Preparation of amorphous and crystalline titanium dioxide on FTO: ITS characterization and photo- catalytic effect on eriochrome black T

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In this work, thin films of TiO_2 were electrodeposited by photocatalytic efficiency of glass materials coated with TiO_2 as an additive layer on FTO substrates. We have studied the characterization of TiO_2 electrodeposited on FTO by several methods such as cyclic voltammetry, X-ray diffraction (XRD), scanning electron microscopy SEM, the energy dispersive spectroscopy device (EDS) and microscopy atomic force (AFM). The crystalline deposits were used as catalysts for the photocatalytic oxidation of black dye Eriochrome black T, under an irradiation source (UV lamp 365 nm). The results revealed that the dye undergone slight degradation under UV illumination. Using the spectrophotometer measurements, the rate of discoloration was estimated from the residual concentration.

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1. Introduction

Much scientific research has been carried out on the subject of oxidation of organic matter, and among the methods used is the oxidation of metal oxides, for example elements deposited on the surface of titanium dioxide can interact with radicals free formed under the excitement of ultraviolet rays.

Metallic oxides, nanocrystalline titanium dioxide (TiO_2) is one of the most studied materials due to its important applications in cleaning the environment [1,12].

Among the methods used in the preparation of the TiO_2 thin films is vacuum evaporation, sputtering, chemical vapor deposition (CVD), sol-gel method, liquid-phase deposition (LPD), hydrothermal method.

Atomic layer deposition (PCA) and electrochemical deposition are relatively simple and inexpensive techniques compared to other preparation techniques [13,18]. Both are transparent metal oxides, and therefore ideal as transparent electrodes because FTO has a variable working function, it is rarely used as an insulated lower electrode. TiO_2 is used for the transparent material deposited on the FTO substrate.

Modification of experimental parameters and conditions, which allow to control variables such as applied potential, pH and working temperature, leads to the generation of desirable films of TiO_2which is a P-type semiconductor.

The position of the cathode electrode of thin-film nanoparticles of titanium hydroxide on a non-commercial transparent conductive oxide (OCT) and the characterization by several methods

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studied in detail and demonstrated by a large number of researchers for many years [9][19,20].

In this study, the application test of the FTO glass coated with a thin film to reduce the black Eriochrome T using the irradiation of the UV lamp for different times.

2. Experimental procedure

2.1. Material and products

To prepare the mesoporous TiO_2 films for photoanode we used indium tin oxide (FTO) coated glass plate, as substrate materials, TiO_2 (sigma Aldrish), H_2SO_4(sigma Aldrish), KC1(sigma Aldrish), $TiOSO_4$ (sigma Aldrish), CH_3COCH_3 (sigma Aldrish).

2.2. Solution preparation

An aqueous solution prepared using 0.02 M $TiOSO_4$, was dissolved in 0.03M of H_20_2 and 0.1M KNO_3, and a few drops of 0.5M nitric acid were added to maintain pH = 1.6 at ambient temperature [19], the non-commercial fluorine-doped tin oxide (FTO) electrode [1], which served as the working electrode, a platinum Pt wire served as the counter electrode (CE) and a Saturated calomel electrode (ECS) was used as a reference. The deposition times were 60 min, under potentiostatic condition in the solution cited above, a bias voltage E = -1 V was applied at room temperature.

The $TiO(OH)_2H_20$ gel film deposited on the FTO electrode, then was subjected to heat treatment in air at 450 °C for 1 h. The deposited and annealed films were characterized using X-ray diffraction (XRD), was performed using a Philips automatic powder diffractometer (Bragg-Brentano arrangement, fixed slit mode) using radiation filtered by CuKa and scintillation. Scanning electron micrographs were obtained using a JEOL JSM 6390 microscope equipped with an energy dispersive spectroscopy (EDS) installation.

2.3. TiO_2electro deposition medium

In an aqueous medium, an amount of titanium oxo-sulfate is dissolved to obtain the deposit of TiO_2 on FTO.

