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Solar Hydrogen Production by Artificial Photosynthesis in Photoreactor for Sustainable Mobility

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Abstract. The thermo-industrial human society is mainly based on fuels. Currently, societies are fully dependent on fossil fuels which cause climate change that threaten human race. Solar fuels are well suited technologies to face these challenges. Long-term solar energy storage based on chemical fuel production from water (and potentially CO_2) has a significant importance to decarbonize our societies. Artificial photosynthesis is especially adapted to produce solar fuels, such as hydrogen, methane, ethanol, etc. This study focuses on hydrogen production. Water splitting with photolysis reaction is possible thanks to photocatalysts that absorb light and produce hydrogen. Modeling the hydrogen production is based on 3 main physics fields because the process is limited and controlled by radiative transfer. Electromagnetism is used to determine radiative properties. Then, radiative transfer allows to calculate photon absorption rates. Finally, the thermokinetic coupling law establishes a relation between photon absorption rate and hydrogen production rate. Experimentally, hydrogen production is operated in a dedicated laboratory-scale benchmark photoreactor. Photon flux density is controlled by a LED panel and hydrogen pressure variation is monitored with a pressure sensor. It is then possible to calculate experimental hydrogen production rates. The model predicts a non-linear thermokinetic coupling law, which fits well experimental results. Consequently, we demonstrated that the concept of incident solar flux density dilution is an important feature for process optimization. Several dilution technologies from TRL 3 to 5 are implemented in our laboratory thanks to the new PAVIN solar platform. They aim to validate high-efficiency technologies thanks to solar flux dilution.

Keywords: Solar hydrogen, Artificial photosynthesis, Photoreactor, Radiative transfer, Water Photolysis, Solar flux dilution process

Introduction

In 2020 the International Energy Agency [1] report that the total energy consumption in the world was around 420 EJ and 65% of the final energy demand is directly provided by fossil fuels, with associated production of greenhouse gases. This energy consumption would increase during 21st century. Moreover, the total consumption of electricity in the world is only about 20% of the final energy demand and 60% of this electricity is produced from fossil fuels and must be decarbonize. This means that electricity is restricted to specific applications and that energy is mainly used in the form of storable chemical energy carriers. This demonstrates that our needs for the production of renewable and sustainable chemical energetic vectors (with no CO_2 emissions) is considerable, firstly to substitute fossil fuels in the mobility, buildings heating and industry, and secondly to store electricity and smooth renewable energy intermittency by using chemical fuel (ex: power to gas).

Usable hydraulic, marine, geothermal and wind energies are limited to a potential far lower than our needs at the end of this century and produce almost only electricity. At the opposite, solar energy, biomass and wastes have a great potential in order to produce chemical fuels at large scale (ten times the energy consumption at the end of 21st century). These chemical energy carriers, such as hydrogen, methane, methanol, or ethanol, can be provided, in a limited way, by processes using wastes and biomass. The main method to product them would be the conversion of H_2O (and CO_2) from solar energy if the challenge to reach high efficiencies and enough quantities is met.

Thermochemical cycles propose a first interesting way to produce hydrogen thanks to high temperature using concentration solar plants. The water dissociation is operated by several chemical reactions, hydrogen and oxygen are produced during these reactions and intermediates chemicals are reused inside the cycle.

Another promising alternative way of producing hydrogen is artificial photosynthesis. Its basic principle is to generate excitons thanks to radiation absorption and use them for redox reactions, like natural photosynthesis, but with inert and synthetic catalysts [2]. Artificial photosynthesis has the advantage of being a one-step photoreactive process with theoretical maximum thermodynamic efficiency about 40% [2], but the corresponding technology is facing two clearly identified scientific challenges. The first one lies in the field of chemistry and aims to produce efficient, stable, and cheap photocatalysts. Different approaches are explored: semiconductor, molecular, or hybrid catalysts [3]. The second challenge, related to energy and process engineering, aims at developing solar processes allowing to reach kinetic and thermodynamic efficiency as high as possible in order to reduce the installation's volume and ground's solar collector surface required for future industrialization. Our research team is expert in the field of photoreactive process engineering and we develop original high efficiency photoreactors and photoelectrochemical cells, based on multi-scale knowledge models allowing to simulate and extrapolate the technologies based on inverse design (i.e., starting from the model to reach the optimal conception).

