



MOLECULAR ASSEMBLIES AND NANOSTRUCTURED SEMICONDUCTORS FOR PHOTOINDUCED WATER SPLITTING

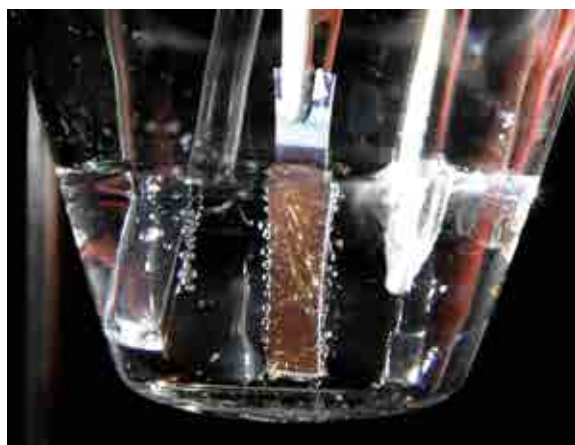


Fig. 1
Photoinduced water splitting from a triple-junction silicon solar cell (3J) modified with a $\text{Fe}^{(III)}$ water oxidation catalyst

THE CONTRIBUTION DESCRIBES THE APPLICATION OF PHOTOELECTROCHEMICAL DEVICES BASED ON n-TYPE METAL OXIDES AND TRIPLE JUNCTION PHOTOVOLTAIC CELLS, FUNCTIONALIZED WITH OXYGEN EVOLVING CATALYSTS, TO PHOTOINDUCED WATER SPLITTING. RESULTS ON THE FUNCTIONALIZATION OF SEMICONDUCTOR PHOTOANODES WITH VISIBLE ABSORBING MOLECULAR ASSEMBLIES ARE ALSO DISCUSSED

World demand for energy is projected to more than double by 2050 and to more than triple by the end of the century and incremental improvements in existing energy networks will not be adequate to supply this demand in a sustainable way [1]. Sunlight provides by far the largest of all carbon-neutral energy sources and could represent the final solution to the energetic problem. Solar energy conversion systems fall into three categories according to their primary energy product: solar electricity, solar thermal systems and solar fuels. Each of these three generic approaches has untapped capability well beyond its present usage.

In the field of photoactive nanostructured materials and interfaces, novel highly ordered semiconductor nanostructures are drawing an increasing interest, both under the fundamental and applicative point of view, due to improved charge transfer kinetics with respect to more conventional sintered nanoparticle substrates. These features, coupled to low cost and ease of fabrication, stand as a good promise for the realization of solar devices capable of solar hydrogen production at a useful rate. Solar hydrogen generation from aqueous solutions is a very attractive field of research, allowing the production of inexhaustible renewable

fuel without emission of pollutants and greenhouse gases. Compared to electricity, hydrogen is a valuable chemical which can be stored and used when needed either in fuel cells, thermal combustion or in industrially pivotal chemical reactions [2, 3]. Among the different approaches to solar water splitting currently investigated in the literature (e.g. molecular level charge separators and catalysts [4-6], photoactive colloidal systems [7, 8]), photoelectrochemical water splitting employing semiconductor electrodes is one of the most viable and efficient [9-11]. The reactions taking place at the electrodes of the photoelectrochemical cell (PEC)

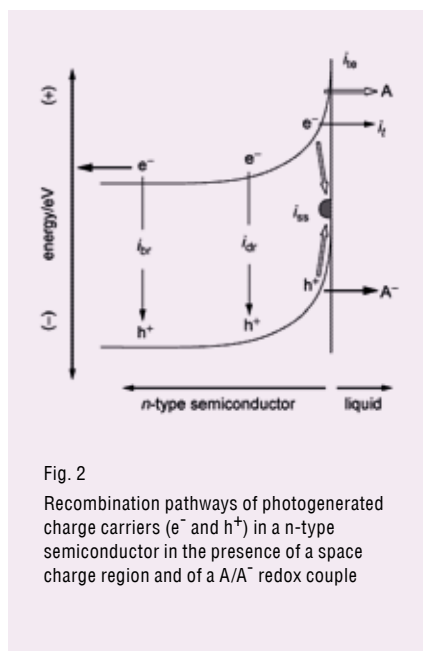
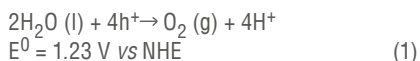


