

Nanoscale Effects in Water Splitting Photocatalysis

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Abstract From a conceptual standpoint, the water photoelectrolysis reaction is the simplest way to convert solar energy into fuel. It is widely believed that nanostructured photocatalysts can improve the efficiency of the process and lower the costs. Indeed, nanostructured light absorbers have several advantages over traditional materials. This includes shorter charge transport pathways and larger redox active surface areas. It is also possible to adjust the energetics of small particles via the quantum size effect or with adsorbed ions. At the same time, nanostructured absorbers have significant disadvantages over conventional ones. The larger surface area promotes defect recombination and reduces the photovoltage that can be drawn from the absorber. The smaller size of the particles also makes electron–hole separation more difficult to achieve. This chapter discusses these issues using selected examples from the literature and from the laboratory of the author.

Keywords Fermi Level • Junction • Metal Oxide • Recombination • Surface Photovoltage

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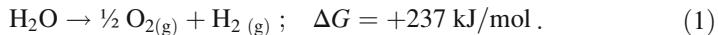
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1 Photoelectrochemical Water Splitting as a Pathway to Sustainable Energy

The goal of keeping global temperature increases below 2°C compared to pre-industrial times requires the rapid deployment of carbon free energy technology that can compete with the price of fossil fuels. The solar energy received on the Earth's surface meets current and future human energy demand [1, 2]. Solar energy can be converted into electricity with up to 46% efficiency using the photovoltaic cells that are available today [3]. However, electricity is difficult to store and distribute over long distances. These problems can be avoided by converting the photochemical energy directly into fuel. The simplest scheme employs the photoelectrolysis reaction shown in (1) to produce hydrogen from water:



Hydrogen from this reaction could become the central energy carrier of a hydrogen-based economy [2]. Alternatively, it could be used as an electron source for the exothermic formation of conventional fuels using atmospheric CO₂ as a carbon feedstock. The technology for creating hydrogen by oxidation of water (solar water splitting) already exists in the form of multi-junction photovoltaic systems coupled to water electrolyzers. These can achieve over 18% energy efficiency [4] but they are so expensive that nobody uses them – especially not anyone living on less than \$10 a day, i.e., the majority of people in the world [5, 6]. Photovoltaics based on lead iodide perovskite might be a promising alternative [7] if problems with photo- and thermal stability, scaling, and lead toxicity can be resolved [8]. Potential cost savings are also possible with photoelectrochemical cells (PEC) that combine photovoltaic and electrolytic functions in one unit (Fig. 1) [9]. PECs can reach efficiencies of up to 12.4% [10], about half of the theoretical efficiency limit for these devices (24.4% for a tandem [11, 12] and 30% for a multijunction device [4]). However, issues with stability continue to plague these devices [13, 14].

Of all known solar hydrogen technologies, solar water electrolysis with *suspended photocatalysts* (PCs) has the greatest potential to induce a revolution in fuel production on this planet. Photocatalysts generate hydrogen and oxygen upon exposure of a particle-water mixture to sunlight (Fig. 2a) [15–24]. Because of the total integration of components for light absorption, charge separation, and

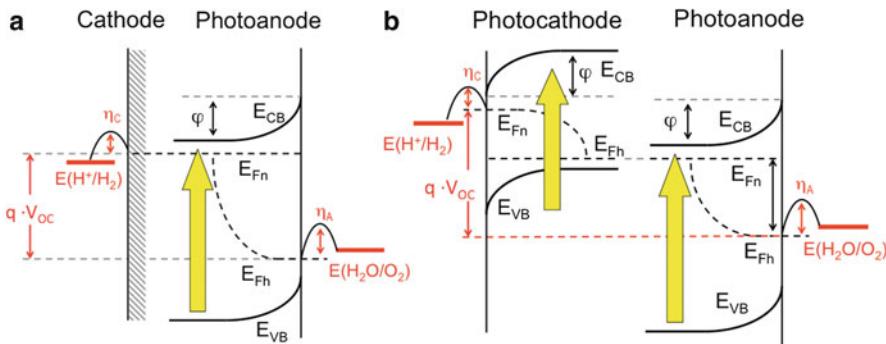


Fig. 1 Energetics of (a) type 1 (single absorber) and (b) type 2 (dual absorber, tandem) suspended photocatalysts for water photoelectrolysis. For photochemical water splitting, the quasi Fermi levels E_{Fn} and E_{Fh} of the illuminated catalysts need to be above and below the water redox potentials. Band bending φ , maximum possible energy output ($q \times V_{OC}$), and electrochemical overpotentials for anodic η_A and cathodic η_C processes are also shown

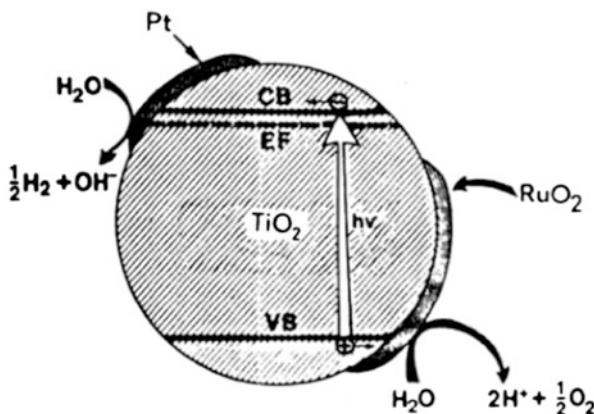


Fig. 2 Photoelectrochemical diode after Duonghong et al. Reproduced with permission from [42]. Copyright 1981, American Chemical Society

water electrolysis, PCs are nearly one order of magnitude cheaper than photoelectrochemical cells at equal efficiency [25, 26]. At 10% energy efficiency, PCs could deliver hydrogen at a cost of \$1.63 per kg, and outcompete oil as an energy carrier.

Photocatalysts operate as either type 1 (Schottky) or type 2 (tandem) devices (Fig. 1) [9, 27–31]. In type 1 PCs, light absorption and charge separation occur at a single absorber particle connected to one or several co-catalysts to complete the circuit for water electrolysis. The ideal limiting Solar-to-Hydrogen (STH) efficiency of this Schottky-type configuration is $\eta = 14.4\%$, based on a light absorber with a 2.0 eV band gap and conversion losses of $E_{Loss} = 0.8$ eV per electron [11, 12]. Actual type 1 photocatalysts such as NiO-modified La:KTaO₃ [32] and Cr/Rh-

modified GaN:ZnO (QE = 2.5%, pure water, visible light) [33–35] achieve less than 0.1% STH because of low sunlight absorption (E_G of La:KTaO₃ is 3.6 eV) and recombination losses at the surfaces of the particles. A number of other catalysts, including In_{1-x}Ni_xTaO₄ ($x = 0\text{--}0.2$) [36, 37], CoO [38], and Cu₂O [39], have also been reported. However, their performance has not yet been reproduced in the literature and remains in question [40, 41].

The type 2 photocatalyst is based on the tandem (or Z-scheme) concept shown in Fig. 1b. Here, two (or more) separate light absorbers are connected in series. Because the device voltage is divided into several contributions, semiconductors with smaller band gaps can be used which absorb a much greater fraction of the solar flux [43]. The ideal limiting STH efficiency of a dual absorber configuration is 24.4% (for a combination of absorbers with band gaps of 2.25 and 1.77 eV). This is nearly twice that of the Schottky junction catalysts [11, 12]. However, because of the greater complexity (two absorbers instead of one), functional tandem PCs have only been known for about 15 years [16]. Of these, the combination of Rh:SrTiO₃ and BiVO₄ connected with a Fe^{3+/2+} redox shuttle, gives the highest STH efficiency (0.1%) [44].

Currently, there are three main strategies to develop more efficient, more stable, and less expensive PCs. One is to encapsulate traditional absorber materials from photovoltaics (e.g., IV, III/V, II–VI semiconductors) with protecting layers to inhibit photocorrosion. This strategy has recently been applied to silicon, GaAs, and GaP photoanodes [45], and to cuprous oxide photocathodes [46], with reasonable success. Another approach involves the development of new metal oxide materials that combine suitable properties (visible band gap, high carrier mobilities, long carrier lifetimes) with greater chemical stability for photoelectrochemical water splitting. Such materials can be made by directed synthesis, sometimes guided by theory [47], or they can be made by combinatorial approaches, as described by Bruce Parkinson [48–50], Eric McFarland [51], and Nathan Lewis [52]. The third strategy is to exploit scaling laws and specific effects at the nanoscale [53–56] to overcome the limiting problems of metal oxide absorbers, such as their short electron-hole lifetimes and low mobility. This nanostructuring strategy has gained significant interest in the last 20 years [57–67] and is the focus of this chapter.

2 Brief History of Nanoscale Water Splitting Photocatalysis

The photosynthetic systems of bacteria are the earliest examples of nanostructured solar energy conversion devices; they date back to the beginning of life on this planet [68]. In contrast, artificial nanostructures for solar energy to fuel conversion have emerged only in the last three decades. The first experimental work dates back to 1968, when Boddy established photoelectrochemical water oxidation with an

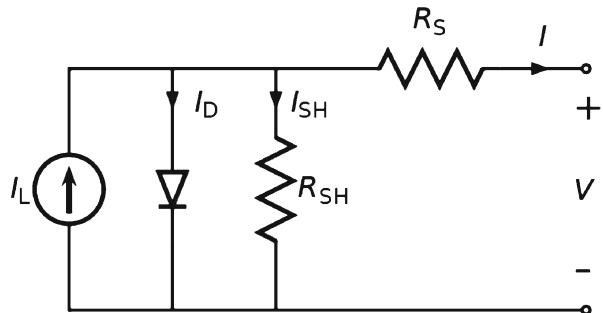
illuminated TiO_2 electrode [69], and Freund and Gomez reported similar reactions on ZnO , TiO_2 , and WO_3 [70]. However, the potential of the reaction for artificial photosynthesis was only recognized broadly with Fujishima and Honda's report in Nature [71, 72]. The idea to carry out this process with 'miniaturized photoelectrochemical cells' suspended in water gained traction after Arthur Nozik formulated the concept of 'photochemical diodes' [29]. This was quickly followed by experimental demonstrations of photocatalytic effects in suspended semiconductor particles by Bard [43], and on 'colloidal microelectrodes' by Henglein [54, 73]. In 1979, Michael Grätzel reported photocatalytic water oxidation by a suspended RuO_2 nanoparticle in the presence of a $[\text{Ru}(\text{bipy})_3]^{2+}$ complex for visible light absorption and methyl viologen (MV^{2+}) as sacrificial electron acceptor [74]. An improved system consisted of a TiO_2 colloidal light absorber and Pt and RuO_2 co-catalysts for water reduction and oxidation, respectively (Fig. 2) [42]. Even though water splitting was not achieved in this system (O_2 evolution was later attributed to air contamination) [28, 75], the structure exemplifies the design principles of a 'photochemical diode' [76]. Contemporary research on nanoscale water splitting catalysts is motivated by the prospect of extracting charge carriers more efficiently and thereby overcoming the limitations of metal oxide absorbers (short carrier lifetimes and low mobility). The underlying concepts are the topics for the next sections.

