

PHOTO-ELECTROCHEMICAL QUANTUM EFFICIENCY OF TiO₂ THIN FILMS : EFFECT OF CRISTAL STRUCTURE, PLASMA HYDROGENATION AND SURFACE PHOTOETCHING

Reçu le 04/07/2004 – Accepté le 15/09/2007

Résumé

L'utilisation des matériaux semi-conducteurs dans la détoxification photoelectrochimique de l'eau est devenue un champs de recherche très important. Pour cela, des couches minces de TiO₂ dont la taille des grains nanométrique avec une dimension variant entre 18 nm et 45 nm ont été synthétisées à basse température. On a trouvé par le moyen des mesures de voltamétrie cyclique et de coulométrie que le meilleurs rendement quantique photoelectrochimique sous une lumière UV monochromatique de longueur d'onde 365 nm et une solution de NaOH 0.1N a été obtenu dans le cas des couches déposées par oxydation thermique dont le rendement atteint 28% comparé aux couches déposées par spray ultrasonique et dip coating dont le rendement est moins de 20%. La structure cristalline a une influence sur la photodegradation du méthanol. La structure recommandée pour cette tâche est l'anatase en particulier celle obtenue par la méthode du dip coating dont le rendement augmente après l'addition du méthanol de plus de deux fois comparé à la solution de NaOH 0.1N sans méthanol. Le rendement quantique photoelectrochimique de ces couches est relié au nombre de dips et au recuit final sous air à 550°C pendant une heure. Le recuit n'a pas d'effet sur le rendement des films mais diminue leur activité photocatalytique comme le montre les mesures du photocourant lié à la photodegradation du méthanol. Ce recuit n'a pas d'effet sur la structure cristalline du matériau. La spectroscopie d'impédance d'une couche déposée en six dips avec et sans méthanol montre que le recuit fait augmenter le dopage et diminuer légèrement le rendement quantique. Ceci implique l'importance de la morphologie de la surface dont la rugosité a diminué comme le montre la Microscopie Electronique à Balayage. L'effet de la concentration du précurseur dans l'éthanol a été recherchée en utilisant des films synthétisées à 550°C. Le rendement quantique augmente faiblement en fonction de la concentration du précurseur. Il tend vers la saturation aux grandes concentrations du précurseur. En ajoutant le méthanol à la solution de NaOH 0.1N, la courbe du rendement passe par un maximum pour la proportion 1 à 9. La voltamétrie cyclique et la spectroscopie d'impédance ont montré que l'incorporation de l'hydrogène par plasma dans les couches de TiO₂ fait diminuer le rendement quantique photoelectrochimique dans NaOH 0.1N et augmenter la concentration du dopage. Le rendement quantique photoelectrochimique dans un electrolyte NaOH 0.1N des couches photodécapées dans H₂SO₄ à pleine lumière UV a augmenté deux fois plus que celle non photodécapée (14% à 26.7%).

Mots clés: Structure cristalline, hydrogénation, photoetching, rendement quantique photoelectrochimique

Abstract

The use of semi-conducting materials in the photoelectrochemical detoxification of water became a very important research field. For this purpose, TiO₂ nanostructures thin films with size of 18 nm to 45nm have been synthesized at low temperature. It is found by means of cyclic voltametry and coulometry measurements that the best photoelectrochemical quantum efficiency under UV monochromatic light with a wavelength of 365 nm and a solution of NaOH 0.1N is obtained in the case of thermal oxidation deposition method which can reach 28% compared to ultrasonic spray and dip coating methods of which the quantum is less than 20%. The crystal structure has an influence on the photo-degradation of methanol. The crystal structure which is recommended for this task is the anatase one, especially in the dipping case when the quantum increases after addition of methanol more than twice compared to the solution of NaOH without methanol. The photoelectrochemical quantum efficiency of these films is related to the number of dips and annealing under air at 550°C during one hour. The annealing has no effect on the quantum efficiency of the films, but decreases there photocatalytic activity as showed by the measure of the photocurrent related to methanol photodegradation. The annealing has no effect on the crystal structure of the material. The impedance spectroscopy of six dips deposited films with and without methanol shows that the annealing increases the doping and weakly decreases the film quantum efficiency. This implies, the importance of surface morphology which the rough is decreasing as showed by scanning electron microscopy. The effect of the precursor concentration in ethanol have been investigated by using films, synthesized at T=550°C. The quantum efficiency increases weakly according the precursor concentration. It tends towards a saturation at great concentrations of precursor. In Na OH with methanol added, it passes by a maximum at a proportion 1 to 9. The cyclic voltametry and the impedance spectroscopy showed that the incorporation of hydrogen by plasma in TiO₂ films decreases photoelectrochemical quantum efficiency in NaOH electrolyte and increases the doping concentration. The photoelectrochemical quantum efficiency in NaOH electrolyte of photoetched films in H₂SO₄ at full UV light increased two times greater than of non photoetched one (26.7% versus 14%).

Keywords: crystal structure, hydrogenation, photoetching, photoelectrochemical quantum efficiency.

ملخص

إن استعمال المواد نصف الناقلية في تطهير المياه بواسطة الكهروكيمياة الضوئية أصبح مجالاً هاماً جداً للبحث. من أجل ذلك، فقد تم ترسيب شرائح رقيقة من ثاني أكسيد التيتانيوم نانو بلورية في درجة حرارة منخفضة حيث أبعاد الحبيبات تتراوح بين 18 و 45 نانومتر. لقد وجدنا باستعمال قياسات الفولتمترية الدورية والكولومترية أن أحسن مردود كهروكيميائي ضوئي تحت إضاءة وحيدة اللون فوق بنفسجية طول موجتها 365 نانومتر ومحلول من NaOH 0.1N يكون في حالة شرائح التيتانيوم المرسبة بطريقة الأكسدة الحرارية حيث بلغ المردود 28 % مقارنة مع طريقتي الرش والغمس الحراريتين إذ لم يتجاوز المردود 20 % . إن للطبيعة البلورية تأثير في الإلتلاف الضوئي للميثانول حيث تبين أن الطبيعة أناتاز (Anatase) هي المطلوبة وخاصة المحصل عليها بطريقة الغمس أين يزداد المردود أكثر من مرتين بعد إضافة الميثانول إلى محلول NaOH 0.1N مقارنة بنفس المحلول بدون إضافة للميثانول. إن المردود الكمي الكهروكيميائي ضوئي لهذه الشرائح له علاقة بعدد الغمسات وبالتسخين عند الانتهاء من الترسيب تحت درجة 550 °C لمدة ساعة. هذا التسخين لا يؤثر على المردود الكمي للشرائح ولكنه يقلص من نشاطها الفوتوكاتاليتي كما تبين ذلك قياسات التيار المتعلق بالإلتلاف الضوئي للميثانول. كما أن التسخين الأخير لا يغير من الطبيعة البلورية للشرائح. وباستعمال سيكترسكوبيا الممانعة لشرائح ذات ست غمسات في حالة إضافة الميثانول إلى المحلول وفي حالة عدم إضافته وجدنا أن التسخين يزيد في كثافة التطعيم و ينقص قليلاً في المردود الكمي للشرائح، وهذا يؤكد أهمية تشكل السطح الذي أصبح أقل ملاسمة كما تبين ذلك المجهرية الإلكترونية الماسحة. لقد تم بحث تأثير تركيز محلول التيتانيوم في الإلتانول باستعمال شرائح مرسبة في درجة 550°C وتم التأكد من أن المردود الكمي يزداد ببطء بزيادة التركيز و يؤول إلى قيمة ثابتة عند التراكيز الكبيرة. وأما في حالة إضافة الميثانول إلى محلول NaOH 0.1N ، فإن منحني المردود الكمي يمر بقيمة عظمى عند النسبة 1 إلى 9. لقد بينت الدراسة الفولتمترية الدورية و سيكترسكوبيا الممانعة أن إدخال الهيدروجين في شرائح ثاني أكسيد التيتانيوم عن طريق البلازما يعمل على تقليص المردود الكمي في محلول NaOH 0.1N في الوقت الذي يزيد في كثافة التطعيم. إن المردود الكمي في محلول NaOH 0.1N للشرائح المصقولة في H₂SO₄ تحت إضاءة فوق بنفسجية شاملة إزداد مرتين مقارنة مع التي لم يتم صقلها (من 14% إلى 26.7%).

