SYNTHESIS, STRUCTURAL CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF TIO_2 NANOPARTICLES

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ABSTRACT

Titanium dioxide (TiO_2) nanoparticles were synthesized via sol-gel process (soft chemistry), using the metal alkoxide as precursor. TiO_2 is a promising material especially when it is reduced to the nanometric scale, but many parameters influence its nanoscale synthesis. In this work, the influence of calcination time was studied.

The structure, morphology and size of the synthesized particles were determined by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

The XRD diffractograms revealed an anatase structure of the as prepared TiO_2, with a nanometric size. The average particle size of TiO_2, synthesized in ethanol as a solvent, is estimated to be 17 nm. An increase of calcination time induced an increase of the particle size to 21 nm, while keeping the anatase phase unchanged. FTIR measurements confirmed the pure anatase phase of TiO_2 and the SEM micrographs displayed the aggregation of the nanoscale particles. The photocatalytic activity of synthesized nanoparticles was investigated by degradation of methylene blue dye by TiO_2 nanoparticles under ultraviolet radiation.

KEYWORDS: TiO_2, photocatalysis, nanoparticles, Sol-gel.

RESUME

Dans ce travail, les nanoparticules de dioxyde de titane (TiO_2) ont été synthétisées via le procédé sol-gel (chimie douce), utilisant l'alcoxyde de métal comme précurseur. Le TiO_2 est un matériau prometteur surtout lorsqu'il est réduit à l'échelle nanométrique, mais beaucoup de paramètres influent sur celui-ci. Dans ce travail, plusieurs temps de calcination ont été étudiés. La structure, la morphologie et la taille des particules synthétisées ont été réalisées par diffraction des rayons X (DRX), spectroscopie infrarouge à transformée de Fourier (IRTF) et microscope électronique à balayage (MEB).

Les diffractogrammes de DRX ont révèle une structure anatase du TiO_2 avec des tailles nanométriques. La taille moyenne des cristallites est de 17 nm pour le TiO_2, synthétisé dans l'éthanol comme solvant. L'augmentation de la durée de la calcination entraîne une augmentation de la taille (21 nm). Les mesures FTIR confirment la structure anatase de TiO_2. Les images MEB ont montré que la taille des particules, agglomérés en aggrégats, est nanométrique.

L'activité photo-catalytique des nanoparticules synthétisées a été étudiée par photo-dégradation du colorant bleu de méthylène sous rayonnement ultraviolet.

MOTS CLES: TiO_2, photocatalytique, nanoparticule, Sol-gel.

ملخص

في هذا العمل تم تصنيع جسيمات ثاني أكسيد التيتانيوم (TiO_2) النانومترية عن طريق سول-جال

(الكيمياء اللينة)، وذلك باستخدام الالكوكسيد المعدني كسلائف. لأن TiO_2هو مادة واعدة خاصة عندما يتم تخفيضه إلى مقياس نانومتر، فالكثير من العوامل تؤثر

على هذا. لذلك تم دراسة العديد من اوقات التكليس.

تمت دراسة الهيكل، المورفولوجيا وحجم الجسيمات من العينات بواسطة الأشعة السينية، الأشعة تحت الحمراء والمجهر الالكتروني الماسح.
الأشعة السينية كشفت عن هيكل أناتاس من TiO_2 عند استخدام الإيثانول و حجم الجسيمات التي تأسست هو 17نانومتر كما ان زيادة وقت التكليس دون تغيير درجة الحرارة يسبب زيادة حجم البلورات (21 نانومتر). وتؤكد نتائج الأشعة تحت الحمراء هيكل أناتاس النقي من TiO_2. وأكدت الصور المجهرية حجم نانومتر ي للجسيمات ولكن في وجود التكتل.
تم التحقق في النشاط التحفيزي الضوئي للجسيمات النانوية عبر دراسة الانحلا ل الضوئي لصبغة الميثيلين الأزرق تحت الأشعة فوق البنفسجية.

الكلمات المفتاحية للبحث: TiO_2، التحفيز الضوئي، جسيمات نانومترية، سول –جال

1 INTRODUCTION

It is important to realize that the changes of climate and global warming not only affect our non-renewable resources but also put us in front of serious problems. Equally important, the environment's contamination especially water pollution is becoming a serious problem that affects our planet. Dyes are often not toxic but some of their degradation products may be carcinogenic. Consequently, they can affect the aquatic life and also cause short- and long-term damage to the environment. Actually, environmental nanotechnologies play an important part in determining current environmental engineering and science development [1, 2]. Heterogeneous semi-conductor photocatalysis emerged as a destructive technology used for the total elimination of organic pollutants present in water [3, 4].

