NANO-OPTICAL PROPERTIES OF THE SYNTHESIZED MATERIAL LIKE TiO_2

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Abstract:
This paper reveals that the photocatalytic efficiency of hydrogenated TiO_2 nanoplumes studied by measuring dye degradation in water. Nanoplumes were synthesized by peroxide etching of Ti films with different thicknesses. Structural characterization was carried out by scanning electron microscopy and transmission electron microscopy. We investigated in detail the nano-optical properties of the synthesized material and related them to the efficiency of UV photodegradation of methylene blue dye. The obtained results show that TiO_2 nanoplumes act as an effective antireflective layer increasing the UV photocatalytic yield of the film.

This paper use the method of possibility to synthesize black TiO_2 by an easier method. The hydrogen peroxide etching of Ti films as an easy, rapid, and low-cost method to synthesize hydrogenated TiO_2 nanoplumes with significant photocatalytic properties under UV and visible light irradiation.

The main findings of this paper immersed in a solution (2 mL) containing MB and de-ionized water (starting concentration: 1.3×10^{-5} M). The mixture was irradiated by an 8 W UV lamp (350–400 nm wavelength range) with a irradiance of 1 mW/cm^2, for a total time of 3 h. Every 30 min of irradiation the solutions were measured with an UV–vis spectrophotometer in the 500–800 nm wavelength range. The degradation of MB was evaluated by the absorbance peak at 664 nm, according to the Lambert–Beer law. The decomposition of the dye in absence of any material was also measured as a reference. Before each measurement, the samples were irradiated by the UV lamp for 50 min in order to remove the hydrocarbons localized on the sample surface.

Keywords: Black titania; nanostructures; photocatalysis; titanium dioxide (TiO_2)

Introduction

Today water, energy, and food are the most urgent problems of humanity. Since the seminal work of Honda and Fujishima in 1972 where photo-induced decomposition of water was discovered [1], semiconductor photocatalysis has shown great potential not only for renewable energy generation but also in sustainable technology to remove dangerous contaminants from water [2-6]. In this context, TiO_2 is one of the most extensively studied materials. However, TiO_2 is characterized by a wide band gap (ca. 3 eV) resulting in a poor absorption of light in the visible region. Different approaches were proposed to overcome this limit: the inhibition of the recombination of photogenerated electrons and holes, the increase of the exposed surface area, and the decrease of the band-gap energy.

Recently, Chen et al. were able to synthesize black TiO_2 with a large optical absorption in the visible and infrared region. The amorphous shell on a crystalline nanoparticle core, causes the formation of intragap states, which are responsible for the high absorption of visible light (and consequently of the black color). Unfortunately, the synthesis of this remarkable material requires high pressures of H_2 (up to 20 bar) and long annealing treatments (up to 5 days).

Here we report the nano-optical properties of the TiO_2 nanoplumes and their correlation with the efficiency of UV photodegradation of methylene blue (MB). The obtained results show that TiO_2 nanoplumes act as effective antireflective layer increasing the UV photocatalytic yield.

Results and Discussion:

In order to observe the morphology of the films we analyzed the Ti samples after different etching times by SEM in plan view. Two Ti film thicknesses, 70 nm and 430 nm, were used. Hereafter, we will call the samples Ti (70-x_i) and Ti (430-x_i), where x_i is the time of etching. A statistical analysis showed that the roughness of the surface and the porosity of the structure increase with the etching time.

The total reflectance spectra of Ti (70-60) and Ti (70-150) present a shift in the reflectance peak, from 302 to 314 nm. This shift may be related to the variation on the sample thickness, due to the different chemical etching time. Although the measured spectra include wavelengths from 200 to 800 nm we will focus on the UV region, since the light source of photocatalytic experiments emits in this range (dashed vertical line). In this region the absolute values of reflectance for Ti (70-60) and Ti (70-150) are about 10%. The total reflectance of Ti (430-150) and Ti (430-190) exhibits an almost completely suppression, below 5% in the UV range, and a 50% decrease between 410 and 700 nm compared to the previous two samples. The oscillations of the spectra are due to optical interference. Ti (430-190) exhibits a high exposed surface area due to the longer chemical etching and the lowest reflectivity in the UV-A region. Both parameters affect the photocatalytic properties of the sample making it particularly active in the presence of MB.

As shown before, the defects introduced in the material by the chemical etching (in particular, Ti^{3+} and OH groups) are responsible for a blurring of the valence and conduction bands. Consequently, a reduction of the optical gap was reported. Ascertained of the high photocatalytic activity of the Ti (430-190) sample due to its structural and optical properties, we interpreted the *R* and *T* measurements in terms of the Fresnel formulae, regardless of the effects of depolarization due to the roughness and non-uniformity of the surface. We assumed that the sample is constituted by two layers on a quartz substrate, namely a titanium oxide layer and a metallic titanium layer (from the top to the bottom).