الكلمات المفتاحية: الطبيعة البلورية، الهدرجة، الصقل الضوئي- المردود الكهروكيميائي ضوئي

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Introduction

The use of semi-conducting materials in the photoelectrochemical detoxification of water became a very important field of research based on original experiment by A. Fujishima and K. Honda (1972) [1].

In this experiments the Authors have shown the decomposition of water into O_2 and H_2 gas in a photoelectrochemical cell with an n-TiO₂ electrode. This kind of electrode presents a good chemical stability and the valence band level of this material permit a good charge transfer at liquid/TiO₂ interface [2].

This decomposition is based on electron-hole generation followed by their separation in the space charge electric field which move the electron to the bulk and the hole to the solution .

The photo-generation is achieved by the use of light with a wavelength under 400 nm corresponding to 3.2 eV band gap.

K. Bernard and A. Bard (1978) [4] have decomposed the acetic acid and carboxylic acid into CO₂ and alkenes opening the way of the organic compounds decomposition in water.

Because of its photoelectrochemical properties. Titanium dioxide is an attractive material for the purification of waste and drinking water [5].

At the beginning TiO₂ powder was used with the problem of his separation from water after treatment. This problem is resolved by using thin solid film of this [6].

TiO₂ thin solid films have been deposited by different methods such as electrodeposition [7], thermal oxidation and dip coating [8], spin coating [9], and aerosol spray pyrolysis [10].

This easy last method presents a high interest to investigate the photoelectrochemical quantum and stability of films with good adhesion. His low cost allows to obtain large uniform area.

Aerosol spray pyrolysis is a method of preparing particles by decomposing droplets of Titanium precursor in gas phase on heated substrate.

The droplets are generated by an ultrasonic generator.

Thermal oxidation and dip coating are also used to synthesize TiO₂ because of there simplicity. The first one is based on heating Titanium substrate in oxygen or air atmosphere. The second one consists to dip the Ti substrate into the precursor solution and heating it in a conventional furnace to obtain a thin film of TiO₂ after thermal decomposition of the precursor. This operation is repeated several times.

The morphology of films depends on the deposition conditions such as starting solution, temperature of droplets decomposition , nature of substrate, carrier gas etc...

In this work, we have prepared TiO₂ thin films by the above different methods to investigate the crystal structure and its influence on photocatalytic properties. For the photodegradation we have added methanol 0.1M as a toxic pollutant to solution of NaOH 0.1N[11].

We also deal with TiO₂ films surface treatment as plasma hydrogenation and photoetching in H₂SO₄ related to the doping concentration increasing and surface porosity to achieve good photoelectrochemical quantum.

II- Experimental

In this work we used two kinds of substrate: commercial Titanium (technical quality, Weber) and F-doped SnO₂ coated glass with surface resistivity of 9 Ω (Solems) in order to compare photoresponse property in both case.

The sizes of samples are 4cmx1cmx1mm.

All substrates were cleaned ultrasonically in trichloroethylene, acetone, ethanol and water and dried in a stream of Argon. Glass and F-SnO₂ / glass substrate were additionally etched in 5% for 1mn rinsed with water and dried with Argon.

Titanium substrates were additionally etched in a mixture of HF, HNO₃ and H₂O for 30s rinsed with water and dried with Argon.

From a solution of di-isopropoxytitanium bis-acetylacetonate (TiC₁₆H₂₈O₆),75% in isopropanol (Fluka), isopropanol was evaporated and replaced by absolute ethanol (EtOH). The final precursor solution was :10% TiC₁₆H₂₈O₆ in ethanol. All other chemicals were of analytical grade and used without further purification. Water was purified with a Millipore apparatus.

The precursor solution of Titanium is used as starting solution in spray method to generate small droplets.

The nebulisation is achieved by an ultrasonic generator (Holmes). The precursor is carried to the heated substrate by Nitrogen gas saturated with ethanol vapour in a debit of 2l/min.

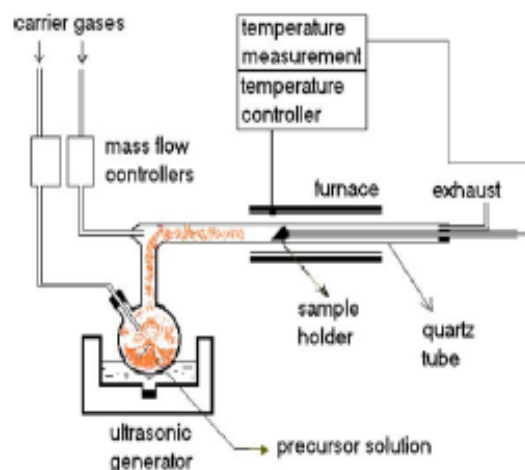


Fig.1- Schematics of the aerosol pyrolysis apparatus employed for the deposition of TiO₂ films.

The small droplets are applied on the substrate in a silica reactor, at a temperature 460° C in order to avoid rutile phase.

The same precursor solution of Titanium is used in dipping method.

The anatase phase has good activity towards photodegradation of organic compounds in water [12,13].

The crystal structure and the grain size of the films were determined by X diffraction of CuK α radiations. This analyse was performed directly on the films with a Philips diffractometer using the Bragg-Brentano method.

Plasma hydrogenation of films is achieved in generator at 250°C for 1 hour, 1mb of hydrogen pressure and 30 Watts of power.

For comparison goal we have deposited some films by thermal oxidation method of a Titanium substrate in O₂ atmosphere at 550°C during 1 hour and 1 atm as pressure.

The calculation of photoelectrochemical quantum is based on photocurrent measurement versus voltage (cyclic voltametry) using a Hamamatsu S1337-1010BQ calibrated photodiode. A 150 W medium pressure mercury lamp in combination with a 365 nm interferential filter was used for illumination The supporting electrolyte used is NaOH 0.1M.

