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Bleaching of Methylene Blue by Hydrated Titanium Dioxide

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ABSTRACT: Hydrated titanium dioxide, h-TiO_2, was prepared by hydrolysis of $TiCl_4$ with concentrated NH_3 solution. Due to its considerably high surface area h-TiO_2 can adsorb a large amount of methylene blue on its surface, about nine times as much of Degussa P25. It can photocatalyze the decomposition of methylene blue, albeit slightly inferior to Degussa P25 if adsorption is excluded. In the presence of dilute H_2O_2 and with UV light, h-TiO_2 can bleach methylene blue as well as Degussa P25. However, under similar conditions, but without UV light, h-TiO_2 can bleach methylene blue much better than Degussa P25.

KEYWORDS: photocatalyst, titanium dioxide, amorphous titanium dioxide, methylene blue, dye degradation, adsorption.

INTRODUCTION

Titanium dioxide has been the prevailing photocatalyst in heterogeneous photocatalysis due to its being chemically and biologically inert, non-toxic, inexpensive, and environmentally safe. Some metal sulfides may also be photocatalytic, but they have some weakness in terms of corrosion. Iron oxide may be inexpensive, but it can also be corroded. Zinc oxide is probably the closest competitor of titanium dioxide but its weaknesses are instability in some solutions and a tendency for its hydroxide to cover its surface, causing lower photocatalytic activities.[1-6]

Titanium dioxide exists in three crystal structures (anatase, rutile, brookite) and each behaves differently. Even the same form if prepared by different methods can also show different properties due to different surface area, porosity, and functional groups at the surface. This fact was borne out in the study of phenol degradations by titanium dioxide prepared differently with different crystallinities.[7] In another report involving the degradation of trichloroethylene and dichloroacetic acid by twelve titanium dioxides commercially available, the initial rate of decomposition was shown to depend on the anatase crystallinity, while rutile showed low photocatalytic activity.[4] Later studies used titanium dioxide in the anatase form as photocatalyst, for example, in the degradation of oxalate,[8] the remote bleaching of methylene blue (MB),[9] and the photocatalytic oxidation of heptane in the gas-phase.[10] Besides anatase, another commercial titanium dioxide known as Degussa P25, a non-porous powder with surface area ~51 m^2/g, is also prevalent as a photocatalyst. P25 is a mixture of anatase (~80%) and rutile (~20%), and shows high photocatalytic activity compared with other forms of titanium dioxide. Many works have employed P25 as their main photocatalyst such as in the degradation of colored organics (including MB) in water,[11] the degradation of monocrotophos,[12] the degradation of microcystin,[13,14] the degradation of oxalic acid,[15] studies to identify the MB degradation pathways,[16,17] and the degradation of acid blue 74.[18] There have been, however, only a few works that studied or mentioned amorphous titanium dioxide. Among those, the most notable one was by Ohtani *et al*. which found that, in the oxidation and dehydrogenation of 2-propanol, amorphous titanium dioxide had negligible photocatalytic activity and the main source of the photocatalytic activity came from titanium dioxide in the anatase form.[19]

All the titanium dioxides used in the above mentioned works were either supplied commercially or synthesized in-house. No matter what their sources, these oxides were all precalcined, usually at around 300 – 400°C, before use. This means a considerable amount of the TiO_2 powder would turn to anatase or even to rutile if calcined at higher temperature. Calcination would also drive off the water molecules which adhered to TiO_2 surface as an OH moiety bound to Ti atom at the surface. The titanium dioxide used in this work, hereinafter referred to as " h-TiO_2 ", was synthesized without calcination so its composition mostly consisted of an amorphous form with a small amount of anatase mixed in. Since no calcination was employed, h-TiO_2 powder was mostly present in an amorphous form with some hydrated water molecules. Its surface area was also significantly higher than that of commercially available anatse / rutile or P25 due to its amorphous morphology. It would be interesting to see if h-TiO_2 would work as the photocatalyst. Simple synthesis with elimination of the calcination step would mean lower costs for chemicals and energy consumption and a shorter lapse time between the in-house synthesis and the application stages.

MATERIALS AND METHODS

Synthesis of H-TiO_2

The main chemicals are titanium tetrachloride and titanium dioxide (anatase), AR grade, from Carlo Erba (Rodano, Italy); methylene blue from Riedel de Haën (Seelze, Germany); and titanium dioxide (Degussa P25) from Degussa AG (Frankfurt, Germany). All other reagents were AR grade from various suppliers.

