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Effect Of Nanoparticle Size on The Photoelectrochemical Property of Anatase Nanocrystals in Photocatalysis

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Abstract—Using light energy to make electrochemical reaction, photocatalysis is among the most promising technology for water treatment. In heterogeneous catalysis, electrochemical reactions occur at the liquid/solid of gas/solid interface. The development of materials with a high surface area (nanomaterials) has then been considered as the best route achieving an efficient system. In this paper, we studied the effect of the crystal size on the photoelectrochemical properties of anatase. Two synthesis routes were used to get nanoparticles with different size and the comparison of their efficiency for the degradation of rhodamine B under ultraviolet (UV) light excitation showed that crystallite size is most important than surface area consideration. Comparing results obtained under UV lamp and under sunlight excitation, we also demonstrated that photocatalysis is more efficient under sunlight radiation.

Keywords— Photocatalysis, anatase, TiO_2, size effects, nanocrystals, nanomaterials.

I. INTRODUCTION

Energy and environments are considered to be two of the most important chalenges of our area and photoelectrochemistry-based technologies are among the most promising to solve these problems. Photoelectrochemistry enables the use of a natural energy source (sunlight) to make chemical reactions. These chemical reactions can be used to clean environment, or to produce fuels (as hydrogen for example), as in heterogeneous photocatalysis [1]. One of the most important examples of the application, for heterogeneous photocatalysis is the depollution of water through the photodegradation of organic pollutants [2]. The key, in heterogeneous catalysis, is the material used as photocatalyst. The material must exhibits a semi-conductor property to be able to absorb incident photon. The band gap value of the material determines the part of sunlight which can be exploited. This parameter strongly affects the efficiency of the process. The stability of the material is another important factor. Finally, the price of the material should be low to enable its potential use at an industrial scale. Different materials have been studied for this purpose in the last decades [3]. Among them, titanium dioxide is one of the best candidates. Several aspects of the process occurring in photocatalysis have been broadly investigated with this material [4]. TiO_2 is a semi-conductor with a band gap range from 3 to 3.2 eV, depending of the crystalline phase. This oxide is stable in the air and in aqueous media. It is widely available because produced

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in a large scale in the industry for various applications. Titanium dioxide exits in three crystalline phases: anatase, brookyte and rutile [5]. The photocatalytic activity of anatase and bookite are comparable and the rutile is the less interesting in photocatalysis [6]. Among the anatase and the brookite phases, the former is the most used because the simplicity of its synthesis in pure phase. Using solution chemistry, the synthesis of anatase nanoparticles has been reported by sol-gel [7], microemulsion [8], precipitation [9], hydrothermal [10], biological methods [11]…. Among these methods, the precipitation of amorphous precursor room temperature, followed by crystallization at different temperature is one of most interesting. This method allows the synthesis of pure anatase phase nanoparticles at different size, at low cost, and in a simple manner. In a previous work [12], we have synthesized nanocristalline anatase materials (~ 5nm) using a room temperature synthesis method. The photocatalytic property of this material has been investigated under white light (sun simulator) using rhodamine B and the results showed that for an undoped material, 60% of the initial concentration of the dye can be degraded after 120 minutes. In photocatalysis, the nanometric size has always been considered to be beneficial because when the size of the material decrease, the surface to volume ratio increases, then, reactions occurring at the material/solution interface is expected be more efficient. In this study, our goal was then to verify this assumption by comparing the results of different materials with different size at nanometric scale. The efficiency of the photocatalysis under real condition using sunlight as excitation source has also been studied.

II. EXPERIMENTAL SECTION

2.1. Synthesis

Nanocristaline anatase TiO_2 was synthesized using a two step synthesis method.

- In the first step, titanium isopropoxide was added dropwise into distilled water at room temperature and under magnetic stirring. White precipitates are spontaneously formed in the solution and the whole is stirred two hours. The final solution is filtered and the solid is washed two times with water and one time with ethanol. The solid product is recovered by filtration, and dried at room temperature for one week. The product obtained after the first step (called intermediate product in the next) appears as a white powder of amorphous titania.
- In the second step, two different methods are used to crystallize the material. One method consists to crystallize the material at room temperature in an aqueous media during 2 months. The second method consists to crystallize the material using a thermal annealing at different temperature, from 400 to 600°C.