Among many candidates for photo catalysts, TiO2 is almost the only suitable material for the industrial use due to its most efficient photo activity, the highest stability and the lowest cost [5].In addition, TiO2 has wide applications, in various areas such as environment, purification, separation, and solar energy cells [6, 7]. TiO2 is classified as a powerful photocatalyst that can break down almost any organic compound when exposed to sunlight. It is considered by some researchers close to an ideal semiconductor for photocatalysis. [8, 9]. The proprieties of TiO2 are closely related to the crystalline structure, the size and the morphology [10].

Several techniques have been developed to synthesize semiconductor nanoparticles. Among this techniques, Sol-gel process and colloid chemistry offer opportunities for synthesis of transparent materials embedding semiconductors nanocrystals [11]. For extensive applications, it is indispensable to use a simple synthesis technique that allows a good control of the nanoparticles size and shape [12]

In the light of past and recent research , sol–gel process is currently recognized as one of the most important chemical technique for the synthesis of TiO2 nanoparticles, due to lowest cost, low processing temperature, high homogeneity, stability, easy and convenient way to control the size of synthesized nanoparticles [13].

This process is based on the hydrolysis/condensation of a titanium precursor to produce a sol and then a gel. Subsequently, after solvent evaporation, a xerogel is obtained which is milled and heated to produce highly crystalline TiO2 nanopowders [14].The present work focuses on the use of sol-gel method to synthesize TiO2 with nanometric size, as well as to investigate the effect of calcination temperature and time [15].

Finally, the photocatalytic reactivity under UV light was evaluated using methylene blue (MB) as a model organic pollutant.

2 EXPERIMENTAL WORK

As has been noted the Titanium Dioxide (TiO2) nanoparticles were prepared by sol-gel process using Titanium Isopropoxide (TiTP) Ti[OCH(CH3)2]4 as a source of Ti with a purity of 98%, acetic acid CH3COOH 99 % and anhydrous ethanol 99.8%. Methylene Blue (MB) was used in photocatalysis experiments with the characteristics showed in table 1. All reagents from Sigma Aldrich were used as received without further purification.

The TiTp was added drop by drop to a beaker containing a mixture of 50 ml of glacial ethanol and 1/10 of the volume acetic acid. This solution was continually stirred to ensure total homogeneity. This sol was put in an ultrasonic bath for 15 min. Yellow transparent gel was formed. The obtained gel was dried at 100 °C for several hours. In the last step, a yellow block crystal was formed. The powder was heated at 500 °C for several hours, taking samples at 5 and 10 hours respectively, in order to investigate the effect of calcination time upon the nanoparticles sizes and TiO2 phase.

Phase identification of prepared samples were performed using a Burker D2 Phaser powder diffractometer, equipped with an integrated flat panel monitor, and a high-speed transistor drive, using Cu radiation with CuKα radiation (λ=1.5406 A°).

As result, the nanoparticles size was determinate using the scherer's formula:[16]

$$D = \frac{0.9\lambda}{\beta \cos(\theta)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

D : size of particles nm

λ : wavelengths of x-ray 1.54 Å

β : Width at Half of Maximum FWHM

θ :Bragg's angles.

The spectra of FTIR were recorded using a JASCO FTIR 4100 single-beam spectrophotometer connected to a microcomputer. Infrared spectroscopy was used in transmission mode on pellets in KBr.

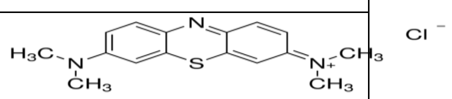
The morphology of synthetized nanoparticles were obtained using a Scanning electron microscopy (SEM) Quanta 250 FEI SEM with a tungsten filament.

The photo-catalytic activity of the nanoparticles was studied by the photo degradation of methylene bleu under UV light, using an UV lamp (BVL-6.L, 6W).

