Enhancing HER rate over Pt-TiO_2 nanoparticles under CPI - role of illumination's parameters

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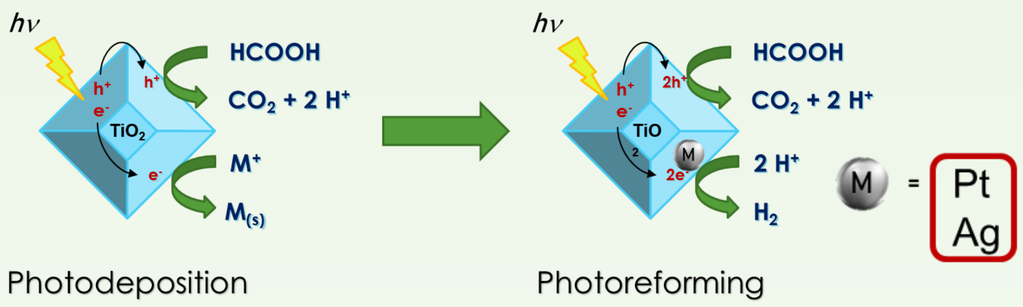
INTRODUCTION

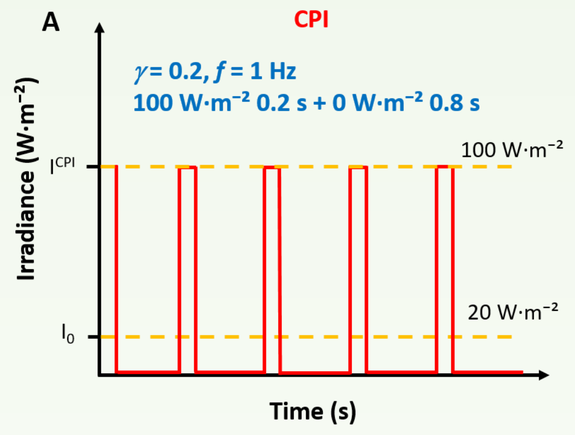
In previous works,[1,2] our group demonstrated the possibility to enhance H_2 production through HCOOH photocatalytic reforming on metal-TiO_2 nanoparticles under Controlled Periodic Illumination (CPI) in respect to continuous illumination, at the same average incident photon flux.

The enhancement was observed only over some specific metals, such as Pt, Pd and Rh. Hydrogen interaction strength (i.e. H absorption/desorption) is strongly dependent on the potential at the metal nanoparticles.[3] We observed that CPI induces oscillations in catalyst's potential, however only when some metals are employed the HER rate can be improved.



Controlled Periodic Illumination

The CPI consists in the modulation of the light intensity reaching the photocatalyst according to a designed wave function, generally a square wave, to alternate light time (t_{ON}) and dark time (t_{OFF}).

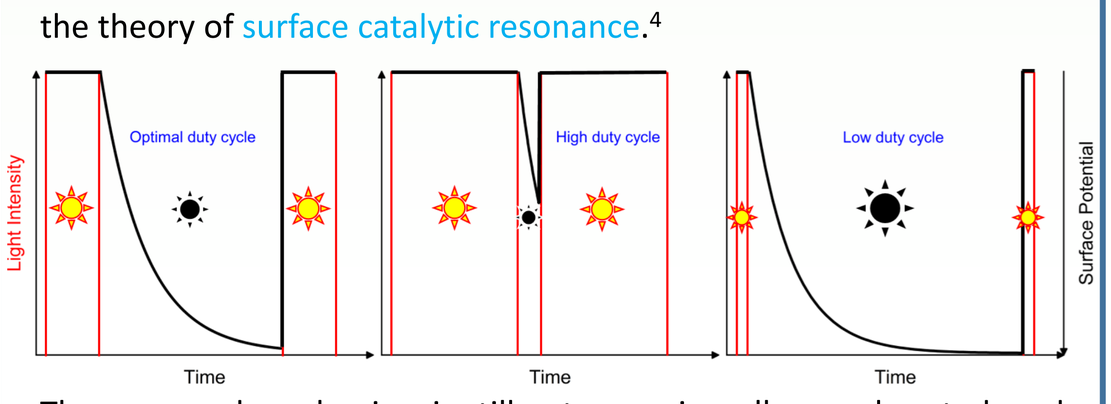


The parameters that describe the square wave are duty cycle (γ = t_{ON}/PERIOD), frequency (f = 1/Period) and the constant incident photon flux during t_{ON} (I^{CPI}).

CONCLUSIONS

In this work we have demonstrated the dependence of HER rate under CPI on frequency and duty cycle on a Pt-TiO2 catalyst, which is also reflected in the current density increase and the OCP decay.

