

Revealing of a Particular Physical Mechanism of Disordered Photocatalytic Structure Functioning

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ABSTRACT

The photocatalytic phenomenon consists in a simultaneous generation of two opposite free charge carrier types, electrons and holes, under a semiconductor photonic excitation. In the case of “classic photocatalysts” (commercial crystalline powder products), the secondary free charge carrier population available at the catalyst surface is significantly less important than the primary one just created by the excitation energetic impact. This fact is due to an intensive recombination of the carriers during their transition to the sample surface. However, the efficient electric charge – both for the secondary and the primary carrier communities – stays statistically well equilibrated in sign. This paper puts in evidence a particular behavior of the composite photocatalytic structures functioning with a pronounced dominance of a single carrier type – for instance, the holes, as shown in this work. The revealed phenomenon seems to be promising for new powerful photocatalysts development. The present research has been realized using silica based amorphous TiO₂ nanocomposites as tests photocatalytic samples.

Keywords: charge carriers, amorphous TiO₂, photocatalysis.

1 INTRODUCTION

The UV-visible light excitation of a semiconductor leads to the creation of free electric carriers (“electron–hole” pairs) due to the passage of valence-band electrons into the semiconductor conduction band through its forbidden zone. Due to the band gap barrier, the electrons and holes are protected against immediate recombination and reach the semiconductor surface in a theoretical 50% / 50% proportion [1]. In order to identify the active facets in crystalline powder photocatalysts, two photochemical reactions are typically quoted in literature: the reducing of Ag⁺ by photogenerated electrons and the oxidation of Pb²⁺ by photogenerated holes [2, 3].

Pronounced photocatalytic activities of amorphous TiO₂ composite materials used for volatile organic compound degradation and bacterial removal were largely discussed in our previous works [4, 5]. The functioning of disordered composite structures as heterogeneous photocatalysts is provided by a reinforced artificial separation of free charge carriers by means of an external electric field [6]. This action leads to a trapping of a

selected free carrier type (electrons, for instance) avoiding so the participation of the immobilized charges in the recombination process. Consequently, the other carrier type (holes, in this example) will dominate at the catalyst surface and so major the photocatalytic phenomenon.

Actually, the disordered photocatalytic structures are not commonly used in practice and the problem of their particular free carrier surface repartition is not yet resolved. The functioning mechanism of amorphous heterogeneous photocatalysts is so not really known.

Lead oxidation and silver reducing photochemical reactions, referred above, can be used as efficient tools in order to investigate the carrier repartition particularities on the surface of disordered photocatalytic structures.

This paper reveals the particular physical behaviour of an *oxidative* amorphous photocatalyst which functions due to the hole predominance on its surface. The opposite type of active material – *reducing* photocatalyst – can also be designed, if necessary.

2 EXPERIMENTAL

Amorphous TiO₂ silica based photocatalysts (particle diameter – 0.25-0.50 μm) were prepared by a technique derived from the Chemical Vapour Deposition method [7] using TiCl₄ (Acros Organics) as the TiO₂ precursor.

The elaborated composite samples (1 g) were lightly agitated in 100 ml of two 0.1 M aqueous solutions containing AgNO₃ (Fluka) and Pb(C₂H₃O₂)₂ (Analyticals Carlo Erba), each for 90 minutes.

In order to test a low energy activation source, an incandescent lamp (Philips, R-60W) with the emission spectrum shown in Figure 1 was chosen. Being placed at 20 cm far from irradiated object, this lamp provides the light intensity equal to 32,200 lux increasing the object temperature up to 45-50°C, approximately.

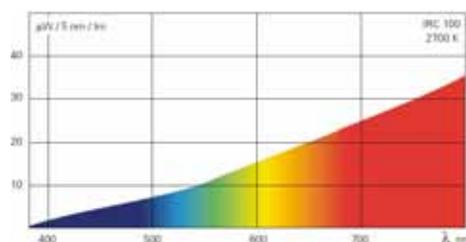
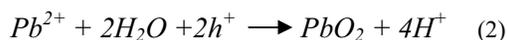


Figure 1: Emission spectrum of incandescent lamps.

After 90 minutes treatment under incandescent irradiation, the samples were filtered, rinsed several times with bi-distilled water, and dried in air at 70°C. Pure silica (Acros Organics) was used as a control sample.

The test reactions were the following:



The changes in solution cation concentrations were followed by atomic absorption spectroscopy (ICP JY 2000 spectrometer). Metallic silver and lead dioxide deposits formed on the photocatalyst surface were qualitatively studied by coupled SEM-EDX analysis (Quanta 200 SEM / FEG microscope).