H-TiO_2 was prepared by slowly adding concentrated ammonia solution (~28%) to the flask containing titanium tetrachloride with constant stirring until white precipitate formed. The precipitate was filtered gravimetrically followed by washing several times with distilled water until the wash was free of chloride and ammonium ions ($AgNO_3$ and NaOH tests , respectively). The white precipitate, h-TiO_2 ,was dried at 105°C for 2 hrs and ground to 200 mesh before used. Characterizations of h-TiO_2 were carried out by x-ray diffraction (XRD) on a PW 3710 mpd control with Ni-filtered Cu Ka radiation, (Philips, Amello, Netherland), fourier transform-infrared spectroscopy (FT-IR) on a EQUINOX55 FTIR (Bruker Optics, Ettlingen, Germany), thermal gravimetric analysis (TGA) on a PE TGA7 (Perkin Elmer, Norwalk, CT, U.S.A.), and the surface area (BET method)* on an Autosorb-1-C (Quantachrome Instruments, Boynton Beach, FL, USA).

Photocatalysis Study

In the photocatalysis studies, TiO_2 powder was placed in an erlenmeyer flask and measured volume of MB solution (1×10^{-4} M) was added. The ratio of TiO_2 to MB solution was 0.5 g of TiO_2 per litre of MB, for instance, 0.025 g of TiO_2 per 50 mL of MB. This mixture was then irradiated under UV-light (blacklight 20 watts, F20T12-BLB, CE, U.S.A.) and magnetically stirred at 500 rpm for a predetermined period. The entire set up was placed in a tightly closed wooden compartment (0.5 m × 0.5 m × 0.5 m) to avoid interference from ambient light. The blacklight tube was attached in a fixed position inside the top side of the compartment. The second tube was attached to the side wall of the compartment. After irradiation the mixture was centrifuged and the clear solution was measured at 656 nm for the absorbance of the remaining MB (UV-Visible Spectrophotometer HP8452 Diode Array, Hewlett Packard, Germany). The concentration of MB after each experiment was determined quantitatively through the calibration graph constructed from standard solutions of MB at various concentrations.

In the studies on the effect of H_2O_2 on photocatalytic activity the same set up was employed as above with one tenth volume (of MB) of 0.2 M H_2O_2 added to the reaction mixtures. Two controlled experiments were also run simultaneously, one containing only MB and H_2O_2 while the other only MB and TiO_2. (Water, of the same volume of H_2O_2, was also added to the latter to correct for the dilution effect which might have occurred from adding H_2O_2.) After irradiation, the mixtures were subjected to the same treatment as above

RESULTS AND DISCUSSION

Characterization of h-TiO_2

XRD data of h-TiO_2 showed weak broad peaks at (2θ) 25.4, 38, 48, 53 and 55 corresponding to the 101, 004, 200, 105, and 211 reflections of TiO_2 in the anatase form (Fig 1).[20] The broad appearance of the peaks indicated that the h-TiO_2 was mainly the amorphous form of TiO_2 with a small amount of anatase mixed in. By using the standard addition method, the anatase form was determined to be around 5%.

The FT-IR spectrum of h-TiO_2 (Fig 2) had a large broad band at 3100-3600 cm^{-1} and rather narrow bands at 1633 and 1440 cm^{-1}. The broad band at 3100-3600 cm^{-1} could be assigned to both ν_{OH} and ν_{NH} (stretching modes) while those at 1633 and 1440 cm^{-1} were assigned to δ_{OH} and δ_{NH} (bending modes) of hydroxyl (OH) and ammonium (NH_4^+) groups, respectively.[21, 22]

The TGA curve of h-TiO_2 (Fig 3) showed a fast decrease in weight in the range 30-150°C, after which the rate of decrease was slow and reached the completion at around 400°C. The overall weight loss was 14.15%, which corresponded to loss of 0.7 molecule of H_2O from $TiO_2.(0.7)H_2O$, or roughly $TiO_2.H_2O$, yielding TiO_2 at the completion of the heating. The abrupt decrease observed at 30-150°C should be the loss of H_2O from the solid. This loss, in fact, should correspond to mixed H_2O and NH_3 (or OH^- and NH_4^+ as identified by FT-IR). Since the amount of NH_3 or NH_4^+

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* The method proposed by Brunauer, Emmett, and Teller in 1938 based on gas adsorption-desorption on the sample surface and calculation thereafter using the so-called BET equation.