We suppose this behaviour to be related to the oscillating catalyst's surface potential during CPI, that enable the system to overcome the optimum efficiency achievable in static conditions, in analogy with the theory of surface catalytic resonance.[4]



The proposed mechanism is still not unequivocally corroborated, and further research is needed for this purpose.

REFERENCES

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2. Sordello, F.; Prozzi, M.; Hodoroaba, V.-D.; Radnik, J.; Pellegrino, F. *Journal of Catalysis* **2024,** 429, 115215.
3. Fang, Y.-H.; Wei, G.-F.; Liu, Z.-P. *The Journal of Physical Chemistry C* **2013,** 117, (15), 7669-7680.
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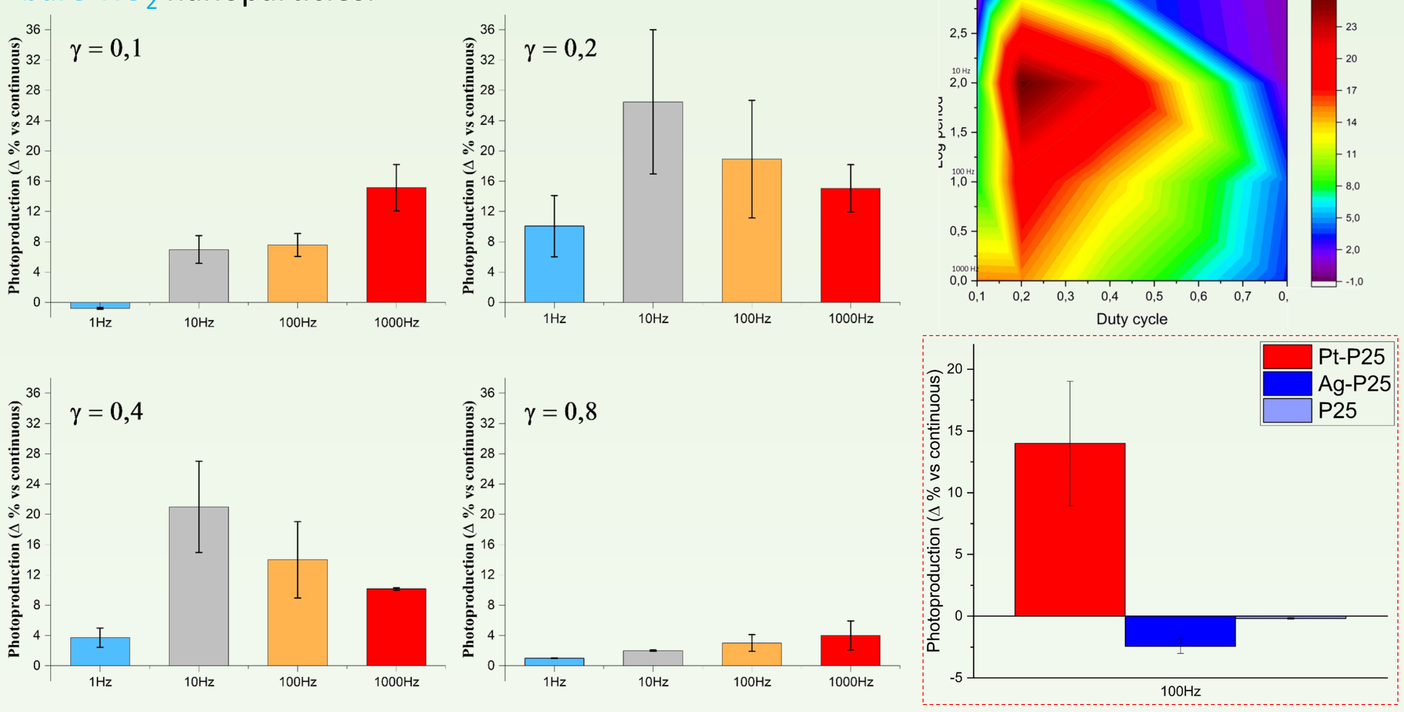
RESULTS

The Pt-TiO_2 catalyst was tested at four different duty cycles and at frequencies from 1 Hz to 1 kHz.