The quantities of lead and silver liberated from the treated samples were determined by ICP measurements. The deposited metals were dissolved by acid treatment of the samples (HCl, 36 % ms. concentration, supplier - ACROS Organics) during 1.5 hour at 65°C, under permanent agitation. The same protocol was used to measure the amount of amorphous TiO₂ on the surface of photocatalytic composites. This technique was not available for Degussa P25 samples (reference material, TiO₂ nanocrystals, 50 nm average diameter [8]) due to well-known handling problems.

The crystalline state of the tested samples was studied by XRD analysis (D8 BRUKER X-ray diffractometer, λ K α Cu = 1,5406Å).

3 RESULTS AND DISCUSSION

Figures 2 and 3 show the evolution of the metal concentrations followed by ICP measurements. Both for lead and silver solutions, the pure silica manifests no chemical activity and the metal concentrations increased only due to solution evaporation (curves -◇- in fig. 2 and -Δ- in fig. 3).

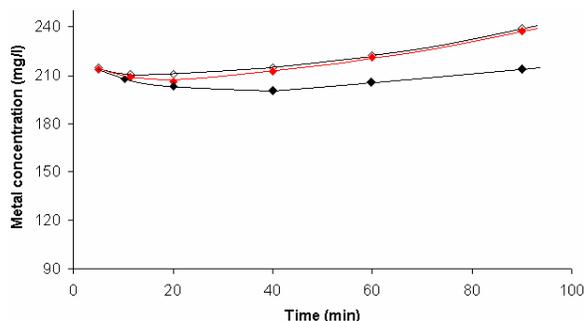


Figure 2: Evolution of Pb²⁺ concentration in Pb(C₂H₃O₂)₂ solution under lighting: -◇- pure silica; -◆- Degussa P25; -●- amorphous TiO₂ photocatalyst.

On the contrary, the TiO₂ composite sample shows a pronounced photochemical activity in the lead solution.

The graphic integration of the ICP curves permit to evaluate the lead concentration decreasing up to approximately 10 % after 90 minutes of irradiation (curves -◇- and -◆-, fig. 2). These results are in a perfect coherence with the ICP data concerning the metal quantities formed on the treated amorphous TiO₂ composite samples (tab. 1). As to Degussa P25, its photoactivity in the Pb²⁺ solution is significantly lower. The graphic integration for the curves -◇- and -◆- (fig. 2) allows to estimate the lead concentration decreasing at the level of 2 %.

| Parameter | Pb | | Ag | |
|---|-------------------|------------------|------------------|------------------|
| | ATS* | P25** | ATS* | P25** |
| | a | b | c | d |
| 1. Metal initial quantity in 100 ml of test solutions, mg | 2070 | | 1080 | |
| 2. TiO ₂ quantity in test samples, mg | 105 | 100 | 105 | 100 |
| 3. Metal quantity on treated sample surfaces, mg | 198.3 | 39.5 | 16.5 | 38.9 |
| 4. Ratio "line 3 / line 2" | 1.88 | 0.39 | 0.16 | 0.38 |
| 5. Metal quantity leaving from test solution, % | 9.6 | 1.9 | 1.5 | 3.6 |
| 6. Free charge carrier contribution in surface deposit (PbO ₂ , Ag ⁰) formation, % | Holes | | Electrons | |
| | 92 | 50 | 8 | 50 |
| 7. Free charge carrier distribution at sample surfaces | 10 h ⁺ | 2 h ⁺ | 1 e ⁻ | 2 e ⁻ |
| 8. Activity ratio ATS / P25: (3a + 3c) / (3b + 3d) | 2.75 | | | |

* Amorphous TiO₂ silica based: ICP data

** Degussa P25: graphic integration results

Table 1: Major results of sample photoactivity tests

In order to explain an important difference in activity between amorphous TiO₂ nanocomposite and Degussa P25 samples, two probable effects can be involved.

Firstly, Degussa P25 nanocrystals need important activation energies, at least higher than 3.2 eV (TiO₂ band gap [9]), to provide free charge carrier. This energetic barrier does not exist in disordered structures and with low excitation impacts the free charge carriers could be potentially provided.

Secondly, the number of free charge carriers at the amorphous TiO₂ surface is 2.75 much greater than in the case of Degussa P25 (tab. 1). This fact may be explained in terms of particular silica Lewis acidity promoting the electron immobilization close to acceptor active sites and so disfavoring the immediate carrier recombination [6].

For the silver solution the amorphous TiO₂ composites show approximately two times less activity than Degussa P25 (tab. 1, fig. 3). This result is in a good coherence with a smaller amount of negative charge carriers at the surfaces of silica based amorphous TiO₂ composites.