0.2 g of TiO2 nanoparticles were added to 100 mL of a solution of Methylene Blue (MB) 5.10−6 M .The suspension was preserved in the dark and stirred for 30 min to allow the adsorption equilibrium to be reached. The solution was then irradiated with a UV lamp emitting 365 nm under continuous stirring.

4 ml samples were taken out of the mixture at 10 min time-intervals and centrifuged for 10 min at 4000 rotation/min. MB concentration was determined by measuring solution absorbance at 665 nm, using an OPTIZEN -1412 VUV/vis spectro-photometer, in 1cm quartz cell, and applying the Beer - Lambert law.

Table 01: Physical Characteristics and Molecular Structure of Methylene Blue

Dye name	Methylene blue
Empirical Formula (HillNotation)	$C_{16}H_{18}ClN_3S$
Molecular Weight	319.85 g/mo l(anhydrous basis)
Colour Index Number	52015
λ_{max}	668nm
Color	Blue
Molecular structure	

3 RESULTS AND DISCUSSION

X-ray analysis showed that TiO2 samples were amorphous before calcination, as shown in figure 1(a). After calcination at 500 °C for 5 and 10 hours respectively, a very high anatase phase is detected for the as-synthesized samples referring to (JCPDS 21-1272), as shown in figure 1(b) and figure 1(c).

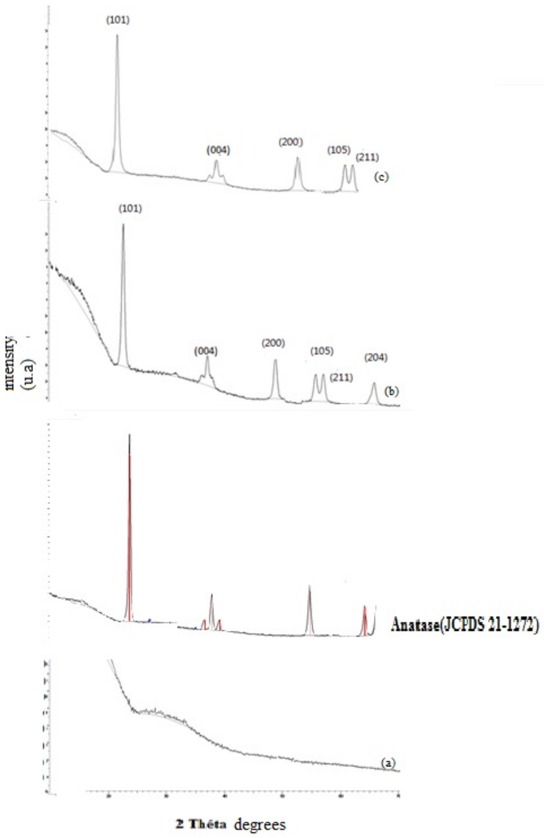


Figure 01: X-ray diffraction pattern of TiO2 prepared by Sol-Gel, (a) before calcination, (b) after calcination at 500 °C for 5h and (c) at 500 °C for 10h and the (JCFDS21-1272) card

The peak at 2θ=25.3° which characterize anatase structure was present in the DRX spectrum of samples as shown in figure 1. The other phases of TiO2 like rutile and brookite were not observed which is in agreement with kheamrutai and al [17] .

In particular, we observe a weak broadening of the diffraction peaks which is due to nanometric grain sizes of TiO2 powder.

The peaks of the XRD spectrum have been fitted by Gaussian functions. Using the Scherrer formula, the size of grains was found nearly 17 nm, for the nanoparticles synthesized in ethanol. Calcination time affected the grain size of TiO2 nanoparticles. Hence, calcination for 10 hours at 500 ° C led to an increase in the grain size of the crystallites to 21 nm. However, no change of the phase was detected [18].

FT-IR spectra obtained after calcination of synthesized TiO2 nanoparticles, recorded in the frequency range of 400-4000 cm-1, are shown in figure 2.

A very broad band appears at 3400 cm-1 which has an important role in the photocatalytic process [19]. That results from a superposition of the vibration bands of hydroxyl groups and the stretching vibrations of adsorbed water molecules. A band at 1626 cm-1 is due to bending of molecular water, and the pic at 560cm-1 for metal-oxygen bond [20, 21].

