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Additional Information

Harnessing Infrared Photons for Photoelectrochemical Hydrogen Generation. A PbS Quantum Dot Based “Quasi-Artificial Leaf”

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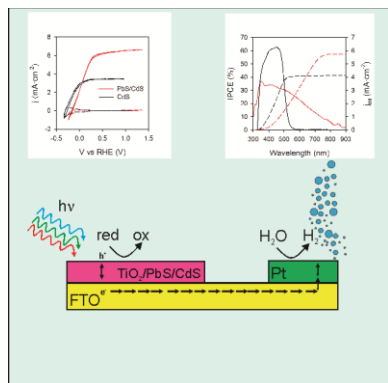
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Abstract

Hydrogen generation by using quantum dot based heterostructures has emerged as a promising strategy to develop artificial photosynthesis devices. In the present study, we sensitize mesoporous TiO₂ electrodes with *in-situ* deposited PbS/CdS quantum dots (QDs), aiming at harvesting light in both the visible and the near infrared for hydrogen generation. This heterostructure exhibits a remarkable photocurrent of 6 mA·cm⁻² leading to 60 ml·cm⁻²·day⁻¹ hydrogen generation. Most importantly, confirmation of the contribution of infrared photons to H₂ generation was provided by the incident-photon-to-current-efficiency (IPCE), and the integrated current was in excellent agreement with that obtained through cyclic voltammetry. The main electronic processes (accumulation, transport and recombination) were identified by impedance spectroscopy, which appears as a simple and reliable methodology to evaluate the limiting factors of these photoelectrodes. Based on this TiO₂/PbS/CdS heterostructure, a “quasi-artificial leaf” has been developed, which has proven to produce hydrogen under simulated solar illumination at (4.30 ± 0.25) ml·cm⁻²·day⁻¹.

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Here we present a Quantum Dot based “quasi-artificial leaf”, based on a TiO₂/PbS/CdS heterostructured nanocomposite electrode, harnessing infrared photons for solar H₂ generation. The device has demonstrated to produce 4.30 ml·cm⁻²·day⁻¹ H₂, confirmed through labeling experiments. The photoelectrochemical characterization of the material also provided an accurate description of the transport and accumulation of charge carriers in the device.

Keywords: Hydrogen generation, quantum dots, lead sulfide, cadmium sulfide, titanium dioxide, impedance spectroscopy

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3 The provision of clean and renewable energy to satisfy the increasing human demands in the
4 XXI century is one of the key challenges to sustain the present global social and economical
5 model.^{1,2} Sunlight offers a huge potentiality for global supply of renewable energy, provided that
6 this energy can be stored for its use upon demand. In this context, photoelectrochemical
7 hydrogen generation by water splitting with semiconductor materials constitutes the simplest
8 conversion scheme, since H₂ can be produced with the only input of water and sunlight and H₂
9 combustion in hydrogen fuel cells leads to electricity with water as the only byproduct, resulting
10 in a CO₂ neutral process.²⁻⁴ The key challenge of this approach relies on whether this goal can be
11 met in a cost-effective way on the terawatt scale.²
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21 Since the seminal report of Fujishima and Honda in 1972 demonstrating the photocatalysis of
22 TiO₂ for H₂ generation,⁵ a dynamic search for the optimum semiconductor material and device
23 configuration was launched, but crystallization of this research activity into a well developed
24 technology has not been achieved yet, mainly because none of the explored materials
25 simultaneously meet the different needed requirements for adequate device operation; i.e. a
26 bandgap comprised between 1.9-2.2 eV, conduction and valence band edges straddling the water
27 oxidation and hydrogen reduction potentials, good conductivity and low cost.^{2,4} The novel
28 developments in the fields of nanoscience and catalysis⁶ have provided key elements and
29 concepts to rationalize the search for promising materials and device architectures.
30 Orthogonalization of light absorption and carrier diffusion,⁷⁻⁹ quantum confinement,¹⁰ band
31 energetics engineering¹¹ and plasmonics^{12,13} appear as fascinating strategies, which can be
32 exploited to enhance the efficiencies of photoelectrochemical hydrogen generation devices.
33 Sensitization of wide oxide semiconductors like ZnO or TiO₂ by chalcogenide quantum dots also
34 provides a convenient heterostructured platform for photoelectrochemical H₂ generation. Indeed,
35 this approach, has showed promising results: Hensel *et al.* showed the synergistic effect of N
36 doping of TiO₂ nanowires and CdSe sensitization leading to photocurrents close to 3 mA·cm⁻².¹⁴
37 Combining ZnO nanowires with CdTe quantum dots, Chen *et al.* obtained photocurrents close to
38 2 mA·cm⁻² using a non-sacrificial hole scavenger.¹⁵ Hierarchical ZnO/WO_x nanowires
39 cosensitized with CdSe/CdS led to promising photocurrents close to 12 mA·cm⁻² and light-to-
40 chemical conversion efficiencies of 6%.¹⁶ More recently, Luo *et al.* have highlighted the
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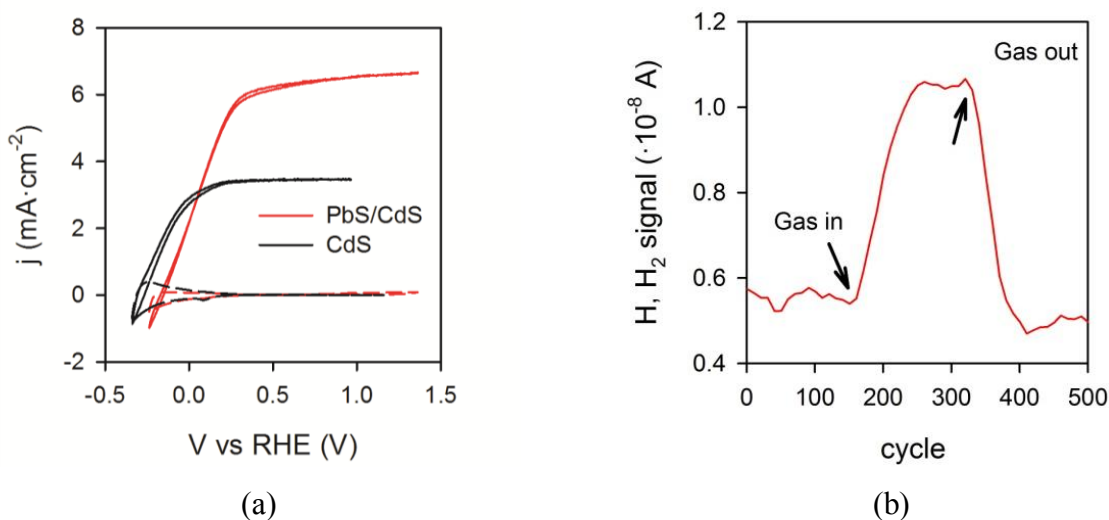
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3 importance of the controlled deposition of the light absorbing semiconductor (CdSe) on inverse
4 opals of TiO₂, achieving photocurrents of 15.7 mA·cm⁻² for hydrogen generation.¹⁷
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9 On the other hand, an optimal exploitation of the solar spectrum for photoelectrochemical energy
10 conversion must entail the use of narrow bandgap semiconductors, like PbS, in order to harness
11 infrared photons for photoelectrochemical conversion. Tada *et al.*¹⁸ have reported a solar-to-
12 hydrogen conversion efficiency of 1.15% and a hydrogen production rate of 5.2 ml·h⁻¹
13 employing a heterostructure based on mesoporous TiO₂ decorated with colloidal PbS quantum
14 dots (under the application of bias). In the present study, we have developed a hybrid
15 architecture based on a TiO₂ mesoporous frame functionalized with *in-situ* grown PbS/CdS QDs,
16 targeting at an unassisted photoelectrochemical hydrogen generation device. The ultimate goal is
17 achieving a system able to convert visible, but also infrared photons into H₂. Great benefit can be
18 derived from the collection of IR photons since they represent practically 50% of the solar
19 spectrum photons.
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30 Colloidal PbS quantum dots have demonstrated to harness the infrared photons towards efficient
31 solar hydrogen production.¹⁸ We have incorporated *in-situ* grown PbS quantum dots onto a
32 mesoporous TiO₂ structure together with CdS quantum dots to both enhance the visible response
33 (see Supporting Information, Figure SI1) and stabilize the whole material.¹⁹ The microscopic
34 inspection of the material by SEM showed the mesoporous TiO₂ structure but did not reveal any
35 morphological details of the PbS/CdS sensitizers (Supporting information, Figure SI2). The
36 presence of PbS QDs was confirmed through XRD spectra carried out on TiO₂/PbS structures
37 (Supporting information, Figure SI3). High resolution TEM images (Supporting information,
38 Figure SI4) reveal that both PbS and CdS appear as scattered nanoparticles (diameter below 10
39 nm) onto the mesoporous TiO₂ network, and covered by a ZnS layer.
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49 The photoelectrochemical behavior of TiO₂/PbS/CdS heterostructures in an aqueous solution
50 containing 0.25 M Na₂S and 0.35 M Na₂SO₃ as sacrificial hole scavenger in the dark and under
51 illumination is showed in Figure 1a. As a reference, results for TiO₂/CdS are also included. It is
52 clear that higher photocurrents are obtained when PbS is included in the heterostructures. At 0V
53 vs RHE, a photocurrent of 2 mA·cm⁻² is obtained for both systems. Saturation of the
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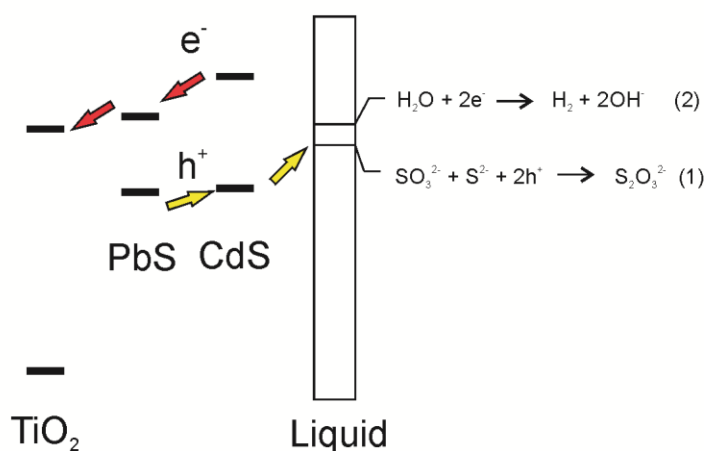
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3 photocurrent takes place at approximately 0.4 V vs RHE, with $6 \text{ mA}\cdot\text{cm}^{-2}$ for $\text{TiO}_2/\text{PbS}/\text{CdS}$ and
4 $3.5 \text{ mA}\cdot\text{cm}^{-2}$ or TiO_2/CdS . This equals $60 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$ and $35 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$ hydrogen
5 generation rate, respectively, assuming a faradaic efficiency unity. The observed positive
6 photocurrents correspond to hole injection from the heterostructured TiO_2/QDs photoanode into
7 the solution. The difference between the anodic and cathodic branches of the dark cyclic
8 voltammetry curve, at potentials below 0V vs RHE (more visible for TiO_2/CdS structure) is due
9 to the chemical capacitance of TiO_2 , consistently with previous studies.²⁰⁻²². Labeling
10 experiments of the evolved gas at the Pt counterelectrode was collected in an inverted burette
11 and analyzed. The results for $\text{TiO}_2/\text{PbS}/\text{CdS}$ are showed Figure 1b clearly indicating that the
12 generated gas is hydrogen. Additionally, the stability of these photoelectrodes was tested by
13 chronoamperometric measurements. The electrodes showed to be stable (no decrease of
14 photocurrent during more than 1 hour, and the loss of performance detected was due to the
15 depletion of the sacrificial agent in the solution (see Supporting Information, Figure SI5).



