Towards Solar Factories: Prospects of Solar-to-Chemical Energy Conversion using Colloidal Semiconductor Photosynthetic Systems

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Towards Solar Factories: Prospects of Solar-to-Chemical Energy Conversion using Colloidal Semiconductor Photosynthetic Systems

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Abstract: Solar-to-chemical (STC) energy conversion is the fundamental process that nurtures Earth's ecosystem, fixing the inexhaustible solar resource into chemical bonds. Photochemical synthesis endows plants with the primary substances for their development; likewise, an artificial mimic of natural systems has long sought to support human civilization in a sustainable way. Intensive efforts have demonstrated light-triggered production of different solar fuels, such as H_2, CO, CH_4 and NH_3, while research on oxidative half-reactions has built up from O_2 generation to organic synthesis, waste degradation and photo-reforming. Nevertheless, while extensive utilization of the radiant chemical potential to promote a manifold of endergonic processes is the common thread of such research, exploration of the chemical space is fragmented by the lack of a common language across different scientific disciplines. Focusing on colloidal semiconductor materials, this Viewpoint discusses an inclusive protocol for the discovery and assessment of STC red-ox reactions, aiming to establish photon-to-molecule as the ultimate paradigm beyond fossil energy exploitation.

Introduction

Solar energy is the ultimate renewable resource that mankind should seek to efficiently harvest for its future sustainable development. It is well known that the total annual global energy requirements are matched by the energy that the Sun shines down to the Earth in about one hour, yet 80% of our consumed energy is provided by fossil fuels[1]. Sadly, this figure of merit has not changed significantly over the last 30 years. High conversion efficiency and scalability are imperative needs for energy generation devices, however, the intermittency and dilution of solar radiation raises storage as a further crucial requirement for renewable technologies. To this extent, the only process able to convert and store solar energy at terawatt-scale is natural photosynthesis. On the contrary, artificial photosynthetic devices perform at high efficiency only at a centimeter scale. Three different strategies are currently investigated, namely electrolysis powered by photovoltaic panels (PV+EC), photoelectrochemical cells (PEC), and photocatalysis (PC). As of now, their technology readiness level is lagging far behind that of solar-to-electricity energy conversion devices. It was projected that photocatalysis-based real-world reactors will techno-economically outcompete the two other configurations[2], [3], consequently, we concentrate this Viewpoint around this solar conversion strategy.

Predominant research efforts in direct solar-to-chemical (STC) energy conversion have been devoted to water splitting, mimicking the process that natural organisms employ to generate reducing equivalents used to process CO_2. On the other hand, the production of oxygen, which is generously discarded as a by-product in natural photosynthesis, elusively hinders overall process efficiency in artificial devices[4]. Its multi-electronic reaction mechanism determines overpotential losses typically in the order of hundreds of mV and further inherent technological challenges pose severe limitations to large-scale control over the explosive H_2/O_2 mixture[5]. Since water is an inexpensive and abundant feedstock, a large scope for process improvement is still urging, yet, the number of complications related to water splitting calls for alternative routes for direct solar fuels generation[6].

In this context, this Viewpoint aims to highlight the perspectives of solar-to-chemical energy conversion opportunities that target solar fuels generation with the simultaneous synthesis of value-added chemicals. In particular, particle-based or colloidal semiconductor photo-active systems have recently provided promising outlooks in such application[7]–[10]. This class of materials merges excellent optoelectronic properties and chemical processability with robust photostability and scalability. Here, the framework of STC energy conversion will be discussed in terms of process efficiency assessment, thermodynamic and spectroscopic aspects, and finally, experimental photoreaction characterization. The proposed inclusive experimental protocol aims, therefore, at the creation of a high-quality data pool, foreseeing the integration of high-throughput computational analytic and predictive tools[11]. Overall, the STC strategy sets a common language which intertwines research communities

working on materials design, energy conversion, organic synthesis, and photoreactor engineering.