2.4. Apparatus

Electrochemical measurements were carried out on a CHI Instruments, Model 900B potentiostat utilizing a conventional three-electrode cell, Fluorine-doped tin oxide conducting glass (FTO) and a platinum coil of large surface were used as working and counter electrode respectively. All potentials quoted in this work are referred to an Ag/AgCl, KCl (sat-d) reference electrode (0.197 V vs. NHE), pH measurements were carried out on a pH-meter-WTW- 330i Germany.

2.5. Structural and morphological characterization

2.5.1. XRD analysis

X-ray diffraction analysis is a non-destructive characterization method that helps determine the nature and organization of the crystal phases present within a material. It was used in our study for the structural characterization of TiO_2 powders and films.

The analyzes are carried out on a Siemens D5000 type two-circle diffractometer equipped with a counter goniometer and operating on the classical Θ-2 Principe (Bragg-Brentano geometry).

The x-ray source is a copper anticathode tube. The emitted beam is polychromatic and the selection of the single Kα copper doublet is ensured by a rear graphite monochromator.

The beam is shaped by means of Soller slits limiting its horizontal divergence, and three diaphragms, limiting its vertical divergence. The sample to be analyzed and the detector are rotated while the x-ray source is stationary. When the former moves by an angle θ the latter moves by 2θ and detects X-rays diffracted from all planes parallel to the surface. The determination of the angle θ and its comparison with the values given by the JCPDS sheet for TiO_2 make it possible to identify the families of planes which diffract. These families of planes are identified by Miller indices (h, k, l), it corresponds to each family of planes an inter reticular distance d_{hkl} which is such

that:

$$2\, d_{hkl} \sin\theta = n\lambda$$

where θ is the diffraction angle, λ the wavelength of the incident X-ray beam coming from the copper anti-cathode (n = 1.5405 Å, corresponding to the doublet Kα1, Kα2 of the copper), n is a natural number representing the order of diffraction.

The size of the crystal domains can be estimated from the widths at mid-height of the main diffraction peaks using the Scherrerrelation:

$$L = \frac{0.9\lambda}{\beta \cos\theta}$$

2.5.2. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to carry out the morphological characterization of the thin films of porous TiO_2 produced as well as of the complete hybrid photovoltaic cells.

The evaluation of the porosity and the homogeneity of the layers was carried out by observation of the surface of the films while transverse sections made it possible to visualize the section of the samples and certain interfaces, while allowing a direct estimate of certain thicknesses of layers.

In general, the samples to be observed are fixed on metal studs, either by means of conductive self-adhesive, or by means of an adhesive. To avoid the disturbances that result from "charging" effects, the use of a conductive silver glue has been necessary in some cases to allow charge discharge to the study. For cross sections, the samples are cut beforehand using a diamond tip, making sure that no additional processing was not necessary, the sections being relatively clean to allow observation under good conditions.

The SEM analyzes were performed on a high resolution JEOL JSM-7400F microscope at the joint microscopy service of the University of Limoges, hosted by the SPCTS laboratory of the European Ceramics Center (G. Trolliard, P. Carles) mechanical contact occurs in the area to be observed.

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Atomic Force Microscopy (AFM)

The interfacial roughness and morphology of the electro-deposited films were investigated by atomic force microscopy (AFM) using an Asylum MFP3D instrument.

3. Results and discussion

Figure 1 shows a DRX model of a catholically galvanized and annealed sample, as can be seen in the spectrum with three peaks appearing at angles 2Ɵ equal to 37.999 62.078 and 65.782 corresponding to Table1. (131), (052), (161), which respectively confirms the formation of TiO_2 according to JPDS maps No. 160617. The average crystallite size is 0.3498 nm, 0.487 nm and 0.559 nm, was estimated from the full width at mid-maximum of the diffraction peak using Scherrer's equation, a SEM photograph of TiO_2.

