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Why dyes should not be used to test the photocatalytic activity of semiconductor oxides

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Many studies focusing on heterogeneous photocatalysis for water treatment report on the synthesis of novel semiconductor oxides (which can often absorb visible light) and their characterisation with a broad range of techniques, as well as the test degradation of a model compound (substrate). The substrate is sometimes a dye that can be easily monitored by spectrophotometry. We discuss herein that the use of dyes in photocatalysis is very problematic. First of all, unless the full absorption spectrum is considered, it is possible to have spectral interferences by transformation intermediates, which may absorb radiation at the wavelength of the dye absorption maximum [1].

Furthermore, dyes have an additional and more substantial problem. When degrading a model compound, one wishes to assess the ability of the photocatalyst to photogenerate reactive transient species such as surface- or sub-surface-trapped holes, hydroxyl radicals (trapped on the photocatalyst surface or free in solution), and/or trapped electrons. These transient species can then react with a wide variety of organic and inorganic substrates, accounting for the photocatalytic activity of the studied material [2]. In contrast, any peculiar effects that the photocatalyst may have toward a particular molecule are usually not of interest (unless the aim is to obtain a selective photocatalytic degradation, which is often not the case). In fact, employing the only molecule (or one of the few) that the photocatalyst can degrade, severely limits the conclusions of such a study.

Many dyes have the ability, when photoexcited, to inject an electron into the conduction band of a semiconductor. This property is widely exploited in the field of dye-sensitised solar cells (DSSC), where dyes are used together with a photocatalyst that is usually a semiconductor oxide such as TiO₂ [3]. In this case, radiation is absorbed by the dye, not the semiconductor oxide [3], differently from the typical photocatalytic set-up where the photocatalyst absorbs radiation to produce reactive transients. In a DSSC, the sensitised dye degradation (which could follow the electron injection by the photoexcited dye into the conduction band of the photocatalyst) is prevented by the design of the device, but this would not be the case for an aqueous suspension. The problem with the degradation pathway of a sensitised dye is that it lacks generality, because (i) it cannot be operational with non-absorbing molecules and (ii) for the electron transfer to be allowed, it requires compatible energy levels between the excited state(s) of the dye and the conduction band of the photocatalyst. Sensitised dye degradation is a confounding factor in the assessment of

photocatalytic activity because, in the irradiated suspension, degradation could be due to either a photocatalytic process (the genuine effect one wants to highlight), a dye sensitisation or both.

When using dyes as model molecules, puzzling results can be obtained. Here we show experiments made using TiO₂ Degussa (now Evonik) Aeroxide P25 (TiO₂ P25) which is well known to absorb radiation up to about 360 nm; thus, visible light excitation is not possible with this material [4]. Rhodamine B was used as substrate. Figure 1 shows that the degradation of Rhodamine B in the presence of TiO₂ P25 took place under different irradiation conditions. Control runs without TiO₂ were also carried out, with limited or negligible Rhodamine degradation. The aqueous suspensions containing TiO₂ were centrifuged before spectrophotometric measures and, by applying the same procedure to non-irradiated samples, insight was obtained into the (very limited) adsorption of the dye onto the TiO₂ itself. Under simulated sunlight (Solarbox, emitting radiation above 320 nm), a semiconductor-type mechanism where TiO₂ absorbs radiation and generates reactive species might be hypothesised. The same explanation is more problematic with the two lamps that emit above 380 nm, because the overlap between the lamp emission and the TiO₂ absorption is, if any, extremely limited. Finally, it is very hard to imagine how a yellow lamp (emitting radiation above 480 nm, with a high emission line at 550 and a broad maximum centred at 580 nm) could be able to photoexcite TiO₂ P25. One should thus conclude that a dye-sensitised process was active, which would be the only operational pathway with the yellow lamp (a partially photocatalytic process cannot be excluded under different conditions). Using phenol as substrate instead of Rhodamine B, no degradation with TiO₂ under yellow light was observed.