STC Efficiency Index

Firstly, the foremost important figure-of-merit for solar-to-chemical energy conversion is its efficiency index, that we conveniently define as follows:

$$\eta_{STC}\ (\%) = \frac{I_{mol} \cdot \mu_{redox}}{P_{AM1.5G} \cdot A} \cdot 100\% \qquad (1)$$

where I_{mol} ($[mol\ s^{-1}]$) is the photoproduct flux or moles of photoproduct per unit of time, μ_{redox} ($[J\ mol^{-1}]$) the chemical potential associated to the redox reaction realized, or the Gibbs free energy change per mole of photoproduct produced, $P_{AM1.5G}$ ($[J\ s^{-1}\ m^{-2}]$) the incident solar power and A ($[m^2]$) the irradiated area. A comprehensive assessment of STC photosynthetic performance should therefore explicitly report each of these terms. Importantly, if any additional electrical or thermal biases are used to promote the photoreaction, such contributions should be added in the denominator. Then, it is worth mentioning the relation between the chemical potential and Gibbs free energy, which is defined as follows:

$$\mu_{redox} = \frac{\Delta G_{redox}}{n} \qquad (2)$$

where ΔG_{redox} is the Gibbs free energy ($[J]$) associated with the redox reaction, and n the number of moles involved in the reaction. The chemical potential, being an intensive property, is independent of the system size and is a fundamentally different concept from the Gibbs free energy, however, nomenclature and symbols used in textbooks and literature often confuse the two physical quantities[12].

The STC index, that is applicable to both PV+EC, PEC and PC configurations, represents a ratio between *power stored* in the photochemical process or the *rate of Gibbs-free energy accumulation*, and power used to promote it. It can be noted that this definition matches the corresponding efficiency index used for solar-to-electricity conversion, where power produced by solar cells is also computed as the product of the flux (charge current - $I\ [C\ s^{-1}]$) and the potential (electrical voltage - $V\ [J\ C^{-1}]$). Furthermore, defining a general term to assess solar fuels and chemicals production, beyond overall water splitting, highlights the limitations imposed by the STH index. The latter quantity is strictly referred to the water dissociation reaction ($\mu_{redox} = 236.7\ kJ\ mol^{-1}$), while the breadth of solar-to-chemical energy research targets instead extensive utilization of the solar energy input, aiming at promoting the synthesis of diverse photoproducts other than H₂ and O₂. Accordingly, the interest of the STC community includes the production of different fuels (CO, CH₄, NH₃, …) along with photosynthetic organic transformations, as schematically shown in Figure 1A. To this extent, H₂ generation was recently promoted along with thiols and Minisci couplings or the oxidation of benzylic alcohol and amines[13], [14]; and CO₂ reduction was demonstrated with the simultaneous synthesis of pinacol[15]. Finally, also photocatalytic pollutants' degradation or photo-reforming of cheap and abundant feedstock like waste plastic or biomass were demonstrated to be extremely strategic when coupled to H₂ production[16]–[18].

Photoreaction Thermodynamics

Whenever a light-triggered redox transformation is realized, a corresponding minimum free energy per mole of photoproduct should be provided to the light-absorbing species to fulfill the reaction thermodynamics. The Nernst relation allows experimental determination of such requirements for the minimum chemical potential to be harvested:

$$\mu_{redox} = -z \cdot \mathcal{F} \cdot V = -z \cdot \mathcal{F} \cdot (V_{red} - V_{ox}) \qquad (3)$$

with z representing the number of electrons transferred per mole of reactant, $\mathcal{F}$ ($[C\ mol^{-1}]$) the Faraday constant and V ($[J\ C^{-1}]$) the cell potential. In the case of decoupled photochemical redox reactions, the total potential is determined by the difference between cathodic (V_{red}) and anodic (V_{ox}) potentials. Such potentials describe reductive and oxidative reaction half-cycles, which occur via parallel electron and hole transfer processes in colloidal semiconductor photosystems[19]. Consequently, such materials can be thought of as closed-circuit photoelectrochemical cells[20].