In the present work we focus on H_2 production by water splitting (which is also the first step to produce more complex fuels such as syngas, methane, methanol, ethanol… by CO_2 photoreduction) using aqueous suspension of photocatalytic semiconductor particles in a photoreactor (a slurry). The purpose of this study is to establish a validated predictive model thanks to a dedicated laboratory-scale benchmark photoreactor. Based on the results, we will discuss the importance of diluting the radiative flux density through optical structures (requiring first a flux concentration step) to achieve high thermodynamic efficiency.

H_2 production from Artificial Photosynthesis

Predictive Model

Modeling of hydrogen production rate and thermodynamic efficiency predictions is based on the coupling between different fields of physics, such as electromagnetism, radiative transfer and thermokinetic (see Figure 1.). Since the process is limited and controlled by radiative transfer, its design is extremely sensitive to boundary conditions and geometry. Thus, the predictive model establishment is needed to optimize the process by inverse design.

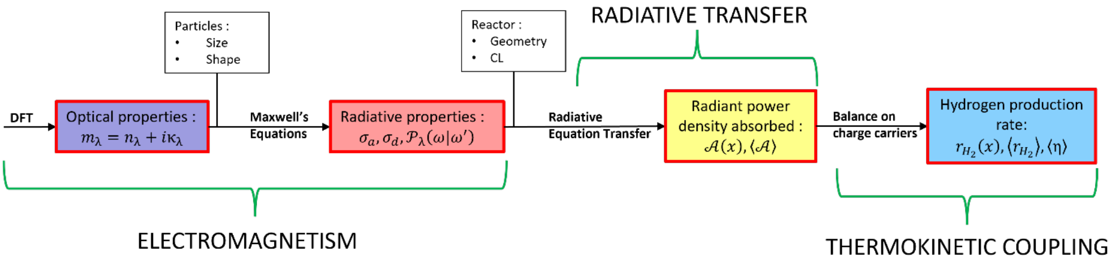

Figure 1. Predictive model structure.

The first physic field is electromagnetism at the photocatalytic-particle scale, which is divided in 2 steps. The output parameters of the *first step* are spectral optical properties of particles which correspond to the particle's complex refractive index $m_\lambda = n_\lambda + i\kappa_\lambda$. Different physical models, DFT (Density Functional Theory) calculations or experimental databases using Kramers-Krönig causality relations are used to predict spectral complex refractive indices. Then, these spectral complex refractive indices are used as input parameters in the next step. The output parameters of the *second step* are spectral radiative properties of particles which correspond to the absorption cross section $\sigma_{a,\lambda}$, the scattering cross section $\sigma_{s,\lambda}$ and the single scattering phase function $p_{\vec{\Omega},\lambda}(\vec{\omega}|\vec{\omega}')$. The Maxwell's equations are solved, and particle's geometry (size and shape) are needed to predict these radiative properties. The Mie theory is well-suited to calculate radiative properties in the case of spherical particles, but not suited for particles with random shapes [4], such as photocatalysts we use to produce hydrogen. Some alternative methods such as the discrete dipole approximation or the matrix transfer method (and associated computer's programs, e.g., ADDA, T-Matrix…) permit to determine radiative properties for these kinds of particles, but they also have some limitations in term of geometry and size parameters that can be treated. The difficulty to predict radiative properties for particles with complex shapes is still a problem of current physics. Then, radiative properties are used as input parameters in the next physics field of the model.

The second physic field is radiative transfer (or photon-transport). Compared to other reactors, photoreactors are limited and governed by radiative transfer in the reaction volume. The output parameter is the photon absorption rate $\mathcal{A}$, it can be per particle $\tilde{\mathcal{A}}[mol_{h\nu}.s^{-1}.part^{-1}]$, specific $\mathcal{A}'\ [mol_{h\nu}.s^{-1}.kg^{-1}]$ or volumetric $\mathcal{A}\ [mol_{h\nu}.s^{-1}.m^{-3}]$ and local $\mathcal{A}(x)$ or volume averaged $\langle\mathcal{A}\rangle$. It represents the rate at which photons are absorbed by particles. The spectral radiative transfer equation is solved to determine $\mathcal{A}$. This equation describes the spatial and angular distribution of the photons in the medium where photocatalysts absorb and scatter radiation. For a given geometry and boundary conditions, the Radiative Transfer Equation (RTE) resolution is performed in path-space, with the Monte Carlo Method, using ray tracing libraries and computer code ensuring that the computation time is insensitive to the phenomenological and geometric complexity. Thus, thanks to this method, the field of $\mathcal{A}$, the absorptivity, the transmittivity and the reflectivity of the medium can be evaluated. Then, the photon absorption rate is used as input parameter in the next physics field.