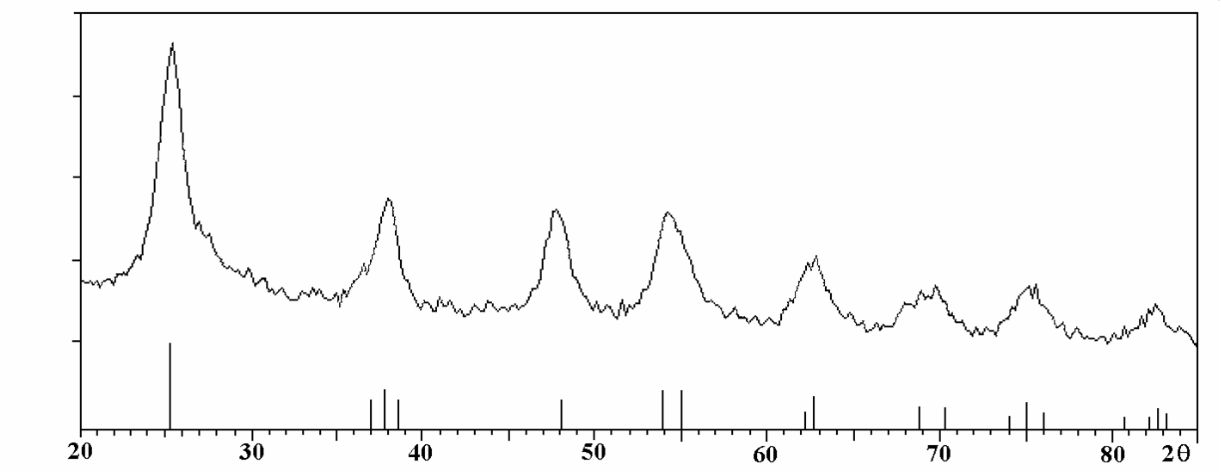

Fig 1. XRD pattern of h-TiO_2 (all the broad peaks belong to anatase).

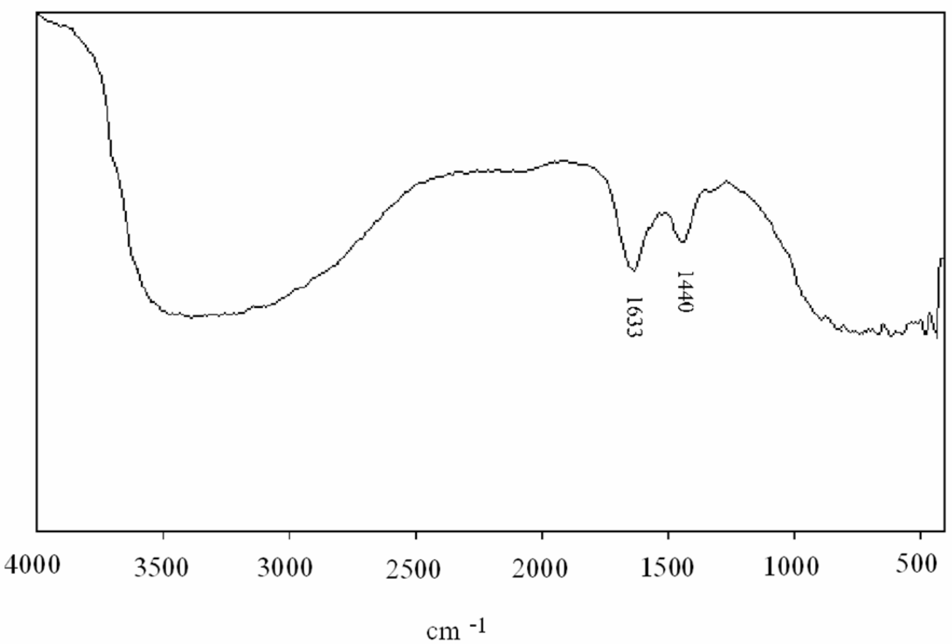

Fig 2. FT-IR spectrum of h-TiO_2.

was almost negligible from elemental analysis, we tentatively put the formula here in the generally accepted hydrated form to the nearest integer as $TiO_2 \cdot H_2O$. Khalil and Zaki obtained similar thermogram (as in Fig 3) but in their system the weight loss was 31% corresponding to losing of 2 molecules of H_2O from $TiO_2 \cdot 2H_2O$.[21]

The BET surface area of h-TiO_2 was 237 m^2/g. Samples of commercially available anatase / rutile and P25 were also measured, their surface areas were similar to those reported in the literatures.