The thermodynamic barrier, expressed by the chemical potential, determines an inherent threshold wavelength below which a semiconductor system cannot promote the photosynthetic reaction. While such a theoretical framework has been well investigated for the water and CO₂ dissociation reactions[21], an equivalent treatment should be conducted for alternative redox reagents used for STC energy conversion. Such practice can indeed intertwine materials design to photosynthetic applications, highlighting the mismatch between materials optoelectronic properties and maximum theoretical efficiencies. Therefore, following on the initial investigation by Bolton, Haught, and Ross[22], [23], we define the threshold wavelength at which sufficient solar chemical potential is transferred to the photoactive system to promote the chemical reaction as follows:

$$\lambda_{thr} = \frac{hc}{\Delta G_{redox}/n_{PS} + E_{loss}} \qquad (4)$$

where h and c represent the Planck and light speed constants, respectively, n_{PS} the number of photosystems used, and E_{loss} expresses the thermodynamic losses associated with the photochemical conversion process. Energy losses account for deviations from the ideal (η_{ideal}) to the maximum conversion efficiency of real-world devices (η_{real})[24], [25]: only a fraction of the total chemical potential at the band-gap energy level (μ_{E_g}) can be *stored* in the photoproduct's chemical bonds (see Figure S1 in the Supporting Information). In particular, energy losses derive from the Second Law of thermodynamics, and are governed by two contributions (see the shaded area in Figure 1): entropic losses, associated with the mismatch between the population of photoexcited charge carriers and available density of states at the band edges[26], and kinetic limitations ensuing from optimum power conversion constrains, yielding dissipative overpotentials [22], [27] (See the Supporting Information for a thorough mathematical analysis). In general, these limit the efficiency of real-world quantum energy conversion devices to a maximum of ~33% for the AM1.5G solar spectrum[24], [28]. Several optical strategies such as hot-carriers harvesting[29], carriers multiplication,[30] and photon up- and down-conversion,[31], [32] have been explored to surpass such limit. Yet, sluggish reaction kinetics already compromise efficiency performance far below η_{real}. In light of this, a clever design of STC redox cycles is
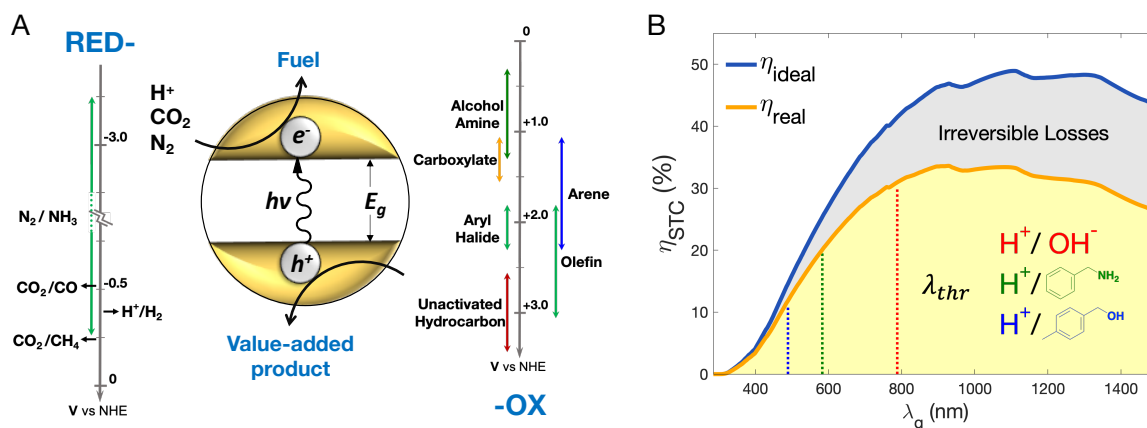
Figure 1. Decoupled photosynthetic red-ox reactions promoted by semiconductor light-absorbers and corresponding Solar-To-Chemical (STC) efficiency limits. (A) Schematic illustration of photo-excited charge carriers (electron/hole, e^-/h^+) across a semiconductor band-gap (E_g). These can promote simultaneous decoupled half-reactions, namely fuels, via reductive processes, and oxidation of organic functional groups to value-added chemicals. (B) Ideal (blue curve) and real (orange curve) solar energy conversion limits, accompanied with the threshold wavelength - λ_{thr} – necessary to promote the decoupled endothermic reduction of protons and oxidation of benzylamine (green dashed line), 4-methylbenzyl alcohol (blue dashed line), as an alternative to overall water splitting (red dashed line).

