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Comparative study of TiO_2 nanoparticles prepared by classical and modified sol-gel methods and their photocatalytic activity

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Abstract

TiO_2 nanoparticles were synthesized via classical and modified sol-gel method by using titanium isoproxide IV (TIP) as precursor. SEM microscopy showed that particles obtained by modified sol-gel route have spherical morphology, besides X-ray diffraction measurements showed that TiO_2 nanoparticles were polycrystalline with anatase phase. Photocatalytic properties of TiO_2 nanoparticles were evaluated via degradation of methylene blue (MB) in aqueous solution under UV irradiation. The results showed that the titania prepared by modified sol-gel using cationic surfactant CTAB have higher photocatalytic activity than the classical method which employed complex agents.

Keywords: *TiO_2 nanoparticles; modified sol-gel; methylene blue; photocatalytic activity.*

1. Introduction

Titanium dioxide is one of the most important materials that has been attracted a wide interest among research and industry communities as a simple, inexpensive and effective photocatalyst. It has been widely used in the photodecomposition of organic pollutants like dyes. TiO_2 mainly exists in three different crystalline phases, namely anatase, rutile and brookite. Anatase and rutile has tetragonal structure where as brookite crystallizes in orthorhombic structure. Among these phases, anatase exhibits higher photocatalytic activities than the other two polymorphs [1,2]. Recently, various studies have been reported the synthesis of TiO_2 nanoparticles with important physiochemical properties such as small size of particles, large specific surface area and pure anatase phase [3,4]. TiO_2 nanoparticles have been synthesized by different methods like hydrothermal [5-7], solvothermal [8-10], sonochemical [11] and sol-gel [12-15]. However, there's a considerable interest in the synthesis of titanium dioxide nanoparticles using sol-gel route because it can product nanomaterials with different properties by controlling some parameters which affect the morphology and the size of particles like solvent nature, molar ratio of water/precursor, temperature and the nature of precursor [16-19]. In this paper we discuss the pure anatase TiO_2 nanoparticles synthesis via classical sol-gel with complex agents as polymer agents and modified sol-gel process by use of surfactants. The choice of modified sol-gel method using surfactant as template was in order to study the role of cationic CTAB in phase purity, size formation and defined morphology which can ameliorate the photo-catalytic activity [20-25]. To sum up, the aim of this work was to compare the photo-catalytic properties of TiO_2 nanoparticles synthesized using the two methods previously mentioned by degradation of methylene blue (MB) in water under UV light irradiation. The photo-catalytic performance of P25 is also studied and compared with that of synthesized TiO_2.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$, 97%) and Cetyltrimethylammonium bromide were purchased from Sigma-Aldrich. Absolute ethanol, acetic acid, ethyl acetate, sodium hydroxide and Milli-Q water (18.2 MΩ cm) were used for the synthesis. Methylene blue (MB), procured from CODEX PANREAC, was chosen as a simple model of a series of thiazin dyes largely used in the industry.

2.2. Preparation of anatase TiO_2 nanoparticles by classical method

3 mL of the Titanium isoproxide (TIP) as a precursor was mixed with 10 mL of solvent (ethyl acetate or mixture of ethanol and acetic acid) and stirred for 30 min. Then the solution was kept 2 days without stirring until formation of precipitate which after, was dried in an oven at 100°C for 3 h, and the obtained xerogel was calcinated at 450°C for 3h. Tow samples (**a** and **b**) were synthesized by ethyl acetate and mixture of ethanol and acetic acid respectively as solvent.

2.3. Preparation of anatase TiO_2 nanoparticles by modified sol-gel method

100 mg of surfactant was dissolved in 50 mL of deionized water with stirring at 40°C for 2h. Then a mixture of (Titanium isoproxide and ethyl acetate for sample **c**, or acetic acid, ethanol and Titanium isoproxide for sample **d**) was slowly added dropwise into the micellar solution. After stirring for 3h at room temperature, a white precipitate was formed and then washed, dried and heated to form anatase phase.

