Annealing Effect on the phase Transformation in Sol-Gel Derived Titania Nanostructures

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Abstract:

This work describes the effect of temperature on the phase transformation of titanium dioxide (TiO_2) prepared using metal organic precursors as starting materials. X-ray diffraction (XRD) was used to investigate the structural properties of TiO_2 gels calcined at different temperatures (300, 500, 700) °C. the results showed that the samples have typical peaks of TiO_2 polycrystalline brookite nanopowders after calcined at (300 °C), which confirmed by (111), (121), (200), (012), (131), (220), (040), (231), (132) and (232) diffraction peaks. Also, XRD diffraction spectra showed the presence of crystallites of anatase with low proportion of rutile phase where calcined at (500 °C), while rutile phase domains at (700 °C). The crystallite size of TiO_2 nanopowders was calculated by Scherer's formula and showed that the crystallite size decreased and then increased with increasing the annealing temperature.

Key words: Phase transformation of nanosized titania powders, Thermal annealing, sol-gel.

Introduction:

Nanostructured materials are currently receiving wide attention due to their special optical, electronic, magnetic, chemical, physical and mechanical properties [1, 2]. Semiconductor nanocrystals have been widely studied for their fundamental properties [3], especially titanium dioxide (TiO_2). Nanosized titanium dioxide materials have been the focus of great interest because they exhibit modified physical-chemical properties in comparison with its bulk [2, 4, 5]. Inexpensiveness, excellent chemical stability nontoxicity, high photo-catalytic property, a wide band gap and high refractive index of TiO_2 make it attractive for practical applications [6-8]. The uses and performance for a given application are strongly influenced by the crystalline structure, the morphology and the size of the particles [5]. There are three main crystalline polymorphs for TiO_2 rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [4, 5, 9], all crystallographic forms of nanocrystalline TiO_2 are of great importance from the view point of applications. Rutile has a high values of refractive index (2.7) and dielectric constant, so it is suitable for optical coating, as dielectric in thin film capacitors in microelectronic devices and as light scattering [6, 8, 10].Rutile is most important white pigment in paint and has other everyday uses as a whitener in toothpaste and the UV absorber in sunscreens [11]. Anatase is mainly used for photocatalytic applications as a gas sensors, photon-electron transfer and it serves as the dye-supporting electron-transporting substrate in a promising class of solar cells [6, 10, 11]. Brookite has been rarely used because its preparation is quite difficult [10, 12]. The rutile structure is very compact and

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thermodynamically most stable phase at all temperatures [8], whereas anatase and brookite phases are thermodynamically metastable and transform exothermally and irreversibly to the rutile phase upon annealing [4, 5, 13]. There are several pathways this phase transformation can take including: anatase to rutile, anatase to brookite to rutile, brookite to rutile, and brookite to anatase to rutile. The transition sequence is dependent on the experimental conditions and the properties of the initial sample including particle size, initial phase and annealing temperature [13, 14].

Since various properties of TiO_2 nanoparticles are definitely dependent on their crystal sizes, morphologies and crystallographic structures. Sol-gel process one of the most successful techniques for preparing nanocrystalline metallic oxide materials due to low cost, ease of fabrication (flexibility) and low processing temperatures [3]. Generally, in a typical sol-gel process, a colloidal suspension or a sol is formed due to the hydrolysis and polymerization reactions of the precursors, which on complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. The wet gel can be converted into nanocrystals with further drying and hydrothermal treatment [7].

The goal of this study is to point out the influence of different annealing temperature on the phase transformation of TiO_2 nanopowders prepared by sol-gel technique.

Materials and methods:-

Chemical reagents:

Tetraisopropyl orthotitanate ($Ti(OC_3H_7)_4$); (TIOT) (≥ 98%) was purchased from Fluka. Ethanol (C_2H_5OH, 99.9%) from GCC, and hydrochloric acid (HCl, 34.5%) from BDH. Deionized water was used for the hydrolysis of (TIOT) and preparation of TiO_2 sol.

Preparation of the samples:

The preparation of TiO_2 particles by the sol-gel technique was performed as follows:

i) A mixture of (6.895×10^{-3} mol) of deionized water and (2.02 ml) of ethanol containing hydrochloric acid (0.06 ml) was added, drop by drop into a premixturer of (6.895×10^{-3} mol) of $Ti(OC_3H_7)_4$ and (2.02 ml) of ethanol at temperature of (11 °C) under stirring for (20 min). A clear yellow sol was obtained.

ii) The TiO_2 sol was heated at (54 °C) for (75 min) in an open vessel, to obtain TiO_2 gel which was broken into small pieces after dried in air. The obtained TiO_2 pieces were calcined for one hour in a furnace at temperature of (300, 500, 700) °C in an ambient atmosphere.