expected to relax the kinetic challenge and boost overall reaction efficiency.

For a given redox reaction, the corresponding ΔG_{redox} will be provided by absorption of photons with $\lambda \leq \lambda_{thr}$. Besides water splitting, we computed λ_{thr} for artificial photosynthetic redox cycles promoting decoupled half-reactions[22], as shown in Figure 1B (see the Supporting Information for detailed calculations). Specifically, we focus on recent reports of solar hydrogen being produced via proton reduction occurring with benzylamine (BnNH$_2$)[14] and 4-methylbenzyl alcohol (4-MBA)[13] oxidative half-reactions.

For these decoupled STC redox cycles, we calculated that a λ_{thr} of $583\,nm$ (H$^+$/ BnNH$_2$) and $489\,nm$ (H$^+$/ 4-MBA) is required. Notably, even redox transformations like conversion of benzylic amines ($V_{ox,BnNH_2} = 1.32\,V\,vs\,NHE$ [33]) and alcohols ($V_{ox,4-MBA} = 1.85\,V\,vs\,NHE$ [34]), that require a larger thermodynamic driving force compared to OH^- oxidation ($V_{ox,OH^-} = 0.82\,V\,vs\,NHE$ at $pH = 7$), yielded remarkable photoproduct formation rates. This is primarily ascribed to the faster and simpler kinetics of the multi-electronic oxidation process, that proceeds via accumulation of 4 charges for water splitting, whereas only 2 holes are needed to oxidize the aforementioned organic moieties.

While fundamental reactions kinetics and mechanisms are unravelled by elaborate spectroscopic techniques, the wide gallery of oxidative organic transformations that may potentially replace water oxidation urges, however, the adoption of rigorous and high-throughput screening techniques. Avoiding serendipitous discovery via predictive methods inevitably requires the use of cheap and readily available tools. In this regard, steady-state and time-resolved photoluminescence studies complement transient absorption spectroscopy in the design and understanding of redox reactions for effective STC energy conversion. Non-luminescent semiconductors are therefore excluded from this treatment; it is, in fact, highly unlikely that photo-excited systems dominated by non-radiative recombination could be efficient solar-to-chemical energy converters[35].

Screening via PhotoLuminescence Quenching Method and Photoreaction Characterisation

In the framework of solar energy harvesting processes, it is intuitive to consider that efficient photosynthetic systems entail excellent light absorption properties by the active component.

Likewise, in order to obtain ideal STC conversion efficiency, it is generally understood that leakages in the form of non-radiative decay are undesirable[25], [36]. This translates to the further requirement of high intrinsic radiative deactivation when a material targets efficient photochemical energy conversion. Leveraging on the importance of optoelectronic properties for STC photosynthetic processes, we advocate the use of steady-state absorption and emission spectroscopy as convenient and fast characterisation and screening techniques.