Photocatalytic Activity

The UV source used in this work was the 20 watt blacklight tube, which emits UV light in the range 346-395 nm with a maximum at 366 nm (Fig 4). Without UV irradiation P25 did not bleach MB, the bleaching occurred only when irradiation was applied. H-TiO_2, however, showed the surprising result that it could bleach MB both with and without irradiation. But, the disappearance of MB color without irradiation was presumably due to adsorption rather than photocatalyzed degradation. This conclusion was supported by observing that the final solution from the irradiated set was clearer and more colorless than that of the non-irradiated set, and if higher concentration of MB was used some color would remained in the final solution of the non-irradiated set. Direct comparison between h-TiO_2 and P25 in bleaching MB over a long period with UV irradiation is shown in Fig 5. At first, this may

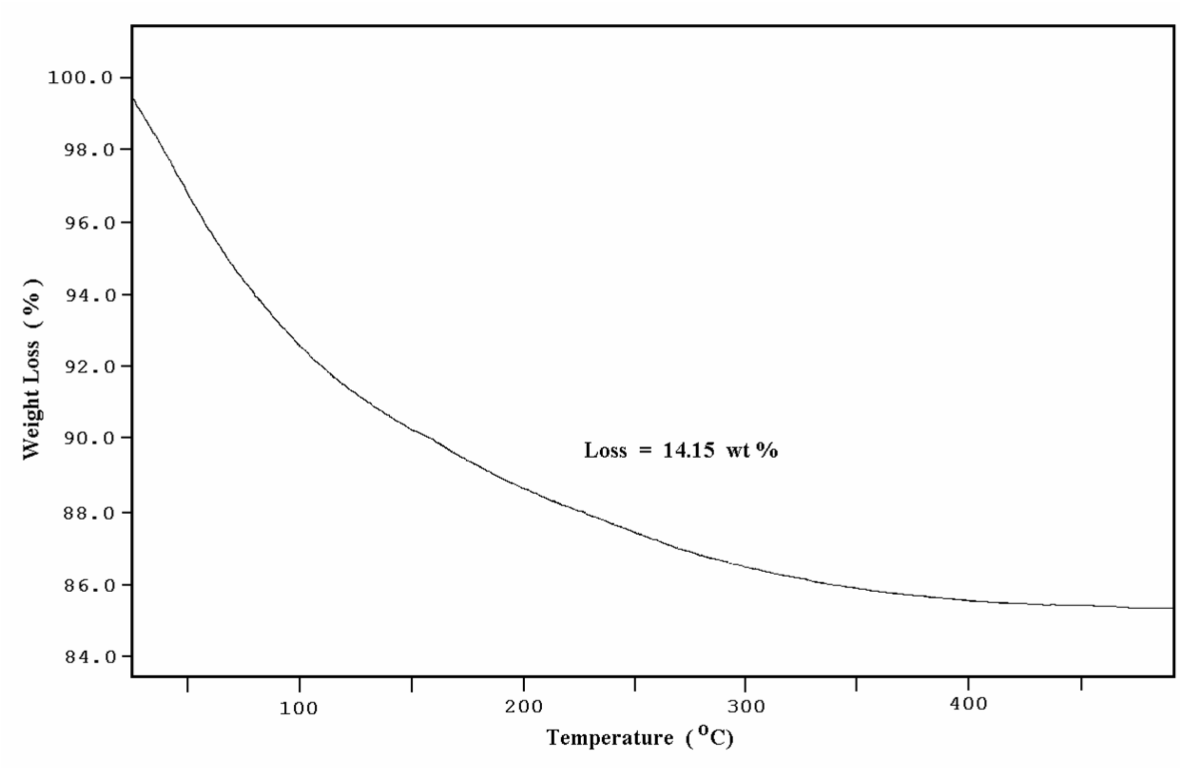

Fig 3. TGA curve for h-TiO_2.