2.4. Characterization

The crystalline phase and purity of the products were characterized by powder X-ray diffraction (XRD) using a Philips (PANALYTICAL X'pert MPD) X-ray diffractometer with Cu $K_{\alpha 1}$ radiation (λ_{Cu}=1.5406 Å). The morphologies were observed with a scanning electron microscope (SEM, Hitachi S-2600N). Absorption spectrum was measured on a UV-vis spectrophotometer (DU-800, BeckMAN Coulter) in the wavelength range of 200-800 nm.

2.5. Photocatalytic activity of TiO_2 nanoparticles

In order to examine the photocatalytic activity of the prepared samples, photocatalytic degradation was tested on the degradation of a standard MB solution under UV light. A 20mg/L MB aqueous solution, which was prepared using distilled water, was employed as model pollutant to measure the photocatalytic activity of the TiO_2 catalysts obtained by the two methods. In a typical experiment, a suspension containing the required amount of the TiO_2 catalyst and 50 mL of an aqueous methylene blue dye was placed in a photocatalytic reactor and stirred for 40 min in the dark prior to irradiation of UV light; to reach adsorption/desorption equilibrium of MB on catalyst surface. The suspension was subsequently irradiated with two UV lamp (λ = 366 nm; HEROLAB company). Then, the reaction mixture was stirred for continuous dispersion of catalysts and at each interval of 20 min, a 3 mL was withdrawn by syringe from the irradiated suspension and centrifuged to separate TiO_2 catalyst from the aqueous solution to analysis.

3. Results and discussion

SEM analyses were performed to examine the morphology of TiO_2 nanoparticles prepared by the two methods: classical and modified sol-gel. Particles obtained by modified sol-gel method (**c** and **d**) were an aggregate of very small defined spheres after treatment at 450°C (Fig. 1). However the classical method without the use of cationic surfactant CTAB provided particles without defined shape.

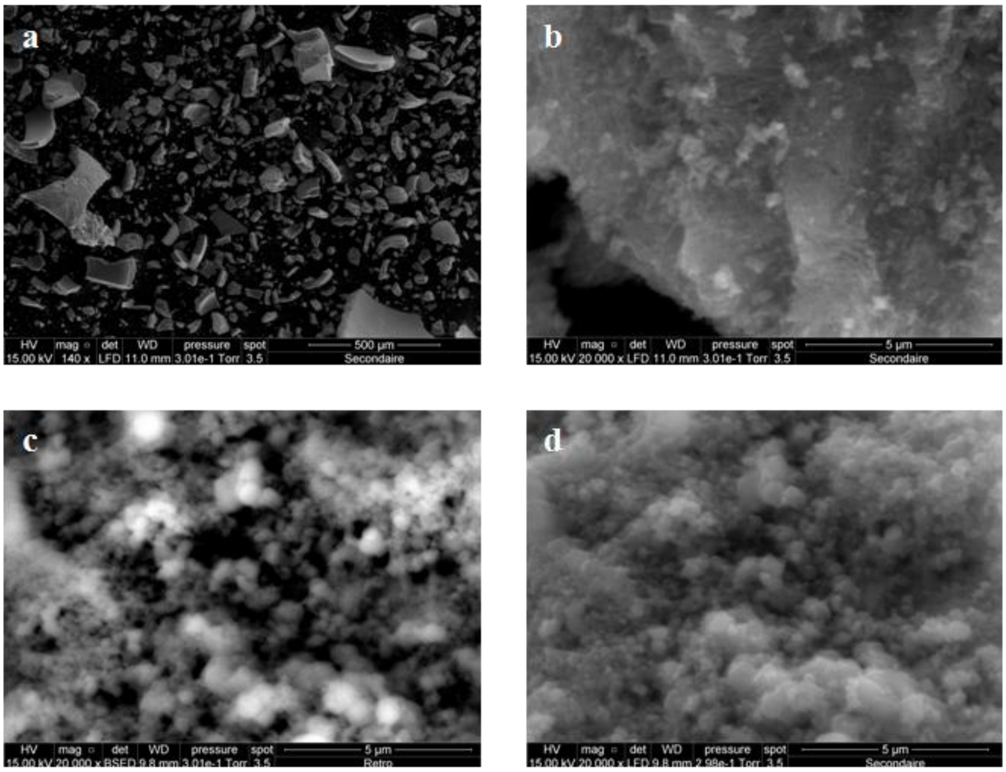

Figure 1: SEM images of TiO_2 particles synthesized by classical method (a, b) and modified sol-gel method (c, d) after calcination at 450°C.