3 Size Dependency of Free Energy Creation in Photocatalysts

The effects of nanostructuring the light absorber on free energy conversion can be illustrated well with an equivalent circuit diagram for a photovoltaic cell. In the diagram in Fig. 3, the light-absorbing component corresponds to a photon-driven current source, and the rectifying (charge separating) component is shown as a diode connected in parallel to it. In addition, there are parallel and serial resistances, R_{SH} and R_{S} . The former is associated with the non-selective charge transfer which leads to leakage or shunting, whereas the latter is produced by the transport of charge carriers from the absorber interior to the interface. For a photovoltaic cell, the load is an electrical device, and for a fuel-producing photocatalyst the load is water electrolysis [77].

In the circuit, I_{SH} , R_{S} , and R_{SH} are dependent upon the physical size of the junction. For two otherwise identical junctions, the one with twice the surface area of the other is expected to have half the shunt resistance and double the leakage current I_{SH} because it has twice the junction area across which current can leak. It also has half the series resistance R_{S} because it has twice the cross-sectional area through which current can flow. For a nanostructured photocatalyst, the decrease in R_{SH} corresponds to the leakage currents J_{et} and J_{T} in Fig. 12. If the leakage current exceeds the generation current I_{L} , water electrolysis comes to a stop. On the other

Fig. 3 Equivalent circuit diagram for a photovoltaic cell. R_{SH} : shunt resistance, R_S : serial resistance, I_{SH} : leakage current, I_L : generation current



hand, the decrease of R_S caused by the reduction in electron-hole transport resistances improves the photocurrent. Finally, as the semiconductor particles approach the nanoscale, reduced space charge layer effectiveness diminishes the rectifying properties. This corresponds to reduction of R_{SH} .

4 Light Absorption

The ability of a material to absorb light is determined by the Lambert–Beer law and the wavelength-dependent absorption coefficient α . The light penetration depth α^{-1} refers to the distance after which the light intensity is reduced to $1/e$ of the incident illumination. For example, for Fe_2O_3 , $\alpha^{-1} = 118 \text{ nm}$ at $\lambda = 550 \text{ nm}$ [7]; for CdTe , $\alpha^{-1} = 106 \text{ nm}$ (550 nm) [78]; and for Si , $\alpha^{-1} = 680 \text{ nm}$ (510 nm). To ensure $>90\%$ absorption of the incident light, the film thickness d must be >2.3 times the value of α^{-1} (Fig. 4). The dimensions of nanostructured photocatalysts are usually smaller than α^{-1} , so each nanoparticle only absorbs a small fraction of the incident light. However, complete light absorption by the suspension can be achieved by adjusting the particle concentration and optical pathlength of the reaction container. Nanostructured surfaces also reduce the reflection losses and increase the light scattering. A solid film with one nanostructured surface (Fig. 4b) increases the horizontal light distribution. A particle suspension (Fig. 4c) increases the light distribution in three dimensions. This occurs by refraction at the surfaces of the particles and by Mie scattering. As a result, the light in a suspension impinges on the particles from all directions. This has an important consequence on the ability of the particles to generate a photovoltage at the solid–liquid interface and to generate the necessary thermodynamic driving force for water electrolysis. According to the Shockley diode equation (2) [77], the open circuit voltage V_{OC} of a solar cell is a logarithmic function of the absorbed flux j_{phot} and of the reverse saturation current j_0 of the diode:

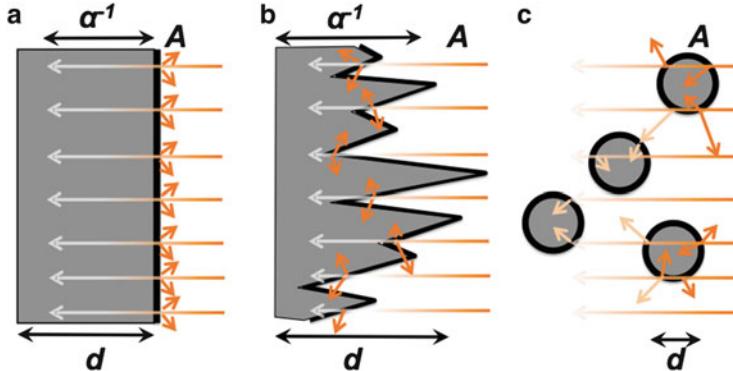


Fig. 4 Light distribution (a) in flat films, (b) in rough films, and (c) in particle suspensions. A : surface area; d : film or particle thickness; α^{-1} : optical penetration depth. *Short arrows* show scattered or reflected light

$$V_{OC} = \frac{kT}{e} \ln\left(\frac{j_{\text{phot}}}{j_0} + 1\right). \quad (2)$$

By increasing the junction area A of the absorber (Fig. 4), the absorbed flux j_{phot} , defined as the photon rate per unit area of the junction, decreases proportionally and the photovoltage drops. For example, if $j_{\text{phot}} >> j_0$, the photovoltage decreases by 0.059 V for every decadic decrease of j_{phot} (i.e., decadic increase of junction area). This has been experimentally observed for silicon microwire arrays [79]. Equation (2) also impacts the construction of photocatalysts. It emphasizes the need to minimize the solid–liquid junction area through inert coatings or by replacing the solid–liquid junction with localized solid-solid junctions on the surface of the light absorber.

5 Majority and Minority Carrier Transport

Photoexcitation produces charge carriers with finite mobility and lifetime, depending on the material, the carrier type, and the light intensity. To drive water redox reactions, these carriers need to reach the material’s interfaces at the electrolyte and at the co-catalysts. In the absence of an external field, charge carriers move by diffusion. Their range is defined by the mean free diffusion length L which depends on the carrier diffusion constant D , the carrier lifetime τ , and a dimensionality factor ($q = 2, 4$, or 6 for one-, two-, or three-dimensional diffusion):

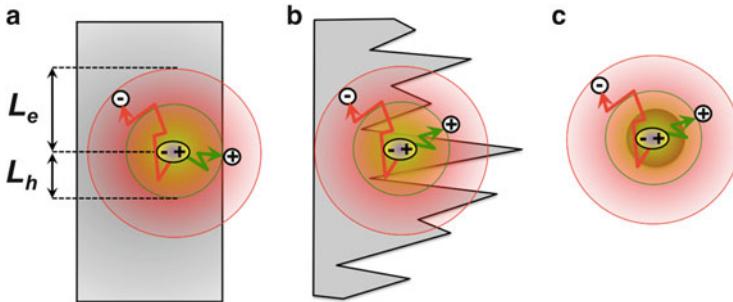


Fig. 5 Charge collection (a) in flat films, (b) in nanostructured films, and (c) in particle suspensions. d : film or particle thickness; L_e : electron diffusion length; L_h : hole diffusion length

$$\overline{L^2} = qD\tau \quad (3)$$

For intrinsic semiconductors, usually $L_e > L_h$ because of the larger diffusion constant D of electrons compared to holes. For example, Si has $D_e = 49 \text{ cm}^2 \text{ s}^{-1}$ and $D_h = 13 \text{ cm}^2 \text{ s}^{-1}$ (calculated from mobilities, $\mu_e = 1,900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $\mu_h = 500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 298 K using the Einstein–Smoluchowski relation) [80] assuming $\tau_e = \tau_h = 10^{-6} \text{ s}$, $L_e = 98 \mu\text{m}$, and $L_h = 51 \mu\text{m}$ for one-dimensional diffusion ($q = 2$). Upon doping, the concentration of the majority carriers increases, and with it their τ and L values. On the other hand, the lifetime and diffusion length of the minority carriers decrease. For optimum collection of both carrier types at the interface, the semiconductor film thickness d has to be in the same range as L_e and L_h (Fig. 5). This can be achieved by increasing the surface roughness of the film, as shown in Fig. 5b. Such a surface nanostructuring approach is particularly useful for first-row transition metal oxides (Fe_2O_3), which suffer from low hole mobility and short hole lifetimes [81, 82]. Ideal electron-hole collection is possible with suspended nanoparticles if their particle size $d < L_e L_h$.

