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INVESTIGATION OF THE EFFECT OF SURFACTANT ON DIP-COATING TiO_2 PHOTOCATALYST

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Abstract: *Titanium oxide film obtained by dip-coating technique and its application as photocatalyst for dye (Methyl orange) and surfactant (Triton X100) are reported. The effect of the addition of Triton X100 on the photocatalytic properties of films has been studied and discussed. The films were investigated by XRD (structure), AFM (morphology) and photocatalytic properties. The surfactant affects the packing density (crystallite aggregation) during deposition improved the photodegradation efficiency. The photocatalytic degradation of Triton X100 is higher than the photocatalytic degradation of Methyl orange (0.0125 mM) due to the affinity to the substrate.*

Key words: *titanium dioxide, thin film, dip-coating, surfactant, photocatalysis.*

1. Introduction

Heterogeneous photocatalysis has become a subject of increasing interest during the past twenty years, mainly in the field of environment protection, in decontamination treatment of wastewater [7], [13]. Usually, the wastewaters contain, among other chemicals, surfactants and dyes that interferes with the photo-degradation process [15]. Surfactants are often participants in the process [4] and, in a real situation, can absorb on the photocatalyst surface, modifying the photo-catalytic activity. Triton X100 is most widely industrial scale used surfactants, including the production of detergents, emulsifiers, wetting agents and dispersants [11].

The majority of research on heterogeneous photocatalysis is based on the application of TiO_2 in a slurry reactor and for treating the dyes [1], [5], [6], [9]. Immobilizing the catalyst as thin film is a pre-requisite for an up-scalable process [8]. Various up-scaling deposition techniques such as sol-gel processes [2], photochemical deposition [3], spray pyrolysis deposition, dip-coating deposition [14] have been investigated for various coating applications.

The surface modification of TiO_2 films for enhancing the photocatalytic efficiency involving the incorporation of other species to increase the surface area maximizes contacting surface exposed to the pollutants [12].

In the present study, we report our recent investigation on photodegradation of the non-ionic surfactant aqueous solution (Triton X100) and dye (Methyl orange) in the presence of TiO_2 thin film illuminated by UV irradiation. The effect of the addition of Triton X100, on the photocatalytic properties of TiO_2 films has been studied and discussed.

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2. Experimental

2.1. Materials and Methods

The materials used for films preparation were TiO_2 Degussa P25 (80% anatase and 20% rutile; specific surface area 55 m^2 g^{-1} and a mean particle size of 25 nm), ethanol and Triton X100 as additive.

The organic compounds used for thin films evaluation photoactivity were:

- Methyl orange (sodium *p*-dimethyl amino azo benzene sulfonate) $C_{14}H_{14}N_3NaO_3S$, M = 327.34 g/mol purchased from Merck. The chemical structure of MO was shown in Table 1. Methyl orange is an anionic dye belongs to the azo group of dyes.

- Triton X100 (*t*-octylphenoxypoly-ethoxyethanol) *t*-oct-C_6H_4-$(OCH_2CH_2)_n$OH, n = 9-10 is a nonionic surfactant; the chemical structure was presented in Table 1. The critical micelle concentration (CMC) is reported between 0.13 and 0.2 g/L (0.2-0.31 mM) [10] and it has an average of 9.5 ethylene oxide units per molecule with an average molecular weight of 646.37 g/mol-Scharlau Chemie. The stock solution of Triton X100 was prepared by dissolving 10 g/L in double distilled water (*Millipore Direct Q3*). The concentration levels studied in our research were below the CMC to avoid the change of the surfactant solution properties at CMC. Initial surfactant dosage was varied between 0.0125 and 0.25 mM. In this range we are working below the critical micellar concentration (CMC), which was determined to be 220 mg/L for Triton X100.

2.2. Preparation of Titanium Oxide Thin Films

Titanium oxide thin films were prepared by dip-coating method, using TiO_2 Degussa P25 in the presence of a surfactant; an aqueous colloid paste was formed by mixing 2g TiO_2 powder with 25 mL of ethanol, and different amount of surfactant. Different types of TiO_2 nanocomposite films were prepared by varying the concentration of Triton X100 (50, 100, 150, 200, 250 ppm) in the paste using a stock solution of Triton X100 (prepared by dissolving 10 g/L in double distilled water). The mixtures were prepared 24 h in advance to ensure full hydration of micelles. The paste was agitated for 10 minute for homogenization. Finally, the glass substrate (1.5x2.5 cm^2) (cleaned using ethanol, distilled water, acetone in successive sonication processes) was immersed in the paste; one side of glass was protected with tape. After drying in air at 60 ºC for about 10 min, the films were annealed in an oven at 400 ºC for 3 h.