The low agglomeration in the case of samples synthesized with cationic surfactant cetyltrimethyl ammonium bromide (CTAB) is may be due to the electrostatic interaction takes place between CTA^+ cations and Ti $(OH)_6^{2-}$ anions. In fact, the cation CTA^+ condense into micelles in which counter ions $Ti(OH)_6^{2-}$are interrelated in the interfaces between the head group to form CTA^+ - Ti $(OH)_6^{2-}$ pair [26].

Figure 2 shows the XRD patterns of TiO_2 powders prepared by the two methods and calcined at 450°C. In all diffractograms, the anatase is the main formed phase according to standard JCPDS card No. 21-1272.

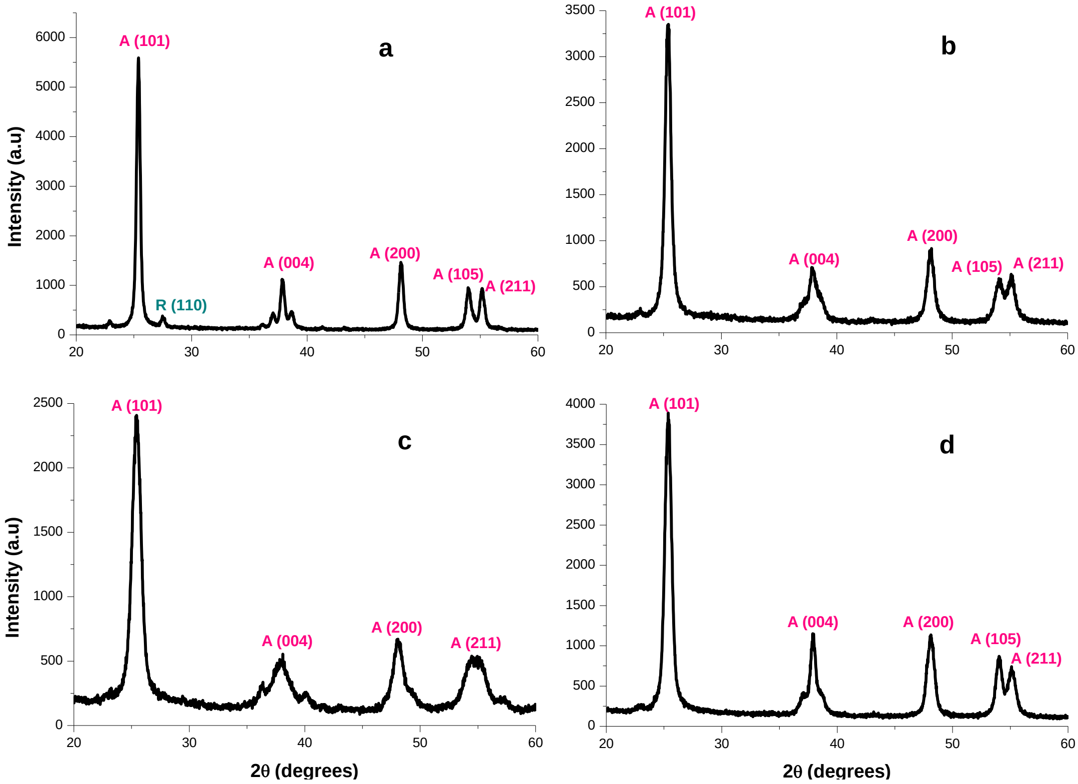

Figure 2: XRD spectra of different TiO_2 nanoparticles obtained after calcinations at 450°C.

