Colloidal Semiconductor Nanocrystals for Artificial Photosynthesis

Colloidal semiconductor nanocrystals for artificial photosynthesis

Francesca S. Freyria[a,b]

Abstract

Light-driven reactions for solar fuels have been receiving tremendous interest, leading of the possibility to store solar energy, our biggest and cleanest renewable energy source. Efficient solar to fuel conversion needs photosynthetic materials with strong absorption and high photocatalytic properties. Colloidal semiconductor nanocrystals are cutting edge materials for this application, thanks to their tunable optical and electronic properties through size, composition, morphology and assembly. In this chapter, some insights on the challenges to improve photocatalytic performance are reported, followed by an overview of different parameters that can be controlled to cope with these limitations. Finally, some devices at the forefront are illustrated.

1. Introduction

During the 2018, the global average annual carbon dioxide concentration reached 407.4 (±0.1 ppm), the highest level of the last 800,000 years. Energy consumption is increasing every year and currently about 81% of world energy supply is from fossil fuels.[1, 2] Acceleration in energy consumption in 2018 was more than 2% driven by high growth in electricity and gas demand. In this scenario, solar energy conversion is a promising approach to solve this problem, especially because the energy from the Sun on the Earth's surface in one hour (4.31020 J) almost matches the current world total energy consumption in a year. Obviously, the solar energy by itself could be able to largely satisfy the entire energy demand of the humankind.[3, 4]

Chemical fuels can be promising candidates for energy storage from intermittent renewable energy source such as sunlight. The formation of high energy C-C and C-H can be a tool to store energy which can release when they undergo combustion [5, 6]. Sunlight is the clean and the most abundant form of energy, but it is diffuse and intermittent so it is necessary to store it.[3, 7–10]

An environmental-friendly way to produce simple fuels (e.g. H_2, CH_3OH, C_2H_5OH) is to use incident solar photon energy to drive energetically uphill reactions such as the water splitting and the reduction of CO_2. In this way it is possible to obtain two great

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F.S. Freyria (✉)

[a] Department of Applied Science and Technology, Corso Duca degli Abruzzi, 24 I-10129 Torino, Italy

[b] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

(✉) Corresponding author. E-mail: francesca.freyria@polito.it// freyria@mit.edu

advantages simultaneously: i) no additional CO_2 is released in the atmosphere; ii) the production of fuels is impressively accelerated. The current natural system takes millions of years to produce fossil fuels, which are quickly burnt by humans, finally emitting huge amount of CO_2 in the atmosphere with climate changes issues. The conversion of CO_2 already present in the atmosphere through a fast process could help to close the carbon cycle and to reach an equilibrium of CO_2 level concentration[4, 6, 8, 11].

Currently there is a huge mismatch between the speed of which humankind emits greenhouses gases, especially CO_2, and the naturally pathway to capture them from the atmosphere. This disequilibrium is at the basis of the anthropogenic climate changes. Renewable energies could help not only to directly produce electricity, such as photovoltaic (PV) devices, hydrothermal and geothermal systems, but also to produce fuels with the same characteristics of fossil fuels. These are called in general "renewable fuels" and when the renewable energy used for the process is the sunlight, they are called "solar fuels". Detz et al. [4] introduced four main categories for the methods to obtain renewable fuels based on how the energy is harvested: concentration, transformation, natural photosynthesis and artificial photosynthesis. Under the last one, there are all the technologies to produce solar fuels through the exploitation of the solar light to drive reactions like water splitting or CO_2 reduction. A simple and cheap method can be accomplished by using particulate semiconductor (SC) materials where both absorption and catalysis occur in the single system. Recent economic calculations have estimated the average cost of H_2 is in the range of 1.6-3-5 $/kg with a solar to hydrogen conversion efficiency (STH) of 5-10% with a stability of 5 years.[12, 13].

Colloidal nanocrystals (NCs), like QDs, are receiving great interest either as photosensitizer or as photocatalyst to drive water splitting and CO_2 reduction reactions. Semiconductor nanocrystals (SC-NCs) have a prodigious extinction coefficient in the solar spectrum, [14] the possibility to tune the band gap up to the NIR-IR range of the solar irradiation,[15, 16] the ability to generate multiple excitons [17], an active and crucial role in energy transfer in hybrid system,[18–21]: all of these features provide the ground for excellent light harvesting materials and photocatalysis [15, 22–25].

2. Photocatalysis/photosynthesis with NCs: mechanisms

To produce and commercialize solar fuels at a viable large scale in a near future, we need a low cost and stable, durable photocatalytic colloid system. The process requires three main passages that all happen on the SC-NC based system: i) absorption of the photons and formation of excitons; ii) migration and charge separation of these photoexcited carriers; iii) surface chemical reactions.[12, 26, 27]

During these steps, there are some challenges to overcome to reach a desirable photocatalytic performance. In the following sections, we are going to describe some of them and to provide some strategies to address them.

Thermodynamics and Kinetics of Photocatalytic solar fuels production

An exciton, i.e. an electron/hole (e^-/h^+) pair bound by Coulomb forces, can be generated upon absorption of incident photon by a semiconductor nanocrystal. To have a catalytic process is necessary that the exciton reaches the reaction centers at the surface of the semiconductor and dissociates into free charges which can react before the recombination [2, 12, 26, 27]. Excitons formation is the first fundamental process in photosynthesis. Photocatalysis and photosynthesis can be classified as light-driven systems, where chemical reactions are promoted by excited states. In the field of solar fuels production, photocatalysis and photosynthesis are often used without a clear distinction: in both processes, we have the absorption and conversion of photons into charge carriers which drive redox reactions at the surface.[28], but the two processes are mainly different from a thermodynamic point of view (Fig.1a). According to IUPAC definition, photocatalysis is:" *change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance—the photocatalyst—that absorbs light and is involved in the chemical transformation of the reaction partners*." [29]

Whereas photosynthesis is: "*a metabolic process involving plants and some types of bacteria (e.g. Chromataceae, Rhodospirillaceae, Chlorobiaceae) in which light energy absorbed by chlorophyll and other photosynthetic pigments results in the reduction of CO_2 followed by the formation of organic compounds. In plants the overall process involves the conversion of CO_2 and H_2O to carbohydrates (and other plant material) and the release of O_2.*"[29]

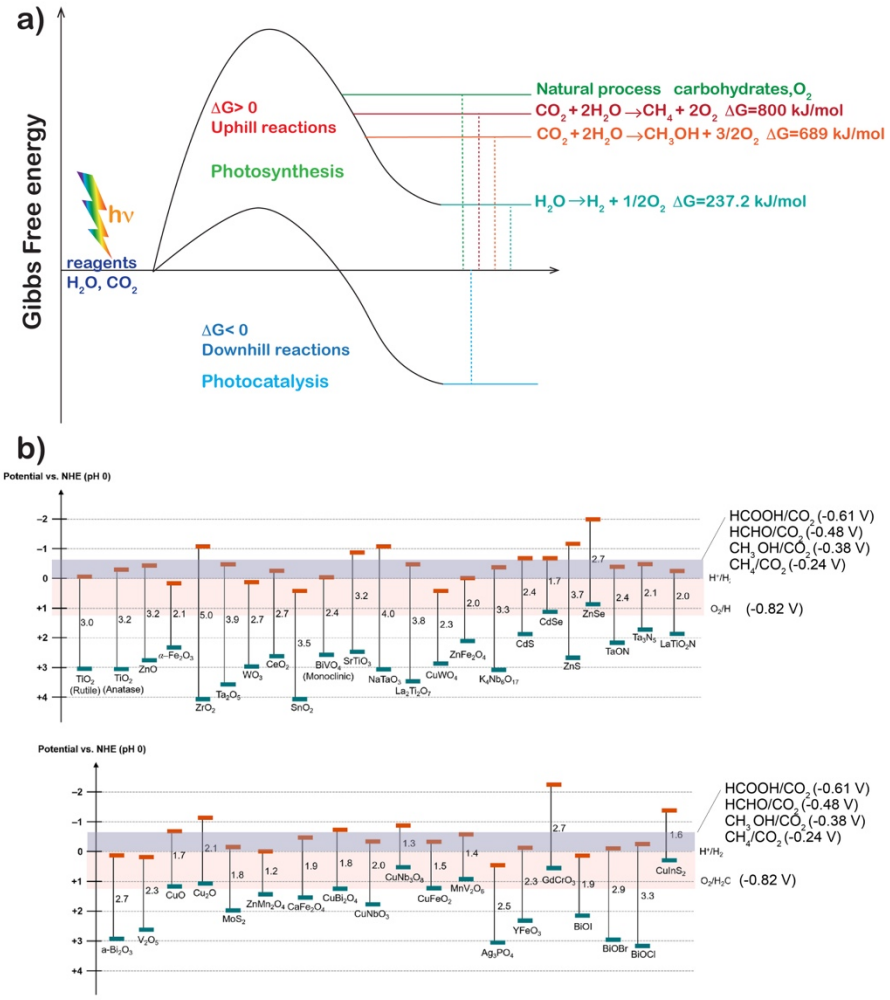

Fig.1 a) Energetics of photocatalysis and photosynthesis, inspired by [27] and [12]; b) Band edge positions of some typical semiconductors with respect to the reduction−oxidation potentials of CO_2 reduction and water splitting reactions, Adapted with permission from (Wang Q, et al. (2020) Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. Chem. Rev. 120:919–985). Copyright (2020) American Chemical Society. [12]

Based on these definitions, in a photocatalytic process light is only used to speed up a thermodynamically spontaneous ($\Delta G < 0$) reaction by reducing the kinetic barriers in

the chemical conversion. In natural photosynthesis, instead, light is an essential ingredient of the reactions allowing processes that otherwise are thermodynamically forbidden ($\Delta G > 0$). In such a case, the reaction occurs only when a light absorber produces e^-/h^+ pairs whose energy is higher than ΔG [27].