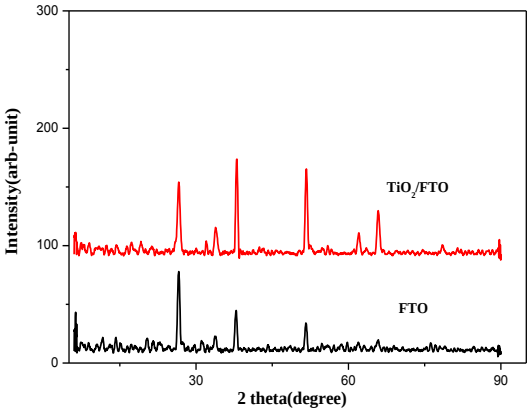

Fig. 1. X-ray diffraction pattern of a FTO, FTO /TiO_2 thin film.

Table 1. Crystallographic parameters of the obtained FTO/TiO_2.

Layer Nembrs	2θ	d (hkl)	hkl	Crystallite size		Lattice constants (Å)	
	(°)	(Å)		(nm)	a	b	c
	38.147	2.359	131	17.092			
Mono Layer	61.929	1.498	052	15.697	5.272	9.219	5.142
	65.806	1.418	161	13.145			
	37.999	2.368	131	15.531			
Double Layer	62.078	1.495	052	17.137	5.419	9.204	5.419
	65.782	1.418	161	13.444			

The images that given by the SEM are represented in Figs 2. a, b, c and d, these figures show that micro-agglomerates have been deposited on the surface of the electrode, the thin film of TiO_2 reveals an open pore structure with the particle size falling mainly in the submicron range.

To study the surface morphology and the roughness of the thin layers of TiO_2 electrodeposited from the various solutions of precursors, atomic force microscopy (AFM) was used on a surface of 25 μm^2.

The AFM technique was used to study the surface morphology and topographic relief of our deposits. Figures 4a and 5 show the top view AFM of a two dimensional thin surface and three dimensional thin surface traces of TiO_2 films, deposited and annealed. Close examination of the images shows that the electrodeposition of TiO_2 on FTO produced changes in the surface topography.

The AFM image of the deposited titanium dioxide (Figure 4) indicates the formation of a rough surface and the root mean square roughness value is 1107.71 nm. The appearance of the AFM image of the annealed film Fig5.appears to be quite similar to the deposited film. These observations agree with our SEM images and the size of the XRD calculation peak, they are in accordance with previous studies [21,22].

Three-dimensional views of thin films of TiO_2 electrodeposited from the various precursor solutions are shown in Figure 4.

Figure 3 reports on 4 different elements present in the FTO / TiO_2 electrode are determined using energy dispersive x-ray analysis. The elements are Si, Sn, Al, O and Ti. These elements are detected at different areas of the same sample.

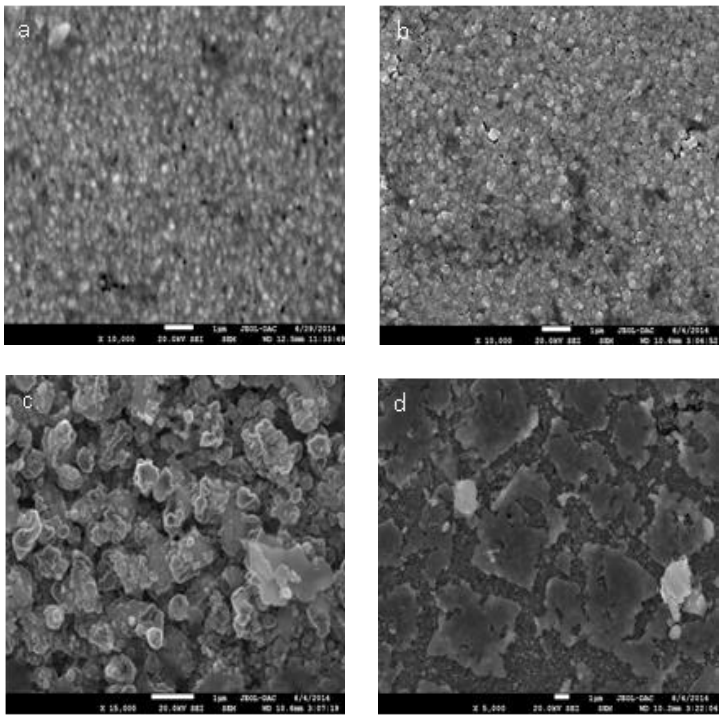

Fig. 2. SEMmicrograph for (a): FTO, (b, c and d) FTO/TiO_2 thin films.