The impact of the absorber size on charge collection has been experimentally verified with nanoparticles and bulk particles of $\text{KC}\text{a}_2\text{Nb}_3\text{O}_{10}$ [83, 84]. Chemical exfoliation of this layered Dion–Jacobson phase affords 1–2 nm thick sheet-like tetrabutylammonium stabilized $\text{HC}\text{a}_2\text{Nb}_3\text{O}_{10}$ nanoparticles, whereas sonication leads to 227 ± 202

$$\text{ER} = \left(\frac{1}{R_G - R_R^L - R_R^S} + \frac{r}{J_{\text{CT}}^-} + \frac{r}{J_{\text{CT}}^+} + \frac{d_{\text{OX}}}{J_{\text{OX}}} + \frac{d_{\text{RED}}}{J_{\text{RED}}} + \frac{1}{R_{\text{OX}}} + \frac{1}{R_{\text{RED}}} \right)^{-1}. \quad (4)$$

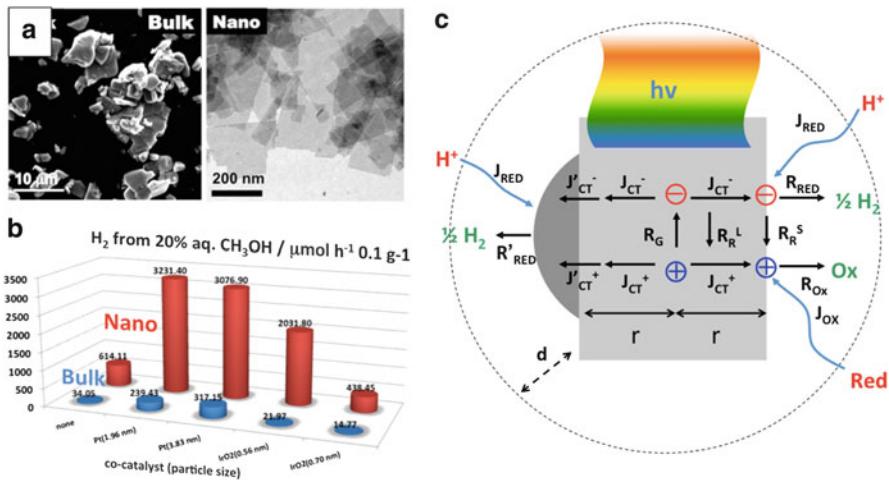


Fig. 6 (a) Electron micrographs of bulk and nanoscale niobate particles. (b) H₂ evolution rates of bare and co-catalyst modified particles. (c) Model to relate the electronic rate of the catalyst (mol s⁻¹ cm⁻³) to the rates for light-induced electron-hole generation (R_G), electron-hole recombination in the lattice (R_R^L) and on the surface (R_R^S), rates for charge and mass transfer to the catalyst-water interface (J_{CT}^+ , J_{MT}), and to the rates for the redox reactions with the substrates (R_{RED} , R_{OX}). Reproduced with permission from [84]. Copyright 2012, American Chemical Society

The model calculates the electronic rate of the catalysts as a sum of the inverse rates of charge generation R_G , charge and mass transport J_{CT} , chemical conversion $J_{OX/RED}$, and charge recombination R_R . This one-dimensional continuity analysis [66, 85–88] is equivalent to Kirchhoff's law, according to which the total resistance of a series of resistors equals the sum of the individual resistances. The analysis shows that the activity of the photocatalysts is limited by the slowest kinetics in the series. Under the experimental conditions (sacrificial donor), these are the rates of charge transport to the water–catalyst interface and of proton reduction. Mass transport in the solution phase does not play a significant role, and neither does surface recombination.

The effect of nanoscaling on the ability to extract short-lived minority carriers is also evident in colloidal Fe₂O₃ dispersions, which catalyze the oxygen evolution reaction with aqueous 0.1 M AgNO₃ as the sacrificial electron acceptor [89]. Even though the performance of the system is limited by silver deposition on the Fe₂O₃ nanocrystals (Fig. 7), a correlation between O₂ production rates and particle size is seen. This can be attributed to improved hole extraction in the smaller nanocrystals [89]. In principle, by reducing the nanocrystal size further, and by increasing the thermodynamic driving force for charge extraction, most metal oxide materials can be turned into photocatalysts. The photocatalytic properties of 2 nm IrO₂ nanocrystals illustrate this principle. Because IrO₂ is metallic [90], the lifetime of the photogenerated holes is on the picosecond time scale. Nevertheless, visible and UV-light induced photocatalytic oxygen evolution from IrO₂ sols can be observed

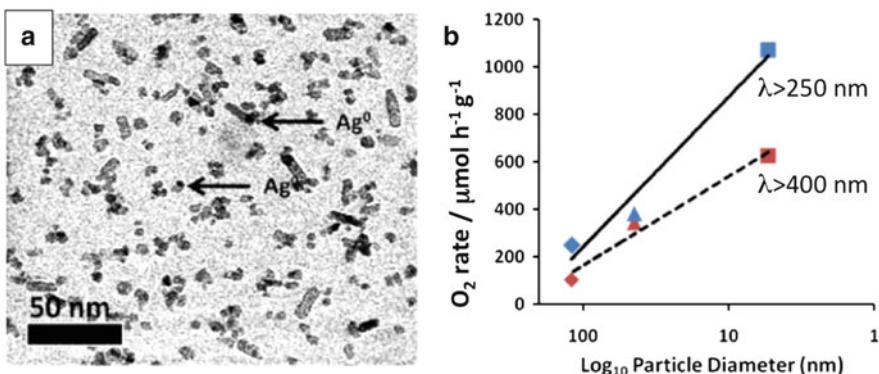


Fig. 7 (a) Silver nanoparticles formed on nano-Fe₂O₃ after irradiation in aqueous AgNO₃. (b) Correlation between Fe₂O₃ particle size and O₂ evolution rate. Reproduced with permission from [89]. Copyright 2011, Royal Society of Chemistry

in the presence of silver nitrate or sodium persulfate sacrificial electron acceptors [91]. However, the quantum efficiency for the process is too low (0.19% at 530 nm) to be useful for solar energy to fuel conversion. This principle also explains photocatalysis with Plasmonic gold nanoparticles.

6 Quantum Size Confinement

The observation of quantum size effects in thin films and quantum dots (QDs) dates back to the work by Dingle [53] and Louis Brus [56]. Quantum size effects not only depend on the material and crystal size, but also the nanocrystal shape [92]. The expanded band gap shifts the conduction and valence band edges to more reducing and more oxidizing potentials, respectively. From Marcus–Gerischer theory it is expected that this increase in thermodynamic driving force raises the rates of interfacial charge transfer and water electrolysis [88, 93, 94]. Increases in solid–solid electron transfer were experimentally confirmed for CdQ(Q=S, Se)-TiO₂ composites [95, 96], and quantitatively described with Marcus theory [97]. In 2013, the author's group established a similar rate dependence for proton reduction with CdSe quantum dots (Fig. 8) [98, 99]. For the study, monodisperse CdSe QDs with diameter 1.8–6.0 nm were synthesized in the presence of 2-mercaptoethanol as a ligand [100], followed by size-selective precipitation with 2-propanol. As can be seen from Fig. 8a, the hydrogen evolution rates from the CdSe QD suspensions in Na₂SO₃ solution show a logarithmic dependence on the crystal diameter.

A logarithmic plot of the rates against the driving force of the reaction is also linear (Fig. 8b). The quasi Fermi energies E_{Fn} were obtained from either the photocurrent onset in photoelectrochemical measurements or extrapolated from the electrochemical reduction peak of the QDs. The trend is expected for free energy-controlled interfacial charge transfer, as described by the Butler–Volmer equation [101]. As

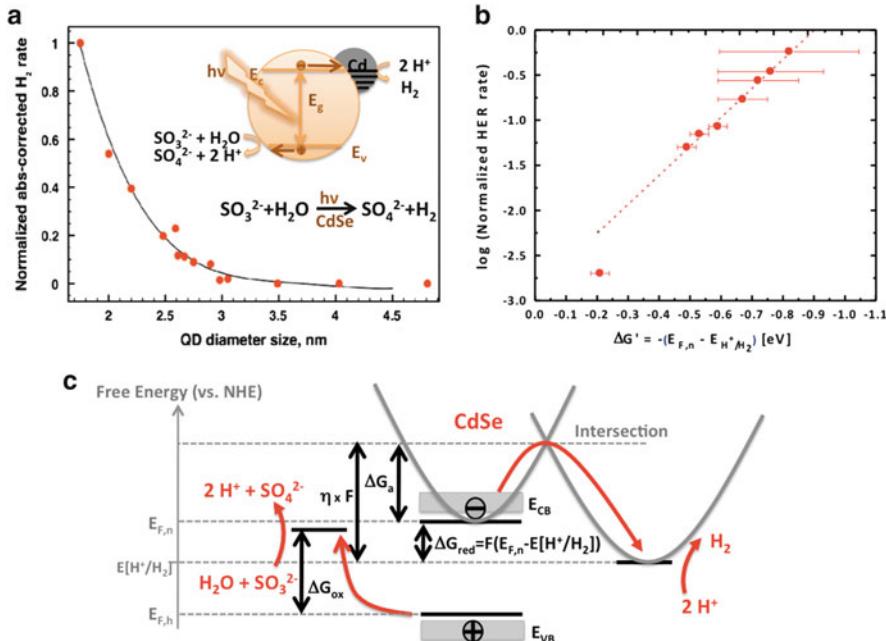


Fig. 8 (a) H₂ evolution rates vs QD size. Rates are normalized with regard to catalyst amount and absorbed photons. Inset: Schematic diagram of hydrogen evolution from CdSe QDs in the presence of sodium sulfite. (b) Weighted least square linear fit (dashed line) of experimental H₂ rates vs Fermi energies from electrochemistry. The lowest point is excluded from the fit because the rate is close to experimental error ($\pm 10^{-3}$) of the H₂ rate measurement. (c) Reaction energy profile for CdSe QD redox system. The kinetic activation energy ΔG_a for proton reduction is controlled by the Gibbs free energy change ΔG_{red} of the reaction, as given by the quasi-Fermi level of electrons under illumination $E_{F,n}$ and the Nernst potential $E[H^+/H_2]$. Reproduced with permission from [99]. Copyright 2013, American Chemical Society

shown in Fig. 8c, there are two half reactions at the QD interface, the oxidation of sulfite and the reduction of protons. The driving force ΔG_{ox} for the oxidation reaction is given by the difference between $E_{F,h}$ and $E[\text{SO}_4^{2-}/\text{SO}_3^{2-}]$ and the driving force for the reduction ΔG_{red} by the difference between $E_{F,n}$ and $E[\text{H}^+/\text{H}_2]$. Compared to ΔG_{red} , ΔG_{ox} for sulfite oxidation is large and relatively constant across the series of QDs. Thus, the proton reduction kinetics are the rate-limiting factor for the photocatalytic hydrogen evolution over CdSe QDs. Overall, these findings establish a quantitative experimental basis for quantum-confinement-controlled proton reduction with semiconductor nanocrystals.