Water splitting and CO_2 reduction are endergonic reactions and the photon energy is necessary to reverse the sign of the associated Gibbs free energy. The rate of the spontaneous reverse reactions may be the limiting factors [27]. Therefore, it would be more appropriate to refer to these processes as photosynthetic processes rather than photocatalytic reactions. On the other hand, in literature, in the majority of the papers, it is more often used the term photocatalysis, especially in presence of reactions that involve sacrificial agents.[2, 27, 30, 31]

When a photon with higher energy of the band gap is absorbed, an electron is promoted from the valence band (VB) to the conduction band (CB) with a subsequent loss of the energy in excess of the band gap due to thermalization process (Fig.2).[28, 32] Not every electron/hole in quasi Fermi levels can be used to promote photocatalytic reactions (Fig.1b). Indeed, not only energy band gap value needs to be larger than the difference in reduction and oxidation potentials of the two half reductions, but the band edge positions also need to be correctly aligned with these redox potentials, having, in practice, the valence band below the oxidation potential whereas the conduction band above the reduction potential of the desired reaction (Fig.2). To promote the electron or the hole transfer it is necessary to guarantee overpotentials. To simplify, we can compare the band edge alignment between the conduction band and valence band of the semiconductor catalyst and the redox reaction to the band alignment on semiconductor junctions. [2, 33, 34] When we have a Type I alignment (straddling configuration) the requirements of overpotentials are verified for both electrons and holes, whereas when we have a Type II alignment (staggered configuration) only one of the half reactions can occur and for the other half reaction, we need to use a sacrificial agent.

For example, if we just consider the band alignment for water splitting, we would need a photocatalyst with the bottom of the conduction band more negative than the redox potential to reduce water molecules to hydrogen (H^+/H_2) and the top of the valence band more positive of the redox potential to oxidize water molecules to oxygen (O_2/H_2O) with an energy band gap between 1.23 eV and 3 eV[31]. (Fig.2, $E°_{w\_red}$ and $E°_{w\_ox}$, in teal color).

Based on the equations 1.1-1.3, the photons in the visible/NIR solar spectrum could have energy enough to carry out the reactions for the water splitting and CO_2 reduction.

$$H_2O \rightarrow H_2 + 1/2\ O_2 \qquad \Delta G^0 = 237\ kJ/mol \xrightarrow{\Delta E^0 = \frac{\Delta G^0}{nF}} \Delta E^0 = 1.23\ eV = 1008\ nm \tag{1.1}$$

$$CO_2 + 2H_2O \rightarrow CH_3OH + 3/2\ O_2 \qquad \Delta G^0 = 689\ kJ/mol \xrightarrow{\Delta E^0 = \frac{\Delta G^0}{nF}} \Delta E^0 = 1.19\ eV = 1041\ nm \tag{1.2}$$

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \qquad \Delta G^0 = 800\ kJ/mol \xrightarrow{\Delta E^0 = \frac{\Delta G^0}{nF}} \Delta E^0 = 1.036\ eV = 1096\ nm \qquad (1.3)$$

Fig.2 reports the main energy loss pathway during photoreaction processes. The first easiest way to lose energy is the not absorption of the photons with lower energy compared to the band gap of the semiconductor [2, 12, 35](Fig.2, event (a)). This is a significant loss channel in semiconductors with large band gap, like TiO_2 (~3.2-3.0 eV), which absorb mostly in the UV or in the visible part of the solar spectrum nearer to the UV [36–39]. On the other hand, photons with a higher energy of the band gap can generate hot charge carriers and the excess of energy is dissipated through thermalization (Fig.2, event (b)). Another crucial loss mechanism is the recombination of the electron/hole pair in the bulk or at the surface before their transfer to the catalytic center (Fig.2, event (c)). Direct semiconductors with a suitable band gap can have a higher transition probability with high absorption coefficients as compared to the indirect semiconductors which result in lower absorption coefficients and a higher probability to generate non-radiative pathways for the e^-/h^+ pairs since phonons are involved.[12] When e^-/h^+ pairs are generated, it is important to avoid their recombination and, especially in direct semiconductors, Auger recombination could become an important channel.[2] The harvested light can be dissipated through radiative recombination (light emission) or through nonradiative recombination (heat generation). The long-lived photogenerated charges that do not undergo recombination can react with absorbed species at the surface. For efficient photocatalytic processes, it is necessary to transfer the charge on the surface and to have a good charge separation in order to run redox reactions with the absorbed species and to avoid back-reactions or recombination.[40] Yet, it is also important to confine away the charge carrier from surface traps since a too strong confinement of a charge carrier can prevent reactions at the surface of the photocatalyst, especially the oxidation of holes which is considered the limiting step in the hydrogen generation.[41] In some cases, the photoluminescence quantum yield and photocatalytic performance might be competitive channels [40, 42]. Quasi-type II or type II core/shell semiconductors (Fig. 5a) can be good configurations to promote charge separation and decrease the charge carriers recombination. The thickness of the shell can positively impact on the quantum yield and the lifetime in the quantum dots due to a drop in nonradiative decay channels with the suppression of the surface traps. In NCs covered by a thick shell, the hole is strongly confined whereas the electron is more delocalized, consequently leading to a decrease of the overlap of the e^- and h^+ wavefunctions and therefore a more charge separation (below further descriptions about these configurations are provided). Another intrinsic loss pathway is the difference in the band alignment between the semiconductor band positions and the redox potential levels of the reaction which is used to transfer the charges instead to run

the photocatalytic reactions (Fig.2, event (d)).[2] A semiconductor NC is stable with respect to the electron reduction if its reduction potential is higher than either its CB or water reduction potential (H^+/H_2) and with respect to the hole reduction, if its oxidation potential is lower than either its VB or the oxidation potential of water (O_2/H_2O) [43]. Photogenerated holes and (less likely) photogenerated electrons can also oxidize or reduce the semiconductor instead than to promote the surface reaction. This happens when the redox potentials of the photocatalyst (nanocrystal itself or ligands at the surface) have a better band alignment than the redox potential of the reaction. This is a common scenario in chalcogenide II-VI semiconductors where the oxidation of the lattice ions or thiol ligands, which then leads to the aggregation of the colloidal photocatalysts, can frequently happen. To avoid photooxidation, holes scavengers are used to prevent the damage of the photocatalyst by removing holes (Fig.2, event (e)).[2]. Yu et al. added amorphous TiO_2 (Ti(IV)) as a hole cocatalyst on the CdS surface to make it stable and Ni(II) as cocatalyst to increase the photocatalytic reactivity. Ti(IV) acts as a h^+ sink and prevents the corrosion of CdS [44]. Moreover, the efficiency of the process is compromised by the thermodynamic feasibility of the reverse reactions (Fig.2, event (f)).

Finally, when the redox reactions happen on the same surface of the colloidal photocatalyst, the separation of the products (e.g. hydrogen and oxygen gases) can generate further energy losses (Fig.2, event (g)) [2].