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44 **Figure 1.-** (a) j - V curves for the $\text{TiO}_2/\text{PbS}/\text{CdS}$ heterostructure in the dark (dashed lines) and
45 under illumination at $100 \text{ mW}\cdot\text{cm}^{-2}$ (solid lines) obtained by cyclic voltammetry in three
46 electrode configuration, the results for TiO_2/CdS are also included as a reference (b) Gas
47 chromatography Mass Spectroscopy plot of the evolved gas for $\text{TiO}_2/\text{PbS}/\text{CdS}$ heterostructure.
48 The signal of H_2 is clearly increased after gas is passed through the system.

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53 The results obtained from the photoelectrochemical characterization showed in Figure 1a suggest
54 that TiO_2 , PbS and CdS form a cascaded structure, and photogenerated electrons at both CdS and
55 PbS can be collected at the contact, although further research is needed to unambiguously
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3 establish this point. Figure 2 shows a proposed energy diagram, based on literature data,^{24,25} in
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5 which the different electronic processes and relevant electrochemical reactions are scheduled.
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7 Further quantification of the position of the energy levels of the conduction and valence band
8
9 edges for QDs is out of the scope of the present study. Extensive discussion of the reaction
10
11 mechanisms has been reported elsewhere.^{14,15,18,23,24} The presence of Na₂S and Na₂SO₃ hole
12
13 scavengers in the electrolyte provides a fast shuttle for the photogenerated holes (reaction 1)
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15 avoiding photocorrosion, while electrons are driven through TiO₂ toward the contact, and then to
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17 the catalytic cathode, where hydrogen generation takes place (reaction 2).



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Figure 2. Energy diagram illustrating the oxidation at PbS/CdS QDs-sensitized TiO₂ particulate anodes. Energy levels were adapted from^{25,26}. The arrows indicate the traffic of electrons and holes.

In order to gain further insight into the charge transfer mechanisms of TiO₂/PbS/CdS heterostructures, chopped light j-V curves were carried out. Figure 3a shows the superimposed chopped and constant light j-V curves. The presence of current transients (spikes) in the chopped light curve provides direct evidence of the participation of surface states in the hole transfer process. Indeed, the presence of these transients has been attributed to the charging (trapping of holes) of surface states, or oxidizing surface species.²⁷⁻²⁹ The presence of surface states for PbS has been also recognized in the recombination process for quantum dot sensitized solar cells.¹⁹ In contrast, we have previously showed that when CdS/CdSe quantum dots are used

as light absorbers, the hole collection efficiency is unity (spikes are not observed in the chopped light j - V curves).³⁰

The contribution of infrared photons to the higher photocurrent measured for $\text{TiO}_2/\text{PbS}/\text{CdS}$ (and hence to the H_2 generation) was assessed by measuring the incident-photon-to-current-efficiency (IPCE) action spectrum in a three electrode configuration, at 0.95 V vs RHE. The results for TiO_2/CdS are also showed as a reference (see Figure 3b). The IPCE action spectrum for TiO_2/CdS extends up to 550 nm, while when PbS is included in the heterostructure, the wavelength range expands beyond 800 nm, confirming the contribution of infrared photons to the photocurrent. Indeed, the IPCE action spectrum practically mimics the optical density, and the APCE (absorbed photon to current efficiency) values are practically identical to IPCE as showed in Supporting Information, Figure SI6, for $\text{TiO}_2/\text{PbS}/\text{CdS}$. Integration of the IPCE spectrum with wavelength led to a total photocurrent of $5.7 \text{ mA}\cdot\text{cm}^{-2}$ and $4.1 \text{ mA}\cdot\text{cm}^{-2}$ for $\text{TiO}_2/\text{PbS}/\text{CdS}$ and TiO_2/CdS , respectively (Figure 3b) in excellent agreement with the maximum photocurrent showed in Figure 1 ($6 \text{ mA}\cdot\text{cm}^{-2}$ and $3.5 \text{ mA}\cdot\text{cm}^{-2}$, respectively).