In metal oxides, quantum confinement effects usually require crystal sizes below 2 nm. That is because electron-hole pairs are less delocalized, and, correspondingly, their Bohr exciton radius is small [82]. Such conditions are fulfilled for 0.71 nm thick WO₃ nanosheets obtained by exfoliation of the layered compound Bi₂W₂O₉ (Fig. 9) [102]. Diffuse reflectance optical spectra reveal an absorption edge of 430 nm, consistent with a band gap of 2.88 eV, compared to 2.68 eV for bulk

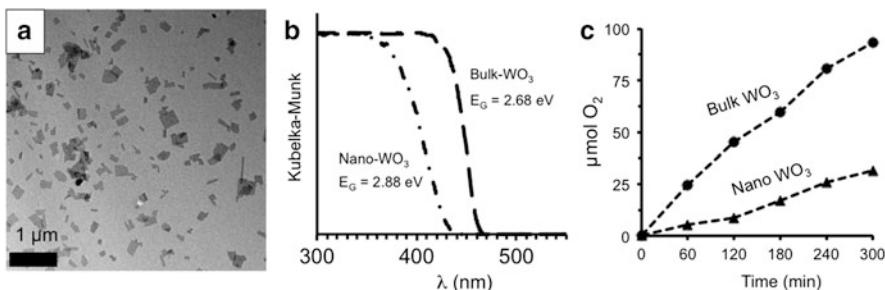


Fig. 9 (a) TEM image of nano-WO₃. (b) Optical absorption of nano-WO₃ and bulk particles. (c) O₂ evolution from aqueous 0.0083 mM AgNO₃ with 50 mg WO₃ and under >400 nm light from 300 W Xe lamp (315 mW cm⁻²). Reproduced with permission from [102]. Copyright 2012, American Chemical Society

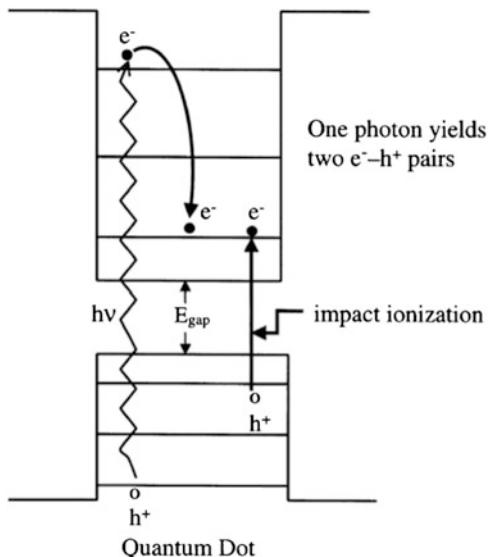
WO₃. Under visible light illumination, the photocatalytic O₂ evolution from such nanosheets is lower than the bulk because of reduced light absorption. However, the quantum efficiency for oxygen evolution at 375 nm (1.55%) exceeds that of the bulk (1.43%). This is because of the greater free energy stored in the nanosheets.

7 Multiple Exciton Generation

The altered electronic structure of strongly size-confined nanocrystals gives rise to multiple exciton generation (MEG), i.e., the formation of several (n) electron hole/pairs after absorption of one photon with an energy n times that of the particle's band gap (Fig. 10). The MEG effect has been made responsible for the abnormally high efficiency of PbSe-sensitized TiO₂ photoelectrochemical cells [103] and PbSe photovoltaic cells [104].

The MEG effect has not yet been demonstrated for water splitting photocatalysts. The problem is that, for MEG, the band gap of the absorber needs to be an integer fraction of the exciting light. For the upper range of solar photons with 3.0 eV, this would correspond to $E_G = 1.50$ or less. Such a low band gap is not sufficient for water electrolysis, considering additional voltage losses from charge transfer and recombination. However, the MEG effect could potentially work for tandem or multi-junction photocatalysts, which utilize several small band gap absorbers in series.

Fig. 10 Enhanced photovoltaic efficiency in QD solar cells by impact ionization (inverse Auger effect). This is promoted in QDs because of the lower rates of carrier relaxation. Reproduced with permission from [105]. Copyright 2002, Elsevier Science Ltd



8 Ion Effects

Because the dimensions of nanomaterials are only a fraction of the space charge layer thickness in solid materials, screening effects from electrolytes and specifically adsorbed ions are dominant. For pure water, the most important ions are hydroxide and hydronium ions, and their effect on metal oxides, including TiO_2 [106] and Fe_2O_3 [107, 108] gives rise to the well-known 59 mV pH^{-1} variation of the flatband potential with the solution pH [109]. In surface water, phosphate, silicate, and fluoride ions are often strongly adsorbing [110], which determines the redox stability of many minerals [109]. In contrast, the flatband potentials of II/VI, III/V, and group IV semiconductors are more susceptible to adsorption of soft ligands, including sulfur [111], HS^- [112, 113], HTe^- [114, 115], and Cl^- [116]. These often bind to specific crystal surfaces [114, 115] and control the open circuit voltage of photoelectrochemical cells [116, 117] and the water redox rate of suspended photocatalysts.

The effect of specifically adsorbed ions follows directly from the definition of the Fermi energy of the electrons E_F in a particle, which is equal to the chemical potential μ minus the electrical potential ϕ of the material (F : Faraday constant) [118].

$$E_F = \mu - \phi F. \quad (5)$$

Adsorbed ions can modify either μ or ϕ , or both. In the literature, proton adsorption is usually considered as an effect on the chemical potential μ . This leads to the known Nernstian dependence of the semiconductor flatband potential on solution

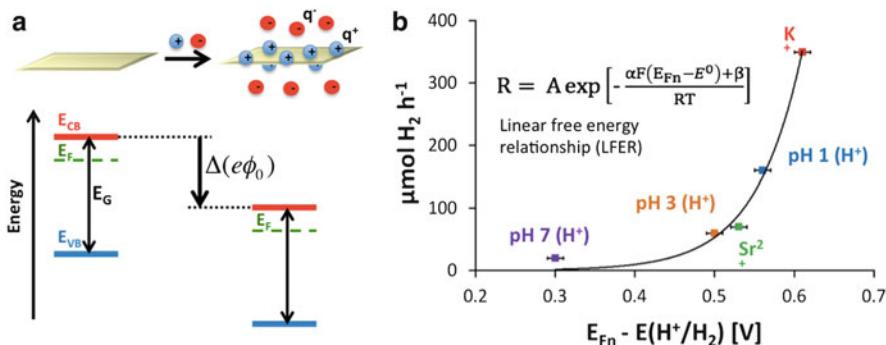


Fig. 11 (a) Effect of specifically adsorbed ions on the energetics of a sheet-like nanocrystal. (b) Calculated rate of hydrogen evolution vs ΔG for electron transfer with illuminated cation modified $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets [123]. Constants: Faraday constant $F = 96,485 \text{ C mol}^{-1}$, ideal gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, free energy parameters $A = 0.0127$, $\alpha = 0.441$, and $\beta = 633 \text{ J mol}^{-1}$. Additional symbols in (6): relative permittivity ϵ and dielectric constant ϵ_0 . Reproduced from [123] with permission from The Royal Society of Chemistry

pH [106, 107, 109]. Equation (5) works because redox reactions with protons are fast, allowing the protons to be in electrochemical equilibrium with the electrons in the particle. For ions such as Al^{3+} (-1.66 V vs NHE) and Mg^{2+} (-2.37 V vs NHE) [119], whose negative reduction potentials preclude reduction in water, an electrostatic approach is more suitable (Fig. 11). Here it can be assumed that ion adsorption to the surface A generates the charge density $\sigma = q/A$, which modifies the surface potential ϕ_0 . Neglecting space charge layer effects, the potential ϕ felt inside the particle is the same as ϕ_0 , causing E_F to change according to (5). The relation between the surface charge density σ and the surface potential ϕ_0 is given by the Grahame equation (for definition of symbols see Fig. 11 caption) [120, 121]:

$$\phi_0 = \frac{2RT}{zF} \sin^{-1} \left(\frac{\sigma}{\sqrt{8RT\epsilon\epsilon_0 c^0}} \right). \quad (6)$$

In it, z and c^0 describe the charge and molar concentration of the counterions in solution, which surround the particle. Specifically, adsorbed cations produce a positive surface potential, shifting the energy bands down to more oxidizing potentials, and anions move the band edges to more reducing potentials. This shifts the Fermi energy in (5) and with it the driving force for photochemical charge transfer. In general, the variation of the electron transfer rate constant with E_F can be understood using free energy relationships [122], including Butler–Volmer [99, 101] and Marcus theory [94].

These theoretical predictions were recently verified for M-modified $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets (M= H^+ , K^+ , Sr^{2+}) [123]. Hydrogen evolution rates from the illuminated nanosheets are plotted in Fig. 11b against the thermodynamic

driving force for proton reduction $F(E_{Fn} - E^0)$, obtained from photoelectrochemistry. The data can be fitted with the linear free energy relationship (LFER) [122] shown in the figure (constants in caption). The numerical values of α and β do not have physical significance, because the fitted rate R ($\mu\text{mol h}^{-1}$) does not convey any information about the value of the rate constant for the process, which depends on the electro-active area of the nanoparticles, the absorbed photons flux, space charge layer effects, and other unknown parameters [30, 124–128]. The model provides a physical explanation for the observed correlation between nanosheet energetics and hydrogen evolution rates, and it confirms the dependence of photocatalytic activity on the presence of specifically adsorbed ions.

9 Interfacial Charge Transfer

The larger specific surface area of nanomaterials promotes charge transfer across the material interfaces (solid–solid and solid–liquid), allowing water redox reactions to occur at lower current densities and, correspondingly, lower overpotentials. This is a direct consequence of the Butler–Volmer equation which relates the current density to the overpotential [101]. This boost is particularly important for the slow, multi-step water oxidation reaction [129, 130], which normally requires highly active and often expensive co-catalysts based on Ir, Rh, or Pt [131]. It is one of the reasons why nanostructured electrocatalysts are so effective [132, 133]. The problem for photocatalysts is that the increase in junction area also increases the rate for reverse charge transfer, as shown by J_T and J_{et} in Fig. 12. These currents oppose the electron drift away from the surface (thick arrow) and reduce the rectifying character of the junction. The effect on the open circuit voltage of the junction is described with the Shockley diode equation (2). Every decadic increase of the reverse saturation current J_0 can be expected to decrease the open circuit voltage by 59 mV. The only way to overcome this fundamental limitation is by making the junction area smaller, as discussed above under Sect. 4.