It is to be noted that Degussa P25 in these experimental conditions does not manifest a high activity level but it functions with well equilibrated electron-hole reparation on its surface (tab.1). This fact corresponds perfectly to the theoretical “fifty-fifty” free charge carrier proportion [1]. In the case of amorphous TiO₂ silica based photocatalysts the free charge carrier repartition on the surface is completely disturbed: 92 % holes / 8 % electrons (tab. 1).

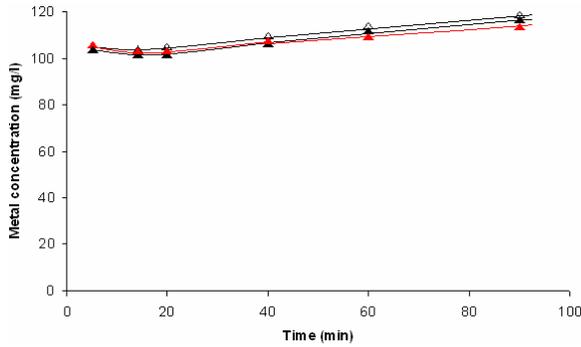


Figure 3: Evolution of Ag⁺ concentration in AgNO₃ solution: –Δ– pure silica; –▲– Degussa P25; –▲– amorphous TiO₂ photocatalyst.

As to the free charge number existing at the sample surfaces, for every four carriers (2 e⁻ and 2 h⁺) available for Degussa P25 eleven carriers (1 e⁻ and 10 h⁺) appear at the surfaces of amorphous TiO₂ composite samples (tab. 1).

The analytical results obtained using the XRD technique show that the TiO₂ silica based photocatalysts are completely amorphous, as compared to Degussa P25 where the anatase and rutile phases are clearly identified (fig. 4).

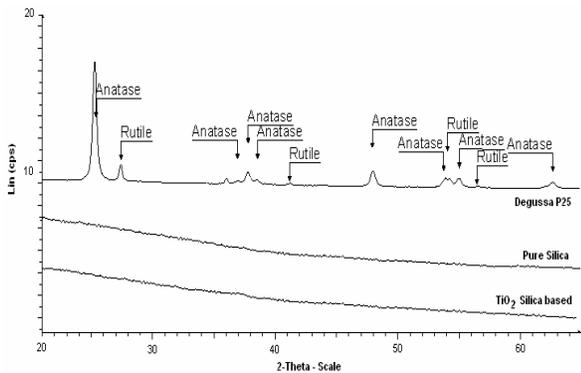


Figure 4: Characterization of the crystalline state of the samples by XRD analysis.

SEM images of the test samples are presented in Figure 5. The used synthesis technique permits to elaborate the TiO₂ aggregates in a spherical form. Their diameters differ from 500 to 2000 nm (Fig. 5 (a)).