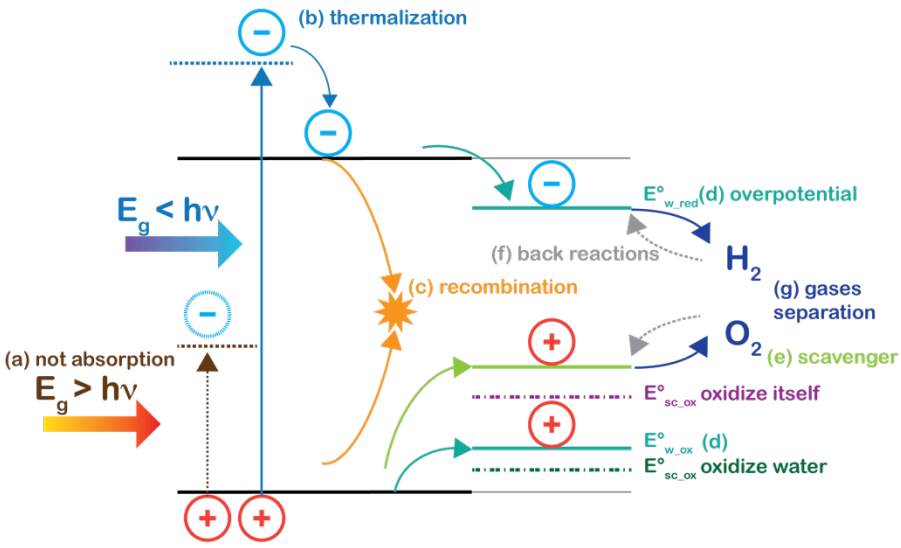

Fig.2 Energy loss processes in SC NCs during solar fuels reactions, based on [2, 43, 45]. Photons with lower energy (a) and with higher energy than the band gap (b); e^-/h^+ recombination; (d) overpotential due to the band position of the NC and the redox levels of water (teal color); Photocorrosion of the SC is determined of the band position of its redox potentials with respect to the water redox potentials: *e.g.*for holes, if the oxidation potential of the water ($E°_{W\_OX}$, teal color) is lower than the oxidation potential of the semiconductor ($E°_{SC\_OX}$, purple), a holes scavenger is necessary (light green level, (e)), if $E°_{SC\_OX} < E°_{W\_OX}$ (dark green color) the water oxidation is instead favorited; possible back reactions (f) and gases separation (g).

Generally, for most of the reactions, thermodynamics and kinetics are independent and there is no correlation between the standard free energy difference from reagents and products and the activation energy of the others. An exception to this general rule occurs in "outer sphere" redox reactions, where in contrast to the "inner sphere" reactions, the compounds are not chemically bounded to each other and remain independently before, during and after the electron transfer.[46] In this type of reactions, according to Marcus theory, thermodynamics influences kinetics since the electron transfer rate increases with increasing thermodynamic driving force, except when the process is in inverted regime. Therefore, a faster electron rate can be achieved with a wide band gap semi-conductor, which absorbs just a small part of the solar spectrum.[47, 48]. This requirement seems to conflict with thermodynamic constraints.[2, 8]

Light absorption and charge migration and separation

Only ~5% of the solar light lies in the UV region (100-400 nm)[49], therefore, to run photocatalytic reactions is important to collect also the visible and the NIR part of the solar radiation. Several architectures have been proposed both to harvest more photons and to respect the thermodynamic and kinetic requirements.

One of the most used approaches to harvest light is to couple the catalyst to another material (sensitizer, upconverting material, plasmonic metal) which is able to absorb the light and deliver excitons/charged carriers to the reaction centers.

A method to do this is to couple a sensitizer (organic/inorganic materials) having a narrow band gap with a wide band gap catalyst (Fig.3a). There are two main mechanisms for the sensitization process.[45, 50] Usually, the sensitizer has a LUMO (e.g. dye, Fig.3a) or a conduction band edge (e.g. quantum dots, Fig.3b) higher than the conduction band edge of the catalyst. Upon light, the photo-generated electrons are injected into the catalyst whereas the photo-generated holes react with holes scavengers present in the system. It is also possible to have a direct excitation of the electrons from the HOMO of the dye to the CB of the catalyst. Based on this approach, especially in the past, several oxides were coupled with dye sensitizers (this is the typical configuration of the dye sensitized solar cell) [51]. The complex of the salt tris(bipyridine)ruthenium(II) chloride, $[Ru(bpy)_3]^{2+}$, has been largely applied as sensitizer either for the reduction or oxidation of the water.[50, 52, 53] Recently, new hybrid systems (organic/inorganic coupling) have been developed where the sensitizer is an inorganic semiconductor nanocrystal whereas the catalyst is an organic molecule. This latter configuration compared to the other one (dye as sensitizer and semiconductor NC) has shown several advantages since semiconductors, like quantum dots, can have i) a very high extinction coefficient and a more tunable band gap and therefore can absorb more light compare to the dyes; ii) a higher stability again corrosion.[22] Moreover, comparing the active sites, molecular photocatalyst can be economically cheaper than semiconductor NCs. [54]

Another method to inject more carries in the photocatalyst is to couple it with plasmonic noble metal nanoparticles (NPs) (Fig.3c), especially silver and gold, in order to exploit the resonant electrons formed during the surface plasmonic resonance (SPR) excitation.[55] In plasmonic metal nanostructures, upon light excitation, when the frequency of photons is similar to the frequency of surface oscillating electrons, a resonant collective oscillation of electrons is formed (SPR), which largely increases the cross section absorbance, more than 10^5 as compared to dye sensitizers. The resonance wavelength is influenced by electron density of the material, its size and shape. These nanoparticles act as a sort of sensitizer by absorbing resonant photons and transfer the SPR electrons to the semiconductor.[55] Therefore, the absorption band of the photocatalytic system is extended as compared to the semiconductor by itself.

Another approach is to couple semiconductors with upconverting nanoparticles to exploit more the solar spectrum, especially the near infrared range (Fig.3d) .[2, 56] Upconverting nanocrystals based on rare-earth elements are formed by a crystal host material where trivalent lanthanide ions are dispersed.[56] Some studies report that efficient upconversion happens through sequential absorption of multiple photons at low energy which are absorbed via long-lived intermediate states between the ground state and the emitting state. The lanthanide-based nanocrystals present a narrowband emission resulting from weak electron-phonon coupling. The crystalline host lattice can influence the photon upconversion creating low phonon energy conditions. The photon upconversion in lanthanides' compounds can happen through excited-state absorption (ESA), energy transfer upconversion (ETU), cooperative sensitization upconversion (CSU) and photon avalanche.[57]

Another easy approach to increase the absorbed photons by the photocatalyst is to introduce interband states to reduce the band gap. In oxides photocatalysts, generally, the O 2p orbitals have low energy giving a large overpotential for water oxidation. The hybridization of O 2p orbitals, with non-metals, , such as S, N, F, S, B, P and C, can lift up the valence band and consequently decrease the energy band gap and make the photocatalytic active under visible light(Fig.3e).[58] Among this, N was found to be the most promising due to its electronegativity, ionic radii, coordination numbers and polarizability, similar to oxygen. N 2p orbitals display potential energy higher than O 2p orbitals and when they are introduced in the photocatalyst structure they can decrease the band gap by lifting up the valence band without perturbing the conduction band.[32]

In d^0 oxides, the band gap can be narrowed by 1.1-1.5 eV by doping with Cu, Ag, Pb, Rh, Ga, Zn, Fe which can also lift the valence band. (Fig.3f). A same approach can be also used to lift down the CB. [12, 59, 60] In QDs, doping with ions as temporary charge carrier trap states can increase the lifetime of excited states and accelerate the rate of the reactions on the surface. QDs can be doped in situ or after, through a cation exchange between the surface and the lattice.[61–63] In core/shell ZnSe/ZnS, Mn^{2+} cations directly added during the synthesis can increase the excited lifetime up 1000 μm [64]. Cu^{+} and Ag^{+} doping can trap carriers in QDs, such as in InP and in CdSe.[65, 66]. Wang et al. reported that the doping of CdS with Ni can increase the selectivity (up to 100%) of CO_2 photoreaction with water while efficiently trapping the photoexcited electrons at the surface and suppressing the hydrogen evolution.[67]

Defects in the lattice can also create interband states and influence the band gap. For example, oxygen vacancies create interstitials $Ti^{4+}$and Ti^{3+} states decreasing the band gap to 1.54 eV and therefore boosting the photocatalytic properties of the TiO_2.[2] Tungsten oxides can also absorb more at higher wavelength when oxygen vacancies are present. In $CuInS_2$ QDs, possible point defects can cause exciton self-trapping with the delocalization of the holes.[68]