The third and last physic field is the formulation of the thermokinetic coupling. The output parameter of this field is the hydrogen production rate r_{H_2}, it can be par particle $\tilde{r}_{H_2}[mol_{H_2}.s^{-1}.part^{-1}]$ or volumetric $r_{H_2}\ [mol_{H_2}.s^{-1}.m^{-3}]$ and local $r_{H_2}(x)$ or volume averaged $\langle r_{H_2}\rangle$. It represents the rate at which hydrogen molecules are produced at the surface of photocatalysts. In order to simplify the modeling, hypotheses were formulated: the particle's model is 0D at steady-state. We only consider the population of charge carriers and not their displacement (no spatial coordinates). This allows to make a balance on charge carrier populations, so the mean volumetric rate of hydrogen production $\langle r_{H_2}\rangle$ at the reactor scale is coupled to the photon absorption rate $\mathcal{A}$ according to the following thermokinetic law [5]:

$$\langle r_{H_2}\rangle = \frac{C_{cat}}{\rho_p}\frac{a_p^2\tilde{\beta}}{V}\int_V dV\left(\sqrt{1+\frac{\rho_m\mathcal{A}(\vec{x})}{a_p^2\tilde{\beta}}\frac{\rho_p}{C_{cat}}}-1\right) \quad with\ \ \tilde{\beta} = \frac{\left([S_2-]k_{ox_1}+[OH^-]\left[SO_3^{2-}\right]^{\frac{1}{2}}k_{ox_2}\right)[H_2O]k_{red}}{4k_{rec}} \qquad (1)$$

This equation clearly establishes the main identifiable and measurable parameters of the coupling process, such as particle's size (specific area $a_p = 6/d_p$), sacrificial donor's concentration ($[S_2-;SO_3^{2-}]$) and oxidation, reduction, recombination rate constants $\left(k_{ox;red;rec}\right)$ - which depend on temperature. The lumped parameter $\tilde{\beta}$ is then identified on different experiments by varying the incident photon flux density and will be reified in further research to learn more about predictive model.

From the knowledge of the mean rate of hydrogen production (Equation (1) or experimental measurements), it is easy to determine the volumetric thermodynamic efficiency of the process [6], as following:

$$\langle \eta_V \rangle = \frac{\langle r_{H_2} \rangle \Delta_r G^0}{\langle \mathcal{A} \rangle \chi} \qquad (2)$$

The kinetic ratio $\frac{\langle r_{H_2} \rangle}{\langle \mathcal{A} \rangle}$ is multiplied by an energetic ratio $\frac{\Delta_r G^0}{\chi}$. $\Delta_r G^0$ is the standard free enthalpy of reaction and χ is the energetic conversion factor which represents the averaged-spectrum energy of photons. This allows to convert kinetic quantity to energetic quantity.

Hydrogen production rate and thermodynamic efficiency are respectively kinetic and energetic outputs of the model. Figure 2 shows local fields of interest. The local thermodynamic efficiency increases when the local hydrogen production rate decreases. That will lead to study the incident light flux dilution principle, as already demonstrated in the field of photocatalysis [7] and for natural photosynthesis engineering [8]. This point is detailed in the "Technology on solar flux dilution" part of this work.

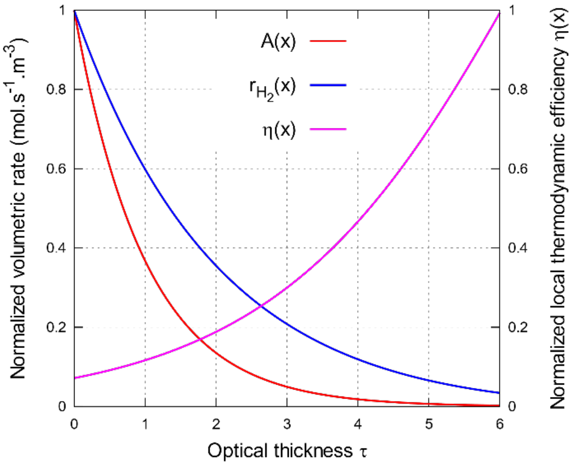

Figure 2. Local field of normalized volumetric photon absorption rate $\mathcal{A}(x)/\mathcal{A}(x)_{max}$, hydrogen volumetric production rate $r_{H_2}(x)/r_{H_2}(x)_{max}$ and thermodynamic efficiency $\eta(x)/\eta(x)_{max}$, for $q_{in} = 2000\ \mu mol.s^{-1}.m^{-3}$ (one sun in the visible spectrum).