10 Electron–Hole Recombination

Electron–hole recombination is the major loss mechanism in excitonic solar cells and in photocatalysts [135]. Photogenerated charge carriers recombine through radiative and nonradiative processes in the bulk phase of the semiconductor, in the depletion region, and at surface defects (Fig. 12) [134, 136–138]. These processes diminish the steady state concentrations of usable charge carriers, their charge transfer rates (thick black arrows in Fig. 12), and the driving force for water electrolysis. Furthermore, the larger specific surface area of the particles promotes non-radiative and interfacial recombination rates. The effect of these parameters on photocatalytic activity and electron–hole lifetime are commonly

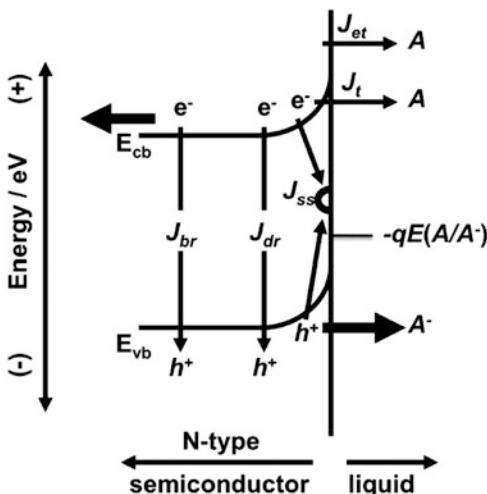


Fig. 12 Recombination pathways for photoexcited carriers in a semiconductor PEC [9, 134]. The arrows signify bulk recombination (J_{br}), depletion-region recombination (J_{dr}), and surface recombination (J_{ss}). Additional loss mechanisms caused by undesired charge transfer are also shown. Electron tunneling through and over the barrier produces the current densities (J_t) and (J_{et}). Electron collection by the back contact and hole collection by the redox couple (e.g., oxidation of water to O_2) are desired processes shown by thick black arrows. Reproduced with permission from [134]. Copyright 2005, American Chemical Society

acknowledged in the literature [89, 139–143], but quantitative studies on this topic are rare [65, 79, 144–148].

We recently employed graphitic carbon nitride $g\text{-C}_3\text{N}_4$ to observe the effect of structure defects on the ability of the material to reduce protons photocatalytically and to generate a photovoltage [149]. Specifically, we observe an inverse relation between the photocatalytic hydrogen production rate from aqueous methanol and the calcination temperature (Fig. 13). Higher temperatures also decrease the photoluminescence (PL) of the material and the photovoltage. Based on the PL and surface photovoltaic (SPV) data, there are two types of defects present near the conduction and valence band edges of the material. These defects promote electron–hole recombination and reduce the ability of the material to generate a photovoltage.

The reduction of surface defects must be a major goal for the future if nanostructured photocatalysts are to be used for unbiased solar water splitting [150]. The literature suggests that performance enhancements can be achieved with chemical treatments. For example, reaction of silicon with HF can suppress surface recombination and improve the performance of photovoltaic devices [138]. For Fe_2O_3 photoanodes it has been shown that application of Al_2O_3 [151] or SnO_2 [152] overlayers also improves the performance. For BiVO_4 photoanodes, both application of an SnO_2 underlayer [153], and incorporation of W dopants boost the electrical power output, which is attributed to reduction of surface recombination

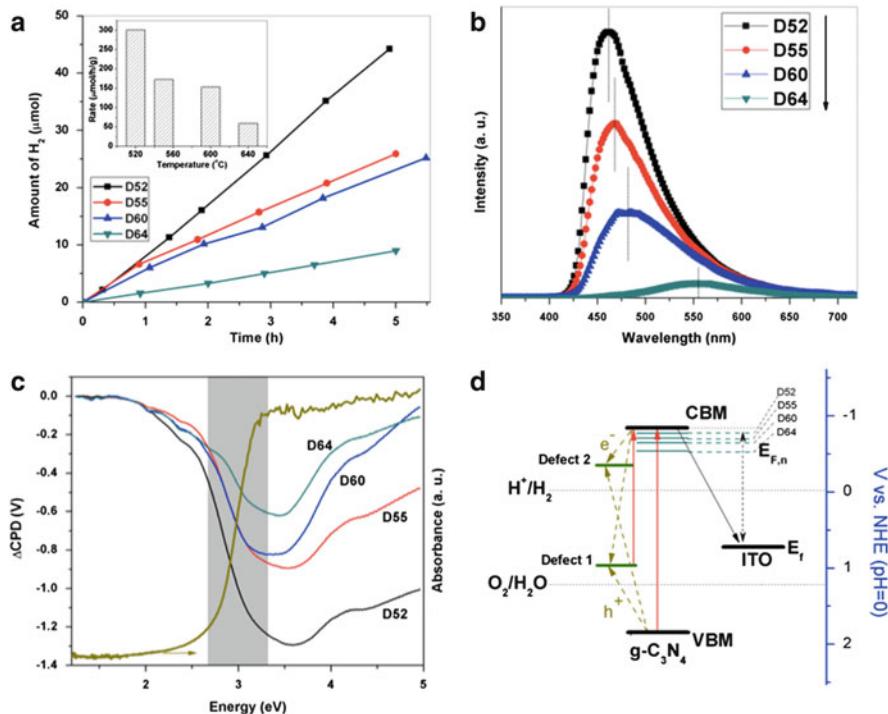


Fig. 13 Properties of g-C₃N₄ prepared at 520, 550, 600, and 640°C. **(a)** H₂ evolution from platinated samples (30 mg) in methanol (20 vol.%) aqueous solution at pH 4.5 under visible light (>400 nm). **(b)** PL spectra at 350 nm excitation. **(c)** SPV spectra of g-C₃N₄ films on ITO substrate with UV-vis spectrum (dark yellow line) of D52. **(d)** Energy diagram of g-C₃N₄ with defect levels at +0.97 V and -0.38 V. Reproduced from [149] with permission from The Royal Society of Chemistry

[154]. Further work is needed to determine the general merit of these and related surface passivation approaches for suspended photocatalysts.

11 Excited State Entropy

Theoretically, the degree of quantum confinement of a light absorber determines the excited state entropy and its free energy [155]. According to (7) [156], the free energy of a semiconductor absorber $\mu_{e,h}$ is determined by the band gap E_G , the temperature, the electron and hole concentrations n_e and n_h , and the effective density of states $N_{\text{CB/VB}}$ near the band edges. The greater the $N_{\text{CB/VB}}$, the more diluted the charge carriers and the higher their entropy loss. In quantum dots, a reduction of $N_{\text{CB/VB}}$ can readily be achieved through quantum size effects (Fig. 14). Here, for $N_{\text{CB}} = 18$, 12, 6, and $n=6$ electrons, the number of microstates

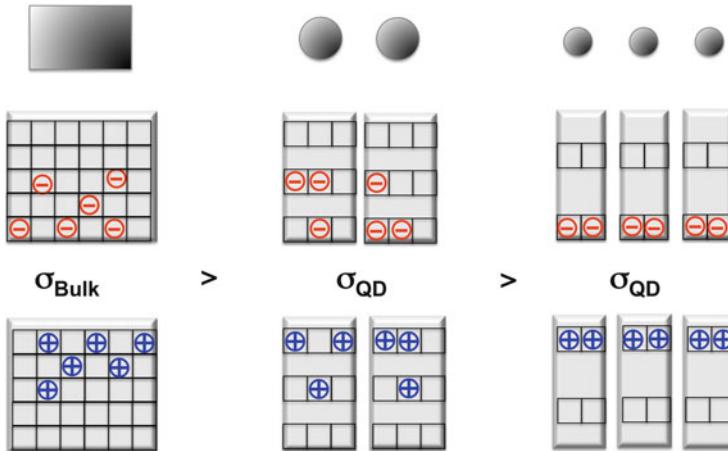


Fig. 14 Effect of quantum sizing on $N_{\text{CV/VB}}$ and entropy for three systems of six electron-hole pairs. Reproduced from [155] with permission from The American Chemical Society

$W_{\text{Tot}} = 18!/(18-6)!6!$, $12!/(12-6)!6!$, $6!/(6-6)!6!$, and the entropy per electron $\sigma = 1.5 \times 10^{-23}$, 1.1×10^{-23} , 0.0 J/K . Thus, the free energy increases with quantum confinement because of the reduction of the effective density of states near the band edges. Physically, this represents a concentration of charge carriers near the band edges. This is in addition to the increase of the potential energy of the charge carriers which results from the widening of the band gap.

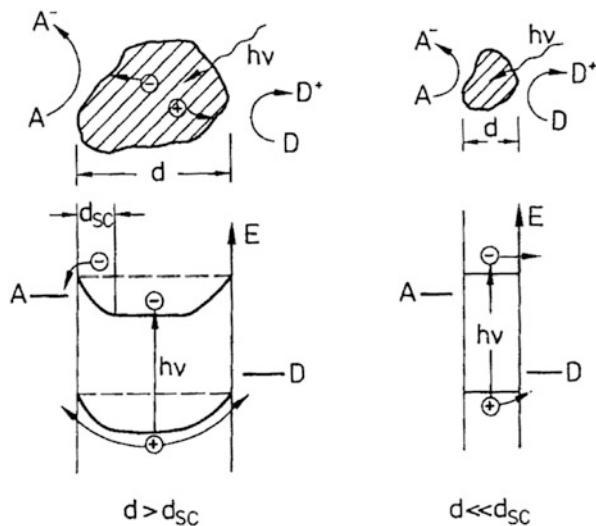
$$\mu_{e,h} = E_G - kT \ln \frac{N_{\text{CB}} N_{\text{VB}}}{n_e n_h}. \quad (7)$$

The entropy effect is difficult to observe in actual photocatalysts because of the presence of other loss mechanisms (e.g., non-radiative recombination). Furthermore, the energetics of nanoscale systems is very sensitive to variations in size, shape, and molecular environment. The corresponding increase in the ground state entropy of polydisperse and randomly packed quantum dots can reverse the entropy reduction of the individual subsystems. Additional entropy losses in particulate absorbers can occur as a result of the redistribution of light. Potentially, these losses can decrease the photovoltage by as much as 315 mV [157].