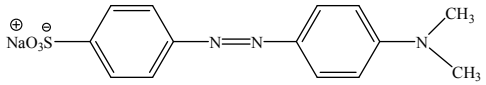
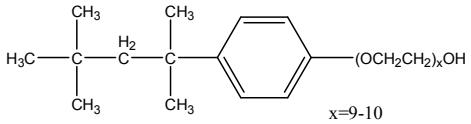
2.3. Characterizations of the Dip-Coating Films

The phase structure, microstructure and surface properties of the films were characterized by using X-ray diffraction (*XRD-Brucker D8 Discover diffractometer with CuKα radiation*) and Atomic Force Microscopy (*AFM-NT-MDT model NTGRA PRIMA EC*). The images were taken in semi-contact mode with "GOLDEN" silicon cantilever (NCSG10, force constant 0.15 N/m, tip radius 10 nm). Scanning was conducted on three different places (a certain area of 5 x 5 μm for each section) chosen randomly at a scanning rate of 1 Hz.

2.4. Evaluation of Photocatalytic Degradation

Photocatalytic activity of the dip-coating films was evaluated from the decomposition of Methyl Orange and Triton X100. In 25 mL of solution the film (sample of 1.5×2.5 cm^2) was added and then irradiated with three F18W/T8 black light tubes (Philips) (UVA light, typically 340-400 nm, with

The compounds used in photodegradation process Table 1

Compound	Chemical structure	λ [nm]	Equation of calibration
Methyl orange		463	y = 0.0017+24.9x
Triton X100		275	$y = -4 \cdot 10^{-3} + 1.689x$

λ_{max} (emission) = 365 nm), for different periods of time.

The Methyl Orange (MO) and Triton X100 residual concentrations were determined by a calibration curve, the maximum absorption wavelength experimentally registered and the equations used for determinate the concentration are given in Table 1.

Absorbance measurements of the solutions were recorded in the range of 200-600 nm, using a UV-Vis spectrophotometer (*Perkin Elmer Lambda 25 UV/VIS*).

The maximum absorbance at 464 nm used to monitor the degradation of MO which is due to the $\pi \rightarrow \pi^*$ transition of the azo group (–N=N–), representing the color of dye solution.

The photodegradation efficiency was evaluated with Eq. (1):

$$\eta = \frac{c_0 - c}{c_0} \cdot 100, \qquad (1)$$

where c_0 represents the initial concentration and c represents the concentration at time t.

Photodegradation tests performed in the dark showed an adsorption rate of 3-4%.

3. Results and Discussion

3.1. Structure

The phase structure, crystallite size and crystallinity of TiO_2 play an important role in photocatalytic activity. The X-ray diffractions (XRD) patterns of the TiO_2 dip-coating films provide the presence of the anatase and rutile phase, as shown in Figure 1.

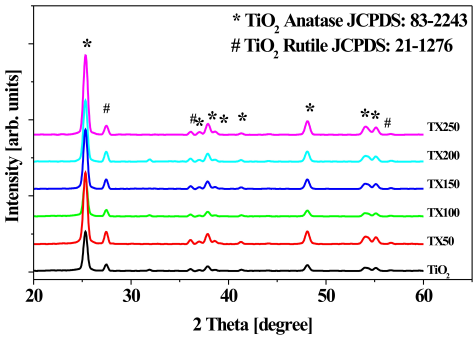


Fig. 1. *The XRD diffraction patterns of films*

The average size of the crystallite was estimated based on the broadening of anatase (101) diffraction peak using the Scherrer equation. The crystallite size of the samples prepared with surfactant TX50, TX100, TX150, TX200 and TX250 is 30.2, 30.3, 30, 30.4 and respectively 30 nm, which were similarly with that (30 nm) of the TiO_2 sample prepared without surfactant. The smaller crystallite size indicates that the Triton X100 can effectively prompt the crystallization and inhibit the grain growth.

3.2. Morphology

Atomic Force Microscopy was used to visualize the morphology of the top surface of the unmodified layer (without surfactant)

(Figure 2a) and modified layer films with a special focus on the organization of the surfactant (Figures 2b-f).

By the AFM technique, we found that the TiO_2 film prepared from dip-coating with surfactant shows a granular nanostructure, and is composed of regular particles of almost the same size (Figure 2).

As clearly seen in these figures, by introducing Triton X-100 the morphology of thin layer changed.

