A Novel, Fast-Responding, Indicator Ink for Thin Film Photocatalytic Surfaces

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ABSTRACT A new photocatalyst indicator ink based on methylene blue (MB) is described that allows the presence and activity of a thin (15 nm) photocatalytic film to be assessed in seconds. The ink is very stable (shelf life > 6 months) and the color change (blue to colorless) striking. The ink utilizes a sacrificial electron donor, glycerol, to trap the photogenerated holes, leaving the photogenerated electrons to react with MB to produce its reduced, leuco, form (LMB). The efficacy of the MB ink is due to the presence of acid in its formulation, which curtails significantly the otherwise usual, rapid reoxidation of LMB by ambient O_2.

KEYWORDS: photocatalysis • methylene blue • indicator Ink • thin film

Semiconductor photocatalysis (SPC) has been the subject of a great deal of research in recent years (1−4). With the current concern over the health effects of pollution, there has been a growing interest in SPC for the remediation of pollutants in water, air, and, in terms of commercial products, particularly on surfaces, especially where sunlight is used as the source of radiation (5).

The general mechanism of SPC (1−4) involves the absorption of ultra-band-gap radiation ($h\nu \geq E_{bg}$) by the semiconductor photocatalyst, almost always TiO_2, producing electron-hole pairs (e^- and h^+), which can then either recombine with liberation of heat or migrate to the surface of the semiconductor material, where they can react with adsorbed species. The photooxidative mineralization of organic pollutants by O_2, sensitized by SPC, is thought to occur by the formation of highly reactive species, such as the hydroxyl ($OH^\bullet$) and superoxide ($O_2^{\bullet -}$) radicals, formed primarily by the oxidation of adsorbed water or hydroxide (6) by photogenerated holes and possibly by the reduction of O_2 by photogenerated electrons. The results of recent studies of the generation and diffusion of gas-phase reactive oxygen species, such as $OH^\bullet$, singlet O_2, and hydrogen peroxide, from the surface of titania are well summarized in two recent reviews (7, 8).

Recent years have seen the emergence of a wide range of commercial products based on SPC, notably, self-cleaning glass, tiles, and paint (9, 10). In almost all cases, the surface-active form is a thin layer (typically 15 nm thick on self-cleaning glass) of titania. Such coatings are usually slow to act and, therefore, difficult to demonstrate readily because of the thinness of the coatings and the usual modest ambient UV irradiance levels associated with sunlight. Although this activity is acceptable for its intended purpose, i.e., maintenance of an initially pristine surface clean, say, for architectural glass, it makes it difficult for routine activity testing (for quality assurance) and demonstration (for promotion of the technology).

There is a real need for a rapid testing method to help identify the presence of a photocatalyst coating and provide a quick assessment of its activity in the laboratory and in the field. Current methods employed in the laboratory are many and are mostly associated with the *photooxidation* of an organic, such as a stearic acid film (11, 12) or a dye (usually methylene blue, MB) in aqueous solution (13). All are slow, cumbersome, and not suitable for testing films on site.

As an alternative, a *photoreductive* test has been proposed recently for the assessment of SPC activity on thin films (14). This test uses a thin coating of an ink in which the UV-irradiated titania film oxidizes the sacrificial electron donor (SED) present in the ink (glycerol usually), leaving the excess of electrons to reduce the ink dye to a different-colored form that is *not air-sensitive*; the latter feature allows the ink to be used under ambient conditions and the testing of films to be carried out on site. Other work shows that the ability of a titania photocatalyst to reduce the redox dye is directly related to its ability to photomineralize an organic, such as stearic acid, on its surface; i.e., as you might expect the two processes—photocatalytic reduction and oxidation—are correlated (15, 16). Under the same conditions, but in the absence of a SED in the ink, the dye takes many hours, if not days, to photobleach. Thus, the photocatalytic, oxidative bleaching of dyes, such as MB, in a dry ink is extremely slow and not viable as a rapid screening method.