12 Electron–Hole Separation

In nanomaterials, carrier separation (arrows in Fig. 12) is more difficult to achieve than in the bulk because at average doping concentrations ($n_0 = 10^{17} \text{ cm}^{-3}$) space charge layers are not effective on the nanoscale [30, 59, 158, 159]. Also, for

Fig. 15 Space charge layers in large and small particles. Reproduced with permission from [30]. Copyright 1994, Springer Berlin/Heidelberg



spherical nanoparticles, the space charge layer thickness d_{sc} cannot exceed the radius $d/2$ of the particle (Fig. 15), which restrains the possible barrier height at the interface. For example, for 16-nm TiO₂ nanocrystals ($\epsilon = 160$) with a charge carrier concentration of $n_0 = 10^{17} \text{ cm}^{-3}$, O'Regan calculated a barrier height of 0.3 meV under maximum depletion [160]. This means that, in the absence of a strong applied bias, the bands in a nanoparticle are essentially flat, as shown in Fig. 15.

In the absence of an interior electrical field, the relative rates of electron-hole injection into the electrolyte are governed by the kinetics of interfacial charge transfer alone [158]. This leads to an increase of undesirable processes (current densities (J_t) and (J_{et}) in Fig. 12) which short-circuit the device. The absence of an internal mechanism for charge separation also increases electron-hole recombination, as discussed above. This is the reason why efficient collection of majority carriers in dye-sensitized cells with nanocrystalline TiO₂ substrates depends on the presence of iodide as an easily oxidizable electron donor [160, 161]. Without iodide, only 4% of electrons can be harvested at the back contact because of recombination with holes on the Ru dye (this corresponds to J_{et} and J_t in Fig. 12). Furthermore, in nanostructures with quantum size effects (e.g., in many metal chalcogenides), the electron-hole pairs are confined to a space smaller than the Bohr exciton radius. This means that additional energy is necessary to separate the charges. This is analogous to organic photovoltaic cells, where a higher exciton binding energy results from the lower dielectric constant of organic polymers [162].

Photochemical labeling can provide information about charge separation in suspended light absorbers [32, 163, 164]. Typically, a photocatalyst is irradiated in the presence of metal salt that forms insoluble deposits (e.g., Pt, Au, MnO_x, IrO_x) after accepting photogenerated electrons or holes. This helps to pinpoint the locations of the photocharges on the absorber surface. For nanosheets derived

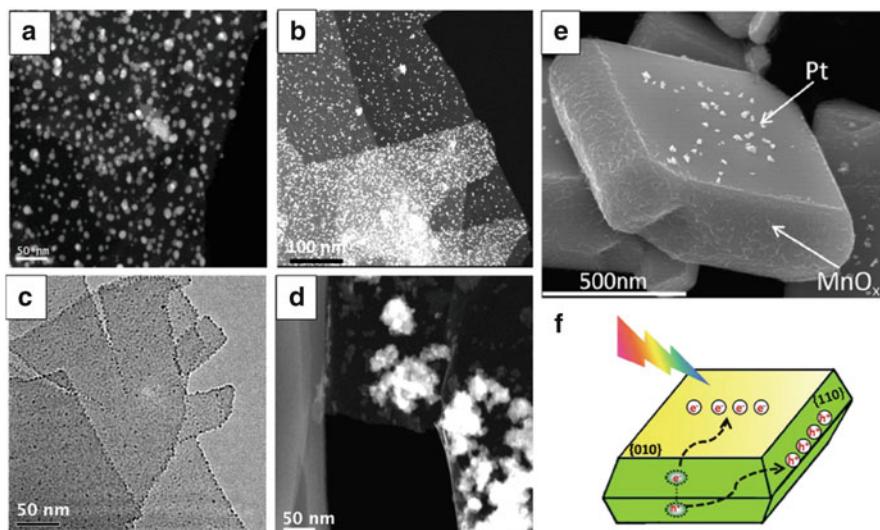


Fig. 16 $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets after labeling with (a) Ag, (b) Pt, (c) IrO_x, and (d) MnO_x [165]. (e) BiVO_4 microcrystals after labeling with Pt and MnO_x (f) [166]. Reproduced from [166] with permission from The Royal Society of Chemistry

from the layered perovskite $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, non-selective labeling results support the lack of intra-sheet charge separation (Fig. 16) [165]. Better charge separation is generally found in microscale particles, especially those where facets with different surface potentials are present. This is shown for BiVO_4 microcrystals in Fig. 16e, f. The selective deposition of Pt and MnO_x suggests that charge carriers accumulate at (010) and (111) facets of the crystal [166].

In ferroelectric materials, local dipoles (Fig. 17) can aid photochemical charge separation [167, 168]. Materials such as BaTiO_3 support a spontaneous electrical polarization that stems from the displacement of mobile cations in the unit cell. Photochemical labeling experiments confirm that these dipoles can guide the accumulation of photochemical charge carriers [169]. The ferroelectric polarization appears to promote photocatalytic reactions [169], but its use for photocatalytic water splitting has not been tested.

Gradient doping provides an alternative way to generate a potential energy gradient inside of small crystals. This approach was recently demonstrated by van de Krol's group for tungsten-doped BiVO_4 films. [170] A tungsten concentration gradient inside the films moves photoelectrons towards the electrode and holes towards the solid–liquid interface. This is an elegant way to control charge separation, but it is probably only usable in defect-tolerant semiconductors, such as BiVO_4 .

For the majority of other metal oxide particles, the use of electron or hole selective acceptors may be a more suitable approach to promote charge separation. Many transparent n- or p-type metal oxides are known to accept electrons or holes

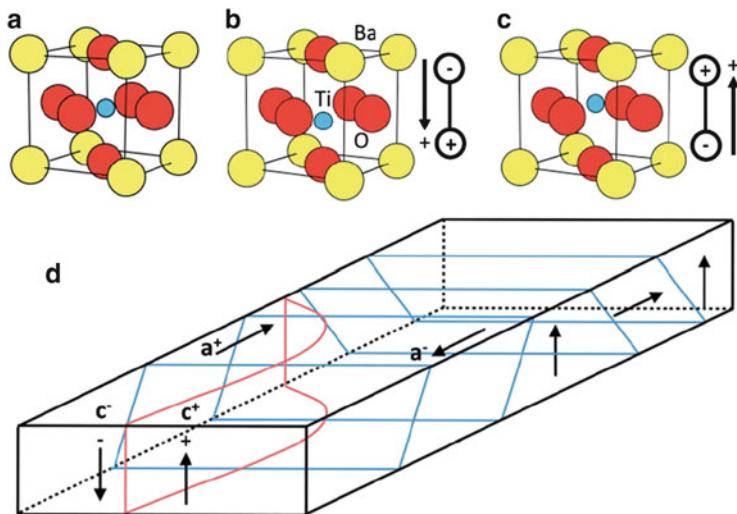


Fig. 17 Cubic unit cell of BaTiO_3 above (a) and below (b, c) the Curie temperature. Note displacement of the central $\text{Ti}(\text{IV})$ ion and corresponding dipoles. (d) Crystal with domains of constant polarization in the *arrow* direction. Reproduced from [169]

selectively [171]. For example, n-SnO₂ underlayers on BiVO₄ photoanodes have been found to boost the photocurrent by 300% [153] and p-type NiO layers on Fe₂O₃ improved the photovoltage by nearly 0.4 V [172]. Many of these metal oxides can be deposited from solution and could potentially be applied to photocatalysts [173].

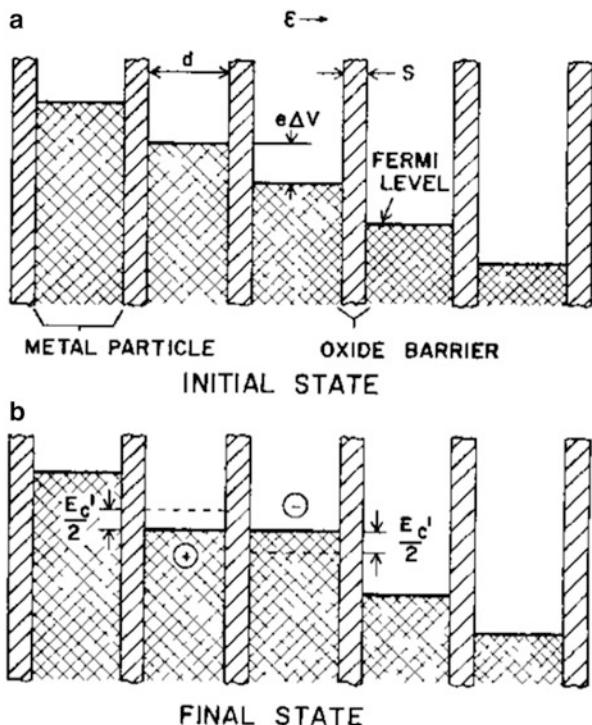
13 Interparticle Charge Transport

In nanocrystalline films, charge carriers move by diffusion instead of drift [59, 174–176]. As a result, charge transport is much slower than it is in the bulk phase, increasing the chances for recombination and back reactions [177]. If the nanoparticles are not fused together, additional barriers arise from interparticle charge transport, which occurs by thermally activated hopping and by electron tunneling (Fig. 18). Charge transport depends on the interparticle distance and the electrostatic charging energy of the donor acceptor nanocrystal couple [178, 179].

The problem of charge transport over macroscopic distance is less important with suspended catalysts. However, it does play a role for charge transport in photocatalyst films, as used for photoelectrochemical measurements, or with immobilized photocatalysts.

Fig. 18 Electron hopping in nanostructured films.