2.2. Characterizations

All synthesized materials were characterized by X-ray diffraction in order to determine their crystalline phase and to calculate their crystallite size. Photoelectrochemical properties of different materials were investigated using UV-Visible spectrometer. UV lamp emitting at 365 nm with a power of 5W was used as irradiation source, to compare the different samples. Sunlight has also been used as light source to investigate the behavior of the material in a real white light condition.

III. RESULTS AND DISCUSSIONS

The formation of precipitates by addition of water to titanium tetraisopropoxide (TTIP) is a well known phenomenon. Indeed, as most of alkoxide reagents, TTIP is highly reactive with water molecules [13], [14], and forms instantaneously an amorphous precipitates. The nature of the precipitate has been reported in the literature as a titanium tetra hydroxide ($Ti(OH)_4$) [15], an hydrated titanium oxide ($TiO_2.1.7H_2O$) or an oxyhydroxy phase ($TiO_{0.5}(OH)_{1.5}.0.2H_2O$) [16]. The differences of weight loss recorded on TGA between these three possibilities are low and no conclusion about the real formula of the amorphous phase can be made. However, as the hydroxide phase is the most reported in the literature, in this publication, we considered the formula $Ti(OH)_4$.

During the crystallization step, the first crystallization method uses a room temperature ageing process, in aqueous solution. This method is based on a dissolution-precipitation mechanism [12] and leads to the formation of nanocristalline anatase particles (~ 5 nm). During this study, the pH of the aging solution has been varied between pH 0.7 and 4.7 and the XRD patterns of the as synthesized samples revealed that the crystalline phase and crystal size depends on the pH (*Fig. 1*).

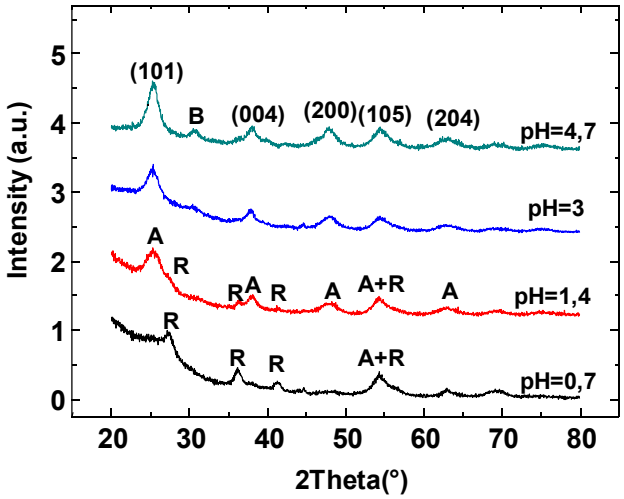

Fig. 1: XRD Patterns of nanocrystalline TiO_2 synthesized at room temperature at pH range from 0.7 to 4.7.

At pH < 3, mixed phase of anatase and the rutile are observed in the samples. At pH ≥ 3, no rutile phase is observed. The crystal size of the anatase phase has been calculated using Scherrer formula and the result has been reported in the *table 1*.

TABLE I: Evolution of the crystallite size in function of the pH of the ageing solution.

pH	**0.7**	**1.4**	**3**	**4.7**
Crystalline phase	Rutile	Anatase + Rutile	Anatase	Anatase + Brookite
Anatase crystal size (nm)	-	3.8 nm	5.06	5.35

As the pH increases, the anatase phase crystal size also increases. These results are in good accordance with those reposted in the literature and can be explained in term of the kinetic of the solid formation which increases with the pH [12]. At low pH, the reaction rate is low and the thermodynamic phase is favored.