The above conclusions are rather straightforward, but only because the irradiation experiments were carried out with a material (TiO₂ P25) that is well known **not** to absorb visible light. However, what if the same experiments had been carried out with a novel photocatalytic material, obtained with a synthetic process aimed at extending light absorption into the visible? It would be tempting to conclude that the photocatalyst worked well under yellow light. Our concern is that such a reasoning is quite widespread, with the potential to provide biased conclusions because of the use of dyes as model molecules. This operational methodology does not allow a straightforward discrimination between a dye-sensitised process and an actual semiconductor mechanism. In other words, the use of dyes may complicate the distinction between promising synthetic approaches for new photocatalysts and strategies that will not work, thereby providing inconclusive data.

To sum up, we recommend not to choose dyes as substrates to test the photocatalytic activity of new materials, because of the potential biases associated with their use. Phenol could be a reasonable choice as substrate, if irradiation is conducted at wavelengths above 300 nm. This compound is very easily monitored by liquid chromatography, and there are also several spectrophotometric techniques allowing its detection. An even better choice would be the couple phenol/salicylic acid in separate experiments, because they would provide insight into the role of hydroxyl radicals and of electron-transfer processes (involving holes) in photocatalytic pathways [5].

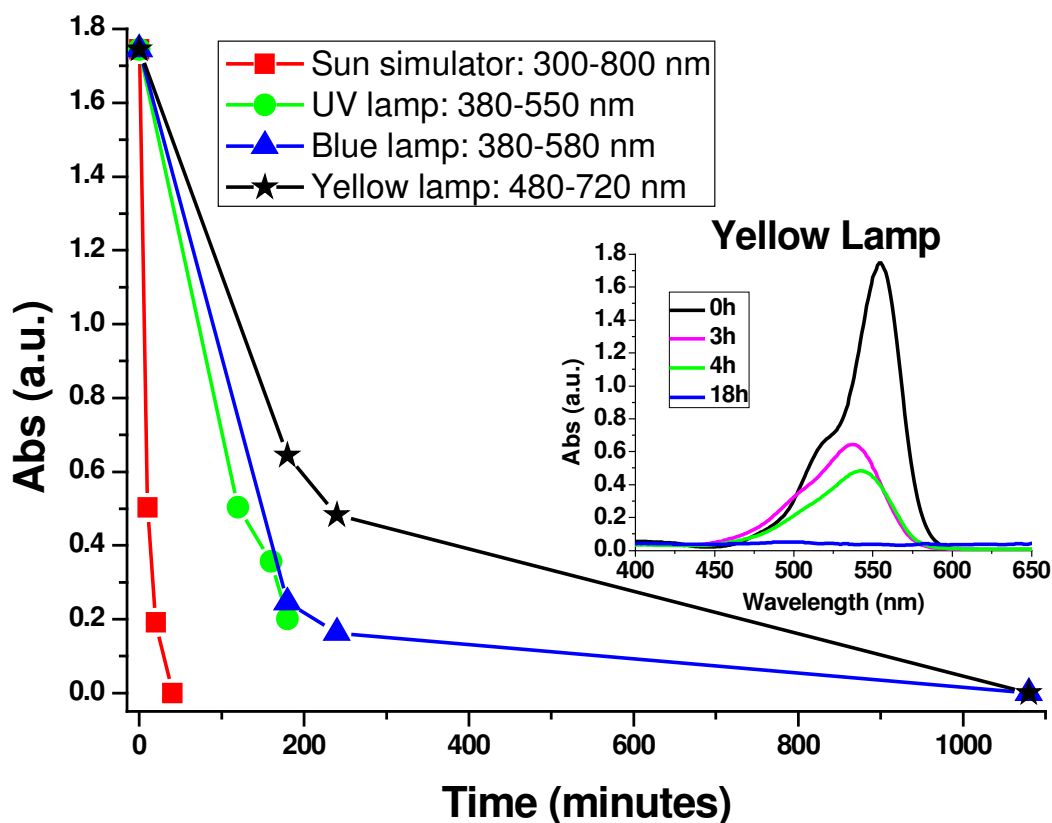


Figure 1. Time trend of Rhodamine B (initial concentration 20-25 μM , assessed at the wavelength of maximum absorption) under different irradiation conditions, in the presence of 2 g L^{-1} TiO_2 . The inset shows the time trend of the Rhodamine B absorption spectrum, upon irradiation with the yellow lamp. The spectral modifications with time suggest the occurrence of coloured transformation intermediates, which would cause an underestimation of the dye degradation. Limited to negligible transformation of Rhodamine B was observed upon irradiation without TiO_2 , under all conditions.

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