Firstly, the assessment of the semiconductor's photoluminescence (PL) efficiency, along with its inter-'molecular' electronic interactions in fluid media, is of cornerstone importance in the design of decoupled STC redox cycles. Chemical fuels are highly reduced compounds necessarily formed via reductive processes. On the other hand, a wider chemical space exists for potential candidate oxidative half-reactions for the synthesis of high-value added chemicals, therefore calling for a convenient and fast selection technique. Since photo-induced electron-transfer (PET) is the inceptive step of light-triggered chemical reactions, we propose this screening to be conducted via PL quenching. Noteworthy, the feasibility of a specific red-ox reaction ensues from the direct assessment of the electronic interaction between the semiconductor and the target molecule. This, in turns, winds up basic thermodynamic considerations concerning redox potential alignments and contributes to a thorough description of photoreaction mechanisms[37], [38]. Drawing from the work by the Glorius group in the field of photoredox catalysis[39], an example of the mechanism-based screening of oxidative organic synthesis via PL quenching is pictured in Figure 2A. Here, radiative decay is probed by steady-state emission spectroscopy of a diluted liquid solution of the light-absorbing unit. Interaction between the excited-state species and the target electron donor is assessed by the simple addition of the organic moiety to the solution. From a practical point of view, an excess of the molecule (millimolar regime) should be added at a screening stage, in order to surpass concentration quenching thresholds discussed later on. Whenever a decrease in the emission intensity signal is detected, the *quencher* molecule can be considered a potential candidate for an organic transformation. Using colloidal CdSe@CdS seeded nanorods, PL screening discloses benzylamine as an efficient quencher, while thiophene evidence no electronic interaction with this semiconductor system. It should be noted that PL quenching
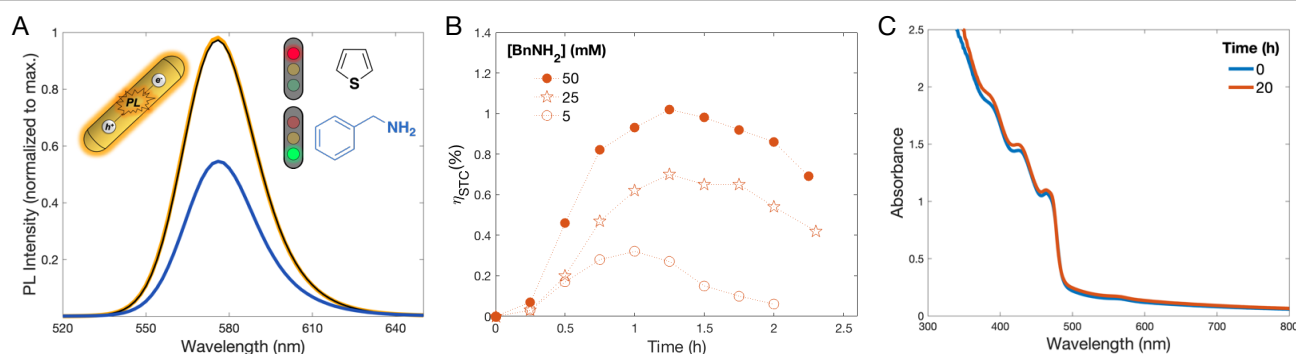
Figure 2. Screening via PL Quenching method and Photosynthetic Reaction Characterization. (A) Photoluminescence (PL) intensity ($\lambda_{exc} = 460\ nm$) of optically matched diluted solutions (H_2O:CH_3CN, 60:40) of CdSe@CdS seeded nanorods (orange curve) with the addition of benzylamine (blue curve), or thiophene (black curve). Photoluminescence quenching is observed only for benzylamine. (B) STC efficiency for the photosynthetic production of H_2 and benzaldehyde using Pt-tipped CdSe@CdS ([Pt-CdSe@CdS] $= 1.4 \cdot 10^{-7}\ M$), at different initial $BnNH_2$ concentration. (C) UV-Vis absorption spectra of the crude reaction mixture before (blue curve) and after (red curve) irradiation