A characteristic peaks were detected for impurities indicating the presence of rutile phase for the sample **a**, which was obtained by classical synthesis route. Nevertheless, XRD spectra of samples (**b**, **c** and **d**) revealed the single phase formation of anatase without any characteristic peaks of impurities. The crystalline size and the average particle size (D) of TiO_2 nanoparticles were estimated from the width of diffraction peak at 25.4° using Debye-Scherrer equation [27]:

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where k is the shape factor (0.94), λ is the wavelength of X-ray irradiation (0.15 nm for CuK_α), β is full width at half maximum (FWHM), Θ is the Bragg's diffraction angle at maximum peak.

The phase content of a sample can be calculated from the integrated intensities of peaks by different equations. If a sample contains only anatase and rutile, the weight fraction of rutile (W_R) can be calculated from the following equation:

$$W_R = \frac{A_R}{0.884\ A_A + A_R}$$

Where A_A represents the integrated intensity of the anatase (101) peak, and A_R the integrated intensity of rutile (110) peak.

The calculated crystallite size and crystalline composition of the materials were given in Table 1. It reveals that particles synthesized by CTAB as template agent are single nanocrystals and exhibit a relatively spherical shape with a size distribution of 14-16 nm than particles obtained via the classical sol-gel using complex agents (acetic acid and ethyl acetate). These results indicate that cationic surfactant CTAB played an important role in improving the decrease of particle size and control of morphology.

Table 1: Characterization parameters of synthesized TiO_2 nanoparticles (crystalline phases: A= anatase and R= Rutile).

Sample	2Theta (deg)	d(Å)	FWHM (°)	XRD particle size (nm)	Crystalline composition (%)
a	25.388	3.508	0.334	24.919	48.85%A+51.15%R
b	25.301	3.520	0.118	70.490	100%A
c	25.548	3.486	0.590	14.050	100%A
d	25.400	3.506	0.511	16.240	100%A

The temporal evolution of the spectral changes taking place during the photodegradation of MB over TiO_2 nanoparticles was displayed in Fig. 3.