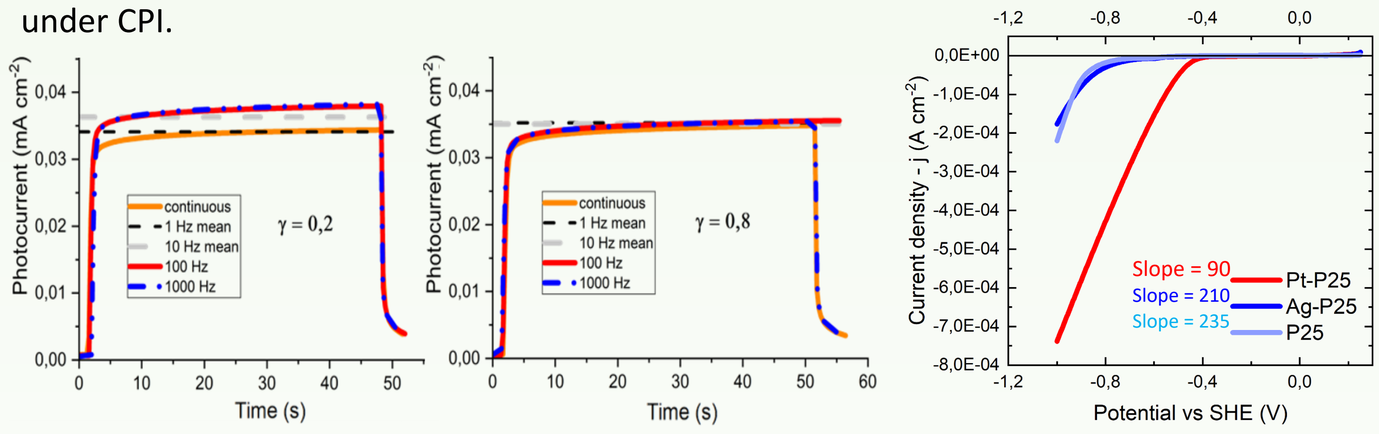
In almost all cases, an increment in HER rate relative to continuous illumination was observed. This result is particularly pronounced above 1 Hz and for intermediate duty cycle (γ = 0.2, γ = 0.4).

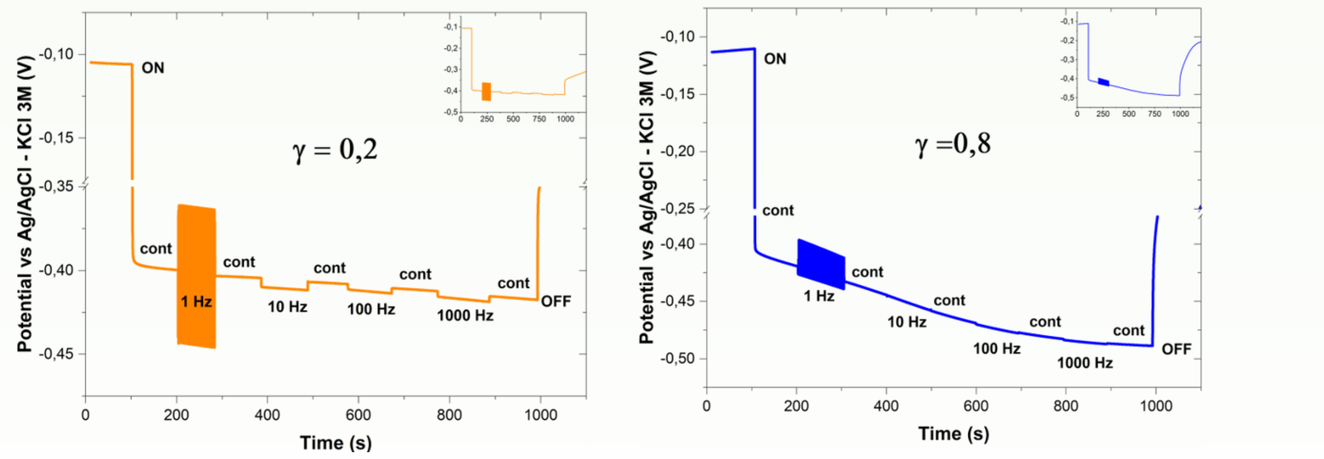
As a comparison, it wasn't possible to observe any increment in HER rate over Ag-TiO_2 and bare TiO_2 nanoparticles.



To get further insight into the mechanism, we performed a photoelectrochemical characterization of the three materials (Pt-TiO_2, Ag-TiO_2 and TiO_2) in form of electrodes.

The periodically irradiated TiO_2 always exhibit an increase in the average charge carrier density depending on the duty cycle and regardless of the employed metal. However, as already observed,[1] only materials with low Tafel slope can effectively improve HER rate under CPI.





To further investigate the charge carriers dynamic under different illumination conditions, EIS measurements were performed at different frequencies for a given duty cycle (A), and at different duty cycles for a given frequency (B). Results clearly show that the electron transfer to the electrolyte is improved under CPI and for low duty cycles.