SOLSTICE	Name of the PhD: **Aurélie ROSSET** Title of the PhD thesis: **Synthesis and characterization of catalytic nanoparticles for solar photocatalysis applications** Dates (start/end): 10/2013 - 05/2017
Supervisors	Kamal DJESSAS, PROMES/UPVD Gael PLANTARD, PROMES/UPVD

Context and objectives

This thesis is part of the development and optimization of a doped and undoped panel of catalysts for the treatment of wastewater based on an Advanced Oxidation Process (AOP), solar heterogeneous photocatalysis. This tertiary process for bio-recalcitrant organic molecules clean-up is limited by the catalysts absorption in the UV range which represent only 5 % of the solar spectrum received on the earth surface. The aim is to compare photocatalytic efficiency under UV, visible and solar irradiation in order to improve efficiency in the UV range, to develop a catalyst, which operates effectively under visible irradiation and to define key parameters governing the photocatalytic activities.

Approach

In this context, a selection of doped or undoped catalysts was realized, by choosing the most efficient ones studied in the literature, working on a wavelength range from 214 nm to 1181 nm (corresponding to energies of 1.05 to 5.8 eV). These undoped catalysts are classified in three categories of materials, namely the disulfides ($CuInSe_2$, $CuInS_2$, WS_2 and MoS_2), sulfides (SnS, CdS, ZnS, and CuS) and oxides (P25, SnO_2, In_2O_3, WO_3, MgO and ZnO). In this selection, a study is performed on doped or undoped ZnO based catalysts. All of ZnO based catalysts are synthesized by the same process, the sol-gel process under supercritical drying conditions. Structural, morphological, chemical, optical and optoelectronical characterizations are carried out to define their physico-chemical parameters in order to control the synthesis conditions of these catalysts.
The morphological and physico-chemical characterizations reveal that the catalysts show a crystalline structure of quality with a single phase and a quasi-stoichiometric chemical composition, except for $Zn_{0,90}Ca_{0,10}O$. Doped ZnO also showed an absorption edge shift toward the visible range.

Main results

Photocatalytic experiments were carried out with a photocatalysis optical bench in the UV, visible and solar range. Particular attention has been paid on a model pollutant, pyrimethanil. In parallel, these experiments are coupled to a kinetic model. In regards to the efficiency of these multiple catalysts, results obtained in the UV range are clearly superior to those of the visible range, knowing that in the latter the quantity of photons is around 50 times higher than in the UV. However, nanoparticles of $Zn_{1-x}M_xO$ (M : Ca, Al, Li, V, In, Co, P…) showed encouraging photocatalytic activities in the visible range. A correlation is shown between the physico-chemical properties of the catalysts (optical band gap) and the radicals production efficiency (Figure). Furthermore, an extensive study is done on $Zn_{0,90}Ca_{0,10}O$ synthesized by sol-gel process under supercritical drying conditions with four different precursors of calcium, $CaSO_4$, $CaCO_3$, $Ca(NO_3)_2$ and $CaCl_2$. All the characterizations carried out indicate that calcium didn't substitute interstitial sites of zinc in the matrix of ZnO for the synthesis with $CaCl_2$ and $Ca(NO_3)_2$ precursors. Furthermore, the presence of Cl^- and NO_3^- ions is harmful in photocatalysis. Only the $Zn_{0,90}Ca_{0,10}O$ synthesized by the $CaCO_3$ precursor allowed integration of the calcium into the ZnO matrix. This study also reveals the presence of structural defects playing a main role on the photocatalytic activities. It was found that the presence of defect in the volume (core defects) in the catalysts is harmful in photocatalysis. This type of defect contributes to the recombination of photo-generated charges. Moreover, the nature of the precursor and doping concentration was identified as the key parameters governing the photocatalytic responses.

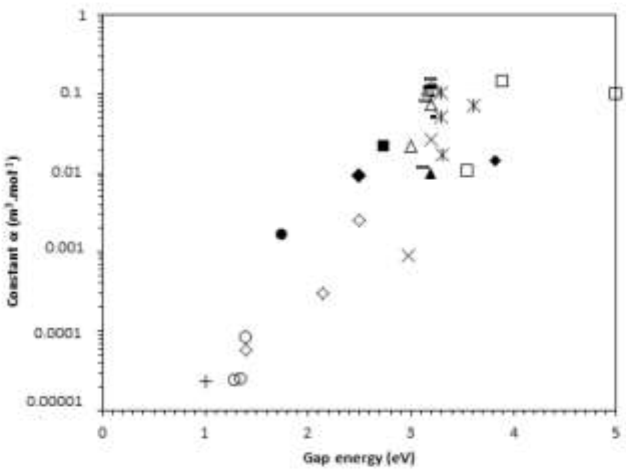

Figure issued from Ref. [1]: Variation of the constant (α) calculated, for the different catalyst studied as a function of the band gap energy of the corresponding catalyst. (□) Oxides, (○) P25, (◊) Sulphides, (○) Disulfides, (+) Selenide, (Δ) Alkali metals alloyed ZnO, (×) Transition metals alloyed ZnO, (⁎) Post-transition metals alloyed ZnO, (-) Non-metals alloyed ZnO and (▭) Alkaline earth metals. Results from the literature are obtained by Lliev and al., with WO_3 (λc = 451 nm) (■), by Sharma and al., with ZnS (λc = 325 nm) (◆), by Bajorowicz and al., with CdS (λc = 496 nm) (◆)and with MoS_2 (λc = 709 nm) (●), and by He and al., with Transition metals alloyed ZnO (λc = 388 nm) (▲).

Publications in scientific journals

[1] A. Rosset, G. Plantard, K. Djessas, V. Goetz, Correlation between gap energy and photocatalytic efficiencies of nanocatalyst under solar irradiation conditions, J. Mater. Sci. Mater. Electron. 28 (2017) 1-10.

[2] A. Rosset, G. Plantard, K. Djessas, V. Goetz, Photocatalytic efficiencies of $Zn_{1-x}M_xO$ coumpounds synthesized with a broad panel of M elements: responses in the UV, visible and solar range. (Submitted to Solar Energy materials and solar cells, October 2017).

Invited lecture

A. Rosset, K. Djessas, G. Plantard, J.L. Gauffier, Synthèse et caractérisation de nanoparticules catalytiques pour une application en photocatalyse solaire, Matériaux 2014, 24-28 Novembre 2014, Montpellier-France (Keynote).