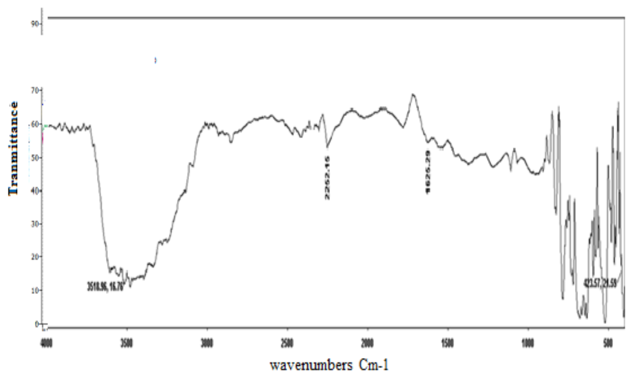


Figure 02: Infrared transmission spectra in the region of the absorption band of hydroxyl of the TiO2 synthetized

As shows in figure 3 (Scanning Electron Microscope (SEM) imagery), the micrographs of as-TiO2 nanoparticles present a perfect nanostructure made up of a collection of crystallites. However, the grain size of nanoparticles characterized by XRD, and calculated using Debye-Sherrer formula are smaller than the results observed by SEM. This can be explained as a result of the agglomeration of nanoparticles.

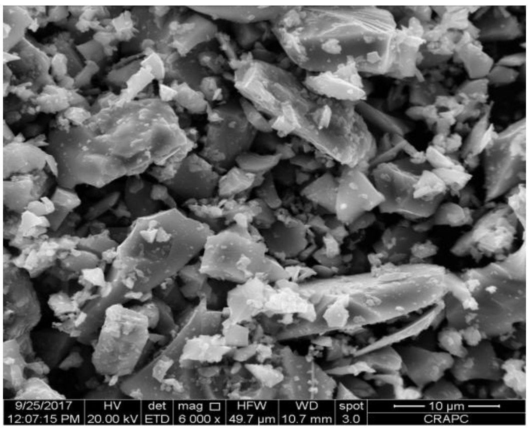


Figure 03: Micrographs SEM of the TiO2 nanoparticles synthetized

Additionally, the photocatalytic activity of the nanoparticles was studied by the photo degradation of methylene blue (MB). The absorbance value obtained for each point which reflects MB concentration at that point was plotted against the irradiation time to obtain the rate of discoloration, as shown in figure 4.

When the solution was irradiated in the absence of TiO2, there was no observable degradation of methylene blue, indicating that no direct photolysis takes place for MB. However, in a non-irradiated solution, there was a slight loss of MB, due to adsorption on TiO2 nanoparticles. Irradiation in the presence of TiO2 leads to a rapid degradation of MB. The concentration decrease reached 80 % after irradiation for 90 min.

The degradation of MB was due exclusively to photocatalysis. The higher photoreactivity of anatase phase compared to rutile or brookite phases is due to the lower capacity to adsorb oxygen, its band gap and higher degree of hydroxylation [9, 22].

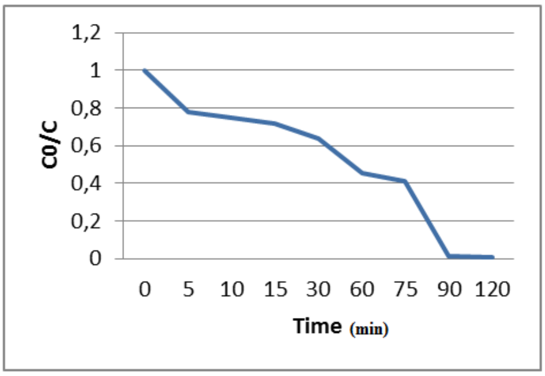


Figure 04: Kinetics of the photocatalytic degradation of methylene bleu on the TiO2 nanoparticles synthetized under UV irradiation

4 CONCLUSION

Nanoparticles of TiO2 were synthesized by sol-gel process using ethanol as solvent, with two calcination times to investigate the effect of this parameter on the crystallinity, size of grain and yield of reaction.

XRD characterization results showed that the anatase structure is obtained at a calcination temperature of 500 °C. We also noted that TiO2 particles size increased with the increase of calcination time. FTIR characterization confirmed a pure structure of TiO2 particles.

SEM micrographs showed a larger scale structure (aggregates) at the nanometric scale.

The synthesized TiO2 nanoparticles displayed an important photocatalytic activity, as determined by a rapid photocatalytic degradation of MB under UV irradiation.

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