Photoelectrochemical quantum is defined as the ratio of the number of electrons moving in the external circuit of the photoelectrochemical cell, to the number of photons arriving on the cell. It is calculated by the following formula :

$$\Phi_c = \Phi_p (I_c/I_p)$$

Φ_c : Quantum efficiency of Cell.

Φ_p : Quantum efficiency of hamamatsu photodiode.

I_c : Current of cell at U= 0.6V

I_p : Current of hamamatsu photodiode at U= 0.6 V

The photoetching of surface films is achieved by the same system but in coulometric mode and H₂SO₄ 0.5M as electrolyte under full light of mercury lamp..

Scanning electron micrographs (SEM) were obtained from a JEOL JSM-840. UV-Vis reflection spectra were measured at near to normal incidence using a home-made setup employing a Xe arc lamp (Oriel), a Jobin-Yvon monochromator, a goniometer (Micro Control) and a Hamamatsu S1336-8BQ photodiode.

The doping concentration and the flat band voltage have been determined by impedance spectroscopy using Mott-Schottky straight line.

III- Results and discussion

III-1) Crystal structure and photocatalytic properties

The X-ray diffraction shows a good stoichiometric TiO₂ with rutile, anatase or mixture of the two phases.

The grain sizes of the samples are nanostructures and vary from 18 to 45 nm; these two parameters are linked to the growth method and associated thermodynamic conditions.

III-1-a) Structure and photocatalytic properties of thermal oxidation films.

Thermal oxidation of titanium under one atmosphere of oxygen pressure at a temperature T=550°C leads to rutile phase as showed by the peak of (110) plans corresponding to $2\theta = 27.415^\circ$ (Fig.2). The other peaks are related to the titanium substrate(Fig.3). The rutile phase is in general chemically more stable than anatase [14].

The measured photoelectrochemical quantum under a radiation $\lambda = 365$ nm is about 28% and is greater than that is measured in the same conditions with TiO₂ growth by thermal oxidation under air. The addition of methanol 0.1M to the solution of NaOH 0.1N has not affected the photocurrent then the photocatalytic activity (Fig.4). This is due essentially to rutile phase of the material [12,13].

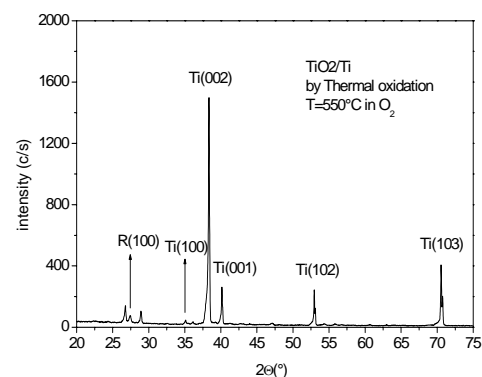


Fig.2- XRD of TiO₂/Ti prepared by thermal oxidation @ T=550°C.R means TiO₂ rutile

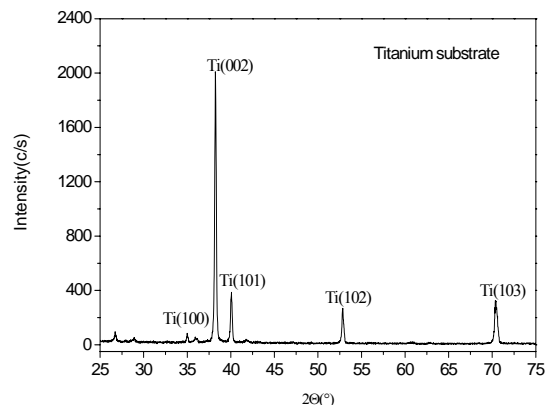


Fig.3- XRD of Ti substrate

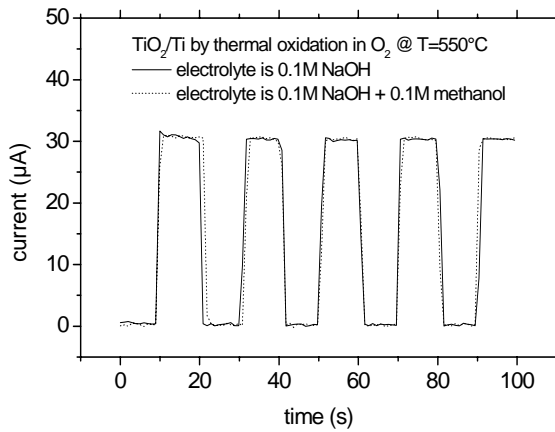


Fig. 4-Coulometric measurement at U=0.6V of films prepared by thermal oxidation

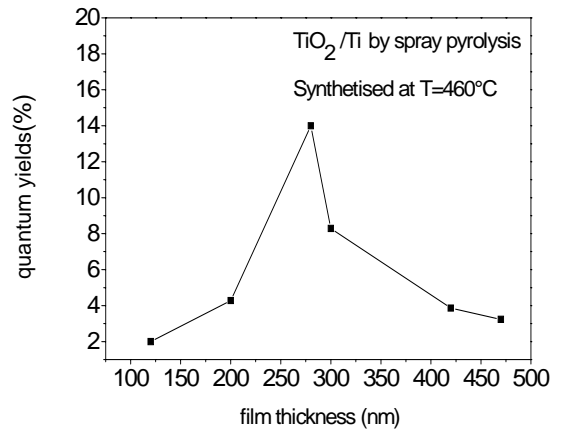


Fig.6- The photoelectrochemical quantum of samples versus thicknesses of TiO₂ spray coated films.

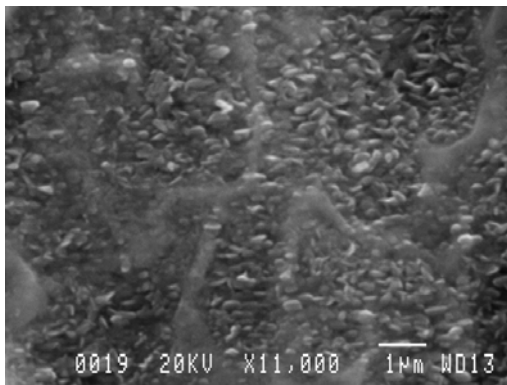


Fig. 5- SEM image of thermal oxidation film.

One can also remind that the photoelectrochemical quantum depends strongly of the grains size of the samples [15].

The sample growth by thermal oxidation under oxygen has a grain size of 30 nm.

The SEM image of the film deposited on Ti substrate is illustrated on Fig. 5.

III-1-b) Structure and photocatalytic properties of ASP (Aerosol spray pyrolysis) films.

The films synthesized by ASP method at 460°C and annealed at 550°C under air or O₂ flux to remove carbon impurity by oxidation. The films thickness influences strongly their photoelectrochemical quantum which is over 4% to 14% (Fig.6). The thickness was performed by reflectivity measurements (Fig.7). It varied from 120nm to 470nm. The material is a mixture of rutile and anatase phase with a great proportion of rutile phase as showed by diffraction lines on (Fig.8).