does not necessarily correlate linearly with STC photosynthetic performance but represents a yes/no entry barrier for further optimization and characterization studies. For the screening step of the proposed protocol, we therefore recommend to simply report which molecules are of potential interest for STC reactions for the particular photosynthetic system used. The inherent advantages of this test can be understood in terms of the high-throughput and speed by which it is accomplished, as demonstrated by its implementation also in flow conditions[40], and fundamental analysis of photoinduced phenomena. Starting from the PL screening test just described, further quencher concentration dependence studies can indeed be performed. These allows the determination of the minimum concentration needed to quench the population of photosynthetic units in the excited-state, according to Stern-Volmer or Langmuir type models[41]. Further time-resolved photophysical investigations tools, whose description goes beyond the scope of this Viewpoint, are invaluable to explore the fundamentals of STC photoreactions, unravelling, for example, the nature of collisional quenching phenomena[38], transient behaviour of photo-generated charges[42], [43] or surface-sensitive phenomena in colloidal systems[44], [45]. Detection of luminescence quenching is, however, a necessary but not sufficient condition to confirm PET as the sole mechanism of interaction between the photosynthetic unit and target organic molecule. Processes like Förster and Dexter energy transfer can also compete with PET in radiative decay processes[46]; yet, their role can be conveniently ruled out by proving absence of spectral overlap between the absorption profile of the quencher and the emission trace of the semiconductor (See Figure S3).

Upon successful exploration of feasible organic transformations to be coupled to, for example, H_2 production, correct evaluation of the photosynthetic performance is the next key step. In the first place, it is worth noting that the reaction rate is proportional to the product of absorbed light intensity and photoreaction quantum yield. While catalyst-mass normalization can artificially inflate reports of photochemical reaction rate[47], efficiency assessment through quantum yield, i.e. moles of photoproducts per einstein of absorbed or incoming photons, is the only reliable metric for comparison between systems. This demands accurate estimation of the incoming photon flux, both in the case of mono- and polychromatic sources. In the latter case, for example, absorbed solar radiation is assessed via absorption spectroscopy, also in the presence of scattering contributions, by overlapping the absorption spectrum of the photosynthetic system and the emission profile of the Sun (See Figure S4). Finally, actinometric

protocols frame the investigation of reaction mechanism, since the photoreaction quantum yield also unfolds important information on radical- or chain-type processes. In this respect, we refer the interested reader to more in-depth discussion from Yoon and Melchiorre[38], [48].

Later, a thorough validation of the light-triggered nature of the photochemical reaction entails analyses of both photoproducts and the photosynthetic unit. It is instructive to notice that the photochemical reaction rate, and consequently the STC efficiency, is strongly affected by the quencher concentration, in a reaction-specific way. This follows from the dependence of luminescence quenching efficiency on substrate concentration. The higher the quencher molarity, the larger the PET rate and accordingly the higher the final STC efficiency, as presented in Figure 2B. Notably, continuous operation is contingent to initial reagent replenishment in batch photoreactors, while flow systems surpass this limitation, along with further process intensification advantages such as multiphase product separation and integration of operando and post-reaction characterization techniques.

Finally, demonstrating the photostability of the systems winds up the comprehensive characterisation of photochemical reactions, that withstand as long as the catalytic component turns over throughout the reaction without light-induced degradation[49]. To this extent, recyclability of the photosynthetic material is indeed demonstrated when, after separation from the reaction mixture, its spectral signatures closely overlap with the one before irradiation. Figure 2C clearly demonstrates this occurrence. The total reaction turnover number (TON), defined as the moles of H_2 produced divided by the moles of photosynthetic unit (in the present case Pt-tipped CdSe@CdS nanorods), is therefore of primary interest in sight of the perspective development of real-world devices, at the expense of reports claiming remarkable turnover frequency (TOF), i.e., maximum rate ($mol\ s^{-1}$) divided by the moles of photosynthetic unit, over a limited amount of time. This is particularly relevant with the increasing adoption of flow technologies, which recently upgraded photochemical reaction conditions in the fields of organic synthesis and water remediation[50]. As a consequence, while photocatalysis has system-specific working principles that hinder benchmarking by means of TOF values[51], characterization of overall photostability through UV-Vis and TON comprise basic, but fundamental, information for STC photosynthetic reaction reports. In conclusion, these parameters, together with the aforementioned STC index and PL quenching screening method, make up the proposed basic protocol to assess STC photosynthetic reactions, as summarized in Table 1.