The number of redox dyes that have reduced forms that are stable in air is very limited, and so far only two dyes have been used to create such inks (14), namely, 2,6-dichloroindophenol (DCIP) and resazurin (RZ). A DCIP ink gives good photoreduction kinetics on commercial self-cleaning glass, such as Activ, but lacks long-term stability upon storage because it hydrolyses in a little more than 3 weeks under ambient conditions (17). In contrast, an RZ ink is stable and fast-acting, but the initial photocatalyzed color change, from

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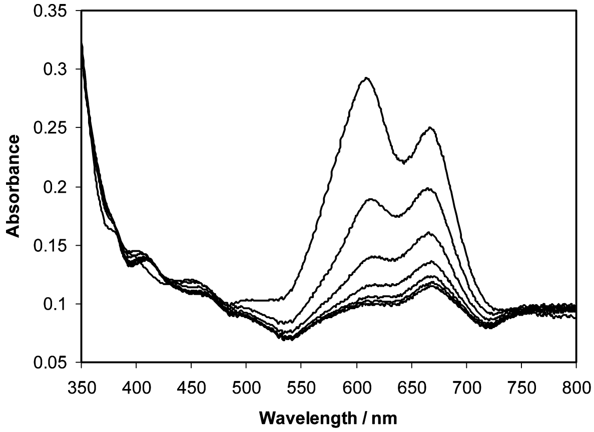

FIGURE 1. UV/vis spectral changes of an *acid* ink of MB coated onto Activ (500 rpm, 15 s) as it is bleached upon irradiation with UV-A (3 mW cm^{-2}) under otherwise ambient conditions. The spectra were recorded every 20 s.

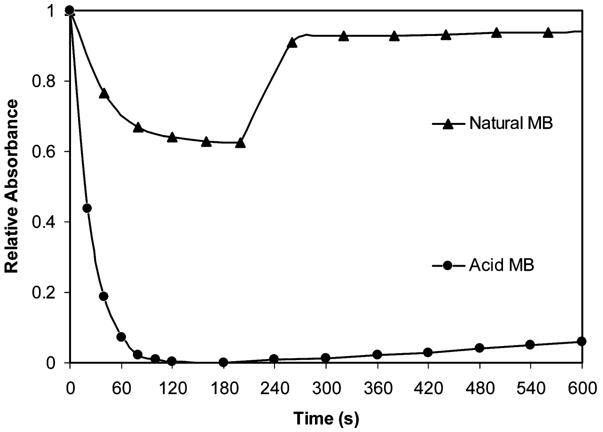

FIGURE 2. Photobleaching and dark recovery profiles of *acid* and *natural* MB inks, cast onto Activ self-cleaning glass. Reaction conditions are as given in Figure 1.

blue to pink, is less definitive than the blue to colorless of the DCIP ink. This paper reports a surprising and promising alternative to these inks using the more commonplace dye MB as the redox dye.

In this work, a typical photocatalyst indicator is made up of 3 g of a 1.5 wt % aqueous solution of hydroxyethylcellulose (medium viscosity, Fluka), 0.3 g of glycerol, and 5 mg of dye (MB, RZ, or DCIP). These three inks are at their *natural* pH (RZ, pH 9.5; DCIP, pH 7.3; MB, pH 5.2), although in one other key formulation, an *acidified* MB ink, was made using 0.01 M HCl, and this is referred to henceforth as the *acid* MB ink. In all cases, the inks were spin-coated onto samples of the commercial self-cleaning glass Activ at 500 rpm for 15 s and then allowed to dry in an oven at 70 °C for 10 min. Other work shows that they can be readily applied using a felt-tip pen, and the dried films produced behave in all respects as the spin-coated films.

Previous work (18) has established that TiO_2 is able to readily effect the photoreduction of MB to leuco-MB (LMB) in solution, provided a SED, such as methanol, is present. However, because LMB is O_2-sensitive and is readily reoxidized to MB, it seems initially unlikely that an effective photocatalyst indicator ink could be created using MB as the redox dye, which, as noted earlier, must produce a reduced form of the dye that is *not* O_2-sensitive. Fortunately, it has long been known that the redox equilibria of dyes, such as MB, are strongly influenced by the pH (19), and others have noted that, in the dark at pH 2, LMB is stable in an air-saturated *solution* for many minutes but is rapidly oxidized to MB^+ at higher pH (20). Thus, it would appear possible that a MB-based photocatalyst indicator ink could be created by *acidifying* the MB ink formulation. A quick study of the performance of an *acid* MB ink coated onto Activ self-cleaning glass revealed that upon irradiation with UV-A light it was possible to effect the complete photoreduction of MB under ambient aerobic conditions, as illustrated by the results in Figure 1.