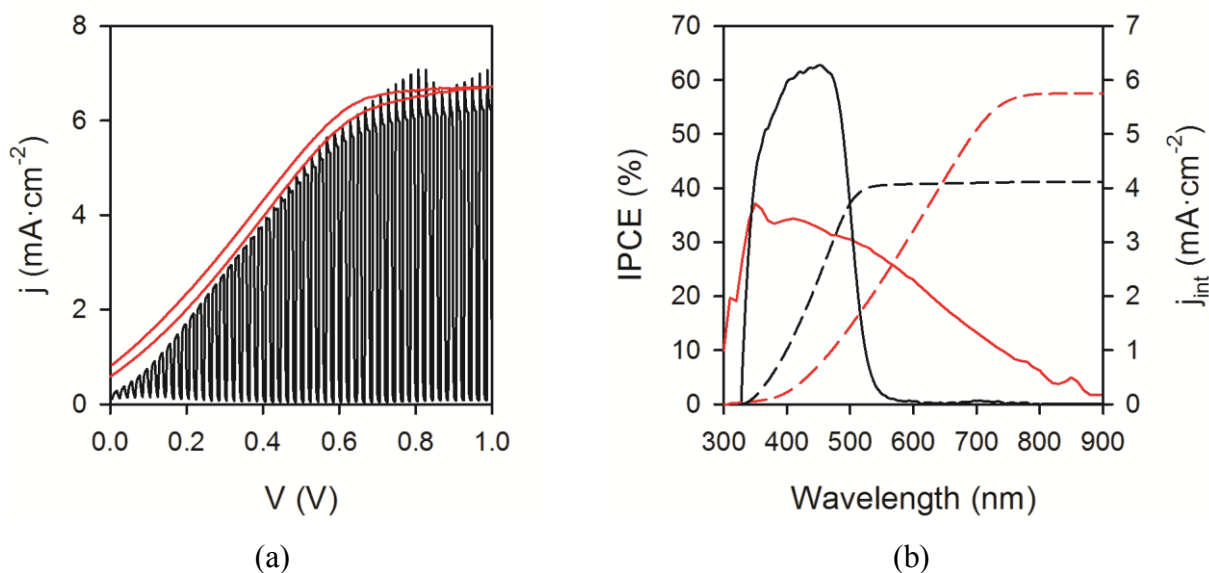


Figure 3.- (a) Chopped light (black) and constant (red) illumination j - V curves in two electrode configuration of the $\text{TiO}_2/\text{PbS}/\text{CdS}$ heterostructured photoanode. (b) IPCE (solid lines) and integrated current (dashed lines) for a $\text{TiO}_2/\text{PbS}/\text{CdS}$ (red) and a reference TiO_2/CdS (black) photoelectrode at 0.95 V vs RHE.

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Further photoelectrochemical characterization of the heterostructured TiO₂/PbS/CdS photoanodes was carried out by impedance spectroscopy measurements in the dark and under illumination. A sound physical model was already developed for similar heterostructured materials,^{19,30-32} which is scheduled as supporting information, Figure SI7. Consequently, this model was directly applied to extract the chemical capacitance of TiO₂, C_{μ} , the recombination resistance, R_{rec} and the transport resistance, R_{tr} of the TiO₂/PbS/CdS architectures. C_{μ} monitors the density of states (DOS) at the Fermi level, and provides the distribution of trap states below the conduction band of TiO₂, R_{tr} is directly proportional to the resistivity of TiO₂ (ρ_{TiO_2}) and R_{rec} is inversely proportional to the recombination rate of electrons at the TiO₂/solution interface.^{20,33,34} The exponential behavior of the transport resistance with voltage in the QD sensitized films follows identical exponential trend as compared to bare and dye sensitized TiO₂, suggesting that electron transport occurs mainly through the TiO₂ nanoparticles rather than through QDs.²¹ Furthermore, the transport resistance (R_{tr}) for TiO₂ is very similar in the dark and under illumination (Figure 4a). This is an expected result, since the conductivity of the TiO₂ nanoparticles is determined by the electron density in the conduction band which, is controlled by the applied potential and not by illumination. The chemical capacitance (Figure 4b) shows the characteristic exponential dependence with potential, reflecting the trap state distribution below the conduction band of TiO₂. This agrees well with the assumption that charge is accumulated and transported mainly through the TiO₂. The behavior of C_{μ} is very similar in the dark and under illumination conditions again, since it is determined by the position of the Fermi level which is governed by the applied bias. The small difference found at the intermediate states between dark and illumination conditions may be due to a capacitive contribution from the accumulation of charges in the QDs.

Finally, the recombination resistance, R_{rec} is governing the photoelectrochemical behavior of the heterostructure, since the total resistance obtained by derivation of the j-V curve, also including series resistances, practically mimics the R_{rec} values obtained by impedance spectroscopy both in the dark (Figure 4c) and under illumination (Figure 4d). Therefore, impedance spectroscopy appears as a very attractive experimental technique to monitor the main processes controlling the performance of these materials.

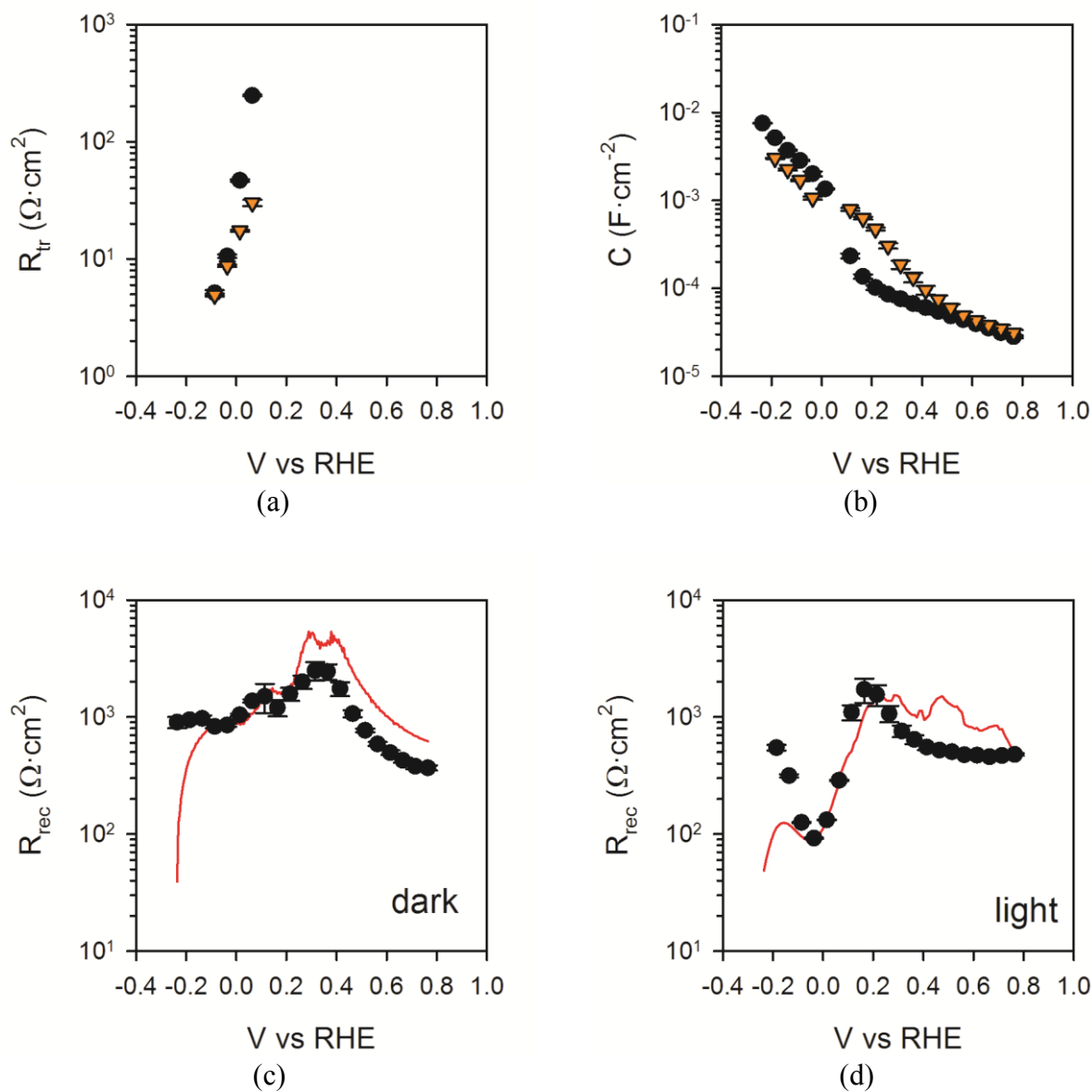


Figure 4.- Parameters extracted after fitting the impedance spectroscopy spectra of the heterostructured $\text{TiO}_2/\text{PbS}/\text{CdS}$ photoanodes, using the model previously developed and showed as Supporting Information, Figure SI7.³⁰⁻³² (a) Transport resistance, R_{tr} , (b) Chemical capacitance, C_{μ} , (c) recombination resistance, R_{rec} as a function of potential both in the dark and (d) under illumination. The red lines in (c) and (d) represent the total resistance extracted from derivation of the j - V curve, $R = \left(\frac{dj}{dV}\right)^{-1}$. Error bars assigned to the experimental points have been obtained from the fitting error.