VIEWPOINT

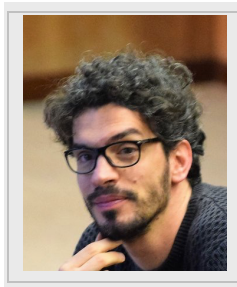| Category	Information to Report
Screening	PL Quenching: Yes/No (for each molecule)
Performance	$\eta_{STC,max}$ (%), $I_{mol,max}$ ($mol\ s^{-1}$), μ_{redox} ($J\ mol^{-1}$), $A\ (m^2)$,
Stability	UV-Vis (Before/After Photoreaction), TON

Table 1. Basic check-list for STC Photoreactions assessment.

The interdisciplinarity underlying the STC research field highlights the unprecedented opportunity for materials and reaction discovery, as well as reactor engineering and computational tools development. In light of this captivating goal, we hope that this Viewpoint could establish a common language transversal to collaborating disciplines, attracting a broad research community in proficiently contributing to both fundamental and applied investigation.

Agosti Amedeo was born in Piacenza, Italy, in 1991. He completed his Bachelor degree in Materials and Nanotechnologies Engineering at Politecnico di Milano, and later moved to ETH Zürich, where he obtained his Master in Materials Science. In 2016 he joined the group of Prof. H.J. Snaith at the University of Oxford, where he worked on Si/perovskite tandem solar cells. In the same year, he undertook doctoral studies at the University of Bologna, where he obtained his PhD in 2020 under the supervision of Prof. Giacomo Bergamini. He is currently a Post-Doctoral Fellow at the Gran Technion Energy Program, interested in developing efficient solar-to-chemical energy conversion technologies.
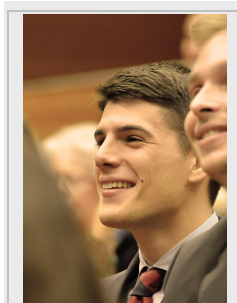
Bergamini Giacomo obtained his PhD in Chemical Science at the University of Bologna in 2007 under the supervision of Prof. Vincenzo Balzani. He is now an associate professor at the Giacomo Ciamician Department in Bologna and is co-author of more than 100 scientific papers in refereed international journals. He is the Coordinator of the H2020-MSCA-ITN-2016 PHOTOTRAIN which aims at converting solar light into usable, sustainable and exploitable forms of chemical energies, such as pharmaceutics, foods and/or solar fuels.

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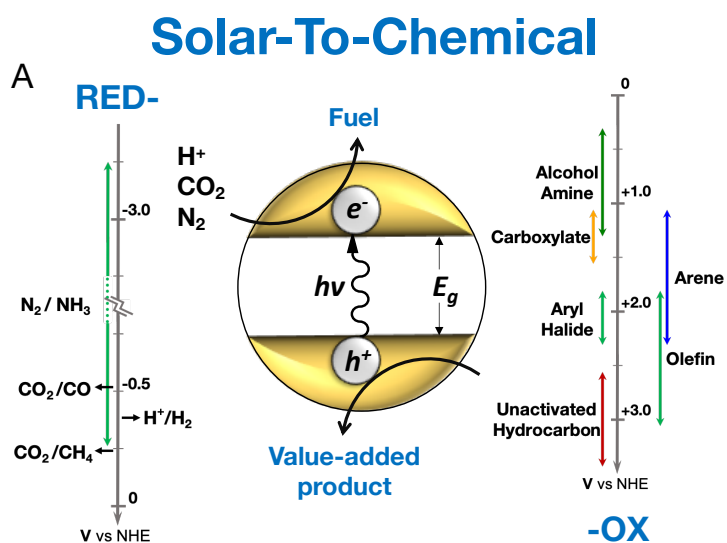
Solar-to-Chemical (STC) energy conversion allows the synthesis of a manifold of red-ox products via decoupled endergonic processes. Focusing on colloidal semiconductor materials, this Viewpoint aims to establish an interdisciplinary experimental protocol, stimulating collaborative research in photon-to-molecule energy conversion.