, while the 'antenna' metal centers are excited at 420 nm. Charge transfer from the radial ruthenium centers to the central metal center is followed by transfer to the substrate [10]. Initially fueled by an interest in the sensitizing properties of prussian blue, a new dye was synthesized containing cyanide groups to link the radial ruthenium centers to the central metal complex [11]. Along this vein, one pyridyl group in the initial single-metal center tris-bipyridyl dye was substituted by two coligands such as cyanide, thiocyanate, or halide. These efforts resulted in the very successful bis-bipyridyl dithiocyanate dye which has been our principal photoabsorber for the past several years, with a better spectral response than the initial tris-bipyridyl sensitizer [12]. Only recently has the use of terpyridyl ligands on the single-metal center ruthenium complex resulted in greater spectral response [13]. Currently, we are evaluating a 'black dye' with panchromatic absorption across the solar spectrum. Other dye formulations evaluated include copper derivatives of chlorophyll and certain phthalocyanines [14][15].

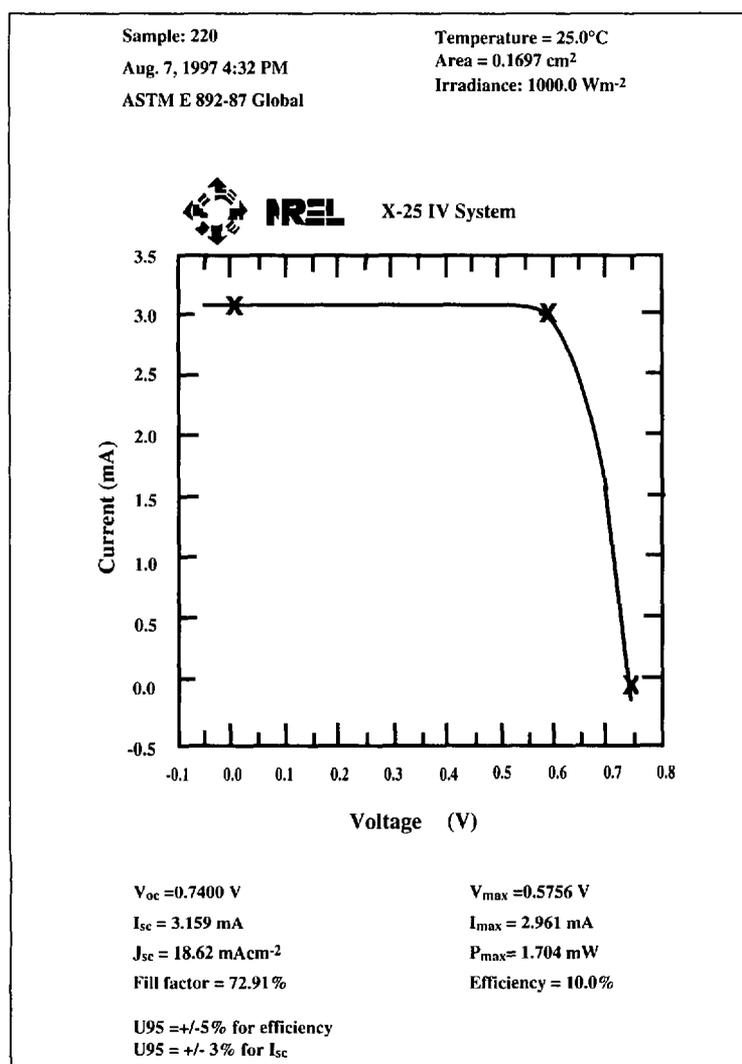


Fig. 2. Current density/voltage characteristic of a typical nanocrystalline photoelectrochemical cell

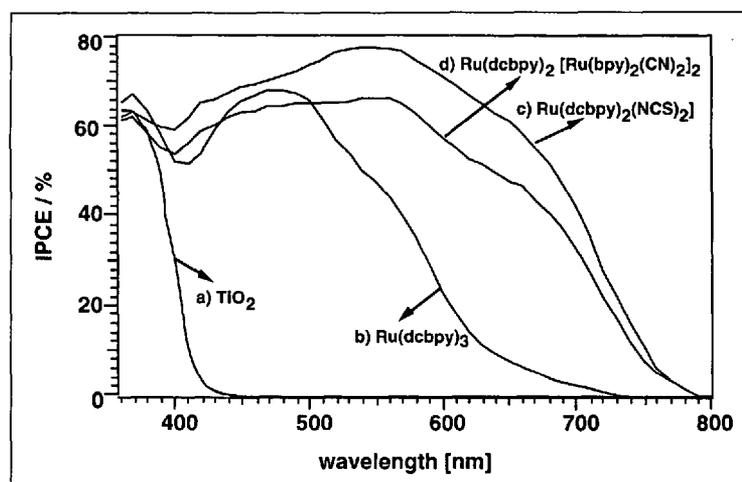


Fig. 3. Evolution of sensitizing dyes, with increased incident photon conversion efficiency at longer wavelengths

4. Electrolytes

The electrolyte typically used in these solar cells is an iodine-containing organic solvent. Alternate electrolytes such as high-viscosity gel and polymer electrolytes have low diffusion coefficients for redox ions, which limits their performance in full sunlight. Recently, we have demonstrated that low-viscosity room-temperature molten salts derived from alkylimidazolium cations can be used successfully as electrolytes in the solar cell [16].