A schematic view is shown as inset in Figure 1. The refractive indexes of the three layers (TiO_2/Ti/quartz) were calculated separately. For the quartz substrate it was assumed to be 1.5. The refractive index of the metallic film was extracted by fitting the reflectance spectrum of the titanium layer before the chemical etching. We assumed that the functional form for the dielectric constant of the metallic film is given by the "Drude free carrier" expression:

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 - \frac{\omega_P^2}{\left(\omega^2 + i\omega\gamma\right)}\right), \quad (1)$$

where ω, ω_P, γ and ε_∞ are, respectively, the light frequency, the plasma frequency, the damping constant, and the low-frequency dielectric constant tabulated for titanium. The refractive index of titanium is calculated by the square root of Equation 1:

$$n(\omega) = \sqrt{\varepsilon(\omega)}. \quad (2)$$

The refractive index of the TiO_2 film was extracted by fitting both the reflectance and transmittance spectra of the Ti (430-190) sample, by using a Forouhi–Bloomer (FB) functional form for amorphous samples:

$$n(\omega) = n_\infty + A\frac{B(\omega-\omega_0)+C+i\Theta(\omega-\omega_g)(\omega-\omega_g)^2}{(\omega-\omega_0)^2+\Gamma^2}, \quad (3)$$

Where

$$B = \frac{\Gamma^2-(\omega_0-\omega_g)^2}{\Gamma}, \quad (4) \qquad C = 2\Gamma(\omega_0-\omega_g) \quad (5)$$

and $\Theta(\omega - \omega_g)$ is a step function, ω_g is the energy gap of the amorphous material, n_∞, A, ω_0, Γ are the "low-frequency" refractive index, the amplitude, the position, and the damping constant of the FB oscillator, respectively. The simulated reflectance and transmittance spectra by the Fresnel formulae are shown in Figure 1 by the dashed and the continuous line, respectively.

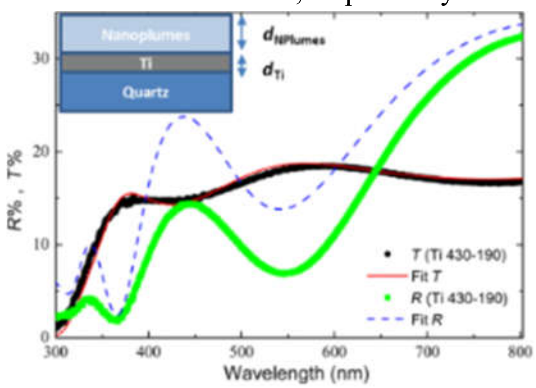

Figure 1: Fitting of the transmittance and reflectance spectra of Ti (430-190).

It is worth noting that the refractive index of the nanoplumes, albeit it depends on the wavelength, does not exceed the value of 1.4. In particular, it is 1.2 at 800 nm, and 1.3 at 300 nm. TiO_2 is known to be a high refractive index material (n = 2.5–2.7), whereas the nanoplumes show a very low refractive index. This result can be correlated to the high porosity and the high content of air into the nanoplumes, so that the refractive index can be considered as an average value of those of air and TiO_2.

The model used to fit the experimental R and T curves shows that the metal Ti layer acts as an efficient reflective layer, whereas the nanoplume layer acts as an antireflective coating. We found an ideal combination of 70 nm of highly reflective metallic Ti under 300 nm of TiO_2 with low refractive index. Moreover, scattering effects improve the light adsorption by the nanoplumes, increasing the generation of electron–hole pairs and, therefore, enhancing the photo catalytic performance.

We wish to underline that the position of the maxima and minima in the measured reflectance and transmittance spectra do not coincide as expected. We found an ideal combination of 70 nm of highly reflective metallic Ti under 300 nm of TiO_2 with low refractive index. Moreover, scattering effects improve the light adsorption by the nanoplumes, increasing the generation of electron–hole pairs and, therefore, enhancing the photocatalytic performance.

Conclusion

In summary, TiO_2 nanoplumes were synthesized by a straightforward method, involving rapid chemical etching of Ti films in a H_2O_2 solution. The present results reveal that the most important nano-optical effect of the synthesized nanoplumes is the suppression of reflectance, particularly in the UV range of the spectra.

The photocatalytic properties of the synthesized material were evaluated by the degradation of methylene blue (MB) dye, a chemical compound commonly used to evaluate the photocatalytic efficiency of a material. The experimental setup was in agreement with the ISO 10678:2010 international standard.

The samples were immersed in a solution (2 mL) containing MB and de-ionized water (starting concentration: 1.3×10^{-5} M). The mixture was irradiated by an 8 W UV lamp (350–400 nm wavelength range) with a irradiance of 1 mW/cm^2, for a total time of 3 h. Every 30 min of irradiation the solutions were measured with an UV–vis spectrophotometer (Perkin-Elmer Lambda 45) in the 500–800 nm wavelength range. The degradation of MB was evaluated by the absorbance peak at 664 nm, according to the Lambert–Beer law. The decomposition of the dye in absence of any material was also measured as a reference. Before each measurement, the samples were irradiated by the UV lamp for 50 min in order to remove the hydrocarbons localized on the sample surface.

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