FREE CHARGE CARRIER NANOCOMPOSITE PHOTOGENERATORS AS PROMISING PHOTOCATALYTIC MATERIALS: WHICH PARAMETERS TO EVALUATE AT FIRST?

Alexis Evstratov, *Cristian Chis*
Ales School of Mining, 6 avenue de Clavieres, 30319 Cedex, Ales, France
alexis.evstratov@ema.fr

The materials which are capable to provide at their surfaces free charge carriers (FCC), electrons and positive holes, under UV or visible light irradiation, can be considered as Free Charge Carrier Photogenerators (FCCP). Some similar terms exist also in modern scientific literature [1, 2].

Theoretically, all the FCCP materials, both in free state and in supported form (composite species), could manifest an interest for the photocatalytic applications. The best performances are usually expected from nanometric scale FCCP because of surface attendance facilities for the free charge carriers generated in extremely small active aggregates.

However, experience shows that it is not the case: some FCCP nanocomposites can not be utilized in photocatalysis. Selecting a product which presents a potential interest as an efficient heterogeneous photocatalyst from a large range of FCCP materials remains so a problem to resolve.

At the same time, not only well known crystalline semiconductors (titanium and zinc oxides, cadmium and zinc sulphide, etc.) dispose photocatalytic capacities. It was proved [3-5] that the disordered structures can also assure the photocatalytic phenomenon.

Excepting a good activity, a promising material for photocatalytic application must conserve its initial catalytic capacity for an important period of time in order to guarantee the process steady state during all the service period.

What is the principle cause of the heterogeneous photocatalyst surface deactivation? We believe that in the case of volatile organic compound (VOC) photoxidation process, the active surface degradation is always caused by parasite acid-base reactions taking place at the same time as target reactions. In the previous example, the products of parasite reactions are represented by surface oligomer compounds formed over Lewis acid centres (acceptor cationic sites) from the VOC precursors having a strong Lewis base behaviour. Moreover, the target reactions aim to the VOC complete oxidation occurring often over the same active sites. For any FCCP, the parasite reaction domination over its surface excludes this species from a potential application as an efficient photocatalytic agent.

In order to be considered as a promising photocatalyst, a FCCP sample has to possess, at least, the following proprieties:

- maximum quantity of photogenerated FCC reaching the active surface;
- limited FCC recombination intensity;
- optimal FCC repartition at its surface (positive hole domination [6]);
- important physical adsorption capacity;
- low Lewis acid reactivity (less parasite reactivity potential);
- important photocatalytic activity in steady state process.

When faced with a novel FCCP product supposed to be applied as photocatalyst in a stedy state process, it is useful to define a mini-list of parameters to be controlled (see the table below). Getting to their states or levels advised in the table, assures good perspectives of the material’s use.

Table: Basic parameter set to be controlled for the FCCP identification as efficient photocatalyst

Lot	N°	Parameter	Advised state / level
Fundamental parameters	1	Free charge carrier repartition at the active surface	Hole domination
	2	Quantum yield	Maximal
	3	Free charge carrier lifetime	Maximal
Reactivity parameters	4	Photocatalytic activity	Maximal
	5	Physical adsorption capacities	Optimal
	6	Acid-base reactivity under lighting (UV-A / sunlight)	Minimal
Other characteristics	7	Surface morphology and active aggregate dimensions	Nanosized aggregates
	8	Crystallinity rate of active components	No strict restrictions
	9	Oxidation rate of active component surface cations	Minimal
	10	Average widths of the optical forbidden zones (for crystalline products)	Optimal

The properties of Degussa P25 (reference photocatalytic product) and of an amorphous TiO_2 silica based nanocomposite material supposed to be applied as heterogeneous photocatalyst are presented and discussed in the paper. The experimental methods and techniques used for the parameter evaluation are also cited.

The mini-list presented above needs to be completed with the kinetic characteristics. Each parameter already cited in the table could be detailed for a more pertinent characterisation of a FCCP material sample as a potential heterogeneous photocatalyst.

References:

[1] A. Jain, A. Kapoor, A new approachto study organic solar cell using Lambert W-function, **Solar Energy Materials & Solar Cells 86** (2005) 197–205.

[2] T. Barfels, H.J. Fitting, A. Gulans, J. Jansons,M. Springis, H. Stolz, I. Tale, A. Veispals, Luminescence and electron transport properties of GaN and AlN layers, **Radiation Measurements 33** (2001) 709–713.

[3] L. Zang, W. Macyk, C. Lange, et al., Amorphous microporous titania modified with metal chloride as photocatalysts for detoxification and charge generation by visible light, H. **Kinch Chem. Eur. J.,** vol.6 (2000) 379-384.

[4] A. Evstratov, C. Chis, P. Gaudon, B. Ducourant, P. Jouffrey, Structures composites nanométriques en état amorphe en tant que photocatalyseurs d'une nouvelle génération, **Récents Progrès en Génie des Procédés**, 92-2005, L-14 (2005) 1-8.

[5] C.J. Lin, J. Chen, S.L. Suib et al., Recovery of bromine from methyl bromide using amorphous MnO_x photocatalysts, **J. of Catalysis**, vol. 161, N°2 (1996) 659-666.

[6] A. Evstratov, C. Chis, J.M. Taulemesse, P. Gaudon and F. Peirano, Revealing of a Particular Physical Mechanism of Disordered Photocatalytic Structure Functioning, **9th Intern. Congress NSTI Nanotech-2006, Proceedings,** vol. 1 (2006) 9-12.