For the second method used to crystallize the materials, thermal treatment has been used. Samples of amorphous intermediates were annealed at 400, 500, 600°C and their XRD characterization (*Fig. 2*) revealed that only a pure anatase phase is observed at 400 and 500°C. At 600°C, the thermodynamic phase, the rutile appears. The formation of the rutile phase at 600°C is not surprising. Indeed, in the literature, the phase transition, from anatase to rutile generally starts above 500°C [17].

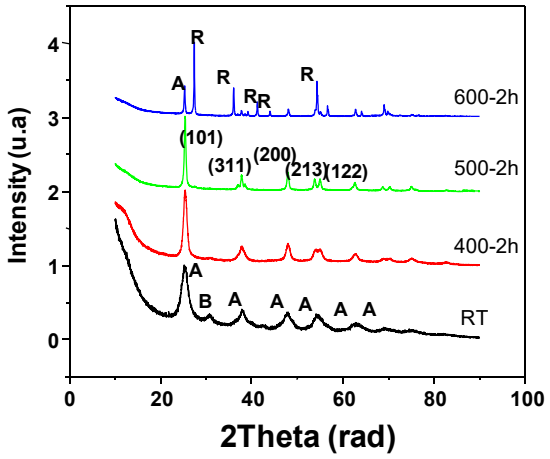

Fig. 2 : Comparison of the XRD patterns of samples annealed at 400-600°C to those of the sample synthesized at room temperature.

From these XRD, their crystallite size has been calculated using Scherrer method, and the results were reported in the *table 2*. Due to the presence of the rutile phase in the sample annealed at 600°C, we did not investigate its photoelectrochemical property.

TABLE 2: Evolution of the crystallite size in function of the annealing temperature.

Temperature	**Room Temperature**	**400°C**	**500°C**	**600°C**
Crystalline phase	Anatase + Brookite	Anatase	Anatase	Anatase + Rutile
Anatase crystallite size (nm)	5.35	7.5	19.8	44.7

The photocalytic performances of different samples were studied, by comparing their ability for the photodegradation of rhodamine B. Under UV lamp, the results were reported in the *Fig. 3*, for room temperature synthesized samples.

For all samples, a decrease of the solution absorbance is observed when the time of exposure to UV lamp increases. In accordance with the Beer-Lambert Law, this decrease of the absorbance is related to the decrease of the Rhodamine B concentration, when the photocatalyst is added to the solution. All samples exhibit the same behavior, but their efficiencies are different. The sample synthesized at pH 4.7 is the most efficient, followed by those synthesized at pH 3. The sample synthesized at pH 1.4 is the less interesting.

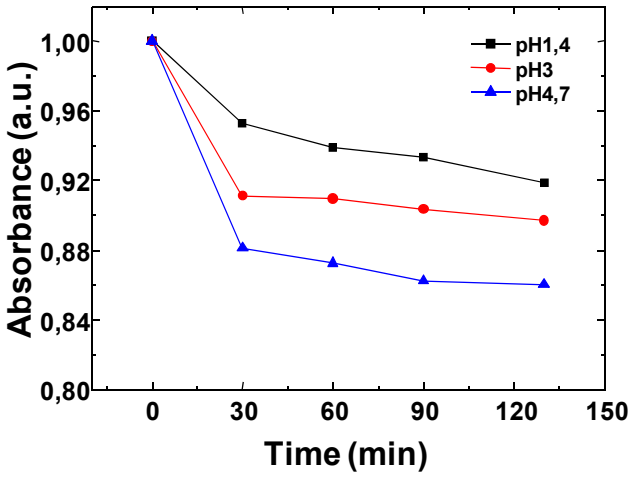

Fig. 3: Evolution of absorbance of a rhodamine B solution in presence of different catalysts synthesized at room temperature, at different pH.

