



## Effect of aggregation of methylene blue dye on TiO<sub>2</sub> surface in self-cleaning studies

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### ABSTRACT

The present paper shows that the aggregation behavior of methylene blue in the monomer, dimer or aggregated forms is responsible for the inconsistency in the photocatalytic performance studies in various photocatalysts materials. The aggregation behavior of MB and its influence on photocatalytic degradation of the dye during photocatalytic performance study has been characterized by UV–visible absorption spectroscopy. The results indicate that the photocatalytic degradation of dyes depends not only on the intrinsic parameters of photocatalysts but also on the aggregation behavior of the pollutant on the catalyst surface.

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### 1. Introduction

There have been efforts in recent years to develop heterogeneous photocatalysts with high photocatalytic activities for their application in solving environmental problems [1]. Recent results in the TiO<sub>2</sub> photocatalysis studies suggest that there is plenty of room for improvement and there is still a lack of fundamental insight into what makes TiO<sub>2</sub> a good photocatalyst [2]. Detailed investigation on the TiO<sub>2</sub> intrinsic parameters such as structure, degree of crystallinity, defects, crystallographic planes, surface hydroxyl and dopants apart from extrinsic parameters like pollutant concentration, pH, temperature, and humidity have been made by several groups. However, there is no report on the influence of model pollutants (dyes) on the surface of the photocatalyst during adsorption as well as photocatalytic reaction, even though adsorption is the primary step in the photocatalytic reactions. Generally, for the evaluation of the performance of a photocatalyst, two types of reactors, viz., slurry-type and immobilized-catalyst-type reactors have been used. As model pollutants, formaldehyde, acetaldehyde, methyl orange, etc., have been used in many of the photocatalytic degradation studies. Methylene blue (MB) has been widely used as a dye in most of the photocatalytic studies in the last two decades [3,4] and it has been accepted as a model pollutant in the Japanese industrial standard JIS R 1703–2:2007 to eval-

uate the self cleaning thin film surfaces. However Yan et al. conclude that MB may not be an appropriate substrate for photocatalytic activity test due to photo-absorption, which could affect the photocatalytic degradation kinetics under visible light [5]. They suggested the possibility that MB could aggregate on the surface of the TiO<sub>2</sub> particles. There is a possibility of aggregation on the surface of TiO<sub>2</sub> particles or thin films while performing the photocatalytic studies on slurry or immobilized-type reactor. The interesting information on the surface may remain hidden on solely analyzing the model pollutant. Thus, there is a need to analyze the pollutant-catalyst interface to completely understand the self cleaning performance.

In this communication, UV–visible absorption spectroscopy is being used to characterize the aggregation behavior of MB and its influence on photocatalytic degradation of the dye during photocatalytic performance study on TiO<sub>2</sub> thin films. This is the first report that shows that the photocatalytic stain removal activity on monomer, dimer and aggregated forms of MB on TiO<sub>2</sub> surface in solid state is based on metachromasy effect of the dye [6].

### 2. Experiments

#### 2.1. Sample preparation

TiO<sub>2</sub> thin films were prepared on well cleaned soda lime glass (SLG) and fused silica (FS) slides by single dip coating process at a constant withdrawal speed of 1 mm/s using the precursor solution prepared from titanium (IV) isopropoxide (TTIP), ethanol and

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diethanolamine, without any further purification as reported by Kumari et al. [7]. Single side coated films were prepared by wiping off one side of the dip coated substrate carefully using ethanol, keeping the film on the other side intact, immediately after withdrawal from the dip coating solution as reported by Sreemany and Sen [8]. The film was allowed to dry at room temperature for 60 min. and fired at 600 °C for 10 min. X-ray diffraction (XRD) studies were carried out on the powder synthesized by firing the same precursor which was used for coating at 600 °C for 10 min. in a quartz plate, in Bruker AXS D8 diffractometer using Cu K $\alpha$  radiation.

## 2.2. Adsorption and photocatalytic degradation

For the adsorption and photocatalytic degradation studies of the dye, methylene blue (MB) of more than 98% purity was used to prepare standard stock solution of 0.3 M (high concentration) and 0.016 M (low concentration) with water that was purified using a Millipore milli-Q lab purification system. The MB adsorption on TiO<sub>2</sub> thin film was studied with high and low concentration stock solutions for 30 min adsorption time in darkness. The films were rinsed with pure water to remove un-adsorbed MB followed by air drying. MB adsorbed TiO<sub>2</sub> thin films were subjected to solar irradiation using an Oriel 300 Watt solar simulator with an air mass filter. The solar irradiation was 118.28 mW/cm<sup>2</sup>. The decomposition of MB adsorbed by the TiO<sub>2</sub> thin film was calculated based on the reduction in the absorption of MB peak using PerkinElmer Lambda 650 UV–visible spectrometer.

## 3. Results and discussion

### 3.1. Structural characterization

Fig. 1(a) is the XRD pattern of the TiO<sub>2</sub> film, which shows that the major fraction of TiO<sub>2</sub> is anatase phase with a small fraction of rutile phase being present. The average crystallite size of anatase was 20 nm as measured by the Scherrer formula after subtracting the contributions from instrumental broadening and lattice strain. Fig. 1(b) shows the high resolution scanning electron micrographs from the fractured surface of the TiO<sub>2</sub>-coated SLG revealing the coating thickness of about 200 nm.