Alternatively, replacing the liquid electrolytes currently used in the nanocrystalline solar cell with solid materials may simplify the sealing process and enables a more facile production process. The electrolyte containing the redox mediator could be replaced by a large band gap p-type semiconductor, *e.g.*, cuprous thiocyanate, CuSCN [17], or cuprous iodide [18]. Alternatively, other hole-transmitting solids may be employed, similar to the amorphous organic compounds used in electroluminescence devices. This is an attractive option which is presently being explored in our laboratory [19].

5. Nanocrystalline Photoelectrodes

The semiconductor oxides used as photoelectrode materials have large surface areas to increase dye uptake, thus maximizing the interfacial region available for interaction with incoming photons. Sol-gel synthesis techniques are used to produce these high-surface area nanoparticles, with dimensions between 10–50 nm. Thin films of these nanoparticles are deposited by screen-printing or doctor blading, resulting in solar cells with respectable efficiencies, as shown in Fig. 2. We have investigated the use of nanocrystalline materials such as TiO₂, Nb₂O₅, ZnO, Ta₂O₅, and Fe₂O₃ for use in the nanocrystalline solar-cell and related applications. The anatase crystal form of titanium dioxide has so far been the most promising candidate for the solar cell photoelectrode material, by virtue of its large band gap (3.2 eV) and its relatively low cost.

We and others have explored the sol-gel synthesis of nanocrystalline anatase for photoelectrode materials [20]. Self-organization of anatase nanoparticles was observed in films made from hydrothermally treated colloidal suspensions, as shown in Fig. 4 [21]. Thin films made from colloids autoclaved at temperatures below 250° display ordered arrays of rod-like particles, with the long axis aligned perpendicular to the substrate. These rod-like particles can be seen in Fig. 5, along with larger particles of varying geometries which apparently frustrate ordering of colloidal particles autoclaved at higher temperatures. The ordering phenomenon has been attributed to interactions between the rod-like particles which are mediated by tetramethylammonium hydroxide (TMAOH) used during hydrothermal growth. Recently, others have observed ordering of hexagonal nanocrystalline titanium-dioxide slabs, also attributed to the directing influence of TMAOH used