Fig. 2

Recombination pathways of photogenerated charge carriers (e^- and h^+) in a n-type semiconductor in the presence of a space charge region and of a A/A^- redox couple

are reported in Equations (1) and (2), where h^+ and e^- are, respectively, the photogenerated holes and electrons:



While the reduction of protons according to (2) is relatively straightforward, water oxidation is a thermodynamically and kinetically demanding reaction, requiring the loss of 4 electrons and 4 protons [12]. Recent advances in the field of photoelectrochemical cells applied to the solar water splitting and hydrogen production are here presented, with meaningful examples and case studies. At the molecular level, significant recent efforts have been directed towards the development of stable dye sensitizers/water oxidation catalyst assemblies and examples of these systems operating under solar irradiation are discussed.

The semiconductor-liquid interface

The phenomenology of semiconductor-liquid interface represents a very interesting and important area in science and technology [13], involving principles of electrochemistry, photochemistry, solid state theory and surface and interface science. The applications are varied, but most are focused on solar energy conver-

sion schemes, through the use of regenerative photoelectrochemical cells, which convert sunlight to electricity, or photoelectrolytic or photoelectrosynthetic cells, in which solar energy is stored into chemical fuels [14]. Other important applications involve the development of photocatalytic processes for selective photooxidation of organic compounds and for environmental remediation. Photoelectrolysis of water using sunlight [15, 16] is extremely attractive for a number of reasons:

- 1) photoproducted hydrogen is a valuable fuel and energy carrier which can be stored more easily than electricity or heat;
- 2) it is non polluting, inexhaustible and flexible with respect to energy conversion in heat (combustion) or electricity (in fuel cells);
- 3) hydrogen is a valuable chemical by itself, being used in large quantities by the industry in chemical processing like ammonia synthesis and petroleum refining.

The thermodynamic upper limit to the energy that can be extracted by the semiconductor/liquid junction is approximately equal to the band gap of the semiconductor, which is related to the open circuit photovoltage (V_{oc}). However the usable free energy collected across a semiconductor/electrolyte junction is not purely limited by thermodynamic quantities, but also by electron transfer kinetics and transport of the photogenerated charge carriers (Fig. 2). The electric field inside the space charge region may have a relevant role in assisting the charge separation at the interface. Holes are attracted towards the electrolyte by the negative charge layer, while electrons are repelled from the surface. As a consequence, photooxidation reactions can take place under illumination at the surface of an n-type semiconductor, while photoreduc-

tion can be carried out at a counter electrode (either p-type semiconductor or metal electrode) wired to the photoactive material.

Photoelectrodes based on anodically grown WO_3

Tungsten (together with Al, Ti, Zr, Bi, Ta, Nb) belongs to the group of the so called valve metals, which passivate and show a very high corrosion resistance in most common aqueous media. The composition of naturally or anodically produced oxide films is essentially identical to the WO_3 .

Due to its electrochromic properties, i.e. a reversible color change upon application of suitable electric potential, tungsten trioxide has been employed and widely used in electronic displays, smart windows, sunroofs and rear and side view mirrors [17, 18]. More recently, due to its chemical stability in acidic aqueous media and interesting photoelectrochemical properties, it has been proposed as promising candidate in water photoelectrolysis processes [19, 20].

Electrochemical anodization of metallic tungsten can be a convenient method for preparing porous photoactive substrates in which the oxide structures are tightly interconnected and strongly bound to the metal collector, both factors concurring to increase the photogenerated charge collection efficiency. The potentiostatic anodization, usually carried out at room temperature (20 ± 5 °C) for several hours (48-72 h), results in the formation of an irregular porous oxide layer 3-5 micron thick, with bundled up structures, particularly evident in SEM imaging (Fig. 3) [21], ca. 300 nm wide, longitudinally crossed by cracks which give to the surface an overall worm-like appearance.