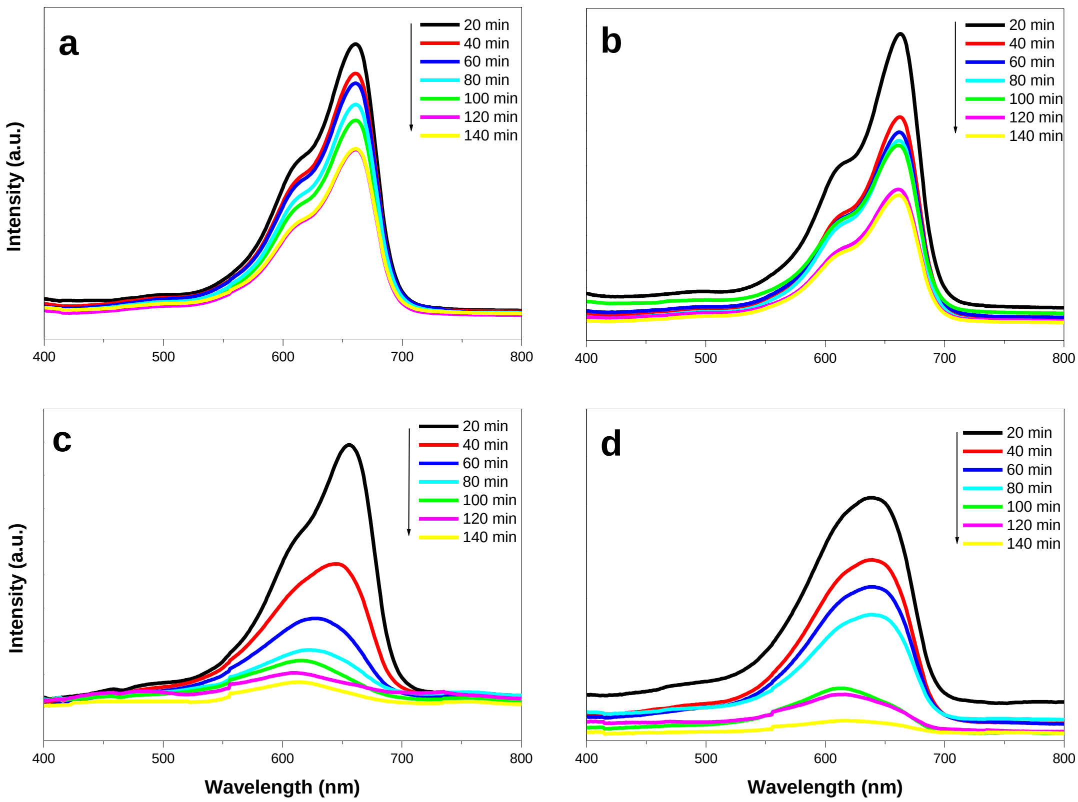

Figure 3: Absorbance of MB reaction solution samples taken at 20min intervals from 400 to 800 nm (initial dye concentration = 20 mg/L, pH= 5, 25°C, catalyst: 0.1g/L).

The maximum absorption peak at 665 nm gradually decreases during the illumination. It is obvious that TiO_2 synthesized by modified sol-gel method (**c** and **d**) exhibited superior photocatalytic activity than those obtained by classical method (**a** and **b**). In case of TiO_2 samples (**c** and **d**), the degradation is fastest and after an irradiation time of about 140 min, the MB is completely decomposed and a colorless solution is obtained.

In Fig. 4 we plotted the change in the concentration of MB (C/C_0) for the different synthesized TiO_2. We also used commercial Degussa TiO_2-P25 as reference to evaluate the photocatalytic performance of our product. A linear decay for the decrease in concentration for all particle sizes was observed. Besides compared with photolysis, it can be concluded that as prepared samples have a photocatalytic activity.

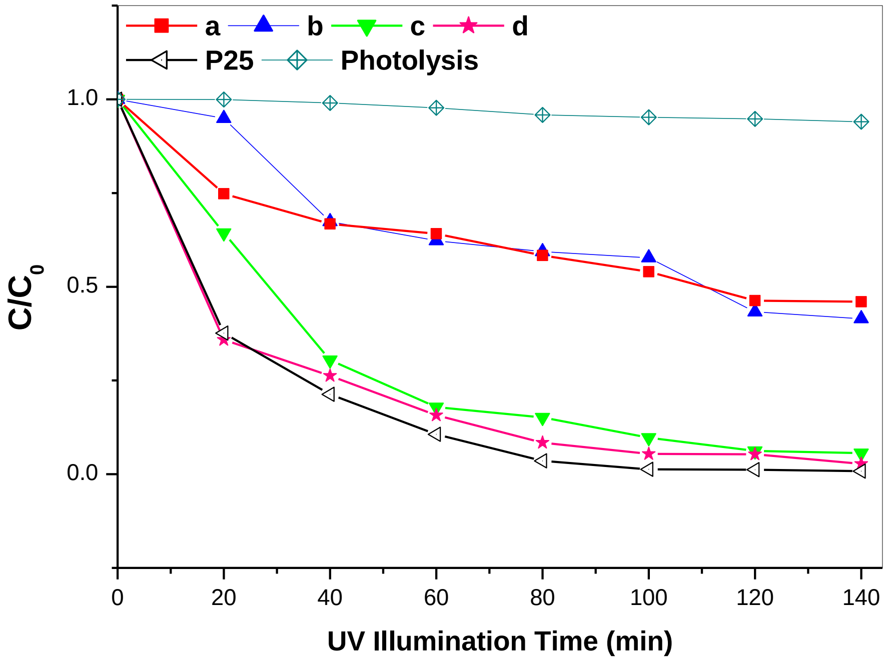

Figure 4: Time-dependent photodegradation of MB under UV irradiation.

Furthermore, the degradation of MB using synthesized TiO_2 photocatalyst (**c** and **d**) obtained by modified sol-gel route was similar to that of P-25, however it was not the case of TiO_2 (**a** and **b**) prepared by classical sol-gel.