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3 From all the above results, TiO₂/PbS/CdS photoanodes show promising capabilities to drive
4 solar H₂ generation. Consequently, we assembled a wireless device, resembling an artificial
5 leaf^{35,36} integrating this heterostructure as scheduled in Figure 5(a). The device is immersed into
6 the aqueous solution, and upon illumination, electro-hole pairs are photogenerated in the light
7 absorber (PbS/CdS QDs). The holes are quickly injected in the solution driving the sacrificial
8 oxidation of SO₃²⁻. On the other hand, photogenerated electrons are transported through the TiO₂
9 mesoporous structure toward the FTO substrate and then to the catalytic cathode, which is
10 composed by a calcined chloroplatinic solution, where hydrogen can evolve. Hydrogen evolution
11 is observed as showed in Figure 5(b) and Supporting Information, audiovisual material. The
12 hydrogen generation rate was 0.18 ml during 1 hour of measurement, which equals (4.30 ± 0.25)
13 ml·cm⁻²·day⁻¹. It is important to highlight that at this stage, this device cannot be strictly termed
14 “artificial leaf” since the use of a sacrificial agent is needed for operation. However, we believe
15 that this “quasi-artificial leaf” constitutes a promising structure for future developments and
16 different optimization strategies are under investigation in our lab to improve the device
17 efficiency, stability and autonomy. Particularly, in order to achieve higher H₂ generation rates,
18 morphological optimization of the TiO₂ structure is an important issue to be addressed, since it
19 has been proven that structures with lower surface area lead to better performance of quantum
20 dot sensitized solar cells based on these structures.^{37,38} Doping has also demonstrated to enhance
21 TiO₂ conductivity and minimize transport losses.¹⁴ Additionally, the presence of PbS enhances
22 charge recombination, (the lower IPCE values in the range 350-550 nm when PbS is included in
23 the structure is a good evidence) and efficient passivation strategies need to be developed as
24 previously done with colloidal PbS QDs.³⁹
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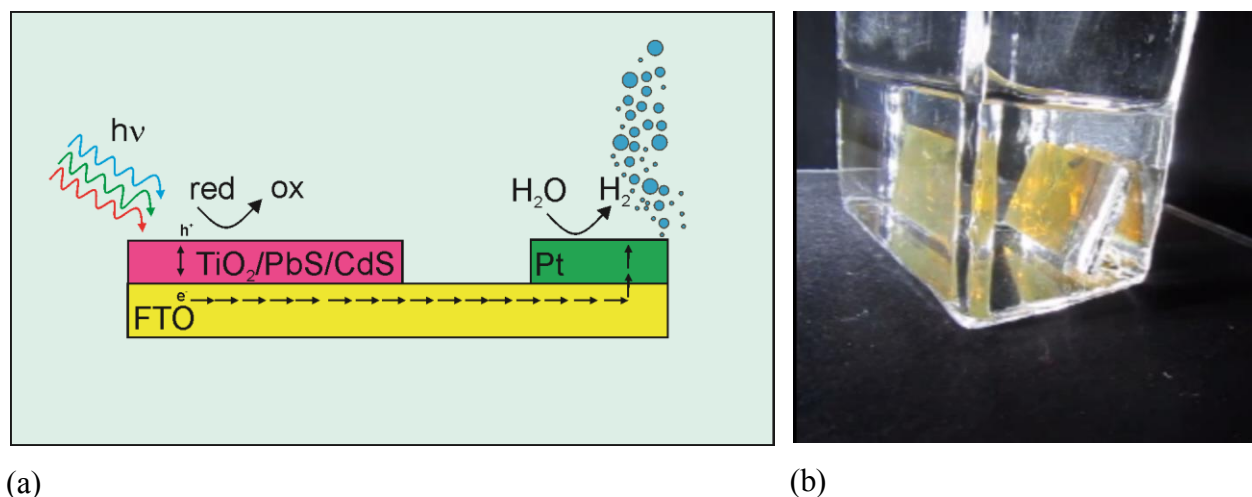


Figure 5.- (a) Scheme of a “quasi-artificial leaf” based on a heterostructured $\text{TiO}_2/\text{PbS}/\text{CdS}$ photoanode and Pt as cathode. (b) The $\text{TiO}_2/\text{PbS}/\text{CdS}$ “quasi-artificial leaf” in a quartz cuvette filled with an aqueous 0.25 M Na_2S and 0.35 M Na_2SO_3 electrolyte evolving H_2 under illumination. A video of the PbS artificial leaf working autonomously is available in Supporting Information.

In summary, $\text{TiO}_2/\text{PbS}/\text{CdS}$ heterostructures have demonstrated to be candidate architectures for solar hydrogen generation ($6 \text{ mA} \cdot \text{cm}^{-2}$ or $60 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$ obtained by cyclic voltammetry in a three electrode configuration under applied bias). Solar IR radiation provides a huge pool of photons, and consequently of usable energy, which can be stored using the appropriate materials, as PbS. Photocurrent and IPCE measurements have confirmed the contribution of infrared photons to the photocurrent leading to H_2 generation. The integrated current perfectly agrees with that obtained by cyclic voltammetry, and an excellent spectral match between photocurrent and light harvesting has been obtained. Additionally, impedance spectroscopy appears as a simple and reliable characterization tool to inspect the limiting factors affecting the photoelectrochemical performance of the device. We showed that the recombination resistance (R_{rec}) controls the dynamics of the system and further improvement of these heterostructures should be focused on strategies leading to the optimization of the TiO_2 architecture and minimization of charge recombination. Furthermore, IS analysis suggests that transport and accumulation of charge in the film mainly takes place within the TiO_2 nanoparticles. Based on this heterostructured material, we have developed a “quasi-artificial leaf”, which has proven to produce autonomously hydrogen under simulated solar illumination at $(4.30 \pm 0.25) \text{ ml} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$. Further developments at our lab focus on the elimination of the sacrificial agent in order

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3 to increase the robustness of the developed photoelectrodes. We believe that the present study
4 constitutes an important milestone for the development of autonomous systems able to generate
5 hydrogen with the only input of visible and IR radiation combining the advances of
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7 nanotechnology and novel optoelectronic concepts.
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10 11 12 **Experimental method**

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14 Commercial titania paste (Solarnix DSL 18NR, Switzerland, 20 nm particle size) was coated on
15 FTO (SnO₂:F , TEC 15) substrate by doctor blade technique and then dried at 80° C. Prior to
16 TiO₂ nanoparticle deposition, the FTO substrates were covered by a compact layer of TiO₂
17 deposited by spray pyrolysis of titanium(IV)bis(acetoacetonato) di(isopropanoxylate). These
18 electrodes were subsequently sintered at 450 °C for 30 min. The thickness of the electrodes was
19 ~12 μm, as measured by contact profilometry. The titania electrodes were sensitized with PbS
20 QDs grown by Successive Ionic Layer Adsorption and Reaction (SILAR).¹⁹ For this purpose a
21 Pb(CH₃COO)₂ 0.02 M ethanolic solution was used as Pb²⁺ source and another one containing
22 Na₂S 9 H₂O 0.02M in methanol/water (50/50 V/V) as sulfide precursor. A single SILAR cycle
23 consisted of 30 seconds dip-coating of the electrode into the lead precursor and then into the
24 sulfide solution, also during 30 seconds. After each precursor bath, the photoanode was
25 thoroughly rinsed by immersion in ethanol and dried. One cycle was sufficient for an adequate
26 PbS sensitization.
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30 For the hybrid PbS/CdS samples, the CdS deposition was carried out immediately after PbS
31 deposition. For CdS SILAR deposition a Cd(CH₃COO)₂ 0.05 M was used as metal precursor and
32 Na₂S 9 H₂O 0.02M in methanol/water (50/50 V/V) as sulfide precursor. SILAR procedure was
33 repeated five times. CdS coating demonstrated to provide an effective protection of PbS from
34 sulfide based electrolytes and an significant enhancement of the stability. After sensitization, all
35 the samples have been coated with ZnS, by dipping alternately into 0.1M Zn(CH₃COO)₂ (in
36 water) and 0.1M Na₂S solutions for 1 min/dip, rinsing with Milli-Q ultrapure water between
37 dips (2 cycles).⁴⁰ Reference “only CdS” samples have been produced, following the same steps
38 described above, except the deposition of PbS.
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3 Structural inspection of the samples was carried out using a JEOL JEM-3100F field emission
4 scanning electron microscope (SEM) and a JEOL JSM 7600F field emission transmission
5 electron microscope (TEM). The crystallographic structure of the samples was tested by X-ray
6 diffraction (XRD). The optical density of the photoelectrodes were recorded between 300 and
7 800 nm by a Cary 500 UV-VIS Varian spectrophotometer.
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14 The transmittance spectra of the photoelectrodes were recorded between 300 and 800 nm by a
15 Cary 500 UV-VIS Varian spectrophotometer. Steady state and chopped light current density
16 voltage (j-V), Electrochemical Impedance Spectroscopy (EIS) and V_{oc} decay measurements were
17 carried out using a FRA equipped PGSTAT-30 from Autolab. A three-electrode configuration
18 was used, where the $TiO_2/PbS/CdS$ photo-electrode was connected to the working electrode, a Pt
19 wire was connected to the counterelectrode and a saturated Ag/AgCl electrode was used as
20 reference. An aqueous solution containing 0.25 M Na_2S and 0.35 M Na_2SO_3 as sacrificial hole
21 scavenger was used as the electrolyte to prevent photocorrosion of the QDs. Nitrogen was
22 bubbled during 30min before testing to avoid the presence of oxygen (electron acceptor) in the
23 solution. The pH of the solution was 13 and all the electrochemical measurements were referred
24 to the reversible hydrogen electrode (RHE) by the equation $V_{RHE} = V_{Ag/AgCl} + 0.197 + pH(0.059)$.
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34 The electrodes were illuminated using a 450 W Xe lamp (Oriel), where the light intensity was
35 adjusted with a thermopile to 100 mW/cm^2 , with illumination through the substrate. EIS
36 measurements were carried out applying 20 mV AC signal and scanning in a frequency range
37 between 400 kHz and 0.1 Hz, at different applied biases. The IPCE measurements were carried
38 out by employing a 300 W Xe lamp coupled with a computer-controlled monochromator; the
39 photoelectrode was polarized at the desired voltage with a Gamry potentiostat and the
40 photocurrent was measured using an optical power meter 70310 from Oriel Instruments.
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46 Labeling experiments of the evolved gases were carried out using gas chromatography mass
47 spectroscopy GC/MS. A quadrupole Pfeiffer Vacuum model Thermostar GSD301T with a mass
48 interval ranging down to 300 uma was used. The evolved gas was collected in an inverted burette
49 and extracted with a gas-tight syringe provided with an exit valve. The quantitative analysis of
50 the evolved gas for the wireless device was carried out by collecting the generated gas under 100
51 $\text{mW}\cdot\text{cm}^{-2}$ illumination with an inverted burette during 1 hour. The obtained result was
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3 extrapolated to 1 day. During this measurement, no addition of fresh electrolyte to the solution
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10 **Acknowledgements**