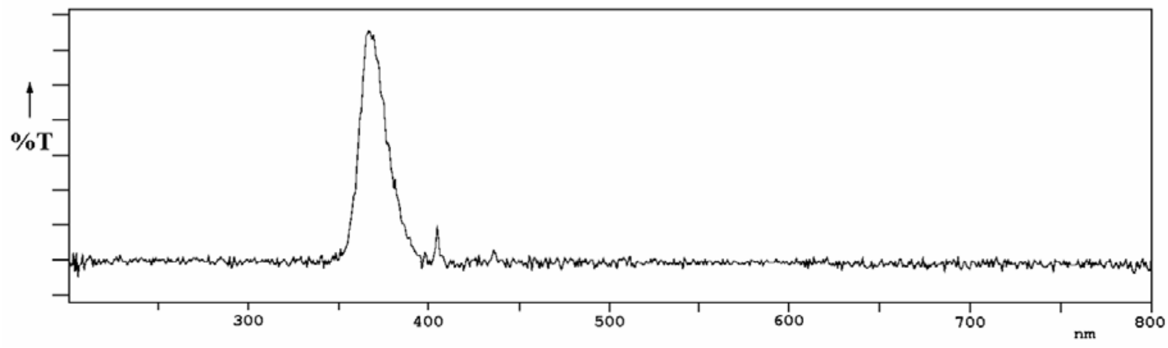

Fig 4. Spectrum of UV light source used in this work.

mislead one to think that h-TiO_2 is a better photocatalyst than P25. This is the result of cooperation, or the synergistic effect,[*] between surface adsorption and photocatalytic properties shown by h-TiO_2. Xu, et al.[23] pointed out that titanium dioxide could adsorb MB on its surface extremely well and in their experiment they even allowed MB to be adsorbed on titanium dioxide until saturation, which took only about 10 minutes, prior to doing the photocatalytic experiment.

The intensity of the UV light could be varied by increasing the number of light tubes from 1 to 2. At higher light intensity, P25 could bleach MB at a much faster rate compared with that at lower intensity. This result agreed with the finding that the rate of the photocatalytic decomposition of 2-chlorophenol was first order with respect to UV light intensity.[25] For h-TiO_2, the rate of bleaching at lower intensity was also increased, but only slightly as shown in Fig 6.

The appearances of the two TiO_2 powders after each experiment were quite different. For h-TiO_2, if allowed to adsorb MB in the dark (only adsorption occurred), the powder was bright blue (the same color as MB solution). In water some of the blue pigment could dissolve, yielding a light blue solution. After

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[**] Similar synergistic effect was also observed in TiO_2-Zeolite system.[24]

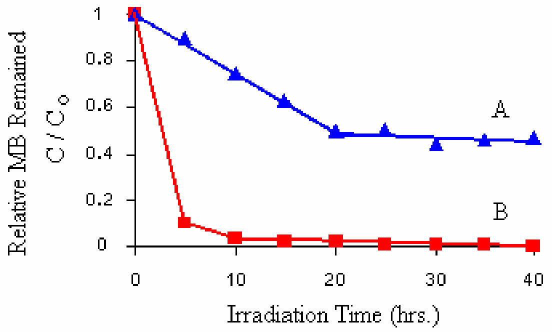

Fig 5. Bleaching of MB (A) P25, (B) h-TiO_2 (including adsorption).

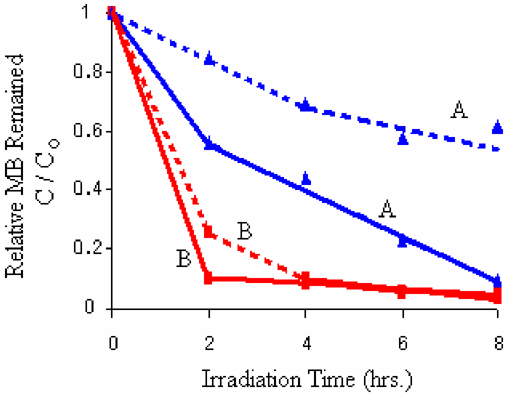

Fig 6. Effect of UV light intensity on (A) P25 and (B) h-TiO_2 (including adsorption). The Dotted line is for 1 blacklight tube, the solid line for 2 blacklight tubes.

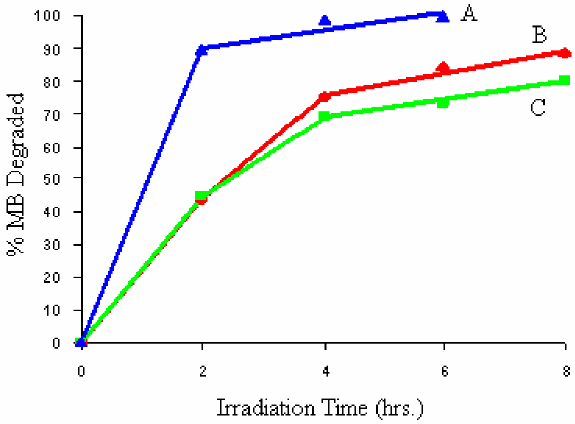

Fig 7. Photocatalytic activity of (A) P25, (B) h-TiO_2 and (C) commercial anatase (excluding adsorption).

photocatalysis reaction, the h-TiO_2 powder was dark purple while that of P25 was pale blue.