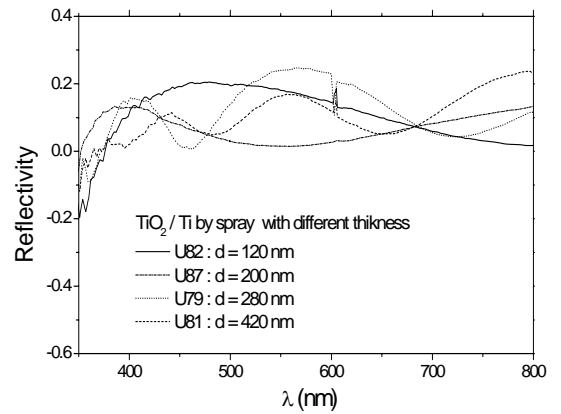


Fig.7- reflectivity measurements of TiO₂/Ti aerosol spray paralysis.

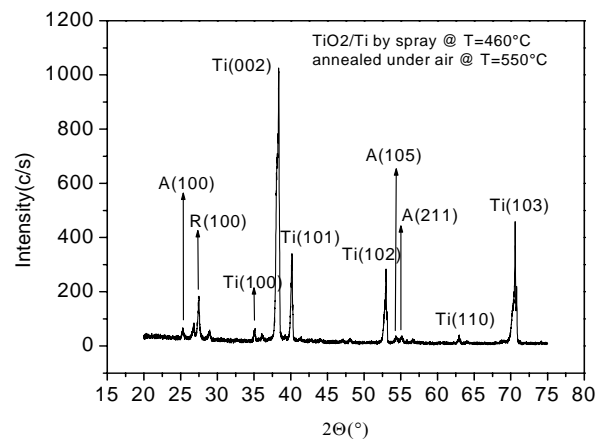


Fig.8-0XRD of TiO₂/Ti prepared by aerosol spray paralysis. R means rutile and A anatase TiO₂.

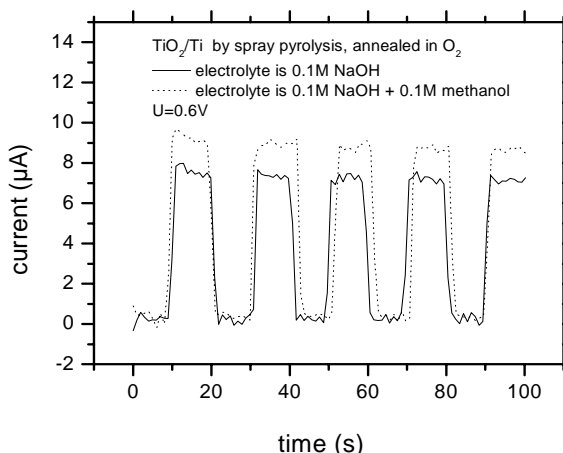
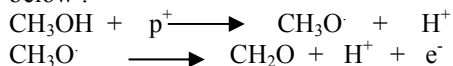


Fig. 9- Coulometric measurements of TiO₂ spray coated. effect of methanol addition in NaOH solution 0.1N

The films are nanometrics with a grain size of 45 nm, which is greater than that measured in the film synthesized by thermal oxidation method.

The photocurrent at different potential V was performed in a (NaOH, 0.1N) and in a (NaOH, 0.1N + methanol, 0.1M) solutions, to appreciate the photocatalytic properties of the films. The measured photocurrent has small value and increases lightly after methanol addition. These results agree with other authors results which prove that photocatalytic properties of anatase are better than those of rutile phase.

The photocurrent light increasing results of the material molecule decomposition following the chemical reaction below :



The photogeneration of a pair (e^- , h^+) and the injection of an electron in the conduction band by the methanol molecule decomposition, lead to a current doubling (two electron by photon $h\nu$) (Fig.9).

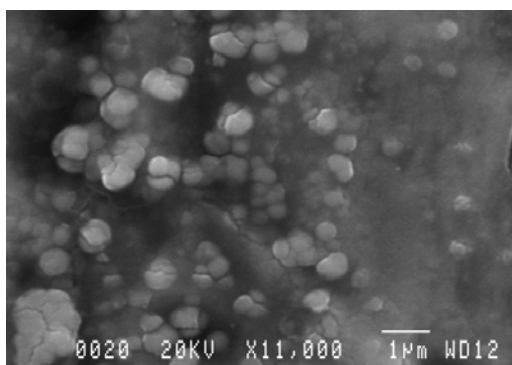


Fig. 10- SEM image of TiO₂ spray coated film.

III-1-c) Structure and photocatalytic properties of dip coating films.

We did not observe this current doubling but the current increases lightly with methanol. The material structure with a presence of rutile phase and with a smooth surface by SEM (Fig.10) and reflectivity measurements, can explain the weak increase of the photocurrent.

The structure of the material prepared by dip coating under air atmosphere at T = 550°C is anatase phase as showed by XRD (Fig.11). We don't observe the rutile phase in these materials.

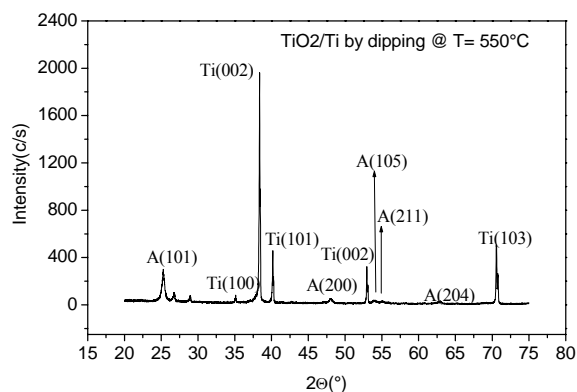


Fig.11- XRD of TiO₂/ Ti prepared by dip coating at T=550°C. A means Anatase phase

In the same preparation conditions, in the ASP method, the material is partly rutile phase. This material is small size (18.3 nm) than those prepared by thermal oxidation (30nm) and ASP (45nm).

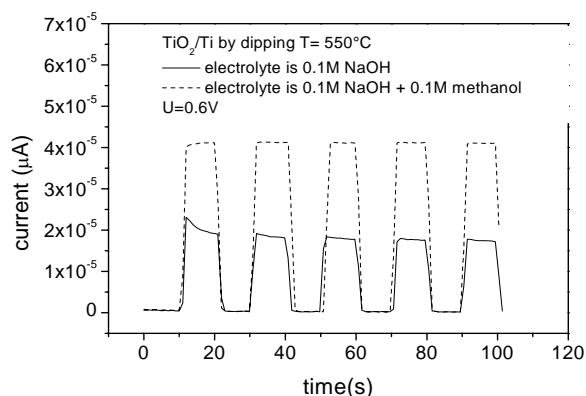


Fig.12- coulometric meaurments of TiO₂ dip coated films at T= 550°C .effect of methanol addition in NaOH solution 0.1N.

We have testing the photocatalytic properties of our films by addition of methanol in the NaOH solutions in this case (0.1M of methanol in the solution) the photoelectrochemical quantum increases to 39% with dip coated films witch are more efficient to decompose the methanol than thermal oxidation and ASP films (Fig.12). This is related to anatase phase and surface roughness of dip coated films (Fig.13).