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31 **Supporting Information Available:** TiO₂/CdS and TiO₂/PbS/CdS light absorption, SEM image,
32 XRD of TiO₂/PbS electrodes, TEM micrograph, stability, IPCE vs. light absorption and APCE,
33 impedance model and a video of the PbS artificial leaf working autonomously. This material is
34 available free of charge *via* the Internet at <http://pubs.acs.org>.
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Figure captions

Figure 1.- (a) j-V curves for the TiO₂/PbS/CdS heterostructure in the dark (dashed lines) and under illumination at 100 mW·cm⁻² (solid lines) in three electrode configuration, TiO₂/CdS is also included as a reference (b) Gas chromatography Mass Spectroscopy plot of the evolved gas for TiO₂/PbS/CdS heterostructure. The signal of H₂ is clearly increased after gas is passed through the system.

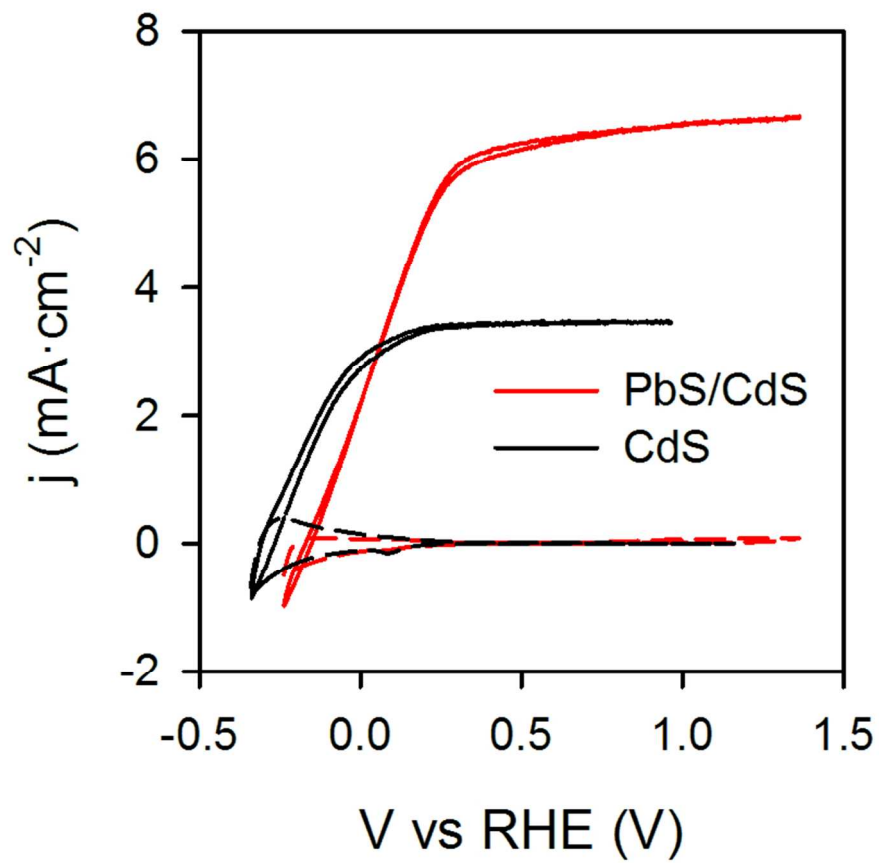
Figure 2. Energy diagram illustrating the oxidation at PbS/CdS QDs-sensitized TiO₂ particulate anodes. Energy levels were adapted from.^{25,26} The arrows indicate the traffic of electrons and holes.

Figure 3.- (a) Chopped light (black) and constant (red) illumination j-V curves in two electrode configuration of the TiO₂/PbS/CdS heterostructured photoanode. (b) IPCE (solid lines) and integrated current (dashed lines) for a TiO₂/PbS/CdS (red) and a reference TiO₂/CdS (black) photoelectrode at 0.95 V vs RHE.

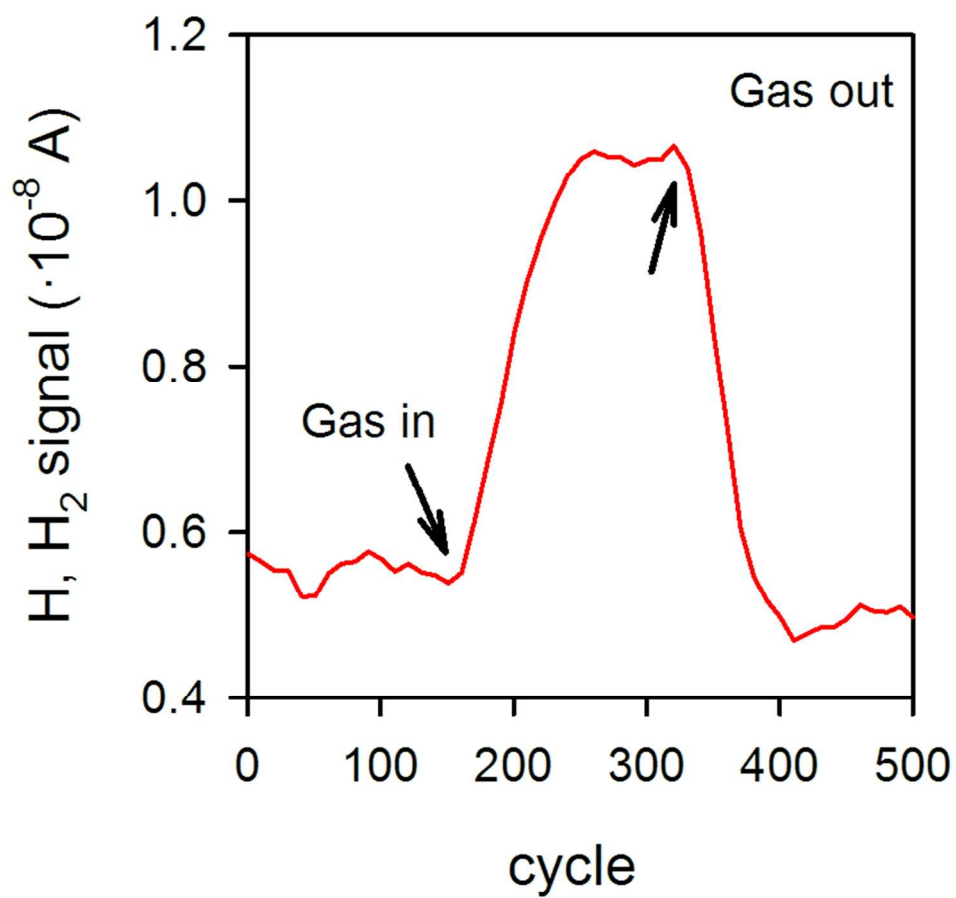
Figure 4.- Parameters extracted after fitting the impedance spectroscopy spectra of the heterostructured TiO₂/PbS/CdS photoanodes, using the model previously developed.³⁰⁻³² (a) Transport resistance, R_{tr}, (b) Chemical capacitance (C_μ), (c) recombination resistance (R_{rec}) as a function of potential both in the dark and (d) under illumination. The red lines in (c) and (d) represent the total resistance extracted from derivation of the j-V curve, $R = \left(\frac{dj}{dV}\right)^{-1}$. Error bars assigned to the experimental points have been obtained from the fitting error.