These results showed that without irradiation h-TiO_2 could reduce the amount of MB by adsorption to some extent, however, the bleaching efficiency increases dramatically through photocatalysis.

Comparing the Photocatalytic Acitivity of h-TiO_2 with Commercial Anatase and P25

In mixing TiO_2 with MB solution for the photocatalysis experiments, the adsorption of MB on the catalyst surface takes place instantly prior to the photocatalytic measurements. Since the purpose was to test and compare the photocatalytic activity alone, so the first adsorption stage must be excluded by allowing the TiO_2 samples (h-TiO_2, commercial anatase, and P25) to adsorb MB until reaching their corresponding saturation point prior to irradiation with UV light (using the higher intensity set up). (The adsorption of these three TiO_2 species were 38.78, 8.45 and 4.28 mg of MB per 1 g of h-TiO_2, commercial anatase (Carlo Erba) and P25, respectively. These values are about ten times higher than that reported by Xu *et al.*, where they reported 3.60 mg of MB per 1 g of amorphous TiO_2 and 0.36 mg for anatase with BET surface area 12.44 m^2/g).[23]

The results from this experiment are shown graphically in Fig 7. Considering only the photocatalytic activity alone, P25 is the best among the three, but the other two are not far behind. From Fig 7, P25 could bleach 89.46% of MB in 2 hrs and rendered the solution colorless (correspond to 99.55%) in 6 hrs. h-TiO_2 and commercial anatase could bleach equally well at about 44% (2 hrs.), but if allowed longer time h-TiO_2 was slightly better. At 8 hrs h-TiO_2 bleached 88.16%, while commercial anatase could bleach only 79.64%. This experiment, therefore, clearly showed that h-TiO_2 does have the photocatalytic property that was comparable to commercial anatase, albeit inferior to P25.

Effect of H_2O_2 on Photocatalytic Activity

The photocatalytic performance can be enhanced by hydrogen peroxide.[11,26] In this respect h-TiO_2 and P25 were compared in the presence of a small amount of H_2O_2 with the result that both h-TiO_2 and P25 performed equally well with H_2O_2 and UV-light, but without UV-light (in the dark) h-TiO_2 was much better than P25 (the catalysts were allowed to adsorb MB until saturation prior to irradiation). These results are shown graphically in Fig 8 where h-TiO_2 and P25 could bleach MB 94.97% and 94.08%, respectively, with the UV-light and H_2O_2. However, in the dark with H_2O_2, h-TiO_2 could bleach MB 95.47% in 1 h.[***] Under this same condition, P25 did not perform that well ; that is only 35.81% after 1 hr and increased to 66.19% and 89.95

[***] Bleaching of methylene blue with h-TiO_2 and H_2O_2 took place very fast. Most of the color faded away in *ca*. 10 min. either with UV light or without. The 1 hr elapsed time here was just to wait for the slower P25, in the dark, to allow the bleaching to proceed far enough to be measurable.