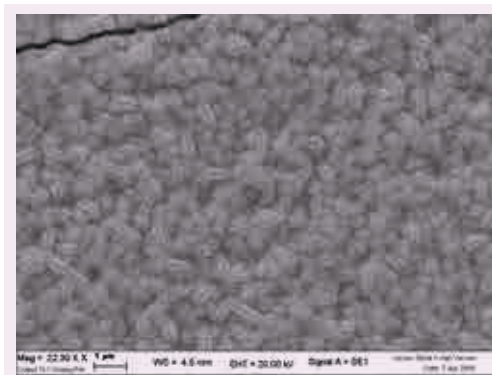


Fig. 3

Top-view SEM image of anodically grown WO_3 after the annealing process at 550 °C for 1 h in air

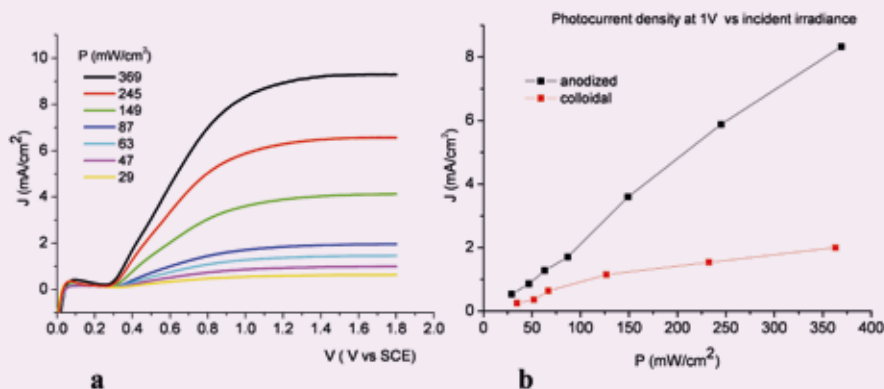


Fig. 4
 a) J-V curves in 1 M H₂SO₄ as a function of the incident irradiance (AM 1.5 G);
 b) photocurrent density taken at 1 V vs SCE vs incident irradiance: anodically grown (black) and sol/gel (red) WO₃ film

After a thermal treatment at 550 °C in air, necessary both to induce crystallinity and to establish good electrical connections between the nanostructures, small angle XRD confirmed the presence of the expected monoclinic phase of WO₃.

As demonstrated by the J-V characteristic recorded in 1 M H₂SO₄ (Fig. 4a), the typical photoelectrochemical performances of the anodically grown oxides are relevant: under varying AM 1.5 G incident irradiation the photocurrent, whose threshold at pH 0 is located at +0.3 V vs SCE, varies in a reasonably linear fashion with the incident irradiance, showing maximum values exceeding 9 mAcm⁻² under 0.37 Wcm⁻² with an average slope of 0.013 Acm⁻²V⁻¹. The advantage of the electrochemically grown WO₃ over a more conventional WO₃ electrode obtained by standard sol-gel methods (colloidal) made by sintered nanoparticles, can be clearly appreciated from Fig. 4b: while the performance of the two electrodes are quite similar at low power intensities, under strong illumination the anodically grown substrate does not show saturation and clearly outperforms the colloidal almost by a x 4 factor.

The photocurrent action spectra (IPCE = number of electrons/number of incident photons) (Fig. 5) recorded in sulfuric acid indicate an high photon to current conversion, approaching 70% in a broad region in the UV and extending deeply in the visible region,

thanks to a secondary maximum at 400 nm (IPCE_{max}=45% at 1.5 V vs SCE) whose onset is located at 490 nm. The IPCE undergoes a significant enhancement in the presence of sacrificial hole scavengers like methanol or formic acid, reaching a value close to 100% in the UV region where the light absorption is complete.

Photoelectrodes based on nanostructured hematite

Nanostructured hematite (α-Fe₂O₃), due to its band gap of ca. 2.2 eV (corresponding of λ=560 nm) and a Valence Band (VB) edge

more positive than the water oxidation potential, has become in the last years one of the most popular semiconductors employed for the fabrication of cheap and earth-abundant photoanodes [9]. Despite these essential characteristics, hematite is known to suffer of electron/hole recombination and very slow hole-transfer kinetic from the bulk oxide to the solution [22]. Some strategies to overcome these negative features commonly involve n-doping with various elements (e.g. Pt, Sn, Si) [23-25], designed to increase electron conductivity of the material, and functionalization of the electrode surface with both oxygen evolving catalyst (OEC) (e.g. IrO₂, Fe-OEC) [26, 27], and conformal overlayer (e.g. Al₂O₃, In₂O₃) [28], to improve water oxidation kinetic resulting either in a photoanodic-onset shift to less positive values or in the enhancement of the photocurrent response, or both. More recently, a new strategy to promote photoconversion efficiency of hematite electrodes has been developed, involving the introduction at the contact between the FTO and the semiconductor film of ultrathin layer of different oxides (e.g. SiO_x, Nb₂O₅, TiO₂) [29] that, having a conduction band significantly higher than hematite, act as tunneling junction. Usually such underlayers (few nanometers in thickness) are used in combination with very thin hematite films (10-30 nm), that do not guarantee high light harvesting efficiency (LHE), but are desirable due to the reduction of the photogenerated holes path to reach the semiconductor-liquid junction (SCLJ) from the bulk. This allows holes to