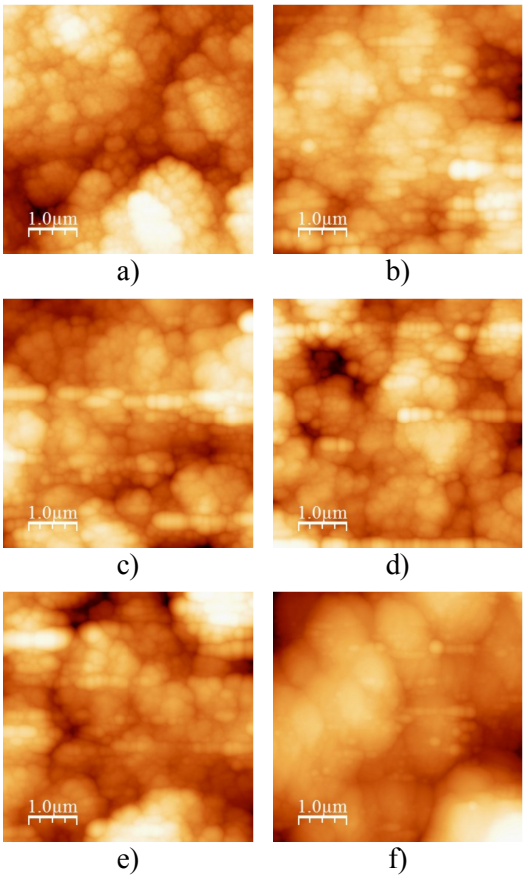


Fig. 2. *The AFM images of films:* (*a*) *TiO_2;* (*b*) *TX50;* (*c*) *TX100;* (*d*) *TX150;* (*e*) *TX200;* (*f*) *TX250*

The films (Figure 2) exhibits a dense, smooth, and compressed skin layer when the Triton X-100 concentration is added in a film below the critical micellar concentration. Probably, higher concentrations of Triton X-100 cause further presence of the micelle-like complex in the thin layer.

The AFM images were analysed using WSxM software, to evaluate the distribution curves of the voids which allows an estimation of the most likely inter-particle voids size (calculated at the half width of the peak), with the following values for the samples: 0.5 µm (sample TiO_2), 0.86 µm (sample TX50), 0.79 µm (sample TX100), 0.64 µm (sample TX150), 0.88 µm (sample TX200) and 0.82 µm (sample TX250).

Triton X-100 not only improves the wettability, but due to its surfactive action, by reducing the surface tension of H_2O, it prevents the films from the cracking that arises from the capillary forces of the liquid evaporating out of the pores.

3.3. Photocatalytic degradation of surfactant and dye

The differences in the photocatalytic activity are likely to be due to differences in the morphology or density of hydroxyl groups on the catalyst's surface, since they will affect the degradation behavior of a pollutant and recombination rate of electron-hole pairs.

The degradation of Triton was dependent on the initial concentration of Triton C_0 (Figure 3). The degradation efficiency of Triton decreased with an increase in C_0, which is attributed to the unavailability and

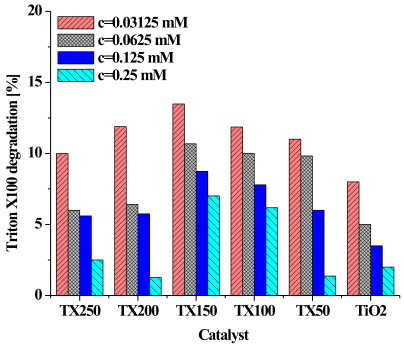


Fig. 3. *The photodegradation of Triton X100 after 3h of irradiation*

inadequacy of the photogenerated oxidizing species in large amounts of the macromolecule surfactant micelle. The degradation efficiency of Triton was enhanced drastically by photocatalysis from 0.03125 mM to 0.25 mM, resulting mainly from the increase in the adsorbed Triton on the surface of the catalyst.

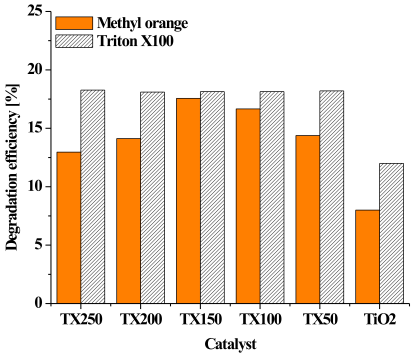


Fig. 4. *Dye and surfactant degradation after 3h of UV irradiation*

The degradation of Triton X100 and Methyl orange after 180 minutes of irradiation as functions of catalysts is shown in Figure 4. The photocatalytic degradation of Triton X100 is higher than the photocatalytic degradation of methyl orange (0.0125 mM) due to the affinity to the substrate and stability of Methyl orange.

4. Conclusions

The present studies have revealed some results for photodegradation of a dye (methyl orange) and a nonionic surfactant (Triton X100).

The surfactant (Triton X100) was used as additive in TiO_2 thin film for improved the photocatalytic activity of thin films. The optimum concentration of Triton X100 in the film was found 150 ppm below the CMC.

From the photocatalytic results, one can find that photocatalytic activity of TiO_2 dip-coating films is strongly dependent on its phase structure, crystallite size, morphology, and surfactant concentration.

The photocatalytic oxidation of Triton X100 in aqueous TiO_2 suspensions and thin film was investigated as a function of initial concentration of Triton X100 in water and the concentration of Triton X100 in the dip-coating film. The TiO_2 dip-coating film could be used for wastewater degradation containing surfactants and dyes.

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