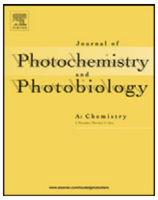
Journal of Photochemistry and Photobiology A: Chemistry 253 (2013) 7–15

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Development of a new qualification method for photocatalytically active surfaces based on a solid state luminescent dye

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ARTICLE INFO

Article history:
Received 11 October 2012
Received in revised form
10 December 2012
Accepted 15 December 2012
Available online 25 December 2012

Keywords:
Semiconductor photocatalysis
Qualification of photocatalytically active surfaces
Testing procedures
Luminescence measurement
Solid-state measurement
Online qualification
Europium(III) complex

ABSTRACT

The authors present a new method for the qualification of photocatalytically “active” surfaces (e.g. TiO_2 coated glasses) comprising a solid-state luminescent dye, which is thoroughly characterized and investigated regarding its behavior on different manufactured photocatalytically active substrates versus inactive reference materials. The dye is an europium(III) complex showing the typical intense $^5D_0 \rightarrow {}^7F_2$ transition with an emission wavelength maximum of 615 nm upon excitation at 350 nm. The dye is deposited as a thin-film reaching from 10 nm to 100 nm onto the substrates using an ultra-high vacuum (UHV) deposition technique. This system is excited with 20 W/m^2 at 365 nm with a LED and the luminescence is time-dependently monitored with a spectrofluorimeter. The dye's luminescence shows only a slight decrease on inactive substrates such as glass or silicon wafers, while showing a significant decay on photocatalytically active TiO_2 substrates. A possible mechanism for the luminescence decay is proposed. This direct method of luminescence degradation is highly sensitive and reproducible. It represents a promising option to be considered in standardization efforts in the field of photocatalysis.

1. Introduction

Photocatalytically “active” coatings receive ongoing attention due to their ability to decompose surface-contaminating organic matter using the photocatalytic oxidation (PCO) effect. Additionally, these surfaces display the so termed “self-cleaning” effect, which corresponds to the UV-induced hydrophilicity, causing particles to be washed off easily, for example by rain in outdoor use. Fortunately, titanium dioxide (TiO_2) can be used for these types of coatings; a material that is already being produced in the million ton scale every year. The reason for this is that the anatase modification of TiO_2 possesses a bandgap E_G that is ideally aligned to absorb short-wavelength light ($\lambda \leq 400$ nm), as visualized in Fig. 1.

The absorption of ultraviolet light leads to the generation of holes (h^+) and electrons (e^-), which can take part in the surface reactions. Depending on the energetic position of the valence band E_{VB} and the conduction band E_{CB}, subsequent reduction and oxidation reactions are possible. The most intensively studied reaction comprises the atmospheric molecules water and oxygen, which can be oxidized, respectively reduced to yield highly reactive oxygen species and radicals [1]. This reaction cascade, which is repeated by the photon absorption, charge generation and charge transport in TiO_2 (anatase) is therefore termed a photocatalytic process. A more detailed description and investigation of the process can be found in literature [2–5].

Especially when concerning the substrate coatings, only a limited surface area is available for this kind of reaction. Within this area minimal structural or morphological differences can play a vital role for the overall performance of the photocatalyst. Reliable testing procedures for different coatings are therefore of importance in ensuring reproducible quality not only for scientific purposes, but even more in industrial applications. There are several common international standards for determining the activity and efficiency of photocatalysts to be used within different areas of application, which are water and air-purification, self-cleaning, and antibacterial activity of semiconducting photocatalytic materials. Recently, Mills et al. [6] gave a fundamental overview of current used standards with their advantages and drawbacks. Beside these standards the established methods for the quantification of photocatalytic properties are mainly the methylene blue test (based on ISO 10678:2010) and the decomposition of stearic acid over a photocatalytic material. While the first one is based on the

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http://dx.doi.org/10.1016/j.jphotochem.2012.12.012

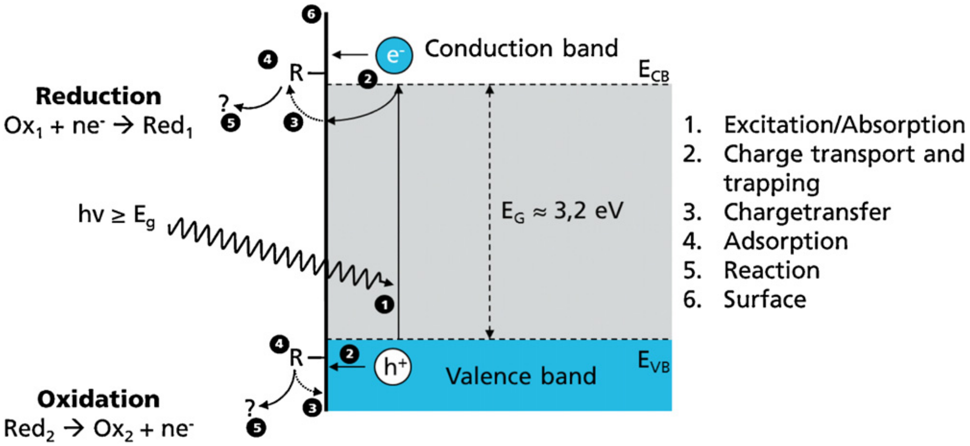

Fig. 1. Photocatalytic generation of radicals at the TiO_2 interface under atmospheric conditions.

decolorization of the redox-dye methylene blue in an aqueous solution, which is in contact to the photocatalyst, the second method features the total mineralization of a solid fatty acid applied as a thin-film by spin-coating or similar techniques, which can be followed by infrared spectroscopy (IR) measurements of the decreasing film-thickness of the fatty acid.