Characterization of Nanoparticles:

X-ray diffraction (XRD) was used to confirm the crystal structure of TiO_2 nanoparticles. XRD analysis was performed using an x-ray diffractometer with Cu-Kα crystal radiation (λ=1.5406 Å) scanning at a rate of (5°/min-1) for (2θ) range of (20°-60°). The full width at half maximum (FWHM) in the XRD has been used to determine the crystallite size by following Scherer's equation [15]:

$$t = \frac{k\,\lambda}{\beta\cos\theta} \quad .....(1)$$

Where:

t is the crystallite size (in nm), K (=0.9) is the Scherer's constant, λ is the x-ray wavelength, β is (FWHM) (in radian) and θ the Bragg's diffraction angle (in degree).

Results and discussion:

The TiO_2 nanocrystalline powder was obtained by controlling hydrolysis procedure of tetraisopropyl orthotitanate, followed by annealing treatment. The purity and the crystal structure were analyzed by XRD, the peak location and relative intensities for TiO_2 are cited from the JCPDS data base. The influence of the thermal annealing temperature on the structure of TiO_2 nanopowder was study using three different temperatures (300, 500, 700) °C.

A thermal treatment is necessary to improve the crystallinity of compounds. When TiO_2 powder is calcined at higher temperature, crystal structure transformations may occur, the transformation temperature depends on the nature and structure of the precursor and the preparation conditions [5].

Nanosize TiO_2 powder prepared by sol-gel method are yellow in color which converted to black when are annealed at (300 °C), indicate to yield brookite TiO_2 phase. Figure (1) shows the XRD pattern for these samples. The peaks located at "d spacing" values (3.456, 2.888, 2.727, 2.491, 2.365, 2.343, 2.304, 1.896, 1.862 and 1.599) nm respond to the (111), (121), (200), (012), (131), (220), (040), (231), (132) and (232) of the brookite titania phase, respectively.

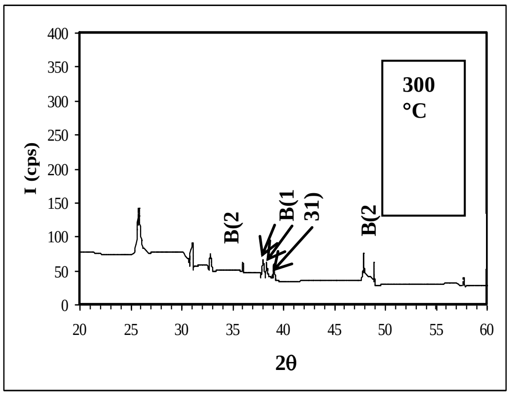

Fig. (1): The XRD pattern of TiO_2 powder annealed at 300 °C.

After annealing at (500 °C); a changed result, being not accordance with that at (300 °C), was obtained, identifying that the powder became white in color and the peaks characteristic of brookite were disappeared and new peaks corresponding to anatase structure with a small proportion of a coexisting rutile structure, as shown in figure (2). The peaks located at (25.489°, 36.186°, 37.81°, 48.129°, 54.426° and 55.326°) respond to the (101), (103), (004), (200), (105) and (211) of the anatase phase, respectively. And the peaks located at (27.654° and 41.532°) are respond to the (110) and (111) of the rutile phase, respectively. At annealing temperature (700 °C) only the peaks for rutile were observed, indicating that anatase completely transformed to rutile through heat treatment. The polycrystalline rutile structure was confirmed by (110), (101), (111), (211) and (220), as shown in figure (3). From these results, it can be said that brookite is directly not transformed to rutile but to rutile via anatase. The results are consistent with the observation of Bakadjieva et al. [4] and Lee et al. [16] who claimed that TiO_2 brookite transforms to rutile via anatase.