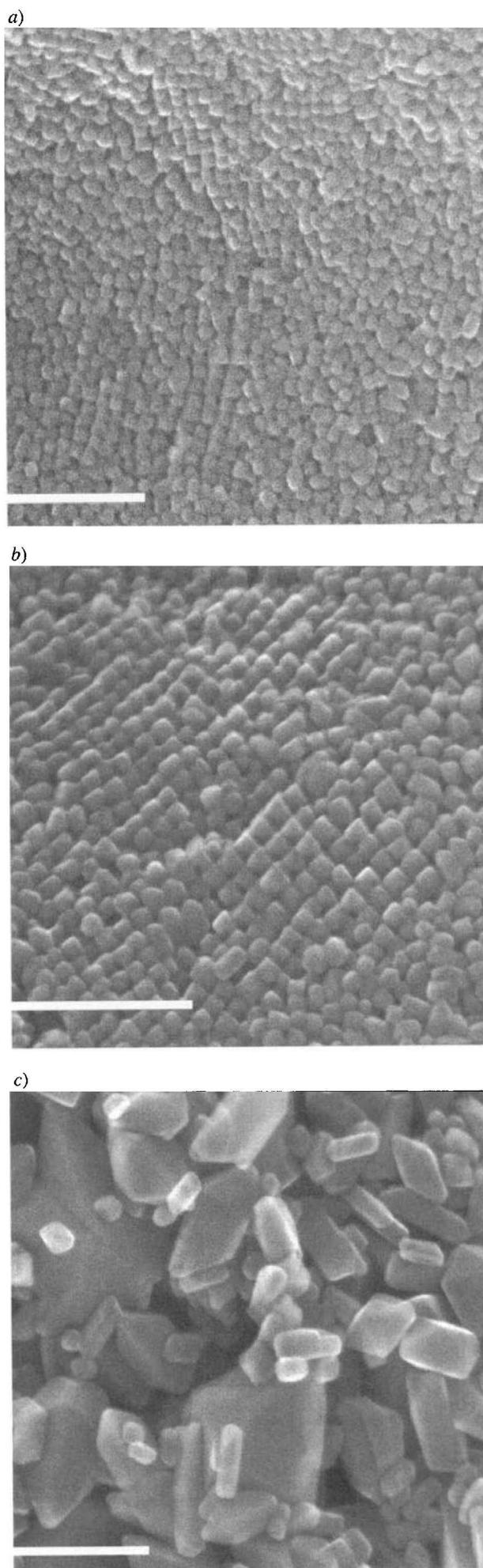


Fig. 4. Scanning Electron Micrographs (SEM) of anatase nanoparticles autoclaved at a) 190°, b) 210°, c) 270°. All scale bars represent 100 nm.

during synthesis [20b]. Interest in ordered thin films of inorganic nanoparticles has increased lately, with the expectation that these structures may yield property enhancements [22].

6. Applications

Numerous applications of nanocrystalline oxide semiconductor films are possible (Fig. 5). Prototypes of small devices powered with dye-sensitized nanocrystalline electrochemical photovoltaic cells are now appearing: e.g., a watch by *SMH Corp.* of Switzerland has been featured recently in the technical press, and industrial progress was reported on upscaling and stability [3][4][23]. The advent of the panchromatic dye facilitates the fabrication of semitransparent devices for windows and other architectural integration, as no color bias is imposed. The opacity of the window can be determined by the photosensitizer concentration. Similarly, the new panchromatic dye could be advantageous for devices such as the recently announced 'smart window' of NREL, in which the photoelectrode, sensitizer, and electrolyte of the EPFL device are associated with an electrochromic counterelectrode [24]. Other devices incorporating specialized counterelectrodes can be projected in the future, such as integrated charge storage devices. These applications will benefit from experience now being acquired in the fabrication of 'rocking chair' secondary cells based on the migration of Li^+ ions from one host, i.e., a TiO_2 -constituting anode to another host cathode, i.e., $\text{NiO}_2/\text{CoO}_2$ or MnO_2 . Studies involving mesoporous TiO_2 films have shown that efficient, reversible, and rapid incorporation of Li occurs due to very short diffusion time for Li^+ in these meso-

scopic oxide structures [25]. A review has recently appeared describing further applications of nanocrystalline films in electrochemistry [14].

7. Conclusions

The dye-sensitized nanocrystalline electrochemical photovoltaic system is at present the only validated competitor to solid-state junction devices for the conversion of solar energy into electricity. This work on photovoltaic cells has also led to innovative developments in electrochromic and photocatalytic devices which utilize nanocrystalline semiconducting thin films as electrode materials.

We would like to acknowledge financial support for our work from the following: the *Swiss Federal Energy Foundation (OFEN)*, a European Union Joule Project (JOR3-CT97-0147: Dye Photovoltaic Cells for Indoor Applications), and the *National Institute for Applied Photovoltaics (INAP, Gelsenkirchen, Germany)*.

Received: June 24, 1998

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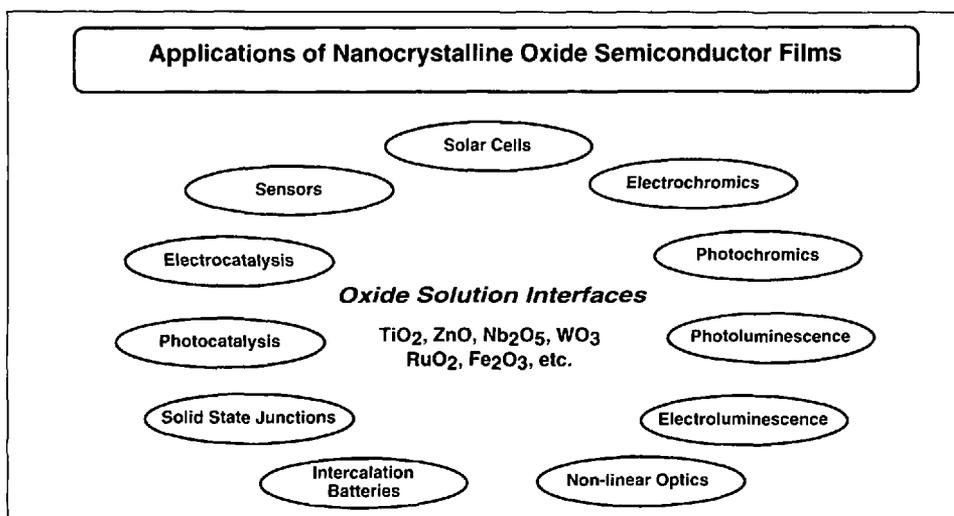


Fig. 5. Applications of nanocrystalline oxide semiconductor films