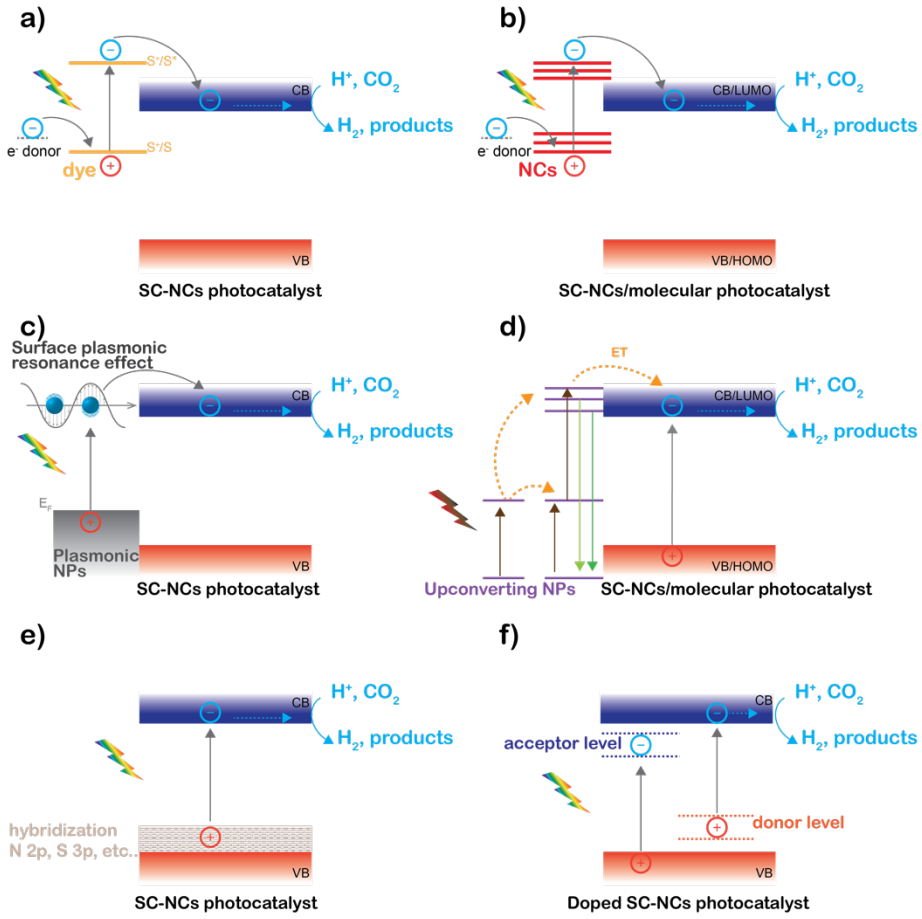

Fig.3 Schematic illustration of different configurations to absorb light and to separate charge in SC-NCs systems for solar fuels reactions, inspired by [2, 12, 45]: a) dye sensitizer; b) SC-NC as sensitizer; c) plasmonic metal semiconductor system; d) energy transfer from upconverting NPs; d) hybridization of orbitals; e) introduction of interband through doping

Z-scheme and other configuration methods

The natural process of photosynthesis can be divided in three main steps: i) solar light harvesting and charge separation in the photosystems I (PS I) and II (PS II); ii) electron transfer between redox parts; iii) products formation (oxygen and carbohydrates) at the reaction sites. [26] The two systems PSI and PSII for each photon

can generate an electron/hole pair although the water splitting process requires 4 electrons/holes whereas the NADP reduction 2 electrons/protons reaction.[8, 69–71] Therefore, a multielectron catalyst at the end of the charge separation is necessary as a bridge between the two reaction processes which require different e^-/h^+ pairs.[8, 9, 71]

A method to mimic the natural photosynthetic process is to recreate the so-called Z-scheme configuration with, generally, two photoexcitation steps. [9, 69, 71, 72]

The classic Z-scheme configuration (Fig. 4a) is two step photoexcitation formed by two photocatalysts having narrow band gap which run separately the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER).[9, 69] In such dual configuration, visible light is sufficient because the band gap of each photocatalyst has to satisfy the overpotential, kinetics and thermodynamics requirements of only half reaction for the water splitting. In Fig. 4a, under visible light e^-/h^+ pairs are generated in both OEP (oxygen evolution photocatalyst) and HEP (electron evolution photocatalyst). After the absorption of a photon in the OEP, the electrons will be excited in the CB by leaving holes in the VB which will oxidize the water oxygen. The electrons, in the CB of the OEP, will be transferred to the VB of the HEP through a shuttle redox couple (ions or molecules) in solution which will firstly reduce the oxidant (OX) to form the electron donors (RED), whereas the photoholes on the HEP surface will be oxidized by converting back the electrons. On the HEP side, the excited electrons in the CB will reduce the water to hydrogen. The main drawbacks of this system are the possible back reactions that can occur, e.g. the shuttle redox couple could react with the VB of the OEP or the CB of HEP [12, 69, 71, 73] A similar approach to separate the charge carriers and transfer them can be obtained with a Type II band alignment, which is similar an inverted Z-scheme without a redox mediator. This approach is commonly applied in photocatalytic systems and it has good potential especially for just one-half reaction to produce solar fuels.

Another method to mimic the natural photosynthesis is to couple a main semiconductor with two cocatalysts where both the HER and the OER can occur (Fig. 4b). In this one-step photoexcited approach, solar light is harvested by the main photocatalyst which should have a suitable band gap to collect a large part of the solar spectrum and a good band alignment with the HE and OE cocatalysts.[54, 71, 73] Important drawbacks are due to the different timescales of the exciton generation and transportation, charge separation and reaction. Typically, from a dynamic point of view, exciton generation has mainly a picosecond timescale, charge separation and transfer to the reactive sites on the surface of the photocatalyst have a microsecond timescale while surface reaction of water splitting is much slower, from microsecond to second timescale, especially the OER. O_2 production occurs at the second timescale since it requires a transfer of four holes to the acceptor and a formation of an O−O double bond core.[23, 26, 45, 74–76] In contrast, H_2 production needs just two electrons and it is in millisecond timescale. This discrepancy of timescale of the two main reactions can

create recombination of the charge carriers and energy losses. For example, in two of the most widely used photocatalysts, TiO_2 and CdS, the carrier lifetimes are on the nanosecond timescale, too short to run these reactions. Therefore, configurations to increase their carrier lifetime, charge separation and the rate of the reactions are necessary. Heterojunction configurations can extend the carrier lifetime. [77] Coupling semiconductor/metal with appropriate band alignment can create barriers for either electrons or holes and avoid back reactions.[78] The metal (generally noble) NPs act as electron sinks and they usually show higher catalytic efficiency than semiconductors. The e^- storage in the metal NPs gives more reductive power to the photocatalyst by shifting to more negative value the apparent Fermi level in the metal-SC composite.[77] In a n-type heterojunction metal/semiconductor configuration, the Fermi level of the metal is lower than of the semiconductor, creating a Schottky barrier due to band bending at the interface. In a p-type heterojunction metal/semiconductor configuration, the barrier avoids the holes to be transferred, whereas the electrons can be easily injected in the metal NP.[2]

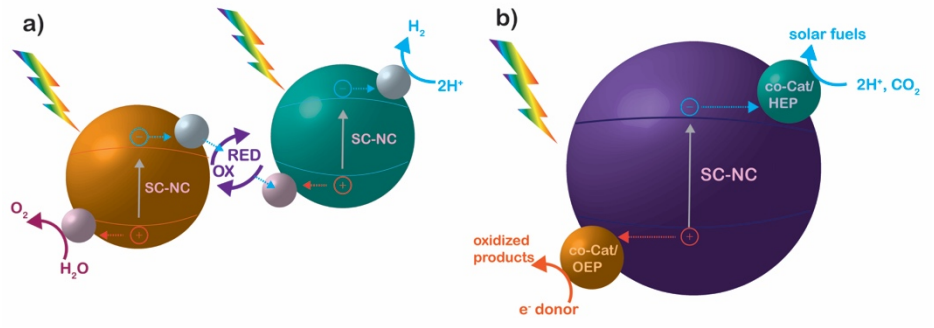

Fig. 4 a) Z-scheme in two steps involving a redox mediator molecules, possible cocatalysts in both the photocatalysts can be present; b) in one step, sketch of semiconductor nanocrystal used as light antenna coupled with two cocatalysts for the reduction and oxidation respectively.

3. Colloidal semiconductors

Colloidal semiconductor nanocrystals, such as quantum dots and perovskite like QDs, can be excellent candidate to be applied in artificial photosystems thanks to their excellent properties to harvest solar light, to generate multiple excitons and to be engineered in their surface properties.[2, 12, 15, 23, 24, 79]

NCs (QDs and perovskite- QDs) coupled with bulk semiconductors.