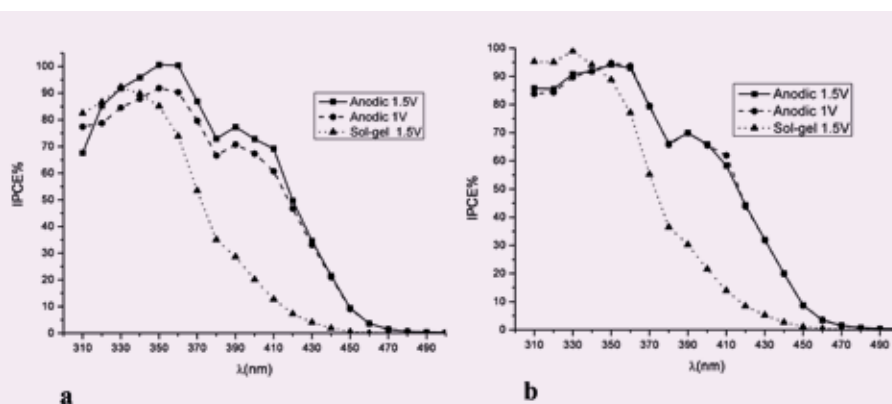


Fig. 5
 Photoaction spectra of anodically grown and sol-gel WO₃ film biased at 1.5 V vs SCE in the presence of sacrificial electron donors, a) 20% of methanol in 1 M sulphuric acid and b) 1 M formic acid/ 1 M sodium formate

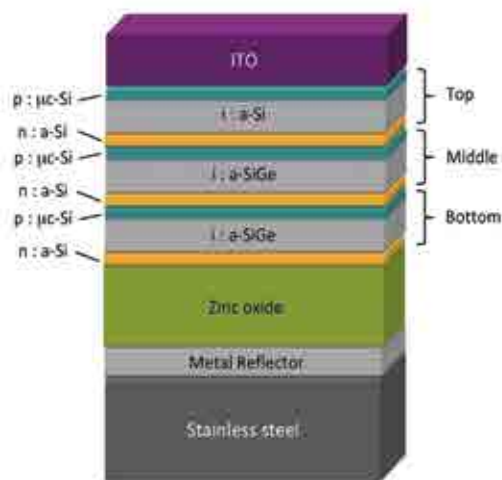


Fig. 6
Schematization of Xunlight®
3J cell

be transferred to the solution with minimized losses due to recombination, finding a compromise between deep light penetration depth ($\alpha^{-1}=118$ nm at $\lambda=550$ nm) and very short hole diffusion length (2-4 nm) [30].

Inspired by this latter strategy, we have recently developed a new photoanode design with a nanometric spin-coated iron oxide underlayer (HTL) coupled with a mesoporous hematite film deposited by electrophoresis (MPH). The electrodes equipped with the thin underlayer was observed to exhibit a four-fold improvement in photoactivity over the simple hematite porous film, reaching a stable photocurrent density of ca. 1 mAcm^{-2} at 0.65 V vs SCE under AM 1.5 G illumination. Further improvement to 1.6 mAcm^{-2} has been observed after decoration of the hematite surface with a Fe(III) oxygen evolving catalyst. These results demonstrate that by combining different iron oxide morphologies it is possible to improve the selectivity of the interfaces towards both electron collection at the back contact and hole transfer to the electrolyte, obtaining an efficient all-iron based photoelectrode entirely realized with simple wet solution procedures.

Triple junction photovoltaic cells functionalized with oxygen evolving catalysts

As previously discussed, photoelectrochemical water oxidation can successfully occur at the surface of illuminated wide-band-gap semiconductors, like TiO_2 [31, 32], WO_3 [33, 34], and Fe_2O_3 [35, 36], by exploiting the ox-

idizing power of holes lying at the top of their valence bands. However, in these systems the Solar To Hydrogen conversion efficiency (STH) is limited by both competitive electron/hole recombination and by the modest spectral sensitivity of these materials, resulting in a reduced amount of effectively harvestable sunlight.