The hydrogen production predicted thanks to the model above is then compared to experimental measures implemented in our dedicated laboratory-scale benchmark photoreactor.

Experimental Apparatus

At small scale, we use a dedicated fully controlled experimental bench developed in the lab [9] which is described on the Figure 3.

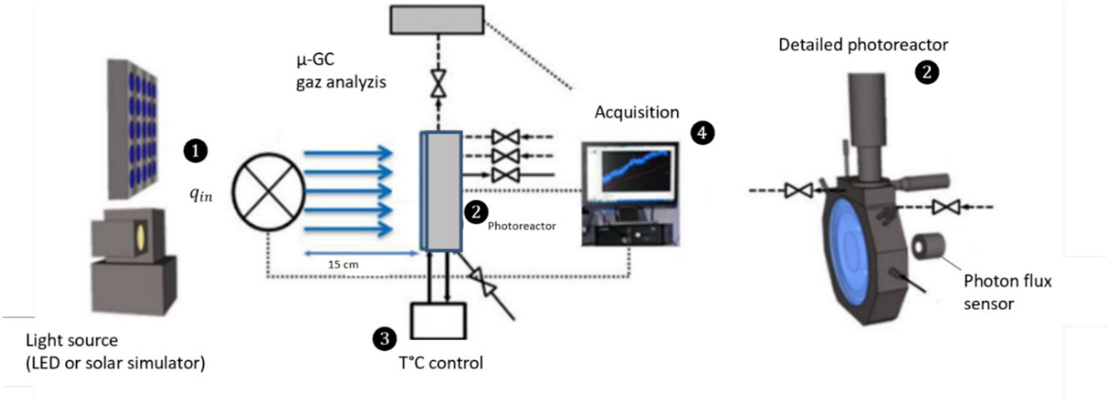

Figure 3. Scheme of the control and measurement chain with benchmark photoreactor.

The experimental apparatus, conceived to validate easily in 1D situation the radiative transfer model before coupling with hydrogen kinetic rate, is composed of 4 main parts:

1. The part ❶ is the light source which irradiates the photoreactor ❷. It could be a LED panel or a solar simulator, with controlled incident photon flux density $\mathrm{q_{in}}$. Results presented in this article were obtained with a normal quasi-collimated blue light LED panel (427 nm). The light source is controlled by the computer acquisition ❹.
2. The part ❷ is the photoreactor in which water photolysis operates. The device is an original sealed toric photoreactor machined in steel, with a 2.5 cm fluid vein thickness. This configuration enables to consider the radiative transfer as a 1D problem. It is filled with an aqueous suspension of photocatalyst particles. As an example of photoreactive system, we used in this study cadmium sulfide CdS particles with or without molybdenum disulfide MoS_2 as proton reduction co-catalyst, but our team also worked with bio-inspired molecular photocatalysts [10-11] or InP quantum dots.
3. The part ❸ is the thermostatic bath controlling the temperature of the photoreactor and the suspension at 35°C.
4. The part ❹ is the computer acquisition. The main part of the monitoring is pressure variation from which it is possible to calculate the hydrogen production rate. We use for this a mass balance on liquid and gas phases at steady state, such as:

$$\langle r_{H_2}\rangle_{exp} = \left[\frac{V_G}{V_L RT} + \frac{1}{H_{H_2|m}}\right]\frac{dP_{H_2}}{dt} \tag{3}$$

The relation is linear and depends on liquid and gas phase volume V_L and V_G, Henry's constant of hydrogen in the medium $H_{H_2|m}$, and temperature T.

A µ-GC gas analyzer is connected to the computer to qualitatively characterize the composition of the gas and check that only hydrogen is produce during experiments.

Once mean volumetric rate of experimental hydrogen production is calculated, it is then possible to compare with the model and validate it.

Comparative Results

To illustrate the predictive character of the proposed knowledge model, results are compared with experiments.