Figure 5.- (a) Scheme of a “quasi-artificial leaf” based on a heterostructured TiO₂/PbS/CdS photoanode and Pt as cathode. (b) The TiO₂/PbS/CdS “quasi-artificial leaf” in a quartz cuvette filled with an aqueous 0.25 M Na₂S and 0.35 M Na₂SO₃ electrolyte evolving H₂ under illumination. A video of the PbS artificial leaf working autonomously is available in Supporting Information, audiovisual material.

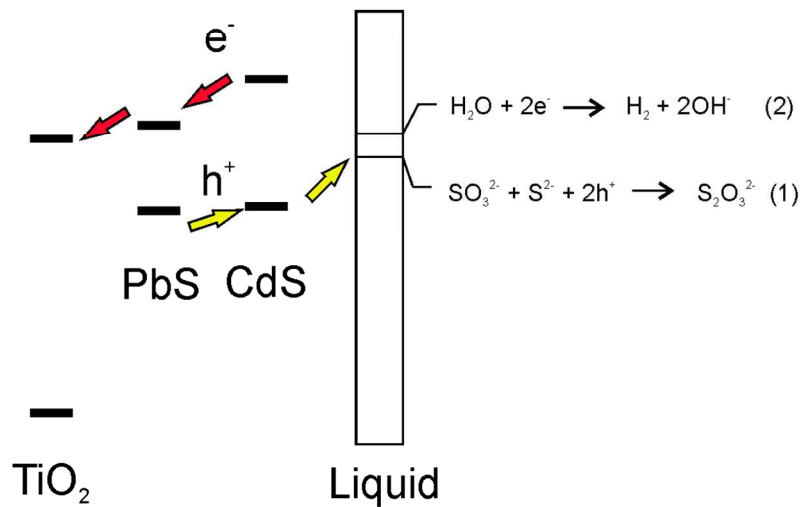
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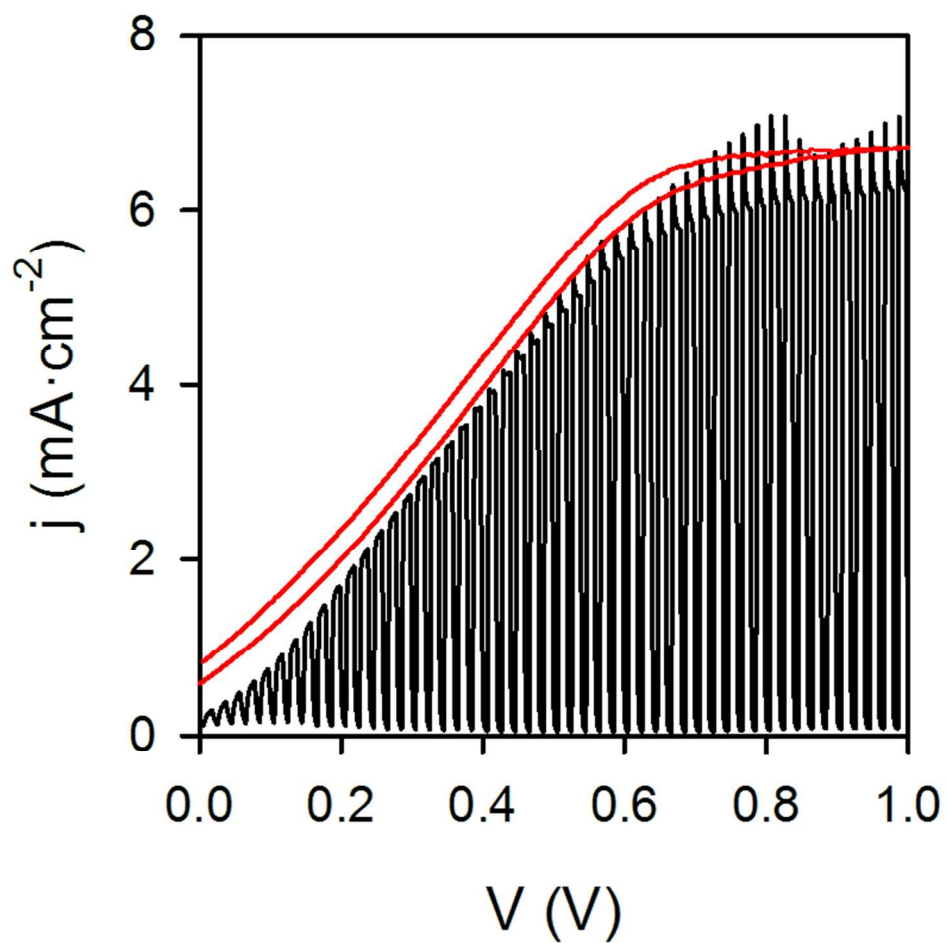
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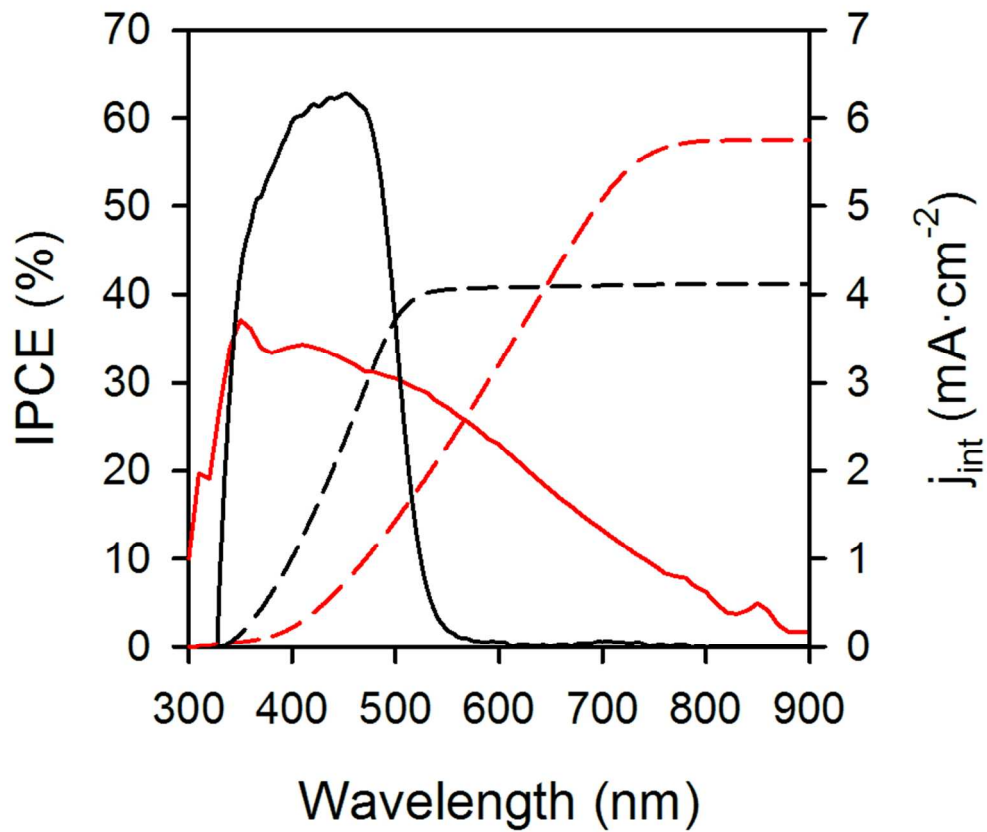