The photobleaching and subsequent dark recovery absorbance versus time profiles of *acid* and *natural* MB inks are shown in Figure 2. Immediately noticeable is the fact that the *natural* MB ink is not photobleached completely during the irradiation process but rather reaches a semibleached steady state after approximately 1 min of UV irradiation, a state that subsequently exhibits a dark recovery that is extremely quick when compared to that of the *acid* ink. In contrast, the *acid* MB ink is rapidly and completely photobleached and recovers its color only very slowly in the dark.

This slower rate of oxidation of LMB by ambient O_2, also observed by others in homogeneous solutions (20), is due, in part at least, to the fact that the overall driving force for the oxidation of LMB by O_2 (which is reduced to H_2O_2) is smaller at pH 2 than at pH 7 by ca. 40 mV because of the complex, but not unusual for a dye, variation in the formal redox potential of the MB/LMB couple as a function of the pH (17, 19). Note, however, that at pH 2 the difference in the formal redox potentials of the two redox couples is large and positive (0.210 V), implying that there is an as-yet-unidentified mechanistic feature that is mainly responsible for the surprising significant decrease in the rate of oxidation of LMB by ambient O_2 at low pH.

In this heterogeneous system, another contributing factor will be that most of LMB ($pK_a = 1.7$) is protonated and so not adsorbed on the highly positively charged surface of titania at pH 2 (pzc = 6.8 (21)). That the photoreductive bleaching of cationic MB by the protonated surface of titania occurs rapidly both in a dried ink and in aqueous solution (18) appears, on coulombic repulsion grounds at least, surprising. Clearly, other factors must dominate, and in support of this, it is worth noting that, over the pH range 3−9, Houas et al. found that the amount of MB adsorbed, n_{ads}, onto P25 increased relatively smoothly by a factor ca. 4, with no simple dependence of n_{ads} on the titania surface charge and that the rate of MB photooxidation behaved similarly (22).

The overall process can be summarized as follows: in both *natural* and *acid* MB inks, the MB is reduced to LMB (i.e., colorless) by photogenerated electrons, while the holes react with the SED, glycerol, in the ink

$$MB^+ + SED \xrightarrow[E_{bg} \ > \ 3.2 \text{ eV}]{TiO_2} LMB + SED_{ox} \qquad (1)$$

where SED_{ox} is glyceric acid or glyceraldehyde.

Under *natural* pH conditions, LMB rapidly reacts with ambient O_2, leading to the regeneration of the MB.

$$LMB + O_2 + H^+ \rightarrow MB^+ + H_2O_2 \qquad (2)$$

As a consequence, UV irradiation of a *natural* MB ink film only leads to its partial bleaching and a subsequent rapid recovery of its color in the dark (see Figure 2). In contrast, in films of the *acid* MB ink (in which the local [HCl] ≈ 0.1 M), reaction 2 is sufficiently slow (20) that photobleaching of the ink is effected rapidly and persistents under ambient conditions, using a UV-A intensity equivalent to that of a mildly sunny day (23).

Most striking about the *acid* MB photocatalyst indicator ink is how it performs when compared to the two previous inks based on RZ and DCIP. Typical times taken to half bleach the inks are given in Table 1 and reveal the *acid* MB ink to be the most effective of them all. This feature, coupled with the stability of the ink formulation (> 6 months), marked color change, and inexpensive nature of the redox dye, makes the *acid* MB ink a promising, new material for assessing the SPC activity of photocatalyst films in situ. In conclusion, the MB acid ink provides a rapid assessment method for thin and/or low-activity photocatalytic films. It can be easily effected by noting by eye the time it takes for the film to lose its color upon irradiation with UV light. As with all photocatalytic assessment tests, it requires a source of UV light, which may be a UV-A lamp in the laboratory or the sun for outdoor work. For comparative studies, a UV meter is needed to provide knowledge of the incident UV irradiance. The water-soluble MB ink and its components do not stain the glass and are easily removed by rainwater or wiping with a damp cloth. Such an ink should prove to be of great help to both the academic and industrial communities working in the field of SPC, especially with regard to the product: quality control, demonstration, and assessment in the field.

Table 1. Observed Photocatalyzed Bleaching (in Air) Half-Lives of the *Natural* DCIP and RZ Inks and an *Acid* MB Ink, Deposited onto Activ (Incident UV-A Intensity 3 mW cm^{-2})

dye	half-life ($t_{1/2}$), s
RZ	132
DCIP	56
MB (∼pH 2)	17

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