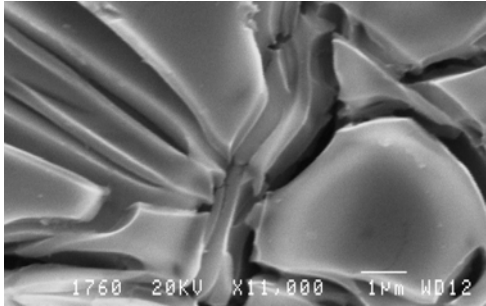


Fig.13- SEM image of TiO₂ dip coated films prepared at T= 550°C

The photoactivity of the material is governed by the kinetic of the interfacial holes transfer to the oxidized species in the solution. The two species are OH/H₂O and MeOH. The ability of MeOH species to capture the holes photogenerated at the interface more efficiently than OH⁻ ions and water explains the increase over twice of the photocurrent with methanol compared to the solution without methanol. This doesn't agree with results of Wahl and al [11] with conventional sol/gel anatase electrode. These authors found the same phenomena with the anatase-rich P25 (80% anatase + 20%rutile).

III- The precursor concentration effect on the photoelectrochemical quantum efficiency of dip coated TiO₂ films.

The effect of the precursor concentration in ethanol is investigated by using films of three dips, synthetised at T=550°C. The Fig-14 shows that the quantum efficiency increases weakly according the precursor concentration. It tends towards a saturation at great concentrations of precursor. In NaOH with methanol added, it passes by a maximum at a proportion 1 to 9. We note also that the photodegradation of methanol is sensitive to change of precursor.

III-2) Effect of the air thermal annealing and the dips number on the quantum efficiency of dip coating elaborated TiO₂.

The curves of Fig-15 give the quantum efficiency according to the dips number. The quantum efficiency presents a maximum at six dips. The photocurrent is increasing with the thickness until that of six dips. Greater than six dips, it decreases because of photo-carriers recombining. A number of layers were annealed at 550°C

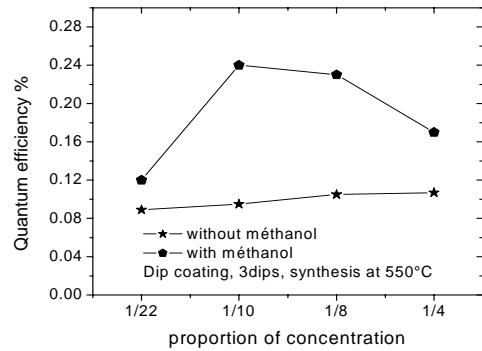


Fig.14- Quantum efficiency versus concentration of precursor with and without methanol

during 60 mn as a final annealing which has no effect on the quantum efficiency as seen on (Fig-15).

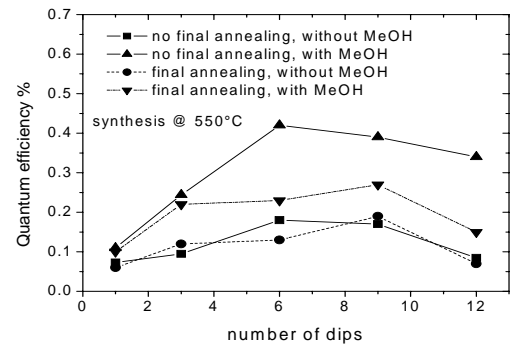


Fig.15. Quantum efficiency according dips number at synthesis temperature at T=550°C.

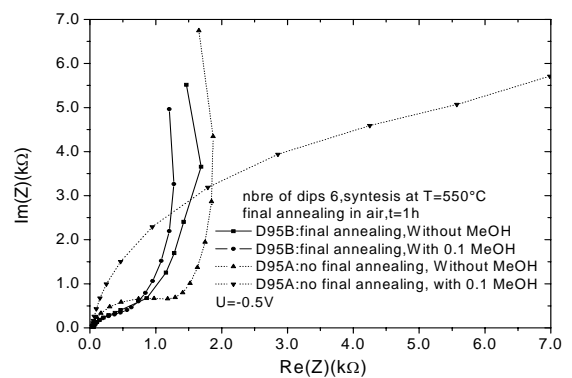


Fig.16. Nyquist diagram of six dips layer with T=550°C as synthesis temperature

The impedance spectroscopy carried out for six dips with and without final annealing, shows a conductivity variation which agrees with a doping increasing (Fig-16). The use of NaOH solution with methanol added increases drastically the quantum efficiency with and without final annealing. We have a methanol photodegradation using anatase TiO₂ layers with rough surface. The increasing of quantum efficiency is less important in the case of final annealing according to the case without final annealing. The final annealing decreases the roughness of the surface as showed in the (Fig-17a and Fig-17b).

The final annealing has no effect on crystal structure and grain size as shown on XRD spectrum (Fig. 18). The anatase peak is in the same position (25.29°) after final annealing with no change of its intensity. The two other peaks (26.78° and 28.92°) correspond to titanium substrate composite.

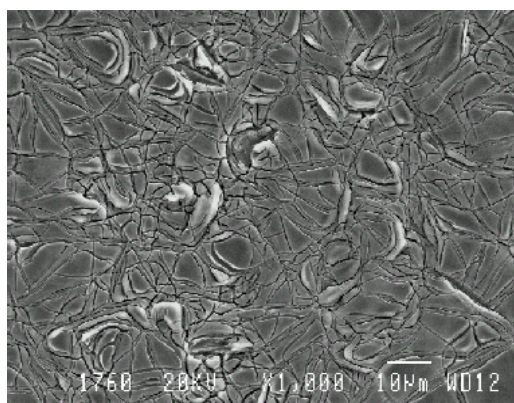


Fig17a- SEM image of six dips layer at 550°C synthesis temperature without final annealing.

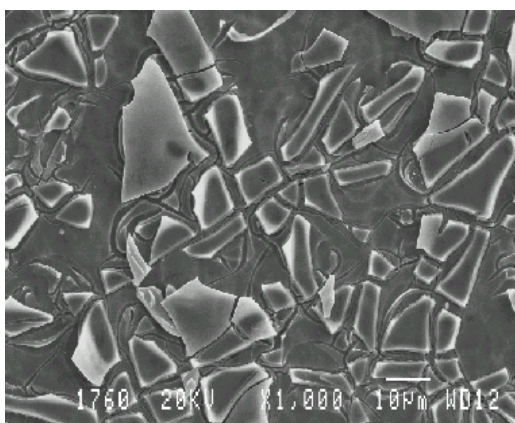


Fig-17b. SEM image of six dips layer at 550°C synthesis temperature with final annealing.