In order to overcome these limitations, Nocera *et al.* coupled triple junction (3J) silicon-based photovoltaic cells to either electro- or photo-electrodeposited oxygen evolving catalysts (OECs), based on modified cobalt oxides (CoPi) [37]. The combination of the excellent electronic properties of silicon (optimal light harvesting, efficient charge collection) with fast water oxidation kinetics ensured by the functionalization with the OEC, yielded PECs delivering more than 3 mAcm^{-2} at 0 V vs the reversible hydrogen electrode (RHE), with STH efficiency $<5\%$, depending on the sample and electrolyte [38].

Following Nocera's work, we started investigating the functionalization of indium tin oxide (ITO) layers of 3J cells, provided by Xunlight® (Fig. 6) [39], with OECs based on Fe(III) compounds [40, 41], obtained by simple Successive Ionic Layer Adsorption and Reaction (SILAR) [42]. Catalyst electrodeposition may in fact result in silicon active layer etching, when biased at positive potentials in non-acidic pH. Besides their well-known catalytic properties in oxidation reactions [43], Fe(III) oxides are very attractive materials, for their low cost, non-toxicity and environmentally benign nature. The proposed SILAR

procedure exhibits several advantages over (photo) electrochemical depositions, since 1) it is fast; 2) it does not require electrochemical equipment or use of toxic chemicals; 3) it can be easily scaled up to large surfaces where defects in the ITO coating and its limited conductivity may cause voltage drops.

The functionalization of ITO surfaces by exploiting fast ionic reactions in aqueous media led to the *in-situ* formation of transparent discontinuous nanometric layers of first row transition metal (Fe, Ni, Co) oxides, exhibiting good catalytic properties towards oxygen evolution in basic environment. Indeed, the Fe-OEC modified ITO electrodes displayed a noticeable electroactivity towards water oxidation in $0.5 \text{ M Na}_2\text{CO}_3$ solutions, with onset potential for water oxidation at ca. 0.7 V vs SCE and a JV slope $>10 \text{ mAcm}^{-2}\text{V}^{-1}$ (Fig. 1). In agreement with these interesting electrocatalytic properties, the best Fe-OEC modified triple junction cells performed water splitting with promising photoanodic stability and STH conversion efficiency of the order of 4-5% in $0.5 \text{ M Na}_2\text{CO}_3$ (pH 11.2) [44], among the highest achieved by photoelectrochemical systems based on photoanodes built with earth-abundant materials and simple chemical procedures.

Dye sensitized photoanodes

The exploitation of molecular level sensitized photoelectrodes in water splitting reactions, requiring specific dyes and surface engineering, is generally less successful than the approach based on stable high band gap semiconductors due to the lack of stability of the molecular assemblies on the SC surface and to efficient charge recombination processes. The main problem in the molecular approach is the development of visible absorbing sensitizers, having sufficient driving force to carry out both charge injection into the semiconductor and hole transfer to a catalyst, achieving the primary charge separated state. In a generic sensitized PEC design, the molecular excitation and excited state formation are followed by electron transfer injection into the conduction band of a semiconductor. In order to promote multi-electron transfer events like water oxidation, multiple redox equivalents must be concentrated in a single site or cluster. In principle, at the cathode, water or CO_2 reduction may occur, giving rise to the production of fuels.

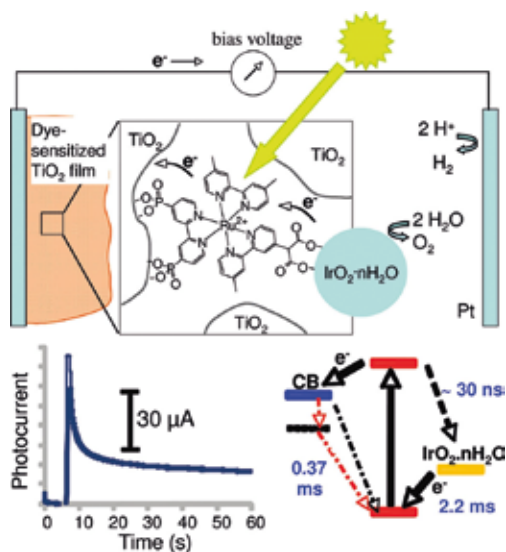


Fig. 7
Top: schematic diagram of an IrO₂ catalyzed water-splitting dye-sensitized photoelectrochemical cell (DSPEC). Bottom left: photocurrent transient showing a steady state photocurrent. Bottom right: energy diagram and time constants for the relevant interfacial electron transfer and excited state deactivation processes