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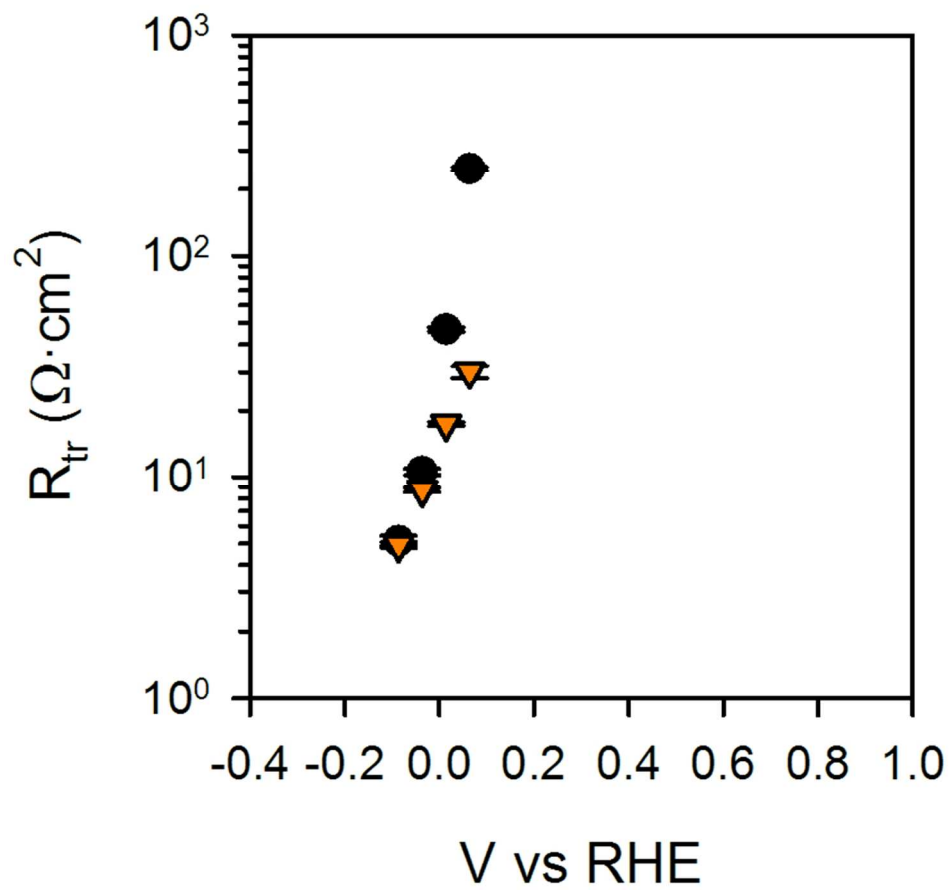
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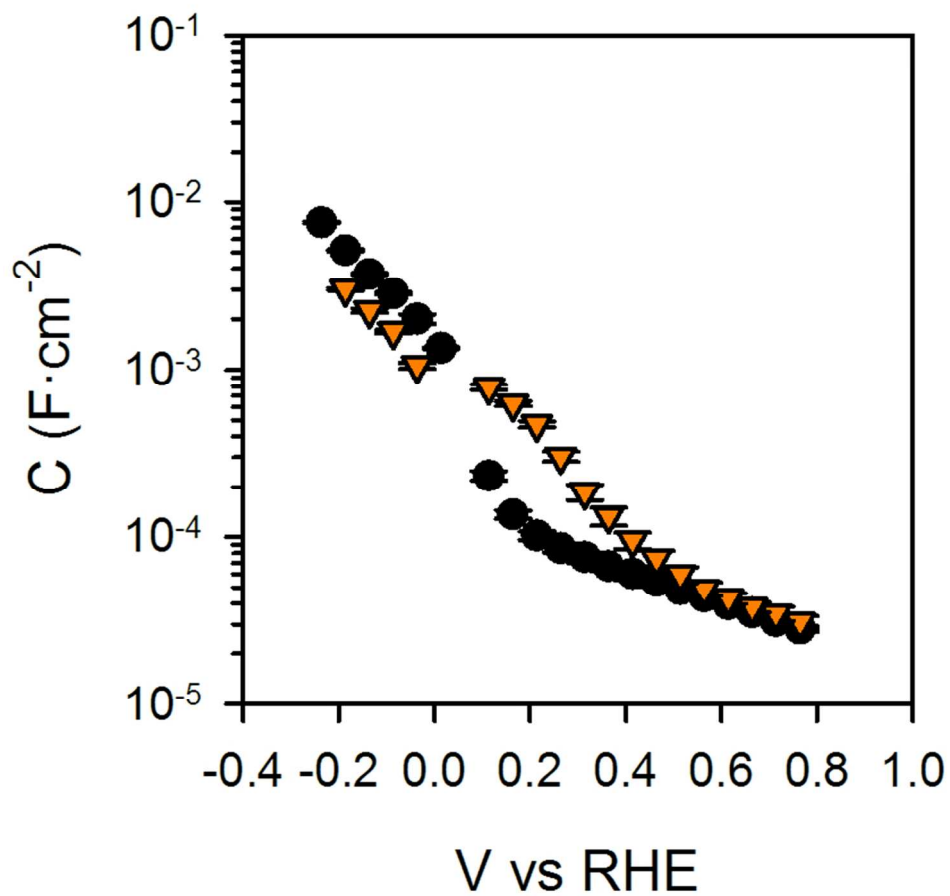
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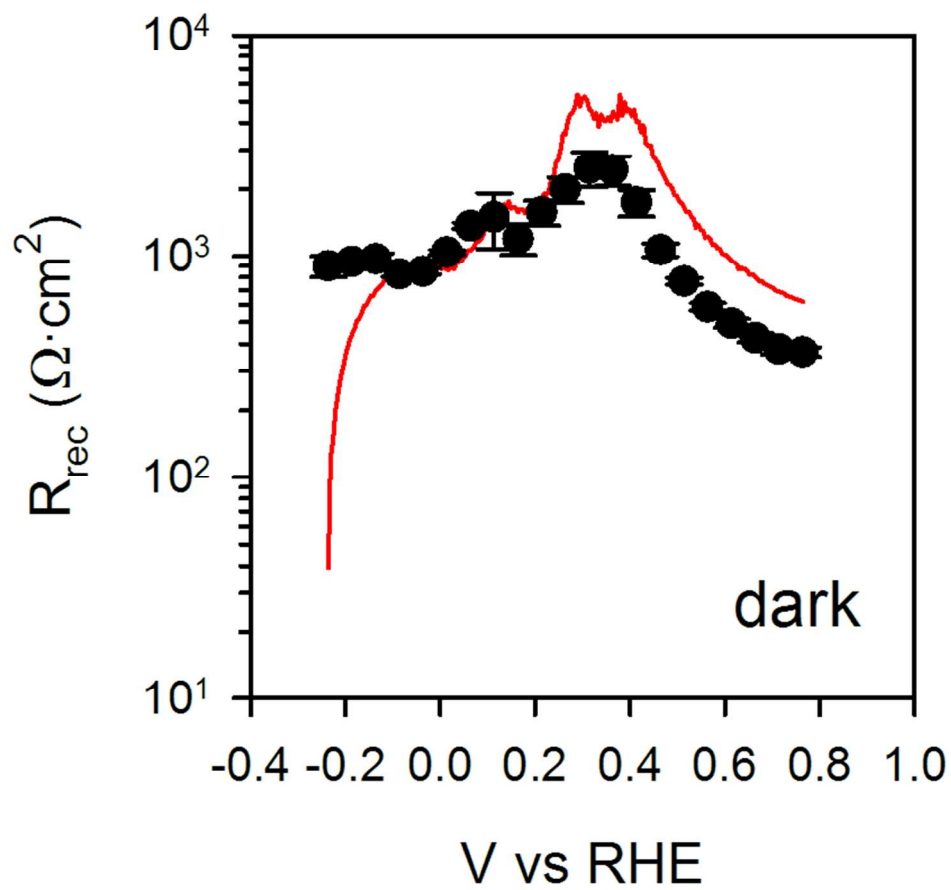
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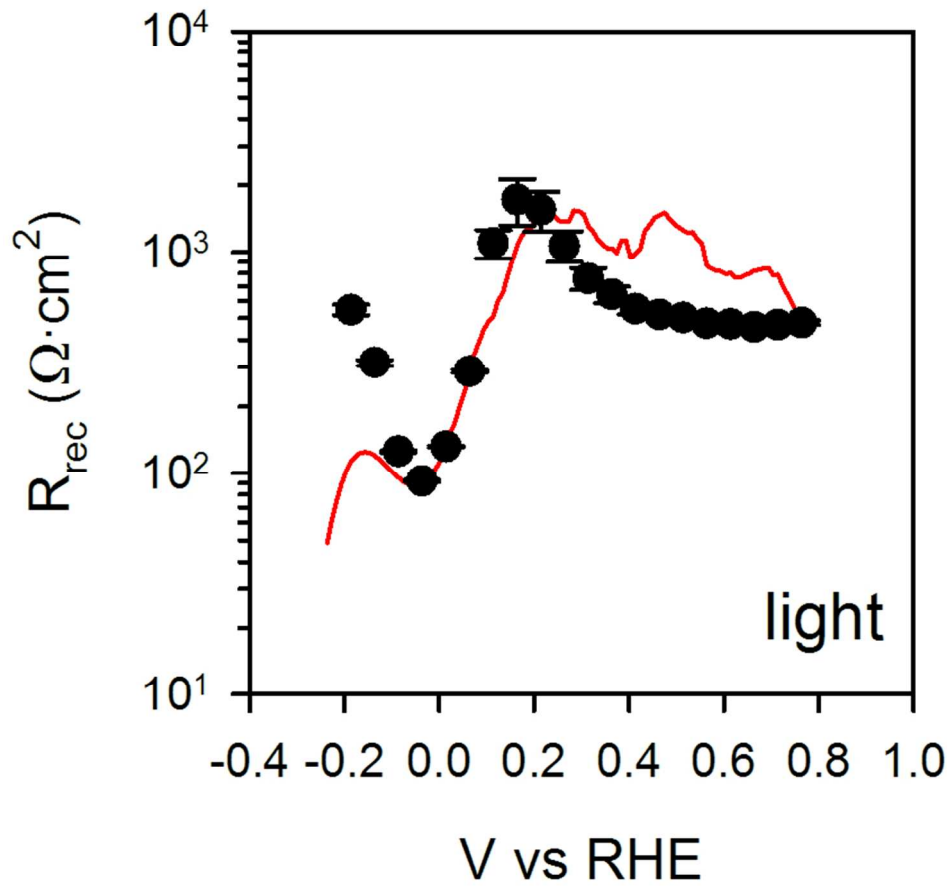
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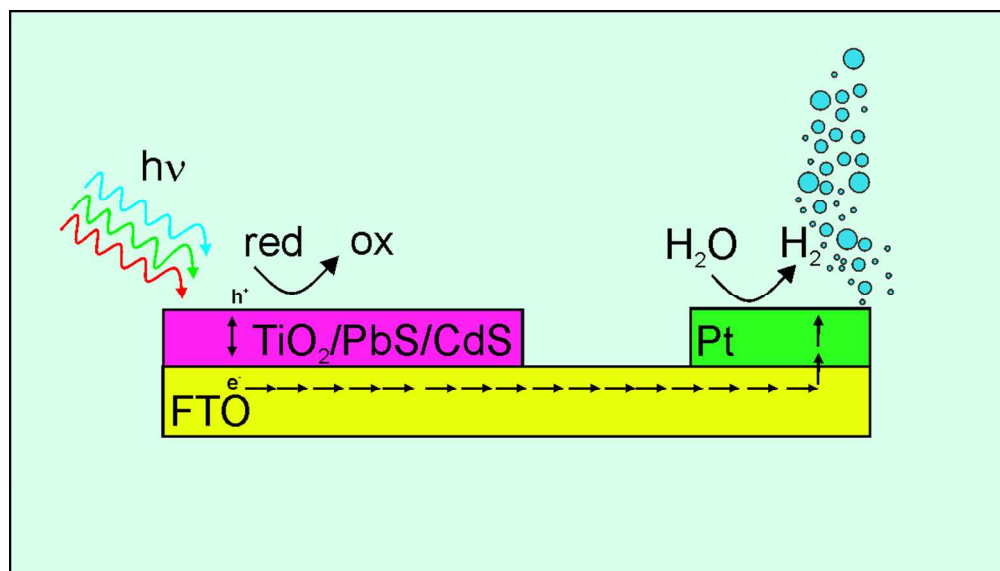
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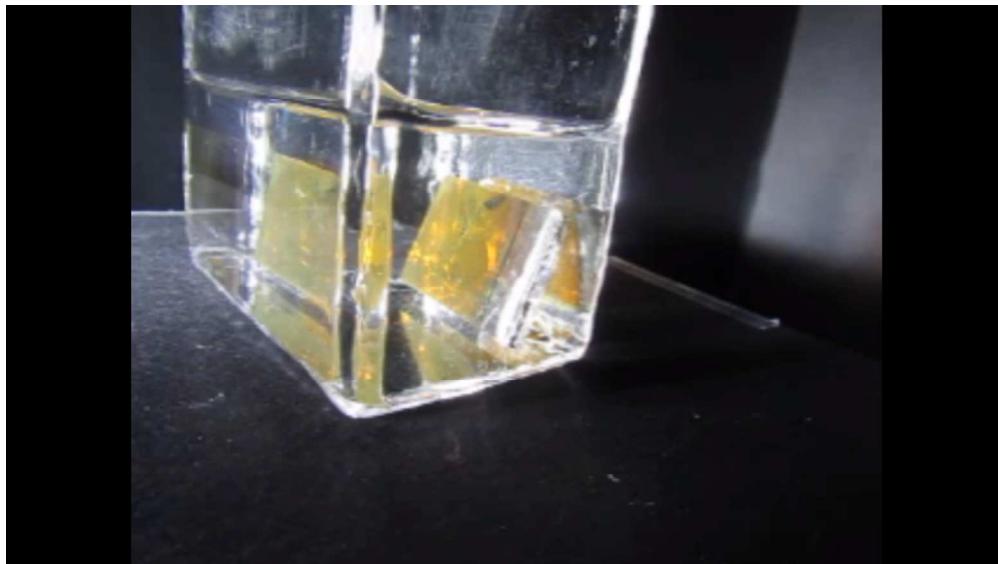