Considering XRD results reported in the *Fig. 1* and *table 1*, this result can be explained in term of cristallinity. Indeed, all the samples were synthesized at room temperature, but at pH 1.4, the material is composed by a mixted phase of anatase / rutile. However, the rutile phase, because of charge carrier mobility reasons, is less efficient than anatase and brookite for photocatalysis [18]. Anatase and brookite phases exhibit similar photoelectrochemical property. For samples prepared at pH 3 and pH 4.7, the difference between the two materials arises from their crystallite size. The latter is well crystallized and it can explain the difference on their photocatalytic performances. To verify this assumption, the photocatalytic performance of one sample synthesized at room temperature, has been compared to those of samples annealed at 400 and 500°C and the result has been reported in the *Fig. 4*.

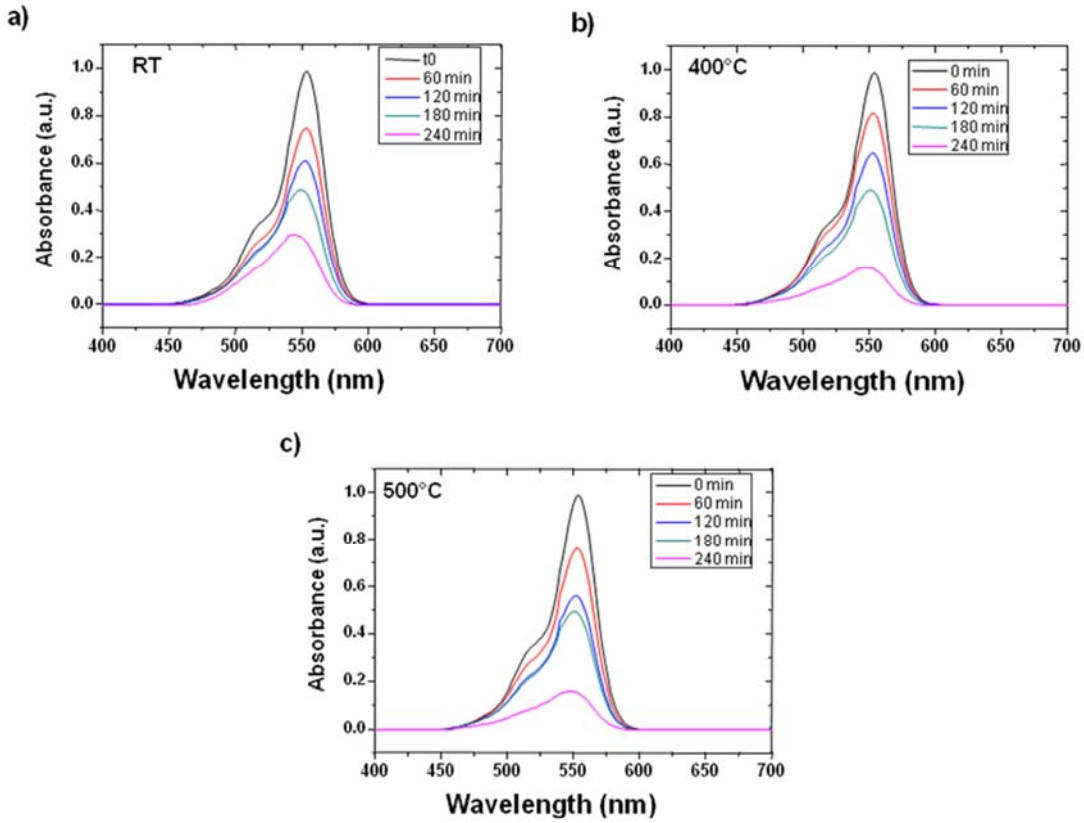

Fig. 4: Evolution of the UV-Vis spectra of solutions containing room temperature a) 400°C b) and 500°C c) synthesized photocatalyst. The radiation source is an UV-lamp.

After 240 min of exposure to an UV lamp, 70% of the initial concentration of the rhodamine B has been degraded by the room temperature synthesized sample. In the solution containing 400 and 500°C, this percentage reaches 83%. These experiments (with the three different materials) have been made rigorously in the same conditions (same temperature, same UV lamp, same batch, same spectrometer….). From this result, we can then conclude that crystallite size affects the photelectrochemical properties of samples and the bigger their crystallite size are, the better is the material performance.