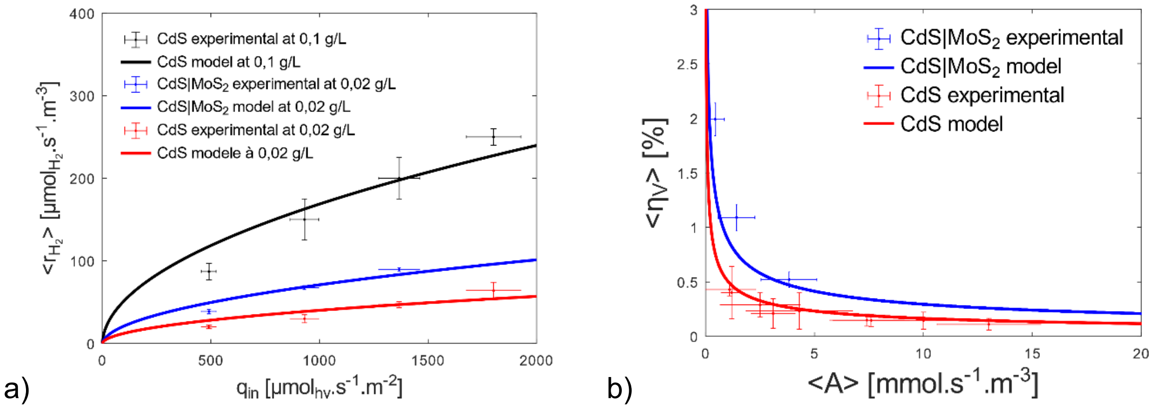

Figure 4. Experimental and model results of a) the mean volumetric rate of hydrogen production $\langle r_{H_2}\rangle$ as a function of incident photon flux density q_{in} for different CdS concentrations, with and without co-catalyst, and b) the thermodynamic efficiency $\langle \eta_V\rangle$ as a function of the mean volumetric rate of photons absorbed $\langle A\rangle$, for 0.02 g/L in CdS concentration, with and without co-catalyst.

For this, we used different photocatalyst concentrations and compositions (doped by co-catalyst) as well as different incident photon flux densities q_{in} (keeping constant the size distribution of particles, temperature, and sacrificial donor concentration).

These results confirm a non-linear relation between the mean hydrogen production rate $\langle r_{H_2} \rangle$ and the incident photon flux density q_{in} (or mean photon absorption rate in case of constant optical thickness) (see Figure 4) as predicted by the theoretical model and discussed for the first time by [12], with only one identified parameter ($\tilde{\beta}$). This results clearly from the increase of the charge-carrier recombination rate when increasing the incident light flux density [12].

Figure 4b also clearly shows that thermodynamic efficiency increases when the mean volumetric photon absorption rate $\langle \mathcal{A} \rangle$ (or incident flux density here in case of constant optical thickness) decreases. To summarize, we confirm here that higher is the incident flux density, higher is the volumetric kinetic rate, but lower is the thermodynamic yield of the process [7, 8, 12]. This suggests to investigate the principle of incident light flux dilution as an important feature for photo-reactive process optimization [8, 12]. This point will be investigated now in the next part of this article.

Technologies on Solar Flux Dilution and PAVIN Platform Facilities

As seen above, the incident light flux dilution is an interesting way to increase thermodynamic efficiency. It seems to be a specific characteristic of photocatalytic processes since on the contrary, light concentration is required for a large part of solar processes.

To quantify the dilution, a dilution factor D is defined, corresponding to the ratio of light distribution area to the light collection area. Distribution and collection of light flux are completely decoupled. Theoretically speaking, by increasing D, it is always possible to design a technology reaching the thermodynamic optimum of a given photo-reactive system (for the CdS/MoS_2 current catalytic system presented here, the maximum thermodynamic yield is 3% from sacrificial donors and 13% for water splitting). Practically, it is then necessary to find a technology with a very high illuminated volumetric specific area for light distribution [8] as using for example optical fibers like on Figure 5b (to increase D and to compensate for the loss in kinetic rate linked to the strong decrease in the incident flux density as seen on Figure. 4a); thus, if the kinetic performance of the photocatalyst is too low, there is no possible realistic design, and this is the reason why in-depth studies on catalysts in chemistry must also be carried out to improve this kind of process.