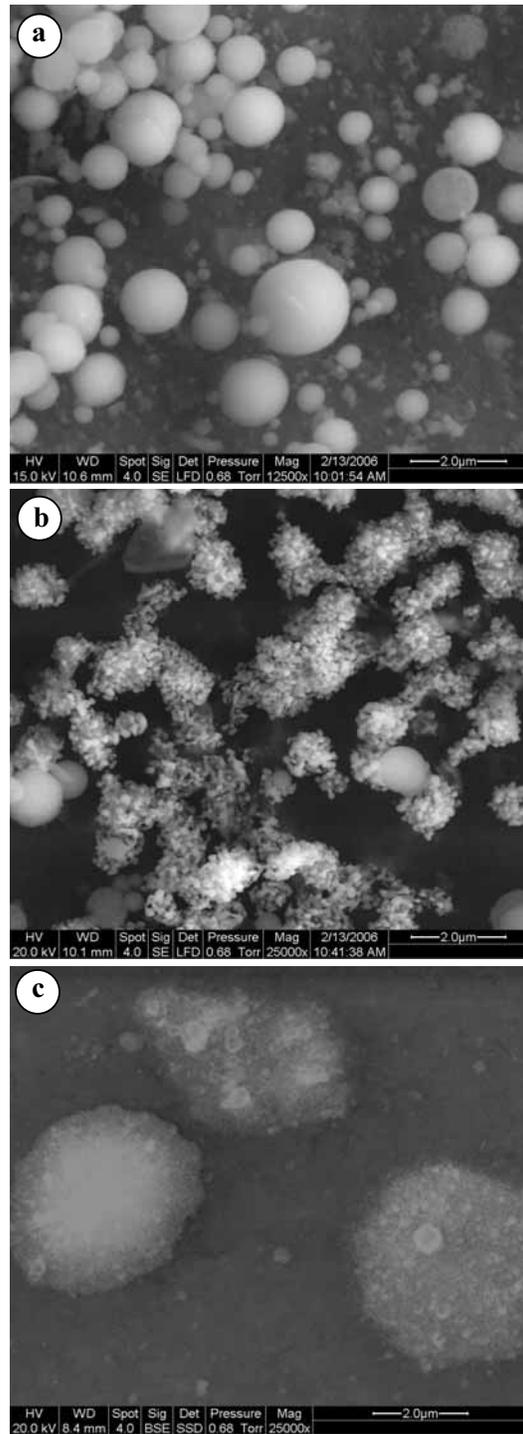


Figure 5: SEM images: a). amorphous TiO₂ silica based photocatalyst; b). amorphous TiO₂ silica based photocatalyst after 90 min irradiation in AgNO₃ agitated solution; c). amorphous TiO₂ silica based photocatalyst after 90 min irradiation in Pb(C₂H₃O₂)₂ agitated solution.

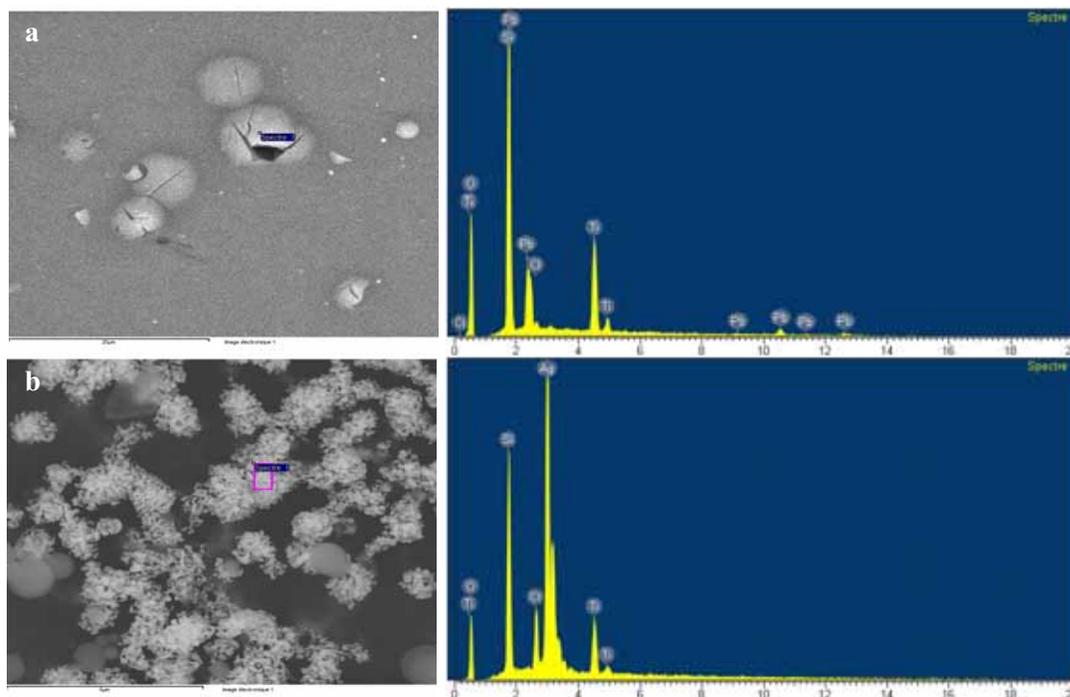


Figure 6. SEM- EDX analysis: a). amorphous TiO_2 silica based photocatalyst after 90 min irradiation in $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ agitated solution; b) amorphous TiO_2 silica based photocatalyst after 90 min irradiation in AgNO_3 agitated solution.

In irradiated AgNO_3 solution the TiO_2 surface aggregates accumulate limited quantities of metallic silver (fig. 5 (b) and tab. 1). On the contrary, significant lead oxide deposits, due to high surface concentration of free holes, justify powerful oxidation capacities of the sample (fig. 5 (c)).

SEM-EDX data confirm the reaction product nature: lead (as lead oxide) and silver are formed at the sample surfaces (fig. 6).

4 CONCLUSION

Disordered TiO_2 silica based nanostructures irradiated by low energy excitation sources manifest an important photocatalytic activity exceeding the one of commercial reference products (e.g., Degussa P25). The mechanism of their functioning is based on a reinforced separation of free charge carriers disfavoring the recombination phenomenon. The carrier surface repartition in the case of these materials is quite particular: instead of the usual “fifty-fifty” proportion, this type of photocatalysts functions with total hole dominance providing its great selectivity in the oxidation processes.

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