This result confirms those reported in the literature, in which for the same material, in spite of having a more defavorable band gap, a well crystalline material exhibits a better photocatalytic performance [19]. The higher surface to volume ratio related to small size of particle do not seem to be more important than the crystallinity [20]. Crystallinity seems to be the key parameter in photocatalysis. Indeed, for nanocrystals, localized levels related to surface defects mediate charge carrier recombination [21].

The photocatalytic performance of samples synthesized at room temperature and at 500°C has also been characterized under sunlight excitation and the results were reported on the Fig. 5.

The same decrease of the solution absorbance is observed for the two materials. Moreover, the 500°C synthesized material is still more efficient than the room synthesized one. However, we can notice that form the same material, the process is faster under sunlight excitation than under UV lamp. For room temperature synthesized sample, it took 240 min to reach 70% of degradation rate under UV lamp. Under sunlight, the process is two times faster.

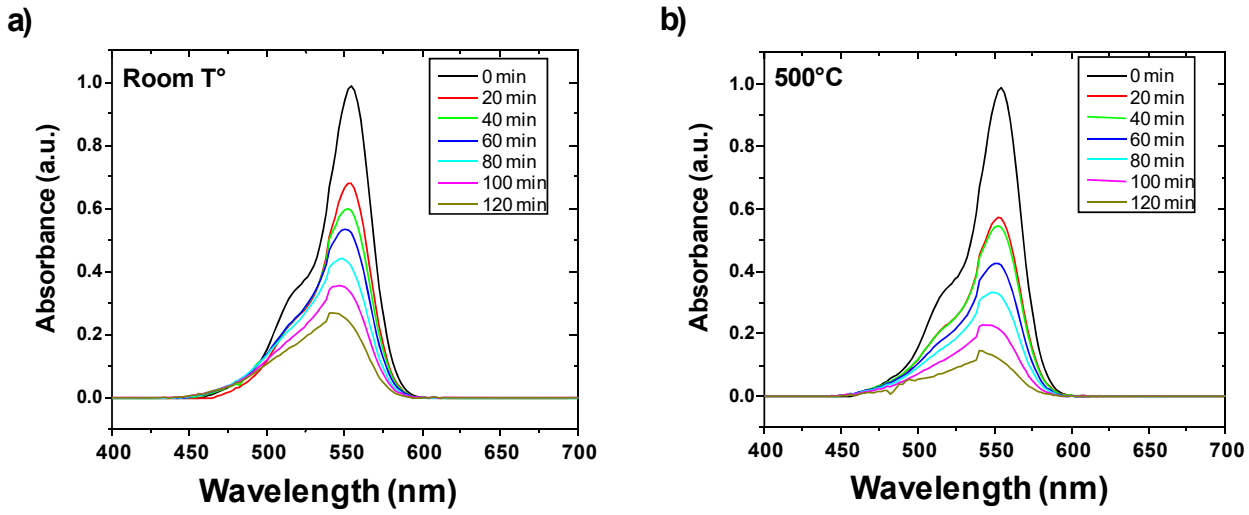

Fig. 5: Evolution of the UV-Vis spectra of the solution of Rhodamine B under sunlight excitation, in presence of Room temperature and 500°C synthesized TiO_2.

The same observation is also be made with the sample synthesized at 500°C. This result can be explained in term of incident photon flux. Under sunlight, the excitation power of photons is higher than under UV lamp, then, more electron – hole pairs are generated, and the reaction rate is faster**.**

IV. Conclusions

In photocataysis, the "nano" size has always been considered as beneficial due to their enhanced surface to volume ratio. In this study, TiO_2 nanoparticles have been synthesized using different method to investigate the effect of their size of their photoelectrochemical properties. Particles from 5 to 17 nm have been studied and it has been demonstrated that higher crystallite size materials exhibits better performance. This result has been explained in term of surface defects density, which act at recombination center.

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