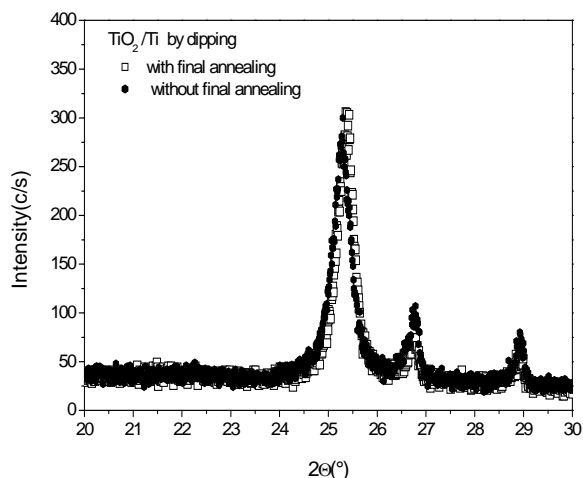


Fig.18- XRD of dip coated films: final annealing effect at T= 550°C for 1h.

III-2) Incorporation of hydrogen by plasma effect in TiO₂ films

The hydrogen incorporation generally increases the TiO₂ conductivity [3,24,25]. In this work we are interesting with the plasma hydrogenation effect on photoelectrochemical quantum of synthesised films.

The I-V curves of TiO₂ and the hydrogenated one shows that the photocurrent generally decreases after hydrogenation (Fig19a-19b-19c-19d). The table I gives the value of the quantum yields for different surface preparation.

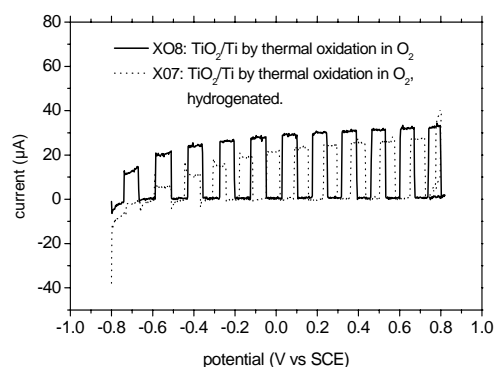


Fig.19a-I-V measurements of TiO₂ films prepared by thermal oxidation in O₂ : hydrogenation effect

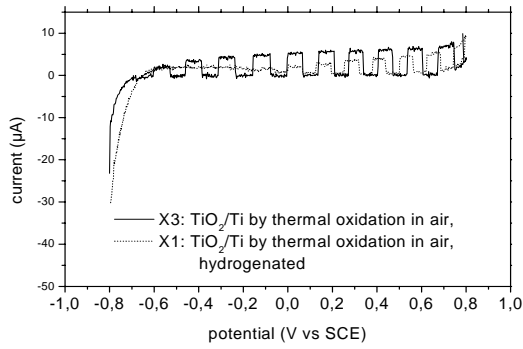


Fig.19b-I-V measurements of TiO₂ films prepared by thermal oxidation in air : hydrogenation effect

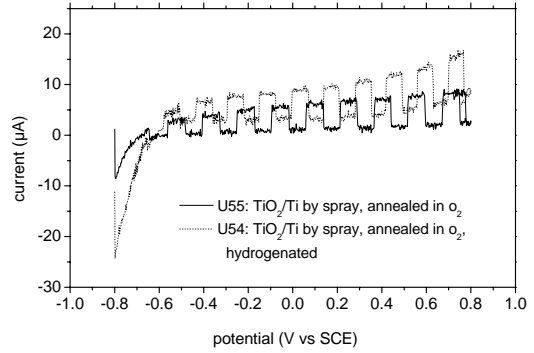


Fig.19c-I-V measurements of TiO₂ films prepared by spray on Ti substrate : hydrogenation effect

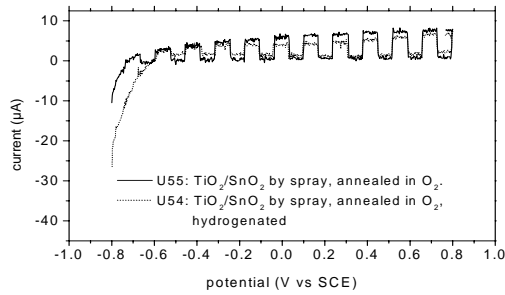


Fig.19d-I-V measurements of TiO₂ films prepared by spray on F-SnO₂ substrate : hydrogenation effect

Table I- Quantum efficiency for different samples

Without hydrogenation			After hydrogenation		
Sample reference	Preparation Conditions	Quantum Efficiency %	Sample reference	Preparation Conditions	Quantum Yields %
XO8	Substrate :Ti Thermal oxydation in O ₂ T=550°C, p=1atm, t=1h	26	XO7	XO8 conditions + plasma Hydrogenation at T=250°C, t=1h, p _{H2} =1mb P=30W	24
X3	Substrate :Ti Thermal oxydation in air T=550°C, p=1atm, t=1h	5.4	X1	X3 conditions + plasma Hydrogenation at T=250°C, t=1h, p _{H2} =1mb P=30W	3.8
U55	Substrat : Ti, Aerosol Spray pyrolysis T=460°C, t=30mn, n, + annealed in O ₂ : T=550°C, t=45mn, p _{O2} =1atm	5.7	U54	U55 conditions + plasma Hydrogenation at T=250°C, t=1h, p _{H2} =1mb P=30W	7
U57	Substrate:SnO ₂ U55 Conditions	6.15	U56	U57 conditions + plasma Hydrogenation at T=250°C, t=1h, p _{H2} =1mb P=30W	4.9

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The Mott-Shottky curves indicate a remarkable decrease of straight slope after hydrogenation that means an increase of doping concentration witch change from 5.2×10^{18} to 5.3×10^{19} cm⁻³ after hydrogenation as observed in the thermal oxidation of Titanium (Fig.20).

The Mott-Schottky curve corresponding to the TiO₂ synthesised by spray doesn't show the same effect. It is screened by strong surface effect after hydrogenation (Fig.21a,21b).

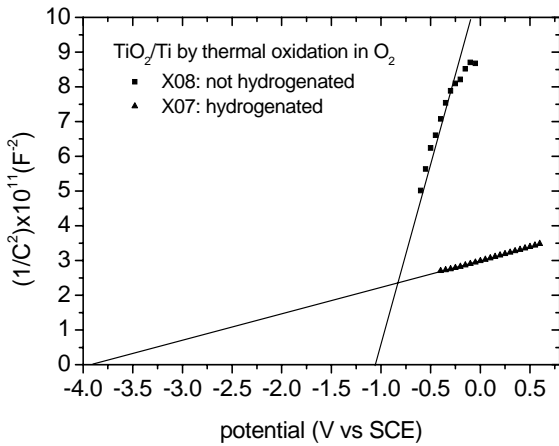


Fig.20-Mott-Shottky measurements of TiO₂ films prepared by thermal oxidation in O₂ : Hydrogenation effect

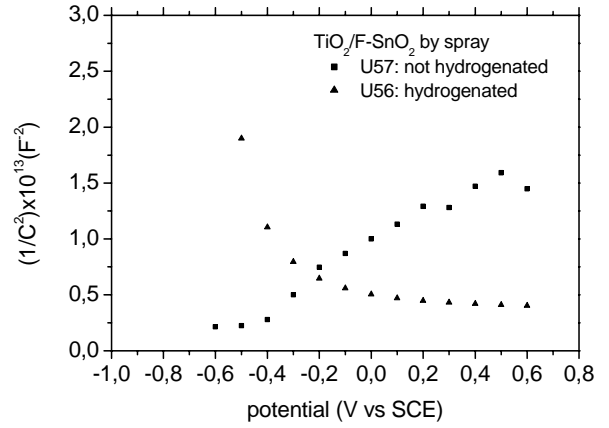


Fig.21b- Mott-Schottky measurements of TiO₂ films prepared on F-SnO₂ by spray :Hydrogenation effect

The doping change increases normally the photocurrent [16]. This effect is not observed. The decrease of the photoelectrochemical quantum after hydrogenation is related in our case to the light absorption decrease as showed in (fig.22).