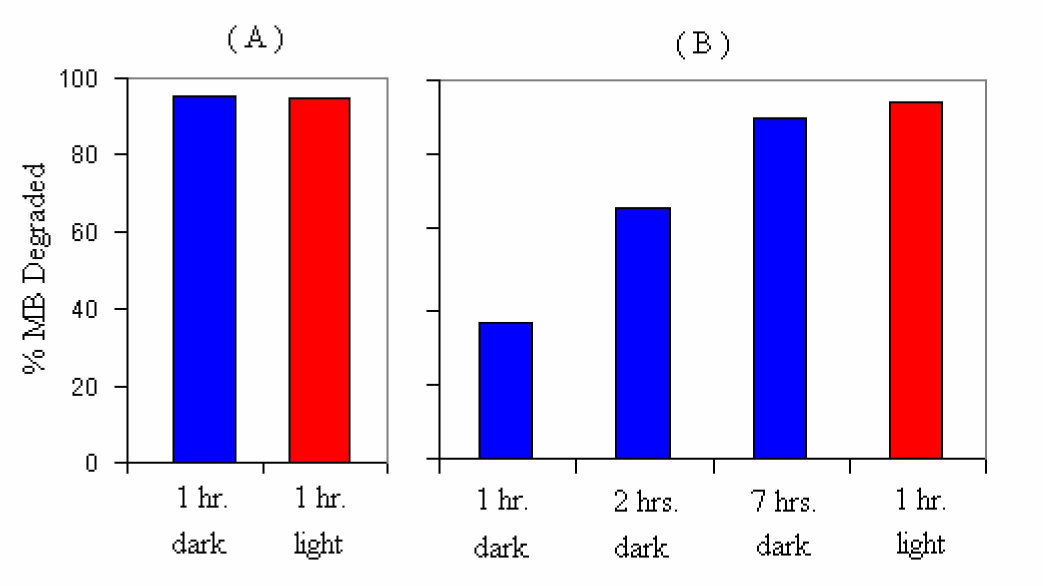

Fig 8. Degradation of MB using (A) h-TiO_2 + H_2O_2 and (B) P25 + H_2O_2.

% after 2 and 7 h., respectively. So h-TiO_2, with the aid of H_2O_2, can decompose MB with no need to use UV light. In the controlled experiments, MB solution alone was irradiated for 1 hr., no bleaching occurred, and in the presence of only H_2O_2 under the same conditions, only 23.5 % bleaching occurred.

H-TiO_2 powder in contact with H_2O_2 turned to a yellowish orange color, while P25 turned to a much fainter yellowish color. This yellowish orange color is typical of a peroxy titanate complex which has peroxide (O_2^{2-}) bonded to the metal ion as a bidentate ligand.[27] After both the photocatalytic and in-the-dark reactions, h-TiO_2 powder turned to dull blue (a trace of yellow color could be seen mixing with the blue color).

Consider that P25 is a better photocatalyst without H_2O_2, but, with H_2O_2, both P25 and h-TiO_2 performed equally well in the presence of UV light while, with H_2O_2, in the absence of UV light h-TiO_2 was better than P25. We believe that to explain these results the surface area is the key factor, since h-TiO_2 has 4.6 times higher surface area than P25.

1. $TiO_2 + hn \rightarrow e^-_{CB} + h^+_{VB}$
2. $O_{2\,(ads)} + e^-_{CB} \rightarrow O_2^{\bullet -}$
3. $(H_2O \leftrightarrow H^+ + OH^-)_{(ads)} + h^+_{VB} \rightarrow H^+ + {}^{\bullet}OH$
4. $O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}$
5. $2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
6. $H_2O_2 + e \rightarrow {}^{\bullet}OH + OH^-$
7. $R_{(ads)} + {}^{\bullet}OH \rightarrow$ degradation products
8. $R'_{(ads)} + h^+_{VB} \rightarrow$ degradation products

Scheme I Possible steps involved in MB degradation by TiO_2 photocatalyst.[17]

1. $O_{2\,(ads)} + e^-_{DB} \rightarrow O_2^{\bullet -}$
2. $O_2^{\bullet -} + H_2O \rightarrow HO_2^{\bullet} + OH^-$
3. $2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
4. $O_2^{\bullet -} + Ti^{4+}_{(s)} \rightarrow Ti^{3+}_{(s)} + O_2$
5. $Ti^{3+}_{(s)} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Ti^{4+}_{(s)}$
6. $MB_{(ads)} + {}^{\bullet}OH \rightarrow$ degradation products

Scheme II Tentative pathway to degrade MB by h-TiO_2 with H_2O_2 in the dark. $Ti^{4+}_{(s)}$, $Ti^{3+}_{(s)}$, and e^-_{DB} represent metal ions and an electron available from dangling bond, respectively, at the solid surface.

In the case of the simple photocatalytic reaction, i.e., with UV light but no H_2O_2, the degradation of MB should go through the interaction with the electron – hole pair (e^-_{CB} - h^+_{VB}) as usual. The recently proposed MB degradation mechanism for the irradiated TiO_2 system is summarized in Scheme I.[17] In step (2) of Scheme I, $O_{2(ads)}$ comes from the O_2 that was present in the system and was adsorbed onto the surface of the catalyst. In the bleaching of MB, step (7) R = MB and since MB has a cationic configuration it should be favorably adsorbed to the negative sites of the h-TiO_2 surface, e.g., $Ti\text{-}O^{(-)}$ and subsequently attacked by the very active ${}^{\cdot}OH$ moiety, leading to the destruction of the MB molecule. We believe this scheme holds true in our work as well both with P25 and h-TiO_2 when irradiated with UV light – both with and without H_2O_2. With H_2O_2, the hydroxyl radical can form in higher concentrations and take part in the degradation process, thus, accelerating the photocatalized degradation.