It is known that the methylene blue test is an inappropriate method for measuring the self-cleaning properties of photocatalysts, where solid–solid and solid–air interfaces dominate [7–9]. Several problems arise if the measurement is not performed under well-controlled conditions [10]. The dye adsorption of methylene blue and the pH value of the solution play a key role in the interpretation of the observed kinetics [11]. If this method is considered to be used for the correct determination of the photocatalytic activity, there are many facts to be considered, such as the dye purity, stirring, and the mechanism of photomineralization of the dye itself [12].

Measurement of mineralization of fatty acids like stearic acid features the generation of CO_2 as a final product of PCO, but suffers from the slow degradation process of the solid. Correlation of known photon flux with decreasing thickness-rate measured by IR or increasing CO_2-generation-rate, also evaluated by IR measurements, can lead to a better understanding of the tested samples.

Another indirect method of measuring the self-cleaning performance is the change of the water contact angle on irradiated photocatalysts. In this method, oleic acid is applied on the surface and the irradiation-dependent change in the wettability of the semiconductor substrate is then measured by water contact angle measurements. When the contact angle is <5°, the measurement is finished. It is proposed that the test simultaneously evaluates the decomposition of the acid and the change of wettability. This test lacks a direct quantity of the photocatalytic activity and it cannot be used for hydrophobic surfaces and for porous substrates or samples with a rough surface.

Due to the difficulties of measuring photocatalytic self-cleaning properties, which have to be overcome to evaluate photocatalysts our group examined a new test method of measuring the photocatalytic activity, as some established methods can provide misleading results. The main idea is to use a luminescence measurement method, with a solid-state luminescent dye being applied as a thin-film on the planar surface of the samples. Due to PCO of the dye the luminescence decreases, which gives a direct link to the activity of the photocatalyst.

The applied dye need to comply several requirements to be used as an appropriate compound for this alternate test method, like (i) high solid-state luminescence and quantum yield, (ii) low photolysis, (iii) low absorption within the excitation-range of the photocatalyst, (iv) no luminescent by-products, (v) easy to handle (thermal evaporation, spin-coating), (vi) high Stokes-shift to avoid auto-catalysis, and (vii) no aggregation on the surface, which can lead to luminescence shifts.

Within this kind of test, undesirable factors like stirring or flow control and the choice or the influence of a solvent can be totally neglected. Thus, there would be a certain “ease of use”. Deposition of the dye takes place by an evaporation or sublimation method. As photocatalytically produced radicals can react at the direct vicinity to the dye surface, but also through diffusion [1], the dye layer is decomposed and the luminescence is thereby reduced. This testing method delivers a possible way of achieving the following desirable characteristics for the self-cleaning tests: (i) it features solid–solid and solid–air interfaces, (ii) sensitive measurement of the oxidation process by luminescence detection techniques, and (iii) online measurement of the decreasing luminescence due to PCO.

The dye material class of choice were metal–organic europium(III) complexes for the following reasons, explained in detail. First, there are only a limited number of neutral organic dyes available, which show strong solid state luminescence. Stacking and other effects often lead to quenching and to low quantum yields in the solid state. The second reason is that a photocatalytic decomposition mechanism of an organic luminescent dye poses additional problems in its interpretation, as there are often multiple pathways possible. Even more important is the fact that europium(III), due to its electronic structure, shows definite emission wavelengths with no λ-shifts. In many complexes [13] the most intense emission is observed at $\lambda = 615$ nm. Due to the antenna effect [14] (Figs. 2 and 3), the organic ligands can efficiently absorb light at lower wavelengths ($\lambda \leq 400$ nm), exciting the ligand to the singlet S_1 state (among other excited states). Migration to the triplet T_1 state is an important follow-up energy transfer mechanism. Subsequent energy transfer to the electronic states of the central europium(III) cation is possible. Emission (at $\lambda = 615$ nm) then takes place from the occupied electronic states to the ground level [15,16]. As stated by Bünzli [16] ligand designers try to keep certain energetic gaps between the singlet–triplett levels and the triplett-rare-earth emission levels to allow for an efficient energy transfer (see Fig. 3). The resulting large Stokes shift ($\lambda \geq 200$ nm) clearly separates the emission from the excitation wavelength, which is an additional benefit for analytical purposes.

On a molecular scale europium(III) complexes can be regarded as spheres with an organic shell and an enclosed luminescent center. Neutral beta-diketonate complexes of europium(III) are well-known in the literature and are comprised of three