Semiconductor nanocrystals are demonstrating to be cutting-edge both as photosensitizers and as photocatalysts. As sensitizer, thanks the possibility to easily tune their band gap by changing the chemical composition or the size/morphology they show high ability to harvest a broad part of the solar spectrum. Several examples are reported in literature of QDs coupled with wide band gap photocatalysts, especially for solar cell applications [80]. For solar fuels generation, PbS QDs coupled on TiO_2 showed to improve the CO_2 conversion up to 5 times since they can absorb light in the NIR range.[81] CdS QDs were also coupled to WO_3 photocatalyst to efficiently separate photoinduced e^-/h^+ pairs, as in Z-scheme without an electron shuttle.[82] Several examples are reported for photoelectrochemical applications (briefly described below) where TiO_2 or NiO_2 photoanodes are coupled with QDs as sensitizer, such as "giant" PbS/CdS[83], thick-shell CdSe/$CdSe_xS_{1-x}$/CdS QDs with pyramidal shape[84]. For example, CdSe/CdSeS alloy/CdS core/shell/shell QD sensitizer of mesoporous TiO_2 photoanode allowed to reach a very high photocurrent density to 17.5 mA/cm^2 under 1 sun illumination with a long stability[85]. More recently, perovskite type QDs or nanocystrals (PQDs or PNCs) [86] have been received an enormous interest thanks to their tunable properties and very easy and low cost synthesis. Their main and important drawback is their instability in air and in water. New hybrid inorganic/organic shells and ligands are under study to make these new materials more stable in atmosphere. In non-aqueous medium, $CsPbBr_3$ QDs on graphene oxide were applied to convert CO_2 by improving electron extraction and transport [87]. They can be also stabilized on metal organic framework (MOF) such as UiO-66(NH_2) and without a sacrificial agent the rate of CO production reached 98.57 μmol/g [24]. Inorganic ligand-capped $CsPbBr_3$ NCs were also immobilized with metal complexes like $[Ni(terpy)_2]^{2+}$ (Ni(tpy)) for CO_2 reduction under visible light where Ni(tpy) suppressed the e^-/h^+ recombination by removing electrons.[88]

Lead free cesium silver bismuth halide double perovskites, $Cs_2AgBiBr_6$, modified with sulphide showed good stability in moisture, light and temperature and a good selectivity in the conversion of CO_2 [89]. Metal halide perovskites (MHPs) are at the forefront as promising class of new materials for solar applications. Huang et al. very recently highlighted some strategies to overcome their stability disadvantages, like the application of halogen acid solution for hydrogen production, the use of low polarity solvents for organic conversion and CO_2 reduction and their encapsulation during water-based processes.[90]

Heterostructures

Especially, heterostructured nanocrystals with the epitaxial coupling of two or more semiconductors have gained attention thanks to the possibility to spatial manipulate the

electron and hole wavefunctions thanks to their fine controllable synthesis [63, 91–93]. The type of band alignment can confine in different domains of the heterostructures photoexcited electrons and holes (Fig. **5**a). In Type I band alignment, both the carriers are confined in the same domain whereas in Type II heterostructure, we have the spatial separation of the photoexcited electron and holes occurs due to the interface between two different SC and this hampers the charge recombination although it increases the confinement and sometimes the unavailability of one charge carrier for surface reactions. In quasi Type II configuration, one carrier (usually the electron) is delocalized over more than one domain whereas the hole is confined in a single domain.[92] (Fig. **5**a)The extended life times of the charge carriers and their spatial separation in quasi Type II and Type II can be useful for photochemical production of fuels. CdSe/CdS and CdSe/ZnS core/shell nanocrystals having a small core and a thin shell show a Type I alignment with both electrons and holes in the core. This configuration can be more appropriated for a light harvest material to transport excitons. Instead, CdTe/CdSe and CdSe/ZnTe core/shell QDs show a Type II alignment where the hole is mostly in the core and the electron in the shell and vice versa respectively.[94] Therefore, the separation of the carriers can be controlled by the morphology, the shell thickness and core dimension.[91, 95–98].

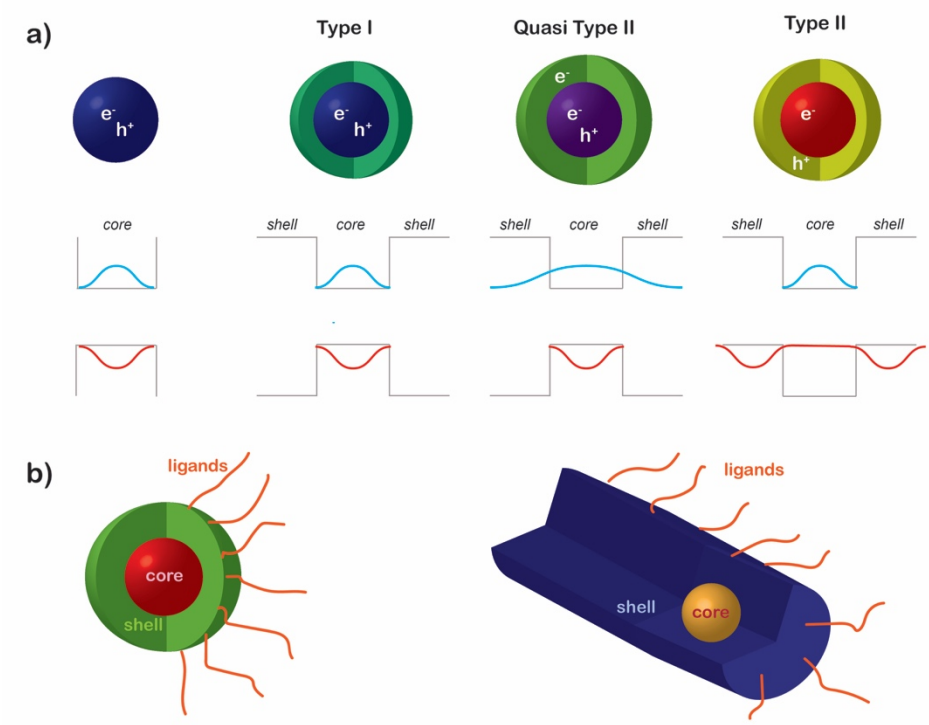

Fig. 5 a) Schematic sketch of different band alignment possibilities in core/shell heterostructures, example of e^-/h^+ wavefunction are reported; b) sketches of spherical core/shell QDs and core/shell nanorods (dot in rod).

Anisotropic morphology, like nanorods [99], can further help to separate the holes and the electrons and facilitate the extraction of one charge carrier. Spherical QDs (Fig. **5**b) can be considered 0D where the exciton is quantum confined in all the three dimensions. Elongated QDs in one direction are called nanorods (NR), and they have a diameter of few nanometers and lengths from 10-100 nm. In these 1D semiconductor nanostructures, the excitons are confined in the radial direction but not always along the axial direction. Thus, NR can present both properties typical of the QDs like the band gap tunability, strong carrier-carrier interactions, interfacial coupling and bulk characteristics like long distance charge transport and separation.[100, 101]. Dukovic's group reported several studies on the carriers dynamics in NRs. In CdS and CdSe NR with nonuniform width (dot in rod) trapped holes localized on undercoordinated chalcogen atoms diffuse with a random walk on the surface of the NRs hopping between trap states, whereas the electrons are more confined into wide-diameter regions of the NRs [92, 102]. Hamby et al. combining CdS NRs in a mixture with *Magnetococcus*

marinus MC-1 (MmOGOR), have shown that NRs are a good sensitizer by providing electrons to enzymatically catalyze the formation of carbon−carbon bonds (2-oxoglutarate) via CO_2 reduction.[103]

Heterostructured NRs composed by two different semiconductors have shown to further spatial separate the charge carriers. Dot in rod (core/shell) heterostructures, like ZnSe/CdS, CdSe/CdS have also shown a fast hole trapping in the CdS rod and electron localization to the bulb which can be manipulated by the chemical composition of the core.[104] More sophisticated heterostructures by creating core/shell semiconductors coupled with (noble) NPs as cocatalyst have gained consideration in photocatalysis, especially for solar fuel production. In platinum-tipped CdSe/CdS NRs, the holes are confined in the core while the electrons can be transferred to the metal NPs on the tip, significantly improving the hydrogen production, with an apparent quantum yield of 20% at 450 nm of excitation.[105] The length of the nanorod can also help in the charge separation as well as the position of the cocatalyst. In bare CdS, increasing the number of the cocatalysts along the rod seems to decrease the hydrogen production although the electron transfer is faster to the metal NP. This is probably because the electron transfer from the cocatalyst to the water reduction reaction is slower as compared to the recombination with the holes. Therefore, tipped CdS NRs showed a better photocatalytic performance.[106] (Fig. **6**)