The only case that requires a different explanation from that above was that h-TiO_2 could also bleach MB in the dark with H_2O_2. Since the catalyst was not irradiated we can logically conclude that the $e^-_{CB} - h^+_{VB}$ pair were not created. Hence, step (1) in Scheme I was not needed, nor were other steps involving h^+_{VB}. Here we can invoke the advantage of using transition metal ions for their flexibility in utilizing electrons in the d orbitals. It is rather common that H_2O_2 can give up hydroxyl radicals in systems with transition metals such as Fe^{2+}, Cu^{2+}.[28,29] Another key feature is the coordination number of the metal ions at the solid surface, which can be less than the saturation number (usually six for transition metal ions) due to the occurence of some dangling bonds at the surface. The Ti atoms at the surface could have a dangling bond with an electron left with it.[****] A dioxygen (O_2) molecule can be adsorbed on the catalyst surface by binding to the metal atom at this empty site and subsequently be reduced to $O_2^{\cdot-}$ by an electron from the dangling bond. This is equivalent to step (2) in Scheme I, except that it did not require irradiation to generate e^-_{CB}. It took advantage of dangling bond at the surface of the transition metal oxide solid. A similar pathway can be proposed here for the degradation of MB by h-TiO_2 with H_2O_2 in the dark, as shown in Scheme II.

In Scheme II, the steps involving the transition metal ion are analogous to the so-called superoxide driven Fenton's reaction with Ti^{3+} / Ti^{4+} replacing Fe^{2+} / Fe^{3+}.[30] Step (3) shows that H_2O_2 was produced and consumed within the process in step (5). Thus, when H_2O_2 was added directly in trace amounts, the bleaching was enhanced even in the dark.

Why did P25 behave differently from h-TiO_2 (with H_2O_2 and in the dark)? There is another property that we have to bring into the scenario, that is, the functional group adhered to the surface of the catalyst, i.e., OH^- as identified by FT-IR. The OH^- groups are present in amorphous TiO_2 more abundantly than in the anatase form.[4] The presence of more OH^- groups means the catalyst is less crystalline, i.e. being more amorphous and hence having high surface area.

The high surface area of the catalyst enables the reactant molecules to be adsorbed more densely on the catalyst surface leading to more rapid reaction. On the other hand, being more amorphous, i.e., low crystallinity, would enhance the rate of e^-_{CB} - h^+_{VB} recombination during irradiation, therefore the amorphous TiO_2 was found to be inferior to anatase as a photocatalyst.[19] P25 has higher crystallinity and less OH^- group at the surface, hence less surface area as evidenced by its low adsorptivity of MB. As a result, the number of H_2O_2 and MB molecules adsorbed on the surface of P25 are much less than that in h-TiO_2. This lower population at the surface should be the main factor to be considered for the fact that P25 (with H_2O_2 and in the dark) bleached MB much slower than h-TiO_2. We have seen that h-TiO_2 is a poorer photocatalyst than P25, but if adsorption is allowed simultaneously the combination of both, the synergistic effect, renders h-TiO_2 more effective than P25 in bleaching MB.

CONCLUSION

Titanium dioxide synthesized in this work, h-TiO_2, exists as a hydrated amorphous form with considerably high surface area and shows an interesting property of being both surface adsorbent and photocatalyst. As a photocatalyst, it can decompose MB when irradiated with UV light, however, it is slightly inferior to P25. With H_2O_2 added h-TiO_2 photocatalyzed the decomposition of MB as well as P25. However, in the dark with H_2O_2, h-TiO_2 could bleach MB far better than P25.

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[****] Dry samples of h-TiO_2 and P25 powder were checked by ESR both at room temperature and at 77 K. No signal was detected for P25 at both temperatures. For h-TiO_2 there was always one small signal detected in the range g = 1.9636-1.8880 (from several samples) at room temperature. One sample showed no signal at room temperature, but at 77 K one signal in the same region was detected. These g values correspond to Ti^{3+} centers in the bulk of TiO_2.[30]

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