### 3.2. Adsorption and aggregation behavior of methylene blue

Fig. 2 shows UV–visible absorption spectra of MB adsorbed on bare SLG and on TiO<sub>2</sub>-coated SLG using lower and higher concentration stock solutions along with that of MB in aqueous solutions. The MB in water shows the characteristic  $\lambda_{\text{max}}$  at 666 nm, which is the reference point in photocatalytic degradation studies in the slurry or immobilized-type reactors. The absorption spectrum of MB adsorbed on bare SLG and TiO<sub>2</sub>-coated SLG exhibit different characteristics when compared to MB dispersed in water (Fig. 2). The characteristic absorption spectrum of aggregated MB by various substrates like clay, quartz and starburst dendrimers was reported by several groups. Bujdak et al. used MB in the charge characterization of clay and found  $\lambda_{\text{max}}$  at 660–690 nm for monomer, at 600 nm for dimers, and at 570–585 nm for H aggregates. Jockusch et al. studied the aggregation of MB on starburst dendrimers and found  $\lambda_{\text{max}}$  at 666 nm for monomer, at 600 nm for dimers/aggregates and at 550 nm for higher order aggregates [9,10].

Similarly in the present adsorption process on bare and TiO<sub>2</sub>-coated SLG using low concentration stock solutions the dimer and monomer  $\lambda_{\text{max}}$  appeared at 610 and 666 nm, respectively. Adsorption in the high concentration stock solution shows aggregates and monomer  $\lambda_{\text{max}}$  around 590 nm and a shoulder at

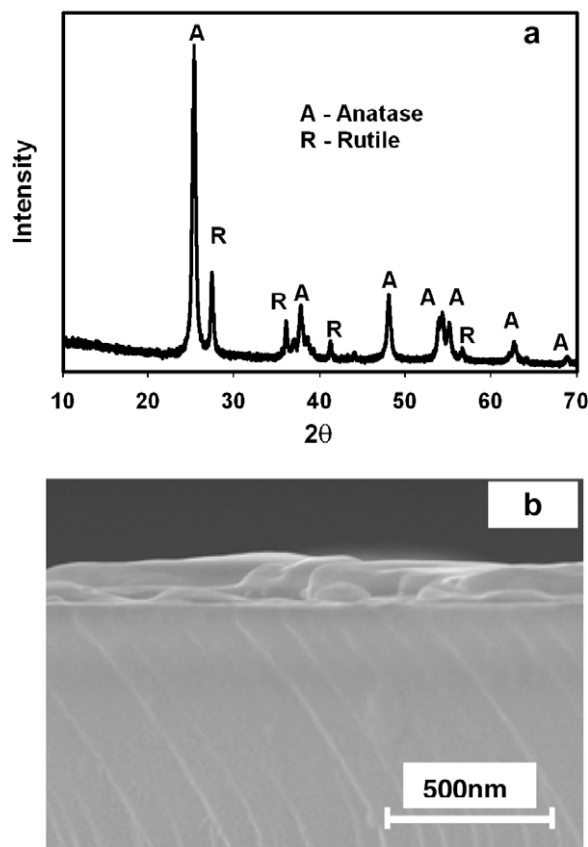


Fig. 1. (a) XRD pattern of the TiO<sub>2</sub> powder synthesized by firing the precursor (which was used for coating) at 600 °C for 10 min. (b) SEM image on the fractured surface of TiO<sub>2</sub>-coated SLG.

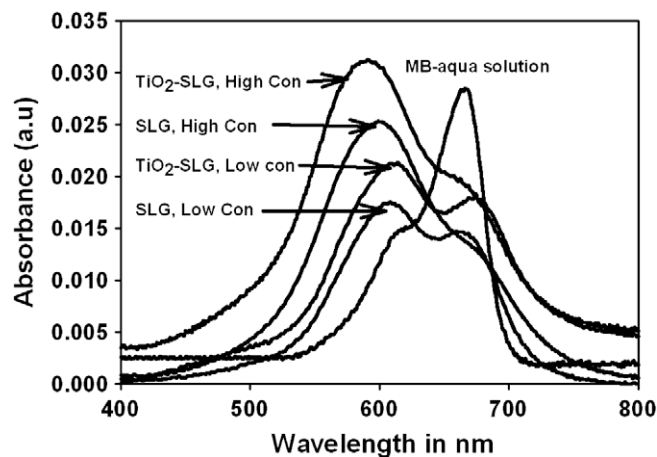


Fig. 2. Spectral absorption of MB bound to SLG and TiO<sub>2</sub>-coated SLG in higher and lower concentration stock solution.

666 nm. From this adsorption process it is clear that the formation of aggregates depends on the surface concentration of MB molecules which is directly proportional to stock solution concentration, which is in good agreement with the results reported in the quantification of the influence of monomer and dimer on a fused silica surface [11]. In these studies too, the  $\lambda_{\text{max}}$  for monomer and dimer appears around 660 and 610 nm, respectively, while the aggregated MB was not observed in fused silica. The same observation was made in the present study, i.e. the aggregated MB was not observed both on FS and TiO<sub>2</sub>-coated FS at low as well

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