In order to calculate the apparent pseudo-first order rate constant for the study of kinetic degradation of MB, the loss of dye was observed as a function of irradiation time and data were fitted to a first-order rate model using the following equation:

$$-\ln\left(\frac{C}{C_0}\right) = K_{app}\ t$$

Where C_0 and C are the concentration of MB at irradiation times 0 and t and k_{app} is a first-order rate constant (min^{-1}).

It was found that the TiO_2 synthesized by modified sol-gel method (**c** and **d**) exhibited a higher apparent pseudo-first order rate constant of 0.0229 and 0.0273 min^{-1} respectively than the TiO_2 particles obtained by classical method (**a** and **b**) which were 0.0063 and 0.0065 min^{-1} respectively (Fig. 5). Besides the apparent pseudo-first order rate constants achieved by samples (c and d) were comparatively close to commercial TiO_2-P25. Based on these findings, it can be concluded that TiO_2 particles synthesized by modified sol-gel method were better performed than TiO_2 obtained by classical method. This is may be due to crystallite size which plays an important role in nanocrystalline TiO_2-based photocatalysts. It was shown that photocatalytic activity increased as the TiO_2 particle size became smaller, especially for sizes less than 30 nm [21,28].

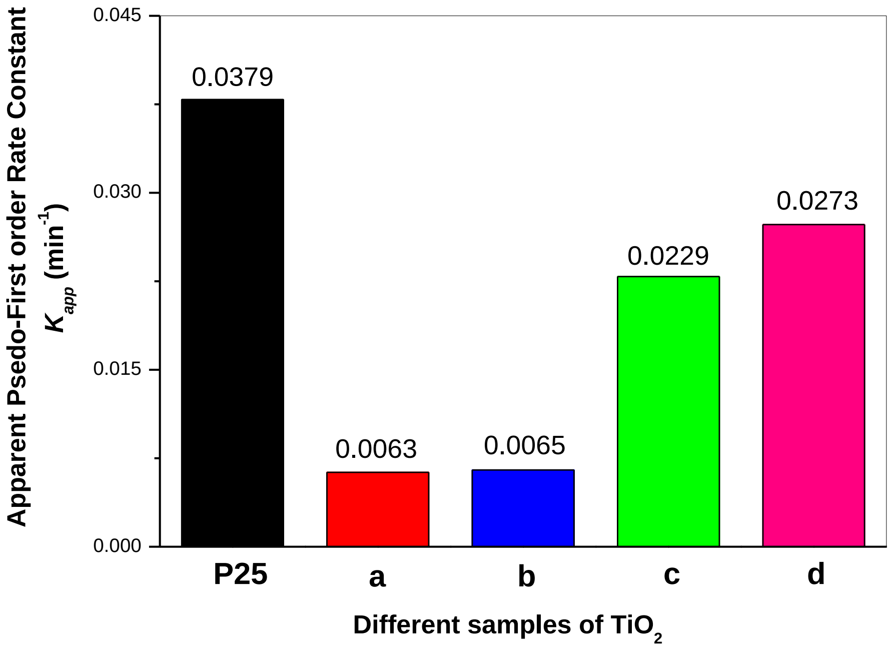

Figure 5: Comparison of apparent pseudo–first order rate constants of synthesized TiO_2 against Commercial TiO_2 - P25.

4. Conclusion

In this study, anatase TiO_2 particles were successfully synthesized via classical and modified sol-gel methods with TIP as precursor. From the above discussion it can be concluded that TiO_2 nanoparticles prepared using CTAB a cationic surfactant showed a lesser particle size with spherical morphology and pure crystalline phase compared to the samples prepared from classical method using complex agents. The size of nanoparticles as well as morphology and single crystalline phase can be controlled by using cationic surfactant than the use of complex agents. The evaluation of the photodegradation of methylene blue (MB), as dye model system, in presence of those particles was evaluated. The best catalysts were (**c** and **d**) which were prepared by modified sol-gel route using surfactant as directing agent. They showed remarkable efficiencies in decolorization process similar to commercial TiO_2 P-25. Overall, the improved efficiency through the photo-catalytic process was attributed to the small size of the TiO_2 particles.

Acknowledgements

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