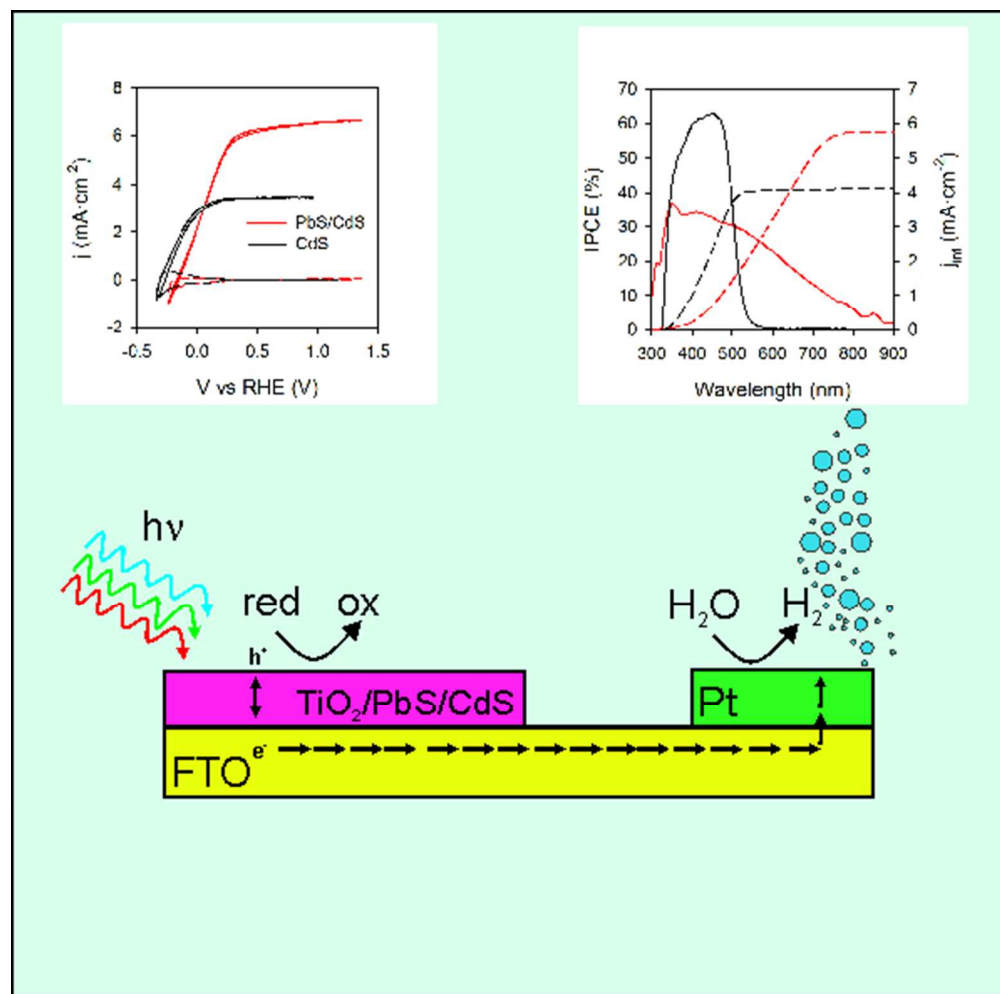
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