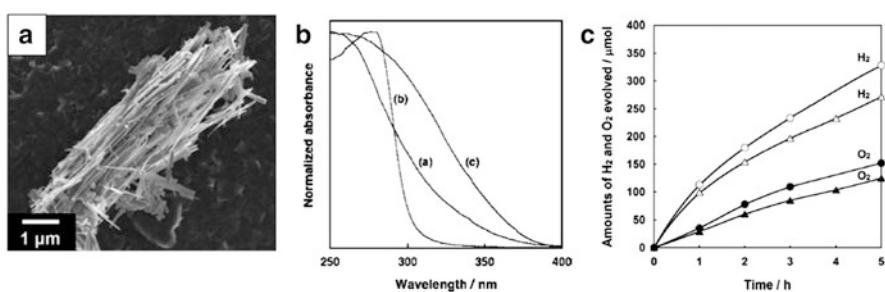
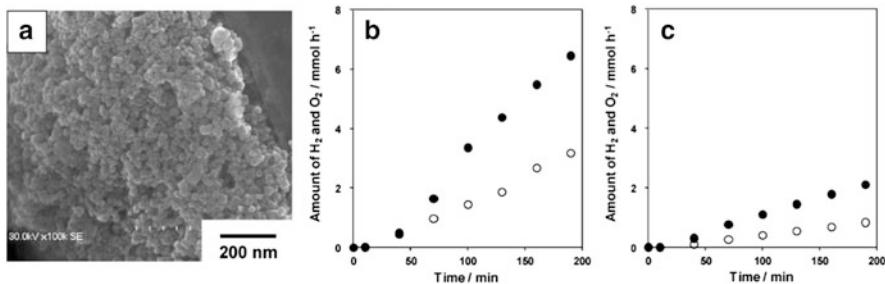
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14 Examples of Nanoscale Photocatalysts for Overall Water Splitting

Because of the problems above, the number of known nanoscale photocatalysts for overall water splitting is limited [57–66]. Only five nanoscale photocatalysts have been reported in the literature. Four of them are Schottky type devices and require ultraviolet light for operation. The most active catalyst was reported by Kondo's group in 2011. It consists of aggregates of NiO_x -loaded NaTaO_3 nanocrystals (Fig. 19) [180]. The catalytic rate of this system was very high (2.0 mmol h^{-1} of H_2 with stoichiometric O_2) but required photons with $>4.0 \text{ eV}$ because of the band gap of bulk NaTaO_3 [32]. The activity of the 20 nm nanoparticles was three times higher than that of the 50 , 100 , and 200 nm particles tested for comparison. This was attributed to the higher surface area of the smallest absorber size and higher crystallinity.

Another system was developed by Akihiko Kudo's group and consists of LiNbO_3 nanowires ($70 \text{ nm} \times 10 \mu\text{m}$) with a band gap of 4.0 eV (Fig. 20) [142]. After modification with 1 mass % RuO_2 co-catalyst, the nanocomposite can split water with 0.7% quantum efficiency at 254 nm (O_2 was evolved in slight excess). The lower activity of the bulk compared to the nanowires was attributed to surface defects resulting from ball-milling.



In a third example (Fig. 21), Yan et al. reported overall water splitting with 3 mass % RuO₂-modified Zn₂GeO₄ nanorods (100 × 150 nm) under UV light from a 400 W Hg UV lamp to excite the large band gap (>4.5 eV) of the material. Here, the H₂ evolution rate was 17.4 μmol h⁻¹ (stoichiometric O₂) with 100 mg of the catalyst [143]. The lower activity of the bulk material is attributed to surface defects and lower surface area.

The last example consists of 6–30 nm SrTiO₃ nanocrystals with a 3.3 eV indirect band gap (Fig. 22) [181]. After modification with an NiO_x co-catalyst, this system produces 19.4 μmol H₂ g⁻¹ h⁻¹ (with stoichiometric O₂) from pure water under >3.2 eV illumination (26.3 mW cm⁻²). The activity of the 30 nm particles was three times higher than the 6 nm particles, probably as a result of surface defects in the latter. These defects are visible as the tail in the absorption spectrum. They resulted from the lower preparation temperature of the 6 nm particles. The 30 nm particles gave 35% lower rates for H₂/O₂ evolution than the bulk particles (synthesized by solid state reaction). This is attributed to a quantum confinement effect,

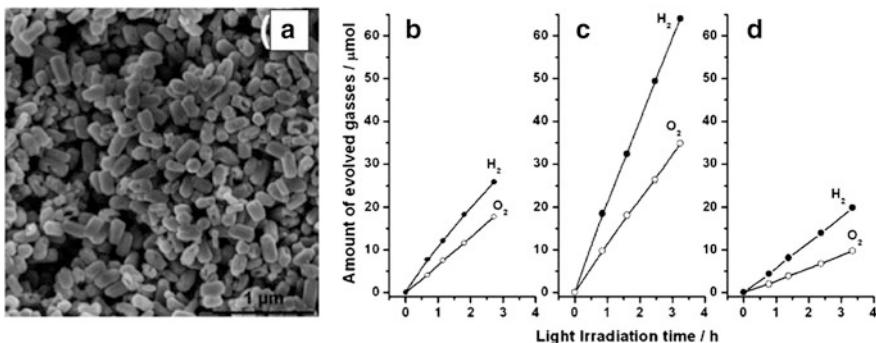


Fig. 21 RuO₂-Zn₂GeO₄ nanoscale photo catalyst. (a) SEM of Zn₂GeO₄. (b) H₂/O₂ evolution from water with particles prepared at 40°C. (c) Same for particles made at 100°C. (d) Same for bulk particles from a solid state reaction at 1,300°C. Conditions: UV irradiation ($\lambda > 200$ nm) of 0.1 catalyst in pure water with a 400-W high-pressure mercury lamp. Reproduced from [143] with permission from The Royal Society of Chemistry

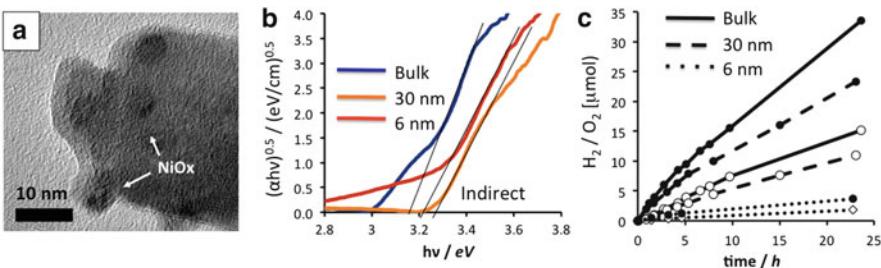


Fig. 22 NiO-SrTiO₃ nanoscale photocatalyst. (a) SEM of NiO-SrTiO₃. (b) Tauc plots for bulk (>100 nm), 30 nm, and 6 nm SrTiO₃ particles. (c) H₂/O₂ evolution from water with 100 mg of catalyst under UV irradiation (250–380 nm at ~26 mW cm⁻² from a 300 W Xe lamp). Reproduced from [181] with permission from The American Chemical Society

which increases the band gap of the smaller particles and reduces the absorbed photons.

In 2014, Kudo's group reported the first nanostructured tandem catalyst for overall water splitting [44]. The system employs physical mixtures of Ru-modified Rh:SrTiO₃ and BiVO₄ powders in the presence of FeCl₃ as a redox shuttle. Whereas 50–70 nm Rh:SrTiO₃ particles gave 16/7.5 μmol h⁻¹ H₂/O₂, 300 nm particles gave 128/64 μmol h⁻¹. This inverse particle size dependency of the efficiency suggests sub-optimal charge separation and recombination in the smaller particles. The best system achieved a quantum efficiency of 3.9–4.2% (at 420 nm) and a solar to hydrogen efficiency of 0.1%.

Finally, in 2014, Peidong Yang's group reported direct water splitting from a mesh consisting of Rh:SrTiO₃ and BiVO₄ nanowires of 100–200 nm diameter

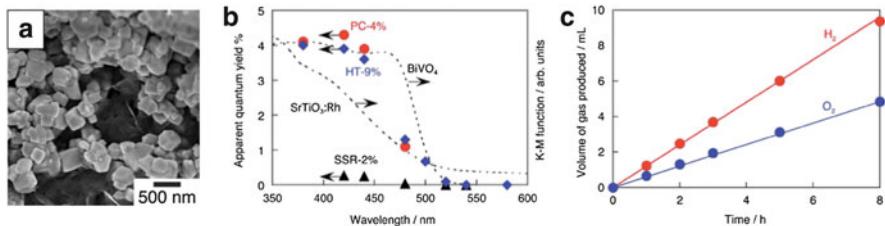


Fig. 23 Sr:SrTiO₃-Pt/BiVO₄ Tandem Photocatalyst system. (a) SEM of Rh:SrTiO₃. (b) Photoaction spectrum for Tandem system. (c) H₂/O₂ evolution under simulated sunlight (AM 1.5). Conditions: 50 mg of catalyst, 2 mM FeCl₃ solution. Reproduced from [44] with permission from The Royal Society of Chemistry

(Fig. 23). However, the H₂/O₂ evolution rate (<0.2 μmol h⁻¹) and the turnover number were too low to designate this process as catalytic [182].

15 Measuring Photovoltage in Nanoscale Photocatalysts

The low performance of the examples above emphasizes the need for a better understanding of charge transfer in nanoscale absorbers. Photoelectrochemistry is the most obvious way to probe photochemical charge separation in photocatalyst particles. However, because electrical contact to a working electrode is necessary, measurements need to be conducted on particle films. As noted above, particle mediated charge transport is generally slow, and reduces photocurrents to the microscale (Fig. 24). There is also a substantial potential drop across the film, which obscures the photovoltage of the individual particle junctions. Recently, Domen demonstrated that these charge transfer problems can be alleviated somewhat by evaporating metal electrode layers directly onto particle films [183–185]. The photocurrents from photoelectrodes made from Sc:La₅Ti₂CuS₅O₇ and LaTiO₂N electrodes are strongly enhanced and reach over -0.5 mA cm^{-2} / $+3.0 \text{ mA cm}^{-2}$ for water reduction/oxidation respectively (A.M. 1.5 illumination, at $+0.3 \text{ V}/+1.2 \text{ V}$ vs RHE). This allows for more accurate studies of junction potentials in small particles.