Figure 3 reports on 4 different elements present in the FTO / TiO_2 electrode are determined using energy dispersive x-ray analysis. The elements are Si, Sn, Al, O and Ti. These elements are detected at different areas of the same sample.

The concentration of the elements is in percentage by weight. It can be noted that the distribution of the elements is not uniform. This means that the molecular composition of the sample is not homogeneous.

EDX analysis suggests the presence of Sn and Ti in relatively large amounts.

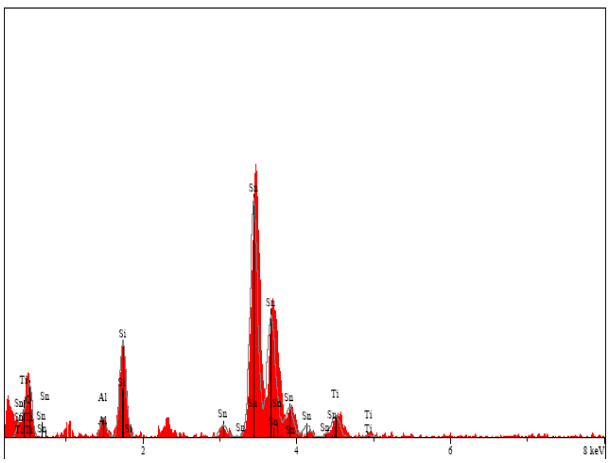

Fig 3. EDS spectrum of titanium deposits on FTO.

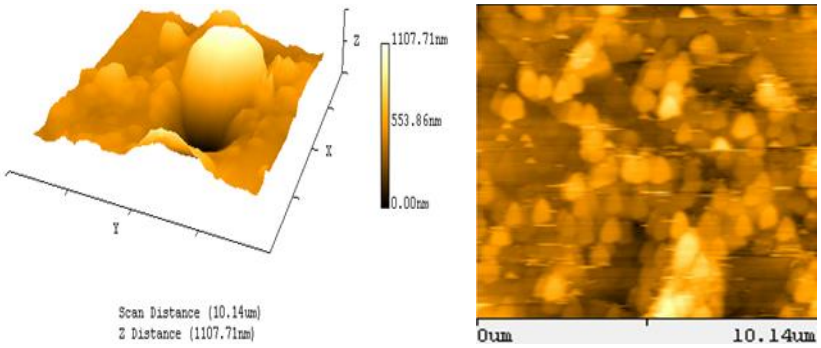

Fig 4. AFM images of three – dimensionalFig 5. AFM images of two-dimensional.

The electrochemical properties of the films have been characterizedby cyclic voltammetry measurements. Figure 6 shows cyclic voltammograms (CVs) of annealed and crystalline titanium oxide films. The two cyclic voltammograms were recorded at a scan rate of 50 mV / s. and a potential range between –350 and 1200 mV with a potentiostatgalvanostat type 301PGZ. In an acidic solution of 0.1 M KNO_3, we can see it on the oxidation peak of the FTO / TiO_2 cable of the modified electrode at 0.1 and 0.5 V successively and a reduction peak at -0, 1 V in the same figure, the non-peak appeared in the FTO electrode.

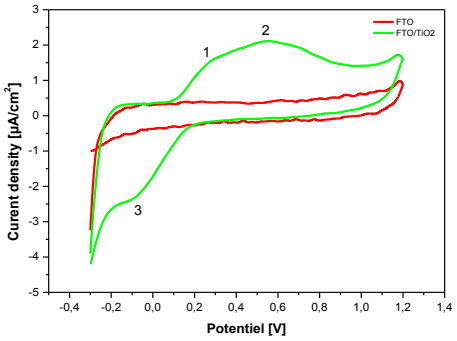

Fig. 6. Cyclicvoltammograms in acidic.