Controlled by radiative transfer, the kinetic and energy performances of photo-reactive processes, as already mentioned, are very dependent on the boundary conditions (dilution of the incident solar flux) and the associated light distribution geometry inside the reaction volume. The objective of this work is therefore to improve the knowledge and the predictive character of solar hydrogen production models in order to be able to use them in inverse design, with a dilution factor adapted to a given location (from simulations over 30 years for example, as the lifetime of the industrial plant). After validating the optical and radiative properties of the photocatalysts, the radiative transfer in the semi-transparent medium and the thermokinetic coupling law for different photocatalyst concentrations, there are still several factors to be mastered before considering the inverse design phase (see Perspectives part) i.e. using the direct predictive model to find the best optimal design under given kinetic or thermodynamic constraint. However, we have a technology transfer tool in the laboratory suitable for testing demonstrators up to TRL 5. This is the PAVIN solar platform equipped with a 3.5 m^2 heliostat and allowing us to design technologies with distribution of diluted solar flux up $D = 100$ (100 m^2 distribution area). The equipment is housed in a building to protect the analytical equipment used to qualify the process on a pilot scale (see Figure. 5). This platform has already made it possible to validate the concept of dilution of the incident solar flux to reach the thermodynamic optimum of natural photosynthesis (microalgae growth) in a 30 L pilot photobioreactor (Figure. 5). It will be used in the same way to design and test a photoreactor producing hydrogen by artificial photosynthesis as soon as the robustness of the knowledge model is proven. Dilution technologies, if well understood and used, can then strongly decrease the land area necessary to a given hydrogen annual production and then to strongly decrease the overall capital costs of this kind of solar industrial plants.

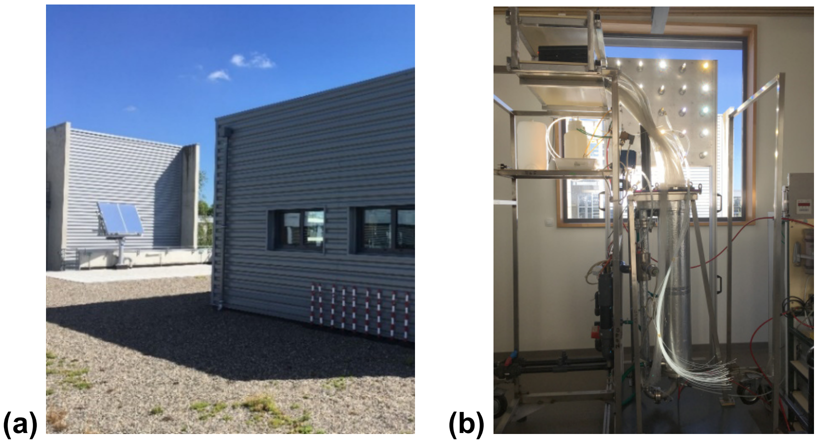

Figure 5. The 400 m^2 solar PAVIN platform dedicated to the development of solar light dilution technologies for solar fuels production at Clermont Auvergne University, France

- **a)** View of the 3.5 m^2 heliostat tracking the sun to the building housing the pilot facilities and their instrumentation.
- **b)** Example of a solar light flux dilution technology at TRL 5 [13-14]: a 30 L photobioreactor with 25 Fresnel lenses and lateral light distribution optical fibers (10 m^2) optimized for microalgae growth with dilution factor D = 50.

Perspectives of this Work

Further research will lead to better understand and describe the predictive model by expressing it as a function of measurable and clearly identified parameters. Especially, we envisage to study extensively the effect of temperature (both experimentally and theoretically) on rate constants of reduction, oxidation and charge carriers recombination appearing in the lumped parameter of the thermokinetic model $\tilde{\beta}$ (Eq. 1). The Marcus-Gerischer theory will be used to modelize electron transfer rate during reduction and oxidation reactions. The effect of co-catalyst content (like MoS_2) will be also considered as an important factor to increase the photocatalyst's efficiency. We have also recently reformulated the thermokinetic coupling model (Eq. 1) in order to independently highlight the size of the photocatalyst particles. Experiments with newly synthesized particles of different sizes will be carried out to validate this functional form (without considering quantum effects, however). Finally, sacrificial donor's concentrations and pH changes could be also investigated.

In another independent work, we will also improve the accuracy of the spectroscopic methods used to validate the radiative properties of the photocatalyst particles used in this work. We envisage to benefit from our generic 3D radiative transfer models to increase the accuracy of experimental results obtained on classical optical bench (transmittances and reflectances measurements).

Thanks to these future results, the new model will be more robust and will be used in inverse design in order to develop a TRL5 photoreactor for PAVIN platform. This prototype will validate that the hydrogen production with maximum thermodynamic efficiency can be reached thanks to solar flux dilution.

Data availability statement

Experimental data are available at: https://hal.archives-ouvertes.fr/tel-03125605, pp. 305-340

Author contributions

G. Foin: Writing original draft – J.-F. Cornet: Supervision – F. Gros, J. Dauchet, T. Vourc'h D. Yaacoub: Writing review and editing.

Competing interests

The authors declare no competing interests.

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