



A comparative study of photocatalysis on highly active columnar TiO₂ nanostructures in-air and in-solution



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ARTICLE INFO

Keywords:

Photocatalysis
TiO₂
Methylene blue
Leuco methylene blue
Reversible
Irreversible

ABSTRACT

While there is continuous progress in development of new photocatalytic thin films and coatings, the lack of a reliable and standard procedure for measuring the photocatalytic performance of such active surfaces makes it difficult to compare results between research groups and different measurement setups. Here, a comparative study was carried out to demonstrate the high photocatalytic activity of sputter-deposited TiO₂ film with self-organized nanocrack networks by using two different analytical approaches: (i) bleaching of a thin Methylene Blue (MB) solid layer on photocatalytic TiO₂ thin film (in-air) and (ii) the decolorization of a MB aqueous solution in the presence of TiO₂ thin film (in-solution). While the decolorization of aqueous MB solution provides an indirect observation of the photocatalytic effect imposed by the TiO₂ film, the use of a solid MB layer as an indicator allows monitoring of photocatalytic reactions at the solid-air interface directly. We showed the applicability of this approach as a complementary and a fast analysis method to reveal the photocatalytic efficiency of thin films by comparing it with the state of the art inks (based on MB and other similar organic dyes) used as photocatalysis indicator.

1. Introduction

The interest in using heterogeneous photocatalysis as an alternative for environmental clean-up is continuously increasing as the water resources diminish enormously and the air pollution threatens the human health seriously [1]. TiO₂ is one of the most widely used photocatalytic materials for environmental remediation applications due to its low cost, chemical inertness, non-toxicity, high photocatalytic activity and recyclability [2]. The band gap of TiO₂ is around 3 eV (3.0 eV for rutile and 3.2 eV for anatase), thus making TiO₂ photoactive under the ultra-violet (UV) radiation [3].

Beside other phases of TiO₂ (brookite and rutile), the anatase is generally proposed as the most efficient polymorph for photocatalytic applications [4]. Thermodynamic and structured-based analysis showed that anatase is the most stable TiO₂ phase at nanoscale due to its relatively lower surface energy [5]. Anatase nanoparticles have been shown to degrade various organic pollutants in water with a high efficiency, thanks to their stability and high surface area [1]. On the other hand, it is a challenge to separate such extremely tiny particles from the water after the photocatalytic clean-up. The difficulty in handling suspended TiO₂ particles and the interest in expanding the use of TiO₂ in air cleaning applications make it obvious that there is a need for robust TiO₂ thin films. In

general, suspended TiO₂ nanoparticles exhibit much higher photocatalytic activity thanks to their high active surface area compared to immobilized TiO₂ nanoparticles or thin films [6]. On the other hand, TiO₂ thin films with highly porous morphology have been shown to exhibit very high photocatalytic performance [7,8]. The morphology and the porosity play a major role on the photocatalytic activity of such surfaces [9]. In addition, both density of surface states and energetic location (energy levels) are very dependent on geometric characteristics of TiO₂ surface [10,11]. Besides geometric factors the incorporation of dopants is an effective approach for the modification of energy states of TiO₂ to get higher photocatalytic efficiency [12]. Especially Au-TiO₂ and Ag-TiO₂ heterostructures have been shown to extend the photocatalytic activity to the visible region and to improve the charge separation and transfer properties which enhance the photocatalytic efficiency [13,14].

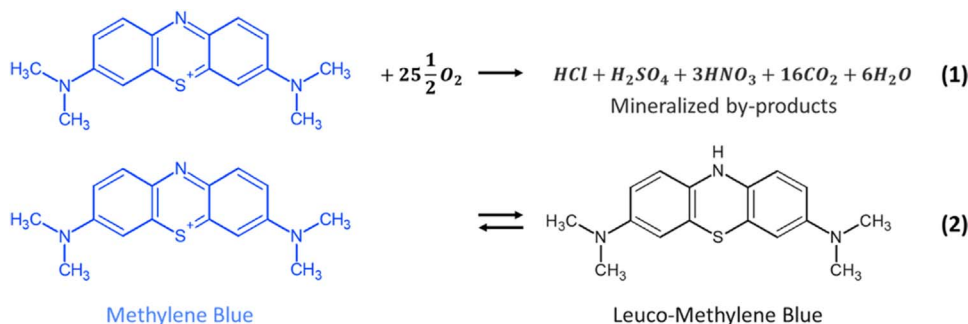
Basically, larger surface area of TiO₂ nanoparticles gains them a higher photocatalytic activity by offering more active sites for catalytic reactions and accommodating higher number of defect states (oxygen vacancies) for the adsorption of water and oxygen. The significant difference between the surface areas of suspended and immobilized photocatalytic nanoparticles (or thin films) must be considered when comparing their performance. There are various standardized methods established by the International Union of Pure and Applied Chemistry

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(IUPAC) for testing photocatalytic activity of particles/particulates suspended in water. In such a typical procedure the surface area of suspended catalysts is usually reported in several m^2/g [15]. It is difficult to achieve such a high surface area in thin film catalysts by simply coating a thin active layer on a planar substrate (where mass ratio between the active layer and the backing substrate is nearly negligible). Furthermore, the quantification of the exact surface area of a thin film is not so trivial. In this regard, most of the methods presented in the literature for the analysis of photocatalytic thin films do not fulfill the requirements of IUPAC standards.