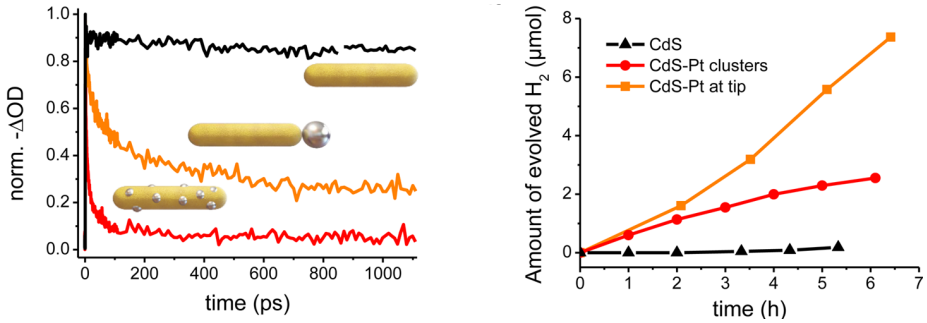

Fig. 6 Hydrogen generation by CdS NRs under illumination in neutral aqueous solution in the presence of sulfite ions. Reprinted with permission from (Simon T, et al (2016) Electron Transfer Rate vs Recombination Losses in Photocatalytic H_2 Generation on Pt-Decorated CdS Nanorods. ACS Energy Lett, 1 (6), 1137-1142). Copyright (2016) American Chemical Society. [106]

In nickel-NPs decorating CdS NRs, Simon at al reported the use of a hydroxyl anion/radical couple as redox shuttle to relay the hole from the NR to the scavenger. This increases the H_2 generation and the photostability of the system.[107]

Fig. **7** shows that no-toxic Type II $CuAlS_2$/ZnS NRs can reduce aqueous bicarbonate ions to acetate and formate under visible light, which can be an interesting and encouraging starting point for these materials to be applied in CO_2 conversion under solar light.[108]. Copper based as well as tin based NCs are a promising and environmental friendly alternative to cadmium/lead based.[109–111]

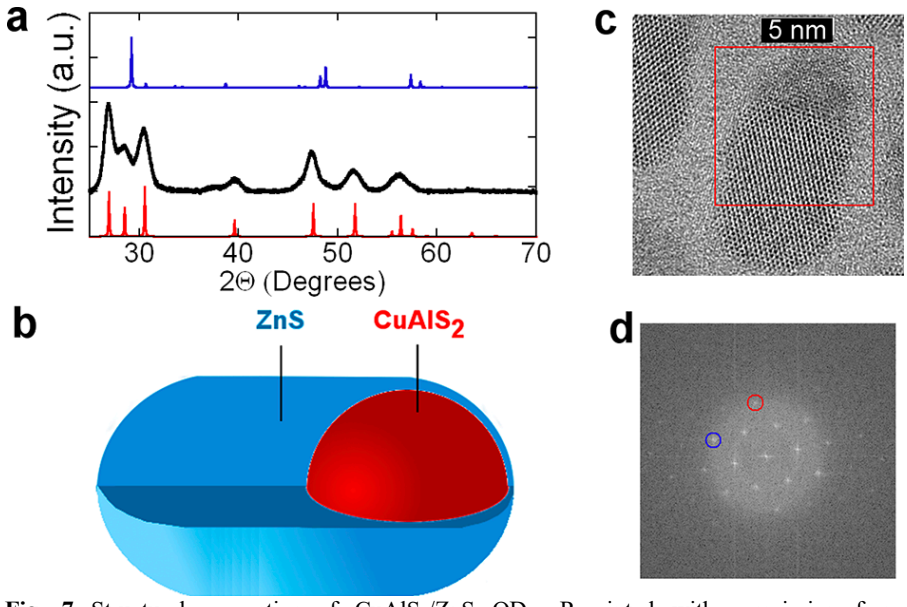

Fig. 7 Structural properties of $CuAlS_2$/ZnS QDs. Reprinted with permission from (Bhattacharyya B, et al (2018) Efficient Photosynthesis of Organics from Aqueous Bicarbonate Ions by Quantum Dots Using Visible Light. ACS Energy Lett, 3 (7) 1508-1514). Copyright (2018) American Chemical Society.[108]

Surface Ligands

The best synthesis route to obtain homogenous in size, morphology, physico-chemical properties nanocrystals is a colloidal approach where NCs are formed in liquid solution.[14] To control the shape and the size and to avoid aggregation and coalescence, stabilizing agents or capping ligands play a crucial role. The type (organic or inorganic), the length, the hydrophobicity, the charge of the ligands dictate several characteristics of the NCs, from optical properties to biological and catalytic properties to their integration in solid devices/substrate.[112–116]. Generally, NCs are synthesized in organic solvents for a better control of the size distribution and morphology. To

transfer them in other more polar solvents or different medium, procedures are ligands exchange or partially replacement during the synthesis.[18, 114]

In homogenous catalysis, metal centers are coordinated with ligands which play an important part creating electrostatic and steric effects that influence the catalytic performance, especially the selectivity.[117] They also have a similar role in heterogenous catalysis with NCs. Capping ligands in NCs have a delicate role since they can either enhance the selectivity and the reaction rate or can have a detrimental effect by blocking adsorption of molecules at the surface.[118] Therefore, to have just positive roles, the coverage of ligands on the surface of the NCs catalysts should not block the active site and should facilitate the interaction between the reactants and the surface of the catalyst and mediate the energy transfer amid NCs and molecules.[113, 119, 120] Their positive effects can be the selectivity control, the chiral modification, the improvement of the adsorption, the surface crowding regulation, the increase of photocatalyst stability as well as the rate and the type of charge transfer.[119] Yu et al. reported an efficient catalytic H_2 production by engineering the ligand of InP and InP/ZnS QDs. Surface S^{2-} ligands showed to increase the photocatalytic performance of the QDs since they can act as hole traps and they can improve the charge separation efficiency of the system. They reported TON values up to 128,000 per InP/ZnS QDs and an internal quantum yield of 31% under green light.[121] (Fig. **8**)

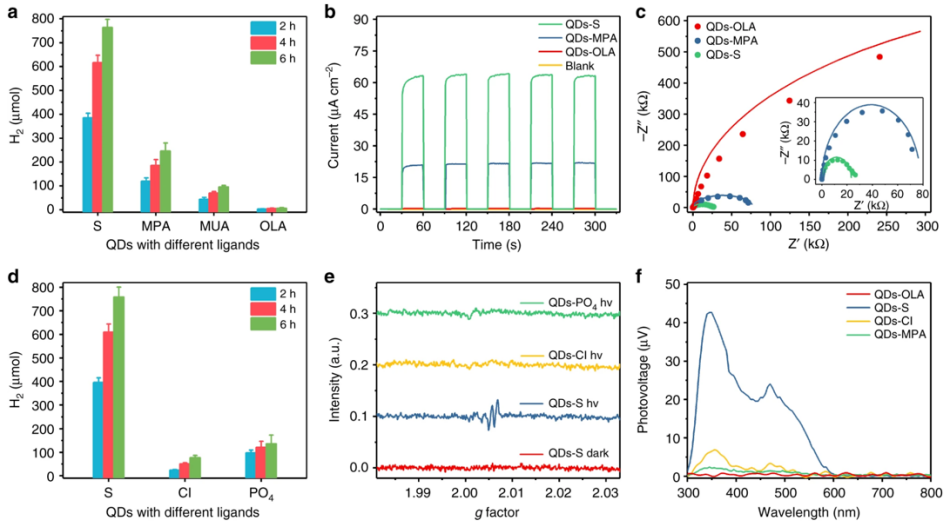

Fig. 8 Influence of different ligands on the hydrogen evolution performance and photophysical properties of InP/ZnS QDs (525 nm, 15 min). Reprinted under the terms of the Creative Commons CC BY [121]

InP based QDs are promising candidate as photocatalyst since their band gap can be tuned in the NIR region, they have a pretty high quantum yield and are Cd and Pb free, which can make them more environmentally compatible. InP/ZnS QDs were applied without any sacrificial agent to photocatalyze under visible light a standard C-C reaction [122]. They can also be covered by an oxide shell, like ZnO, to increase their photostability and to decrease reabsorption losses [123].