An interesting configuration involves the anchoring of hydrated IrO₂ nanoparticles to a phosphonated Ru(II) sensitizer modified with malonate binding groups (Fig. 7) [6, 45]. The hole transfer to the IrO₂ takes place on a millisecond (2.2 ms) time scale, while charge recombination occurs on a sub-millisecond (0.37 ms) time scale. Thus, the competition between hole transfer and recombination is unfavorable to an effective charge separation. Nevertheless, under a small positive bias (≥ 330 mV) a stable photoanodic current of the order of few tens of microamperes is effectively detected, indicating the occurrence of photoinduced water oxidation under steady state conditions. Following a modified strategy, [(N,N'-bis(2-(trimethylammonium)ethylene) perylene 3,4,9,10-tetracarboxylic acid bisimide)(PF₆)₂] (AB005) was recently adsorbed on nanocrystalline WO₃ surfaces via aggregation/hydrophobic forces [46]. Under visible irradiation ($\lambda > 435$ nm), the excited state of AB005 underwent oxidative quenching by electron injection ($k_{inj} > 10^8$ s⁻¹) to WO₃, leaving a strongly positive hole ($E_{ox} \approx 1.7$ V vs SCE) which allows to drive demanding photo-oxidation reactions in photoelectrochemical cells. The casting of IrO₂ nanoparticles (NPs), acting as water oxidation catalysts (WOCs) on the sensitized electrodes, led to a four fold enhancement in photoanodic current, consistent with hole transfer from oxidized AB005 to IrO₂ occurring on the μ s time scale. Although the efficiency is low, these type of devices represent a successful proof of concept of water split-

ting in a sensitized PEC making use of IrO₂ nanoparticles as catalyst.

Other approaches making use of photoanodes functionalized with a chromophoric units covalently bound to a molecular catalyst [47] or functionalized through co-deposition of molecular dyes and catalysts [48] have been reported. In these cases although the efficiencies for water oxidation are reported in the range 3-4%, the long term stability still needs to be demonstrated.

Conclusions

Solar energy is the only renewable and carbon neutral energy source of sufficient scale to replace fossil fuels. Direct conversion of this energy into clean fuels is one of the most important scientific challenges of the XXI century. In this context, hydrogen production from solar water splitting, providing a potentially inexhaustible fuel source and carbon dioxide conversion to organics, is obviously attractive. Although the realization of a molecular level system mimicking natural photosynthesis for the production of solar fuels is certainly fascinating under a fundamental viewpoint, the practical efficiency achievements with respect to water splitting have been so far limited by a small driving force and kinetic complications, arising from the need of realizing a multiple proton coupled charge transfer necessary to simultaneously overcome the demanding kinetics of water oxidation and reduction. Since the experiment of Fujishima and Honda in 1972 [15], the direct use of semiconductor photoelectrodes or nanopar-

ticles have appeared to be an alternative way for achieving photoinduced water splitting, thanks to the possibility of obtaining, with a practically unitary quantum yield, highly energetic charge carriers that can induce the required electrochemical reactions at the solid/electrolyte interface. Photoanodes based on n-type metal oxides like TiO₂, WO₃ and Fe₂O₃ have been intensely studied, since, at appropriate pH, they couple ease of fabrication, high chemical stability in aqueous solution under evolving oxygen conditions and reasonably high incident light to current generation when operated in a photoelectrochemical cell. The results here reported underline that, so far, the winning strategy to obtain photoinduced water splitting in high yield is based on heterogeneous devices based on solid state semiconductors which coupled to suitable catalyst show stability and can operate under high light intensity.

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Sensibilizzatori molecolari e semiconduttori nanostrutturati nell'ossidazione fotoindotta dell'acqua

L'articolo descrive le applicazioni di sistemi fotoelettrochimici basati su ossidi metallici semiconduttori di tipo n e celle fotovoltaiche a tripla giunzione di silicio, modificate con catalizzatori inorganici, per l'ossidazione fotoindotta dell'acqua. Sono inoltre discussi i risultati ottenuti con fotoanodi funzionalizzati con sensibilizzatori molecolari.

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