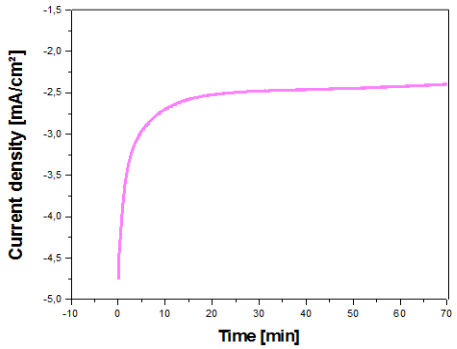

Fig 7. Chronoamperometer voltammograms in acidic KNO_3 0.5 M solution scan rate of 50 mV/s $KNO_3$0.5 M solution scan rate of 50 mV/s.

Figure 8 shows the calibration curve of the maximum values of MAX absorbance as a function of the concentration of the Black Eriochrome T dye, this curve shows a linear relationship of the concentration of the diluted solution using the MAX absorbance values from Table 01

before the initial solution of the UV radiation and after the radiation during the two durations 20 and 30 min. As mentioned below, the result reveals the effect of radiation on the concentration of the dye.

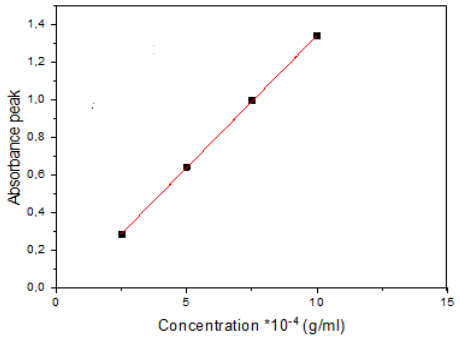

Fig. 8. Calibration curve to calculate Eriochrome Black T concentration.

A solution of dyes Eriochrome Black T known concentration is prepared, then we dip this solution into an electrode FTO/TiO_2 Then calculate the concentration after dipping by UV – method.

Table 2.Test degradation of Eriochrome Black T solution at 20 min and 30 min.

	Initial solution (before UV radiation)	FTO/TiO_2 thin films (after UV radiation)	
		20 min	30 min
MAX values of absorbance peak	1.354	1.323	1.442
Concentration (mg/l)	10.124	9.876	8.785

The photocatalytic degradation of Eriochrome Black T dye in the aqueous phase 10.125 mg/ l under similar experimental conditions. This was done to ensure the use of required amount of catalyst and the absorption of photons for the catalytic process.

It was observed that the rate of the photo-degradation shows a marked increase, Table 2 shows the effect of the catalyst loading on the percentage degradation of Eriochrome Black T dye under visible light illumination, It was observed that with the increase in time the relative concentration of the dye decreases, the percentage degradation rates at 20 and 30 minute is 2 .45 % and 13.5 % respectively.

4. Conclusion

Recurrent cyclic voltammetry, which is an efficient electrochemical method, allowed deposition of TiO_2 layers on FTO from Ti precursor solutions. The precursor effect has been evidenced on the crystal structure nano-sized titanium dioxide on FTO were prepared by The electrodeposition method from a peroxo-titanium solution. The X-ray diffraction (XRD) shows that the as-deposited film was amorphous.

The scanning electron microscopy (SEM) and atomic force microscopy (AFM) showed the homogeneity and medium roughness of the films. The electrochemical behavior of such films shows the characteristic irreversible system, and more electric activity of the as-deposited titanium

(non-heated) films, the testing photo catalysts film to removing some dyes gave a positive results by Spectro photochemical measurements, The absorbance intensity decreased more in TiO_2 presence than in that of carbon graphite. Such tests prove the value of electrodeposited TiO_2 as a photo catalyst for dyes degradation on the TiO_2photocatalyst surface under illumination,. The absorbance intensity decreased more in TiO_2 presence than in that of carbon graphite. Such tests prove the value of electrodeposited TiO_2 as a photo catalyst for dyes degradation.

This study provide in important result given by the characterization of the thin film plotted in the noncommercial plate. The behavior of UV-irradiated for twenty and thirty minute on Eriochrome black T concentration is increased.

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