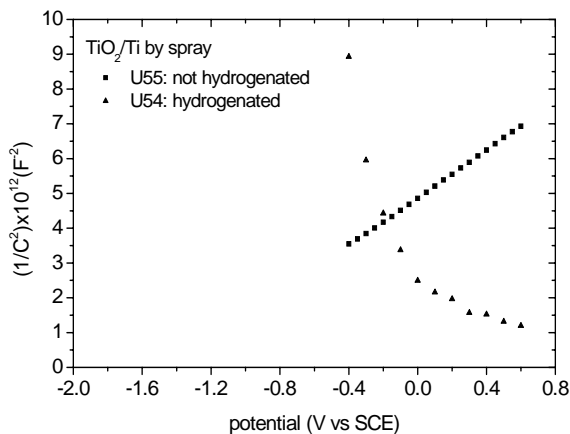


Fig.21a- Mott-Shottky measurements of TiO₂ films prepared on Ti by spray : Hydrogenation effect

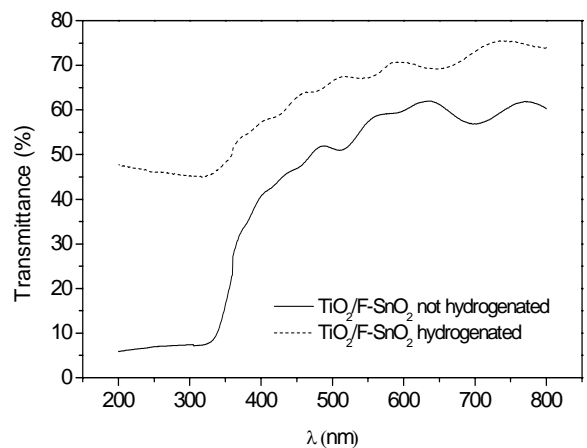


Fig. 22- transmittance measurements of TiO₂/F-SnO₂ films by spray : hydrogenation effect.

The increase of doping concentration after hydrogenation is confirmed by the shift of the open circuit voltage towards positive voltages as shown in all I-V curves.

To compute the doping concentration, we have used the following formula [17]:

$$N_d = \frac{2C^2}{e\epsilon_r\epsilon_0 A^2 (V - V_{fb} - kT/e)}$$

A is the geometric electrode area

$$\epsilon_r = 120$$

III-3) TiO₂ films treatment by photoetching in H₂SO₄.

The photoetching of TiO₂ was made in H₂SO₄ (0.5M) using coulometric mode at fixed potential of 1.4 V. The cyclic voltametry of TiO₂ films and the photoetched one shows that the photocurrent increases by two times in the case of photoetched one. The related photoelectrochemical quantum are 14% and 26.7% before and after photoetching respectively (Fig.23).

This result is explained by the remarkable change of surface morphology which shows an increasing porosity density.

The images (Fig. 24) obtained by scanning electron microscopy shows clearly the appearance of pores on the surface which have an important effect on the photocurrent as explained in the literature [18,19].

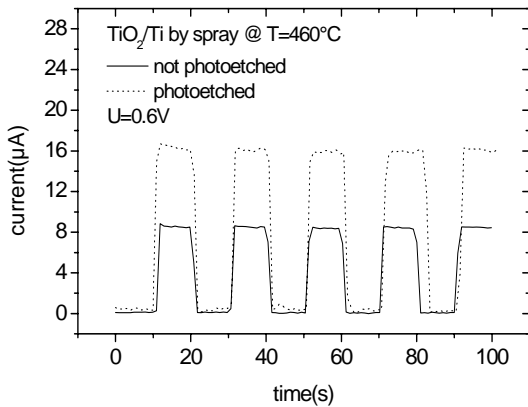


Fig. 23- Photoetching effect of TiO₂/Ti prepared by spray

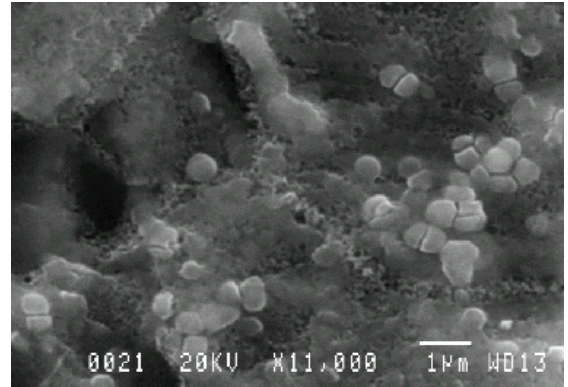
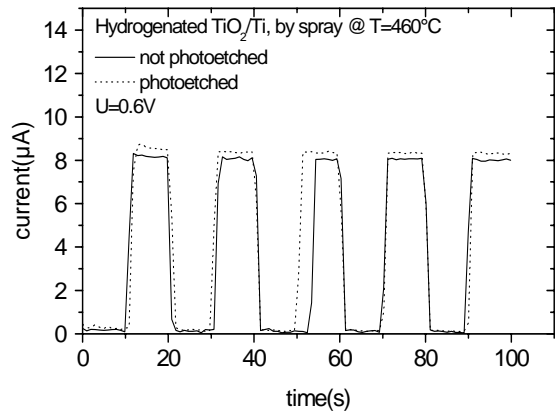


Fig.24- SEM image of TiO₂/Ti prepared by spray, after photoetching

In the hydrogenated films case we have not observed a similar effect of photoetching on photoelectrochemical quantum in the titanium substrate



case as shown on I(V) curves (Fig-25).

Fig. 25- Photoetching effect of hydrogenated TiO₂/Ti prepared by spray

The photocurrent increases after photoetching from 4.5% to 5.5% and 3.5% to 6.1% in the case of no hydrogenated and hydrogenated TiO₂ on F-SnO₂ respectively.

In the hydrogenated sample, the increase of photoelectrochemical quantum can be explained by the effect of surface cleaning. The morphology is not changed, then we can affirmed the strong stability of the surface, it shows spherical particles piled up with a size of ~ 200 nm (Fig.26a,26b). We have also investigated the quality of photoetched films towards methanol

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photodegradation. It is found that the photocurrent changed weakly by increasing or decreasing after addition of 0.1 M Methanol in 0.1M NaOH solution. This is due to surface morphology which is not more rough. The coulometric curves corresponding to different photoetching are presented in figures (27,28,29,30). The table-II reports the quantum yields for different samples.

