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Journée organisée par le Grand Programme de  
Recherche Post-Petroleum Materials

# PPM Thematic Day

## Future Trends in Light-driven Processes

**Thursday May 25<sup>th</sup> 2023, 8h30-17h30**  
**Domaine du Haut Carré,**  
**Auditorium de l'Agora**

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# Sorption mechanism in heterogeneous photocatalysis. The enlightening example of laser-deposition of metals onto bare TiO<sub>2</sub> nanoparticles

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Adsorption mechanisms of reactants are at the heart of heterogeneous photocatalysis efficiencies, and remain the subject of intense discussions.<sup>1,2</sup> Schematically, on the one hand, the Langmuir-Hinshelwood kinetic model (chemisorption),<sup>3</sup> where reagents are supposed to be pre-adsorbed on the photocatalyst surface prior to photo-reaction, is systematically used for bare photocatalysts, such as TiO<sub>2</sub>, despite some inconsistencies in photon flux dependence of reaction rate.<sup>4</sup> On the other hand, Eley-Rideal-like models (physisorption),<sup>5</sup> where reagents diffuse toward the photocatalyst and further react with photoactivated surface states, were advanced to discuss these inconsistencies. We propose to tackle this debate using the much larger range of photon fluxes accessible from lasers, as compared to classical lamps and LEDs, and investigating the kinetics of photodeposition of single metallic (Au, Ag, Pd) nanodots onto bare TiO<sub>2</sub> anatase nanoparticles.<sup>6</sup> Quantitative rescaling of the data sets in laser intensities confirms that a Langmuir-Hinshelwood description leads to inconsistent orders of reaction with respect to light intensity, while the photoactivation of surface states solves these difficulties and then, is much more likely at work.

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- <sup>1</sup> Mills, A., O'Rourke, C., & Moore, K. (2015). Powder semiconductor photocatalysis in aqueous solution: An overview of kinetics-based reaction mechanisms. *Journal of Photochemistry and Photobiology A: Chemistry*, 310, 66-105.
  - <sup>2</sup> Montoya, J. F., Peral, J., & Salvador, P. (2014). Comprehensive kinetic and mechanistic analysis of TiO<sub>2</sub> photocatalytic reactions according to the direct-indirect model:(I) Theoretical approach. *The Journal of Physical Chemistry C*, 118(26), 14266-14275.
  - <sup>3</sup> Ollis, D. F. (2005). Kinetics of liquid phase photocatalyzed reactions: an illuminating approach. *The Journal of Physical Chemistry B*, 109(6), 2439-2444.
  - <sup>4</sup> Emeline, A. V., Ryabchuk, V., & Serpone, N. (2000). Factors affecting the efficiency of a photocatalyzed process in aqueous metal-oxide dispersions: Prospect of distinguishing between two kinetic models. *Journal of Photochemistry and Photobiology A: Chemistry*, 133(1-2), 89-97.
  - <sup>5</sup> Emeline, A. V., Ryabchuk, V. K., & Serpone, N. (2005). Dogmas and misconceptions in heterogeneous photocatalysis. Some enlightened reflections. *The Journal of Physical Chemistry B*, 109(39), 18515-18521.
  - <sup>6</sup> Bai, Q., Shupyk, I., Vauriot, L., Majimel, J., Labrugere, C., Delville, M. H., & Delville, J. P. (2021). Design of metal@ titanium oxide nano-heterodimers by laser-driven photodeposition: growth mechanism and modeling. *ACS nano*, 15(2), 2947-2961.