Ternary Cu based QDs have also shown to be a good no-toxic photocatalyst.[109, 110]. Huang et al. reported the application of $CuInS_2$ (CIS) as sensitizer for a classic rhenium bipyridine complex (Re catalyst) for CO_2 reduction.[124] Through a click chemistry reaction, the CIS QDs were covalently linked to the Re catalyst and this favored a fast electron transfer which promoted formation of reduced Re species, boosting the photocatalytic performance of the hybrid catalyst.[124] (Fig. **9**)

3-mercapto-1-propanol (MPO) capped CIS/ZnS QDs have also shown to be 18 times better sensitizer than the more standard Ir-based organometallic sensitizer for meso-tetraphenylporphyrin iron(III) chloride (FeTTP) in the reduction of CO_2 to CO under 450 nm thanks to the ability to transfer electrons.[125] In hybrid systems, where the NCs are the sensitizers, their surface should be modified for increasing the affinity adsorption of CO_2 and eliminating the co-catalyst. For example, hydride-terminated silicon NCs have a good selectivity to convert gaseous CO_2 to CO.[126] Hydrogen-Si QDs were also used for photoreduction in a 0.01 M CO_2-saturated Na_2CO_3 solution under halogen lamp whereas when the surface is oxidized they can also photocatalyze dye molecules.[127]

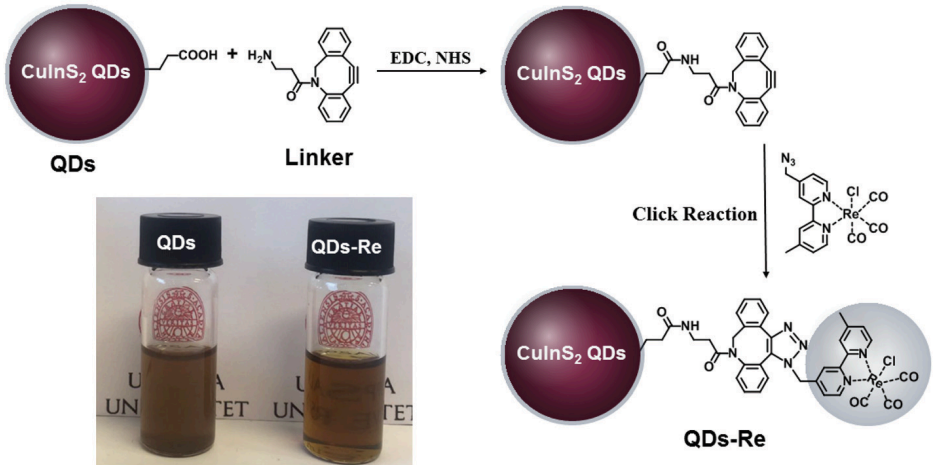

Fig. 9 Schematic routes of the covalently-linked CuInS2 QD–Re hybrid system. In the photograph $CuInS_2$ QDs and the $CuInS_2$ QD–Re hybrid system in DMSO. Reproduced under a Creative Commons Attribution 3.0 Unported Licence. Huang et al. (2018) Covalently linking $CuInS_2$ quantum dots with a Re catalyst by click reaction for photocatalytic CO_2 reduction. Dalt Trans 47:10775–10783. Published by The Royal Society of Chemistry [124]

Bi et al. increased the selectivity of CO_2 conversion by assembling negatively charged CdS QDs with a positively charged dinuclear cobalt catalyst. QDs were made negatively water soluble through ligand exchange with mercaptopropionic acid (MPA). The photocatalytic reduction of CO_2 to CO with this assembly showed good performance under visible light. [128]

Weiss outlined four key strategies to be applied on the surface of colloidal NCs to endorse them as photoredox catalysts or sensitizers of redox catalysts for organic transformations: i) increasing the affinity interaction between the NC and the substrate or cocatalyst in absence of a covalent linkage by tuning surface charge density; ii) optimization of the active sites of the NCs surface thanks to ligand exchange; iii) removing oxidative equivalents from the NC through “hole shuttle” ligands; iv) decreasing the kinetic barrier for proton coupled electron transfer reactions by controlling the protons concentration on the NC surface.[74]

Assembly and energy transfer

A remarkable feature of natural PS is the ability to work with the low photon flux of the sunlight, whose transport to the catalytic centers is efficiency-limiting. Indeed, this issue is overcome by the energy transfer.[25, 26, 75, 129] At the catalytic center, then, the excitons can dissociate into free charges. In natural leaves, the pigments in the antenna complexes of the PSII absorb and transfer the excitation energy to the reaction

center with a diffusion length of some tens of nanometers. The high energy transfer, more than 80% yield in PSII, is able to deliver excitons in the reaction center every 10 ms which allows oxidizing water with 4 holes at very high quantum efficiency.[130]

So far, the majority of sensitized photocatalytic systems is based on the approach 1: sensitizer=1: catalyst or when multiple sensitizers per catalyst are used, for example by coupling multiple sensitizers to single catalysts, like TiO_2, they do not transfer energy among themselves but i) directly to the photocatalyst or ii) they funnel charges instead of energy.[22, 131] Self-assembly of CdSe/CdS QDs binding through polyacrylate ions as surface ligands to platinum NPs as co-catalyst showed to increase the hydrogen evolution initial internal quantum yield of ~65% by facilitating the electron transfer among particles upon irradiation with visible light.[132]

Excitons transfer is more energy-conservative than charge transfer in highly polar solvents, such as water, since excitons can be considered as "neutral particles" that hop from site to site without provoking a reorganization of the molecules typically of the charging and discharging processes.[131] Recently Weiss' group has shown that energy migration among QDs assemblies can boost photocatalytic reactions for solar fuels [131, 133]. Kodaimati et al. demonstrated the feasibility of energy transfer sensitization by coupling together through electrostatic interaction two sets of core/shell QDs, CdSe/ZnS and CdSe/CdS as sensitizer and photocatalyst respectively. By funneling energy from multiple sensitizer QDs to catalytic QDs with a ratio of 4:1 they increased 13 times the reduction efficiency of protons to H_2 compared to the system where energy transfer was absent.[131] Lian et al. applied negatively charged assemblies of core/shell CIS/ZnS QDs to sensitize positively charged trimethylaminofunctionalized iron tetraphenylporphyrin catalysts (FeTMA) to photoconvert CO_2 to CO in water with 450 nm light. The turnover of CO with a selectivity of 99% was 450 after 30h of illumination and the sensitization efficiency was 11 times higher.[133] (Fig. **10**)

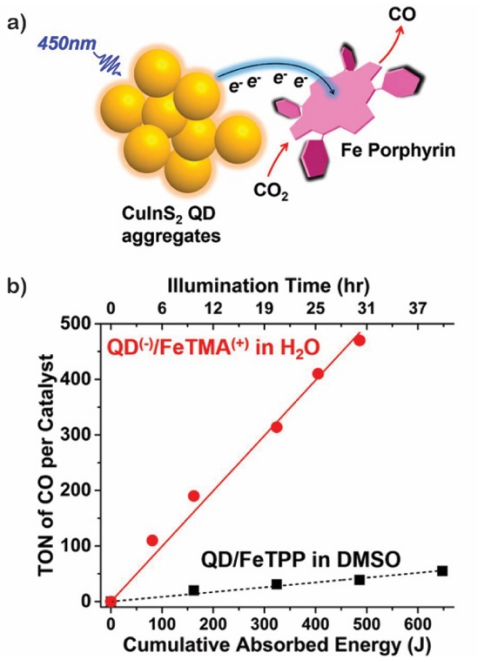

Fig. 10 a) QDs assembly sensitizes Fe-porphyrin catalyst for CO_2 reduction; b) Plot of TON vs absorbed photon energy. Reprinted with permission from (Lian S, et al (2018) Photocatalytically Active Superstructures of Quantum Dots and Iron Porphyrins for Reduction of CO_2 to CO in Water. ACS Nano). Copyright (2018) American Chemical Society [133]

Self-assembly in hybrid heterostructures can help either to faster transfer charged carriers or, even better, to transfer excitons to the catalytic center and allows multielectron reactions to occur also under low photon flux.

4. Device architectures

Current solar-based methods to produce solar fuels

To produce solar fuels or chemicals through solar light and CO_2, several strategies are being applied, such as biocatalytic and thermo-catalytic approaches, and photoelectrochemical techniques. Currently, the three most applied schemes are (Fig. **11**): i) photovoltaic–electrolysis (PV–EC) cell; ii) photoelectrochemical (PEC) cell; iii) photocatalytic (PC) cell due to their comparatively low cost and more simplicity

architecture. In these methods, it is possible to apply either homogeneous or heterogeneous catalysts.[6, 70] In the homogenous system, photocatalyst, sensitizer and possible scavengers are in the same phase of the reactants. In the past, the most molecular (photo)catalysts studied for these applications were based on rare metal center complexes, like Re, Ru and Pd, whereas more recently earth abundant transition metals like Fe, Co, Ni, Mn have been acquiring more attention. Often, the durability of these organometallic complexes-based system is still an issue.[70, 134] Semiconductors as photocatalyst in heterogenous system can be a good alternative, either applied directly in solution or to build photoanode/photocathode.