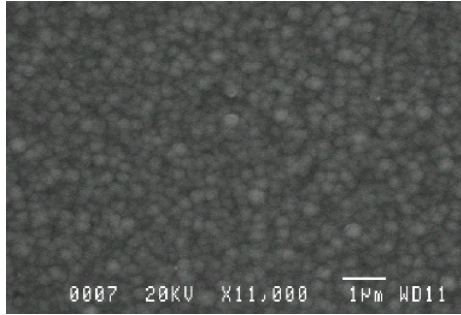


Fig. 26a- Hydrogenated TiO₂/F-SnO₂ without photoetching

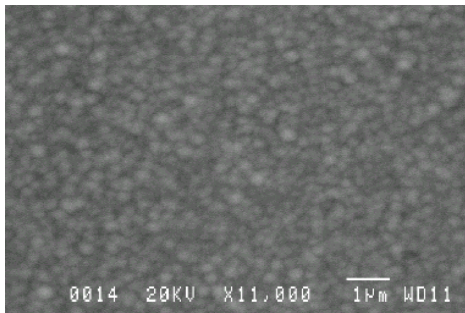


Fig-26b: Hydrogenated TiO₂/F-SnO₂ after photoetching

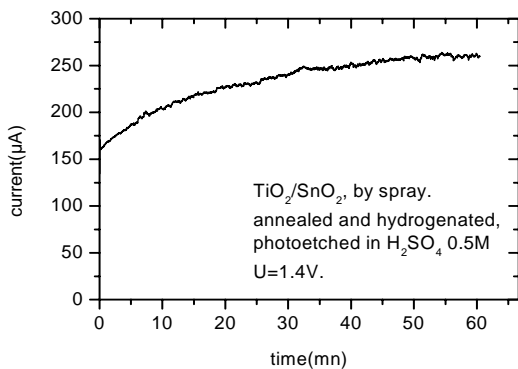


Fig. 27- photoetching of Hydrogenated TiO₂/F-SnO₂

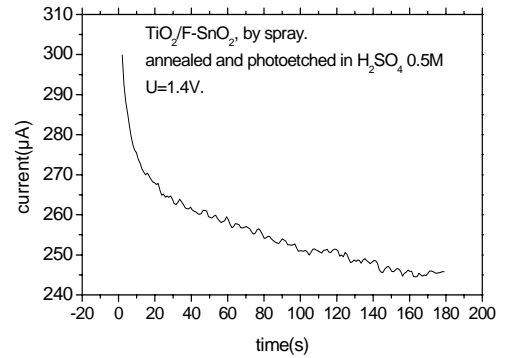


Fig. 28- photoetching of no hydrogenated TiO₂/F-SnO₂

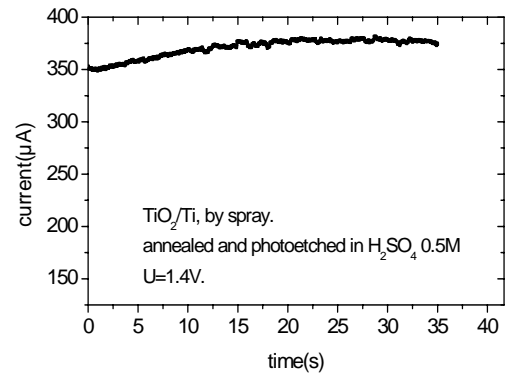


Fig.29- photoetching of hydrogenated TiO₂/Ti

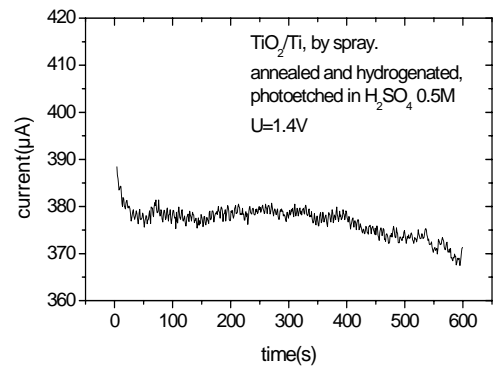


Fig.30- photoetching of no hydrogenated TiO₂/Ti

Table-II: photoetching effect for different samples

Sample	Substrate	Quantum efficiency in %	Comment
U79A	Ti	14.1 26.7	Synthesis at T=460°C, 6 times/30s-1mn, Annealed in air + photoetching in H ₂ SO ₄ 0.5M /U=1.4V/t=1h
U54	Ti	13.2 13.4	Synthesis at T=460°C, t=30 mn, annealed in air/T=550°C/t =1h, hydrogenated at T=250°C,t=1h,P=30W + photoetching in H ₂ SO ₄ 0.5M /U=1.4V/t = 6mn
U57	F-SnO ₂	4.5 5.5	Synthesis at T=460°C,t=30mn, annealed in air/T=550°C/t=1h + photoetching in H ₂ SO ₄ 0.5M /U=1.4V/t = 3mn
U56	F-SnO ₂	3.5 6.1	Synthesis at T=460°C,t=30mn, annealed in air/T=550°C/t=1h, hydrogenated at T=250°C,t=1h,P=30W + photoetching in H ₂ SO ₄ 0.5M /U=1.4V/t = 1h

The interesting case is that of not hydrogenated TiO₂/Ti . We have observed a small increase of photoelectrochemical quantum without photoetching from 14.1% to 14.7% but an improvement of photodégradation activity after photoetching from 26.7% to 29.8% . It is explained by the roughness and porosity of the surface state.

CONCLUSION

In this work, we synthesize nanomaterial and stoichiometric TiO₂ thin films with size of 18 to 45 nm at low temperature by three methods: Thermal oxidation, Aerosol spray pyrolysis and Dip coating.

The photoelectrochemical quantum efficiency is strongly related to the preparation method. In a solution of NaOH 0.1N, the quantum efficiency of thermal oxidation film (28%) is better than that obtained with ultrasonic spray and dip coating films (less than 20%).

The crystal structure influences drastically the methanol photodegradation. The phase which is recommended for this task is the anatase one, especially in the dipping case when the photoelectrochemical quantum efficiency increases after addition of methanol more than twice compared to the solution of NaOH without methanol.

TiO₂ thin film obtained by thermal oxidation have a rutile phase then it does not influence photocatalytic properties.

The photoelectrochemical quantum efficiency of dip coated films is related to the number of dips and annealing under air at 550°C during one hour.

The annealing has no effect on the quantum efficiency of the films, but decreases their photocatalytic activity as showed by the measure of the photocurrent related to methanol photodegradation. The annealing has no effect on the crystal structure of the material.

The effect of the precursor concentration in ethanol is investigated by using films of three dips, synthesized at T=550°C. The quantum efficiency reach a maximum in Na OH with methanol added at a proportion 1 to 9.

The plasma hydrogenation of TiO₂ films deposited by aerosol spray pyrolysis decreases photoelectrochemical quantum efficiency, while the doping concentration is increased.

However this hydrogenation can improve strongly the physicochemical stability especially in the F-SnO₂ substrate case.

In TiO₂ films deposited on Titanium substrate, without plasma hydrogenation, a great effect of the photoetching on photoelectrochemical quantum have been observed (27% versus 14%).

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