Alternatively, surface photovoltage spectroscopy (SPS) can provide a direct assessment of the photovoltage of particle junctions. In SPS, a semi-transparent Kelvin electrode measures the contact potential difference (CPD) of an illuminated photocatalyst film (Fig. 25) as a function of the excitation energy [187, 188]. The measured photovoltage (ΔCPD) is produced by the transfer of free charge carriers or polarization of bound charge carrier pairs (polarons) in the sample [189–191]. Because the technique relies on the detection of voltage and not current, even small concentrations ($<10^{10} \text{ cm}^{-2}$) of charge carriers can be observed [189, 192–197]. This sensitivity exceeds that of photoelectrochemistry by at least 1,000 times. Another advantage of SPS is that it can be performed selectively on solid-

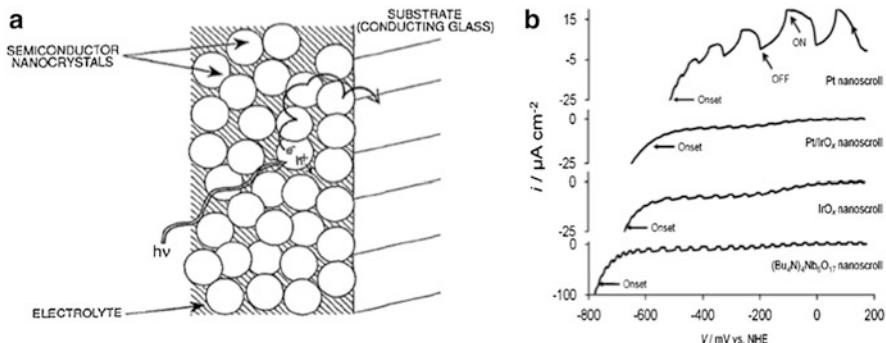


Fig. 24 (a) Charge transport limitation in particulate electrodes. Reproduced from [158] by permission of The Electrochemical Society. (b) Photocurrent scans for niobate nanocrystal films in methanol solution. Reproduced from [186] with permission (2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

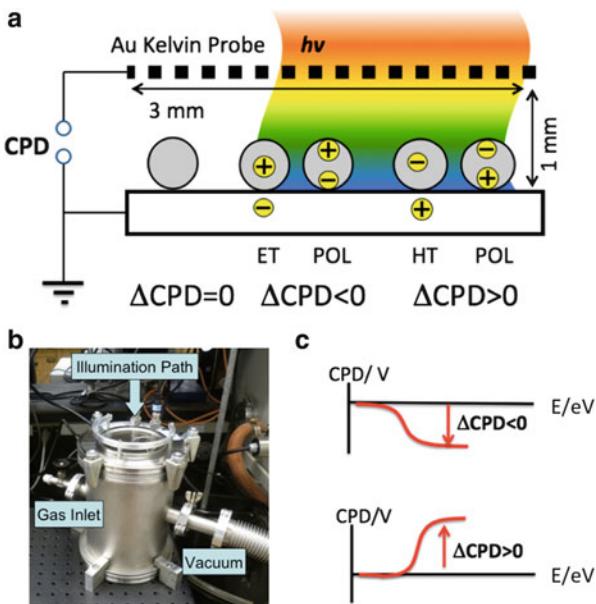


Fig. 25 (a) Geometry of SPV measurement. Contact potential changes are caused by polarization (POL) of electron-hole pairs or by charge transfer (ET/HT) into the substrate. The ΔCPD value can be interpreted as the open circuit voltage of the sample-substrate junction. (b) SPV Instrument. (c) Example spectra. A negative/positive ΔCPD signal corresponds to electron-hole movement towards the substrate. The photo-onset energy provides information about the effective band gap. Reprinted with permission from [190]. Copyright 2014, American Chemical Society

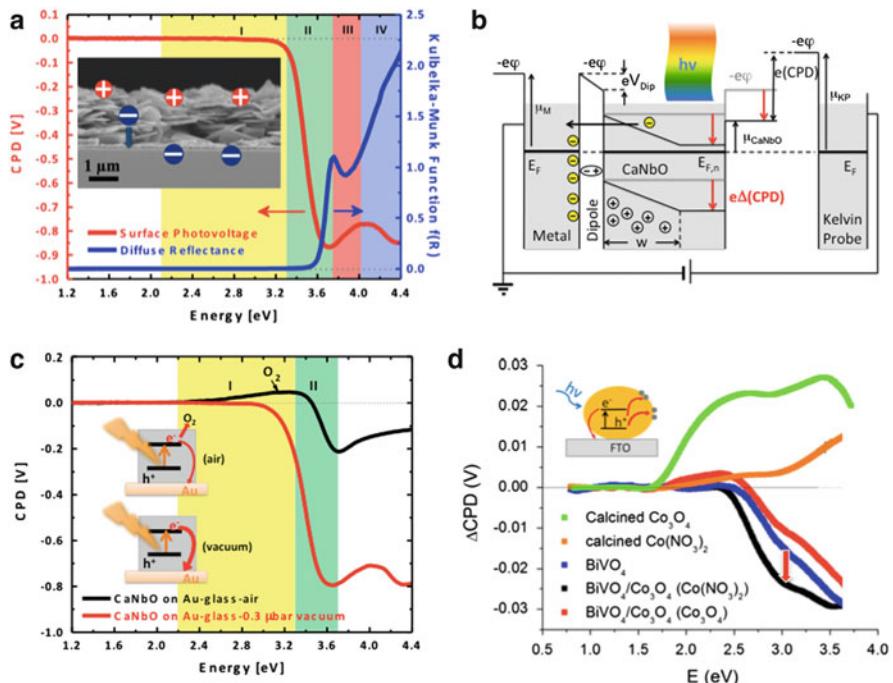


Fig. 26 (a) Surface photovoltage and diffuse reflectance spectra of $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanosheet film on Au (inset: SEM of film). (b) Energy diagram for the metal-nanosheet-Kelvin probe configuration under band gap illumination. Symbols: e : electron charge, φ : electric potential; ΔCPD : light-induced contact potential difference change; w : space charge layer width; μ_i : chemical potential (work function) of $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$, metal substrate, and of Kelvin probe; V_{Dip} : potential drop from interfacial dipole; E_F : Fermi level (electrochemical potential) in the dark; $E_{F,n}$: quasi-Fermi level of electrons under illumination. (c) Photovoltaic spectra of nanosheet film in vacuum and air. Reprinted with permission from [189]. Copyright 2014, American Chemical Society. (d) SPV spectra of Co_3O_4 , BiVO_4 , and Co_3O_4 - BiVO_4 on FTO substrate in vacuum (inset: charge transfer direction). Reproduced from [208] with permission from The Royal Society of Chemistry

solid interfaces without the need for a liquid phase or a redox couple. Because the photovoltage is entirely de-coupled from solid-liquid charge transfer, it allows direct measurement of solid-solid junction potentials.

Thomas Dittrich's group has used SPS extensively over the past decade on nanocrystal [198–200], molecular [201–203], and thin film [204] photovoltaics. However, as shown in the following example, SPS is also well suited for the characterization of nanostructured photocatalysts, where it can provide a quantitative understanding of charge transfer at solid-solid and solid-molecule contacts [189]. Figure 26 illustrates this for $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanocrystals, a known large band gap (3.5 eV) water splitting photocatalyst. [205, 206]. The main signal in the SPV spectrum of this compound is negative and corresponds to photochemical electron transfer from $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$ to the gold substrate. The observed photovoltage (-1.025 V) is controlled by the built-in potential, i.e., $E_F(\text{Au}) -$

$E_{F,n}(\text{HCA}_2\text{Nb}_3\text{O}_{10}) = -5.3 \text{ eV}$ [207] – (-3.5 eV) [205] = -1.8 eV , of the semiconductor–metal junction, as shown in Fig. 26b. The experimental value is lower because of the low illumination intensity and screening effects in the nanocrystal film.

In the presence of air (Fig. 26c) the negative feature II is decreased and partially replaced by a positive signal at 2.4–3.2 eV. This signal belongs to the photo-reduction of oxygen. The low energy of the reduction signal suggests that mid-gap surface defects are involved in electron transfer. The ability to observe these states in the SPV spectrum may promote the understanding of photochemical reactions between photocatalyst and molecules. In Fig. 26d the method is applied to the characterization of a contact between BiVO₄, a known water oxidation photocatalyst [209], and a Co₃O₄ nanoparticle water oxidation co-catalyst. The negative ΔCPD signal of BiVO₄ alone is produced by electron injection into the FTO substrate. Addition of a Co₃O₄ layer boosts the negative signal by 12 mV (red arrow) because of hole (minority carrier) injection into the cobalt oxide [208]. The boost can be interpreted as the photovoltage of the Co₃O₄–BiVO₄ junction. By itself, p-Co₃O₄ has a positive ΔCPD signal which stems from hole majority carrier transfer to the FTO substrate. This confirms the p-type character of this oxide. These examples illustrate how SPS can provide useful information about carrier type and charge separation in nanoscale contacts.

16 Conclusion

Research activity on nanostructured photocatalysts for solar water splitting has increased significantly over the last 30 years. Nanoscaling has been shown to improve charge extraction from absorbers with low carrier mobility and short carrier lifetimes. For selected metal chalcogenides the quantum size effect has been useful for increasing the stored free energy and for enhancing the rate of charge transfer and photocatalytic proton reduction. It was also shown that the energetics of nanoscale absorbers can be controlled with specifically adsorbed ions. At the same time, it has been found that nanoscaling decreases the ability of an absorber to generate free chemical energy from solar energy. The smaller size of the particles makes electron–hole separation more difficult to achieve because of non-selective interfacial charge transfer and reduced electric fields. Additionally, the larger specific area of nanostructures promotes defect recombination, which reduces the concentration of free charge carriers. These issues limit the photocurrent and the photovoltage that can be generated by the absorber, and with it the solar to hydrogen conversion efficiency. Contemporary research should aim to overcome these problems by developing new chemical methods for surface passivation and selective charge transfer and by more quantitatively assessing photovoltage and surface recombination in nanoparticles. The results from such studies not only benefit solar energy conversion but also promote our understanding of interfaces in general, as relevant to electronics, corrosion science, catalysis,

materials science, and geology. We already know that useful solar energy conversion is possible at the nanoscale – the photosynthetic systems of bacteria are the earliest examples of nanostructured solar energy conversion devices [68]. Effective artificial devices are sure to follow once we improve our understanding of nanoscale interfaces.

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