Mostly the photocatalytic activity of TiO_2 nanoparticles or thin films is analyzed by immersing them into a colorful test pollutant, which is mostly an organic dye solution, and observing the decolorization of the solution upon exposing it to UV light. Among various organic dye types Methylene Blue (MB), as the member of thiazine dye group, is most widely used test pollutant [16]. In most TiO_2 photocatalysis studies the decolorization of the aqueous MB solution is used as a gauge to measure the kinetics of mineralization of carbon, nitrogen and sulfur heteroatoms into CO_2 , NH_4^+ , NO_3^- and SO_4^{2-} , respectively (as shown by the photochemical reaction (1) [17]. Although this method is preferred frequently due to its ease of application and low cost, it is not an ideal approach for photocatalytic thin films due to extremely long lasting (several hours) decolorization reaction. Moreover, the decolorization of such an aqueous MB solution may lead to misinterpretation in some cases. In such studies the decolorization of the aqueous MB solution is only attributed to the irreversible photobleaching (1). On the other hand, the decolorization might result from the reversible conversion of MB to its leuco form (LMB) as shown in (2), which is mostly not considered [18]. The reduced LMB is colorless and it is quickly converted back to blue colored MB in the presence of oxygen (oxidation reaction occurs at room temperature) [19].



The $\text{MB} \rightleftharpoons \text{LMB}$ conversion is very sensitive to pH of the environment and in general the addition of a reducing agent is necessary to favor the LMB formation. By using strong reducing agents such as ascorbic acid, or glucose in alkaline medium LMB is stabilized and used as an oxygen indicator in packaging and food industries [20]. The decolorization upon $\text{MB} \rightleftharpoons \text{LMB}$ conversion has been also used as an indicator to monitor photocatalytic activity of TiO_2 thin films [21,22]. Mills et al. developed a MB based ink that acts as a fast (to be assessed in min.) photocatalytic indicator for thin films [23]. The ink utilizes glycose as the sacrificial electron donor (SED) to trap the photo-generated holes, leaving the photogenerated electrons to react with MB to produce LMB. This approach led to several smart ink formulations which claim fast analysis of the photocatalytic performance of thin

films and coatings.

Beside its use as a photocatalytic indicator, recently a MB based ink has been introduced as the rewritable medium [24]. In this and as well as other smart ink applications the color change is attributed to $\text{MB} \rightleftharpoons \text{LMB}$ conversion. On the other hand, the trapped air (in TiO_2 thin film and MB layer) and adsorbed moisture (from the environment) may lead to irreversible photobleaching (mineralization) of the MB in addition to its reversible bleaching [25]. Moreover, the color change through LMB conversion in the presence of a stabilizer cannot be accepted as the direct sign of the remediation of an organic pollutant where a full mineralization is required [26]. For instance, the decolorization of MB solid layers seem to occur totally different in the absence of any stabilizing agent as Ollis et al. presented [27]. They have shown that the full-decolorization of dry MB layer took longer than 8 h. This extremely long decolorization time compared to that reported by Mills et al. [23] and the stability of the colorless state (after UV radiation) in the absence of any stabilizer proves the existence of the irreversible bleaching rather than a reversible bleaching.

Here we report a comparative study of the photocatalytic bleaching of MB in-air and in-solution (aqueous) by highly photocatalytic columnar TiO_2 nanostructures prepared by reactive sputtering. We used thermally controlled cracking as an effective tool to get deep trenches and high aspect ratio (AR) structures in sputter deposited TiO_2 thin film. First a solid MB layer was deposited on prepared TiO_2 structures and the co-existence of reversible and irreversible photocatalytic bleaching of MB layer was shown upon UV exposure. For comparison the photocatalytic activity of the same structures was analyzed by a conventional method which basically monitors decolorization of an aqueous MB solution under UV light. The significance and reliability of both analytic approaches to determine the photocatalytic performance of TiO_2 thin films are discussed in detail.

2. Experimental

2.1. Preparation of TiO_2 thin films

A highly photocatalytic TiO_2 thin film was prepared by pulsed DC reactive sputtering. Metallic titanium (Ti) target was sputtered using a DC planar magnetron source in the presence of argon (process gas) and oxygen (reactive gas). Prior to the sputtering the base pressure of the chamber was adjusted about 5×10^{-5} Pa. To acquire a high sputter yield argon gas (at a flow rate of 250 sccm) was applied directly to the Ti target (at an incident angle of 60°) in the presence of controlled oxygen flow (at a flow rate of 10 sccm). DC power was pulsed at a frequency of 50 kHz with 55% duty cycle to reduce the oxidation and

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