**Photon transport based multi-scale knowledge models for designing efficient photoreactors producing renewable solar photocatalytic hydrogen**

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**Highlights**

* A solar-from-water photocatalytic H2 production engineering is presented.
* A predictive model using multi-level light-matter processes description is proposed.
* Validation is done on an accurate experimental bench using an innovative photoreactor.

**1. Introduction**

 Considering the exhaustion of fossil resources and CO2 emission rise due to their combustion, the use of solar renewable energy is an evidence to cope with the energy demand of Humanity in the future. This resource being naturally fluctuating, it is necessary to convert it into storable energetic vectors. Among solar fuels, one of the first accessible is undoubtedly the H2, whose production can be carried out in slurry photoreactors [1] making use of photocatalytic water splitting [2]. The challenge is huge as the Humanity needs to develop in the same time efficient and cheap semiconductor photocatalysts and optimized solar photo-reactive processes.

**2. Methods**

Multi-scale model: From a chemical engineering point of view and considering that photo-reactive processes are limited and controlled by photon transport and conversion, the understanding and optimization of the elementary process of light-matter interaction at different scales and description levels is essential to develop predictive knowledge models. We present such rigorous and generic models with the objective to conceive, size and optimize highly efficient processes for solar-to-hydrogen energy conversion (yield > 15%) by geometric inverse design. Their multi-scale structuration requires first the determination of the spectral optical properties for the photocatalysts which can be found in experimental databases and/or using density functional theory with Kramers-Krönig causality relations. The second step is aimed at determining spectral radiative properties (phase function, absorption and scattering coefficients) of the photocatalyst particle by solving Maxwell’s equations using Mie theory (for equivalent sphere approximation), with additional information on shape and size distribution that can be experimentally acquired. The last phase consists in solving the photon transport equation (Boltzmann equation) to determine luminance distribution within the system volume for known boundary condition i.e. the spectral incident photon flux density qᴖ and its angular distribution. As a result, the (spectrally averaged) Local A(**x**) and Mean $\left〈A\right〉$ Volumetric Rates of Radiant Energy Absorbed (LVREA and MVREA) are estimated and linked to local H2 reaction rate $r\_{H\_{2}}(x)$ using mechanistic elementary thermokinetics coupling laws. The mean H2 reaction rate $\left〈r\_{H\_{2}}\right〉$ is then obtained by averaging local kinetics over the entire photoreactor volume.

Experimental set up: First, the radiative properties are experimentally validated thanks to transmittance measurements with an integrating sphere. Then, our knowledge model is validated by carrying out a photocatalytic reaction for H2 production in a lab-scale photoreactor [3]. H2 is produced in the gas tight photoreactor illuminated by a LED panel (various spectral distributions) or a solar simulator. Its production rate $\left〈r\_{H\_{2}}\right〉$ is correlated through a detailed mass balance with the pressure increase in the headspace of the reactor measured with a pressure sensor.

**3. Results and discussion**

Experimental result will be presented for the pressure time course (with decompression steps) during H2 production under irradiation of the photoreactor (see figure 1a). It enables to determine the mean H2 volumetric rate $\left〈r\_{H\_{2}}\right〉$. Several accurately controlled values of incident photon flux densities qᴖ [4] are tested for a given photocatalyst concentration. For each qᴖ value corresponds a $\left〈r\_{H\_{2}}\right〉$ value which is plotted as shown in figure 1b. The multi-scale predictive model presented in section 2 is then used to fit the results with the identification of only one lumped parameter.

**(b)**

**(a)**

**Figure 1.** (a) Example of experimental pressure evolution at different photon flux densities qᴖ – (b) Hydrogen mean volumetric rate as a function of incident density photon flux at 0.02 g/L photocatalyst concentration.

New experimental results using costly Pt and cheaper MoS2 as co-catalysts will be also presented.

**4. Conclusions and perspectives**

Predictive results obtained by means of our multi scale model accurately fit with our experimental results for $\left〈r\_{H\_{2}}\right〉$ at different photocatalyst concentrations. The next steps of our study will be: (a) to determine the optical properties of our catalyst by density functional theory; (b) to use other electromagnetic approaches than Mie theory (as T-Matrix and ADDA) to solve Maxwell equations for non-spherical particles of catalysts; (c) to improve the thermokinetics coupling law integrating doping process; and finally (d) test the robustness of our model with natural fluctuating solar light on a new demonstrator under development.

**References**

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