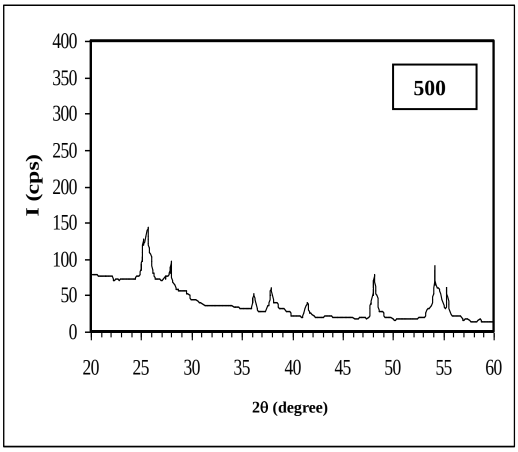

Fig. (2): The XRD pattern of TiO_2 powder annealed at 500 °C.

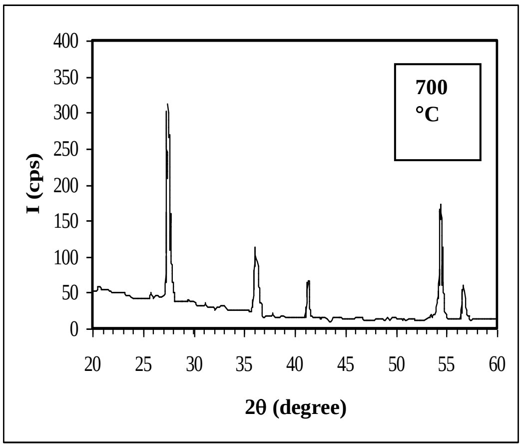

Fig. (3): The XRD pattern of TiO_2 powder annealed at 700 °C.

The crystallite size of the all anatase TiO_2 samples were estimated from XRD patterns using Scherer's equation with their strongest brookite (111), anatase (101) and rutile (110) peaks. All TiO_2 samples have dimensions on the nanometer range, varying from (15.97 nm) for brookite (TiO_2 annealed at 300° C) to (9.53 nm) for anatase and (8.92 nm) for rutile at (500 °C) which increases to (40.79 nm) when annealed at (700 °C).

The obtained data showed that the synthesis of ultrafine titania resulted in anatase and brookite, which on coarsening transformed to rutile after reaching a certain particle size [14], dependent on the experimental conditions. And at (500 °C) the anatase can grow to a size larger than rutile, so the crystallization of rutile is not as well as that of anatase because the relative intensity of rutile phase is lower than that of anatase. This result may be attributed to suppose that anatase may nucleate and grow at the expense of brookite matrix. Based on these result, also the annealing of TiO_2 powder at (700 °C) causes an increasing in the rutile crystallite size; this is coming from the fact that the thermal annealing improves the crystallinity of the particles by rearrangement phenomenon and the increase of the TiO_2 crystallite size.

These results can be interpreted as follows:

The anatase to rutile phase transformation is known to be a nucleation and growth process during which rutile nuclei form within the anatase phase and grow in size with increasing temperature, eventually consuming the surrounding anatase.

Conclusion:

TiO_2 nanopowder with different crystalline phase composition brookite, anatase and rutile and crystallite size have been prepared by controlling the annealing temperature. The annealing of TiO_2 sample showed that brookite phase transform to anatase (with small proportion of rutile) which was finally transformed to chemically stable structure of rutile phase with increasing of annealing temperature.

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دراسة تأثير التلدين في التحولات الطورية لأوكسيد التيتانيوم ذو التركيب الدقيق المحضر بطريقة محلول-جيلاتين

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الخلاصة:

يدرس هذا البحث تأثير درجة الحرارة في التحول الطوري لأوكسيد التيتانيوم المحضر باستعمال المواد العضوية الفلزية كمواد أولية. أُستعملت تقنية حيود الأشعة السينية (XRD) لدراسة الخصائص التركيبية لجل TiO_2 بعد حرقها بدرجات حرارة مختلفة °C (300, 500, 700). بينت النتائج بأن للعينات التركيب المتعدد التبلور لمادة TiO_2 وبطور البروكايت عند حرقها بدرجة (300 °C)، تمثلت بقمم الانعكاس (111)، (121)، (200)، (012)، (131)، (220)، (040)، (231)، (132) و (232). أظهرت أطياف حيود الأشعة السينية ايضاً وجود بلورات من الاناتيس مع نسبة قليلة من طور الروتايل بعد حرقها بدرجة (500 °C)، بينما يسود طور الروتايل على التركيب البلوري عند درجة حرارة (700 °C). حُسب الحجم البلوري لحبيبات TiO_2 الدقيقة التركيب بواسطة معادلة شرر (Scherer) وتبين ان الحجم البلوري يقل ثم يزداد بزيادة درجة حرارة التلدين.