Among the different strategies (Fig. **11**), PV-EC design has the highest technology readiness level and some commercialization devices are already available on the market. PV-EC configuration uses an independent solar cell (but also other renewable energy sources like geothermal or wind) to produce electricity which is directly transferred as direct current to the EC cell where the anode and the cathode perform the water splitting [135](Fig. **11**a). This part could be also in the dark and the solar light could only be used by the PV to produce electricity to "help" the water spilling reaction. Usually the PV panel is connected in series to the electrolyzer to have the same current and voltage from the two independent devices. To increase the stability and avoid degradation, the PV are generally out of the electrolytic liquid.[6] To design efficient PV-EC several parameters have to be considered, like exchange of current density, system resistance, electrode area, light intensity, solar cell efficiency and Tafel slope. Pretty high efficiency, more the 30%, have recently been reached by applying 3-junction solar cells.[136] However, several power losses during the conversion and integration of electrical energy into fuel are still present and the cost of the overall architecture still remains pretty high making the H_2 still too expensive to be compared to fossil fuels and therefore limiting its application on large scale.[136]

Another, less complex method to produce solar fuels is based on PEC cell, wherein the light is absorbed by one or both of the photoelectrodes (Fig. **11**b). The (photo)anode and (photo)cathode are connected and usually only the light absorber side is in contact with the liquid, while the charge collector is isolated. In this system, the two gases, H_2 and O_2, are produced in separate compartments of the vessel keeping the charge balance with a membrane.[135] Different configurations for PEC cells have been developed. The simplest scheme is either an n-type photoanode and a catalytic cathode for H_2 evolution or a p-type photocathode and a catalytic anode for O_2 evolution. However, this basic configuration needs a bias voltage to work and to cope the losses and overvoltage. More complicated configurations consider tandem cells or the PV-PEC.

As photoanode, various of n-type semiconductors have been studied, especially metal-oxides, like TiO_2, Fe_2O_3, WO_3, $BiVO_4$, since they are very stable in water. On the other hand, usually they absorb a small part of the solar light having a wide band gap and a low charge carrier transfer and fast recombination. The most promising are $BiVO_4$,

Fe_2O_3. Semiconductors suitable for photocathode can have a narrower band gap but most of them show lower performances compare to the photoanode electrode.

The simplest and the cheapest solar fuel production configuration is the PC cell (Fig. **11**c), where the semiconductor nanoparticles are dispersed in the liquid. The simplicity of the cells makes them very attractive for a possible large-scale application but so far, they show low production efficiency, especially compared to the PV-EC.

The stability of the sensitizer/photocatalyst hybrid system and the drawback reactions, that are more favorable since the evolution of H_2 and O_2 occurs on the same NCs, are the two main issues that need to be overcome to increase the performance of this system. New architectures for new hybrid heterostructured colloidal NCs have been proposed in the previous sections of this chapter.

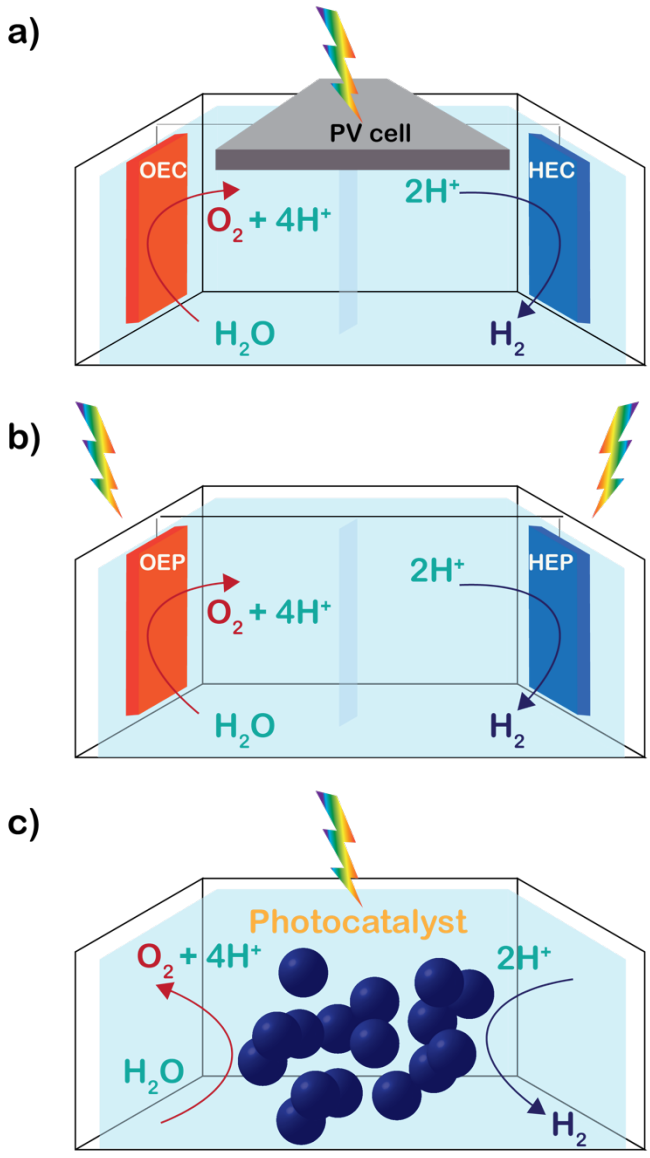

Fig. 11 Main devices configurations, inspired by [6]: a) PV-EC cell; b) PEC cell; c) PC cell

More recent solar-based methods to produce solar fuels

Two remarkable factors in the natural photosynthesis are the light harvesting and the ability to run multielectron reactions under low photon flux. From a technical design point of view for the cell, it is possible to couple devices that harvest the solar light to transfer more photons to devices that run the reaction. Luminescent solar concentrators, waveguide polymeric slabs where luminophores are embedded, can collect, down convert and concentrate solar photons. Liu et al have reported an enhancement of 420% compared to a PEC device alone when a multishell/core QDS LSC was coupled to the photoanode. The better performance is mainly due to a higher stability of the photoanode thanks to the light down-conversion operated by the LSC.[137] Cambié et al have also reported that photomicroreactors channels for photoredox reactions can be integrated in the LSC.[138–140]

5. Summary and outlook

Colloidal photocatalysis has great potential for solar fuel production and other redox reactions (Table 1), showing desirable features either of the homogenous or of the classical heterogenous photocatalysis. Yet it presents also particular challenges, which can be overcome and controlled by tuning several physico-chemical properties of the nanocrystals. Photocatalytic reactions based on multielectron chemistry are very dependent on active sites, defect type and density, surface properties and spatial migration of excitons. Colloidal NCs show excellent light absorption, multiple exciton generation, surface functionalization and charge separation properties which can be easily tuned and controlled by synthesis procedures. By combining a deeper understanding of multielectron chemistry and advanced synthesis strategies, it is possible to design better photocatalytic systems through hybrid coupling, heterostructures, morphologies, surface engineering and self-assembly techniques. For example, it is possible to dope, to create heterojunction through morphological architectures, to couple with metallic NPs and to control assembly to further engineer the energy transfer, spatial charge separation and reactions on the surface.

Table 1 Comparison of organic dyes, bulk semiconductors, and QDs for solar fuel production, inspired by [24]

Photocatalyst	Advantages	Drawbacks	Examples
Molecular compound	straightforward design, synthesis, and characterization	Expensive, sometimes scarcity of metal complex, difficult synthesis, purity	Ru- and Ir- based complexes Fe/Cu based system Earth-Abundant First-Row Transition based systems
Bulk SC	Inexpensive, generally water-based synthesis, easy synthesis, high reaction yield, low toxicity	Wide band gap, mainly absorption in the UV-vis range, low exciton kinetics, fast carrier recombination,	TiO_2, Fe_2O_3, WO_3, $BiVO_4$
NC-SC	properties similar either to homogenous or heterogenous photocatalysts, high light absorption from the UV-vis to the NIR range, simple synthesis, easy tunable photochemical properties, tunable exciton dynamics, multiple exciton generation, fast and long diffusion length of carriers	possible toxicity, discrete stability	QDs, NRs, etc.., perovskite NCs

Colloidal PC system shows a very simple architecture and a low cost since the photocatalyst is directly dispersed in a medium. Some issues need to be overcome in order to increase the efficiency and to make it ready for widespread commercial applications.

Crucial aspects for an ideal photocatalyst are high activity, high stability, low cost and scalability in its production. For a practical use of NCs further researches should focus on the developing new cadmium and lead free QDs, such as InP, ternary Cu- based QDs, Ag- and Zn- based QDs. Moreover, to increase the environmental stability, new surface ligands, shell and functionalization should be investigated as well as to enhance the surface selectivity for solar fuel conversion. The interesting and keep going

progresses in this field push colloidal NCs be promising candidate either for photosensitizer or photocatalyst, which will allow solar to fuel conversion to be applied on a large scale in the near future.

6. Acknowledgements

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