Evaluation the TiO2 phases by Raman spectroscopy and X-ray diffraction

Abstract:

TiO2 reported in all litterateurs with three phases anatase, rutile and brookite which variance in activities and most of chemical properties. The variance in properties represent one of the best strategy to enhance the activities. Thus in this work TiO2 were prepared with different crystal mixture from TiOSO4/H2O2 by change the values of pH for the solution (3, 8, 11 and 14). the synthesized TiO2 were characterized by Raman spectroscopy and X-ray diffraction and that shown different phases for the product. The results of analysis show that Anatase prefer acid solution which change to rutile and brookite or forming amorphous TiO2 with change the pH towards basic solution.

Keywords: TiOSO4/H2O2, Anatase , pH, Raman/XRD, Rutile.

 Introduction:

Their photocatalytic activities of nanomaterials are greatly influenced by the conditions of synthesis such p H, temperature, solvent, and the precipitation reagents. Many elements are used for synthesizing simple or complex molecules for many applications [1[. The method of preparation influences the product properties, especially when required to form specific crystal particles with surface area phase, crystalline and size, all of these forming a surface with new chemical and physical properties [1-2]. Maybe the real reason for the huge attention to studying TiO2 is that three phases with variance in physiochemical behavior encourage use in many applications [3] and that could be caused when changing the conditions of production to form Rutile, Brookite and Anatase [4]. TiO2 is classified as a semiconductor with specific activity for the reaction which catalytic within UV-light and that influences morphology by the preparation method, which is responsible for variance the activity of anatase, rutile and brooklet [5].

The advantages of TiO2 are non-toxicity, low cost with high corrosion resistance and amazing stability were complete with the strong performance of photogenerated carrier redox [6]. The disadvantage is represented by the [7] limited responsibility of TiO2 for absorbing light (UV-region only) and that absolutely reduces the activity of TiO2, causing the wideband gap and high recombination probability. Generally, the ways that depended on enhancing the activity of TiO2 mostly include i- adding ether species such as dye sensitization, or hybrids with other species such as Ag, Pt, Au, Graphite, Graphene and carbon nanotubes [8]. While the ether ii- required create mixture form in the same crystals such make Anatase and Rutile with specific rations to produce inner enhancement between them and the common example is P25 from Degussa \Germany [9]. The significant effect on the final product of the TiO2 phase by chemical precipitation is the pH values of the solution. Thus, the aim of the work was to study the effect of the pH state of the solution on the TiO2 phase at (3, 8, 11, and 14) by X-ray diffraction and Raman spectroscopy.

Experimental:

1. Chemicals

Titanyl sulfate (TiOSO4·2H2O, >98%) was supplied by VEKTON Inc., Russia and hydrogen peroxide H2O2  (40%) and sodium hydroxide were supplied from Sigma, India. The solutions were prepared using distilled water which was prepared in a lab with conductivity of 3 μ S/cm.Synthesis TiO2

Four samples of Titanium dioxide TiO2 were prepared from Titanyl sulfate by a chemical precipitation method. The solution, 2.5 wt.% concentration of TiOSO4, was prepared by dispersion of 2 g in 78 ml of distilled water with stirring and heating at 40 ˚C until the white solution colorless and kept pH =3 by added drops of 0.5 M NaOH, then 12 wt. % hydrogen peroxide 10 mL was dropped slowly for 3 min.  with continues stirring at room temperature for 1h. The red solution was left overnight before filtering and washing the precipitation. The product was dried at 100 ˚C for 3 h. before calcination at 500 ˚C for 2 h. The other three samples were prepared by the same method with changes to p H to 8, 11 and 14. The synthesized TiO2 was characterized by X-ray diffraction and Raman spectroscopy.

Characterization:

Raman spectra were measured with LabRAM HR-800, which supplied by a Nd:YAG laser with wavelength λ = 532 nm , all of it to give spectrum from 50 -1600 cm-1 .A powder diffractometer techniques was depend to using XRD patterns (Philips PW1830) operating with CuKa radiation as a reflection mode and monochromatic from graphite . The angular 2thetas between 20 and 80 degree and Philips PC APD 3.5 program package as analyzed for obtained data.

Results and Discussion:

The evaluation of titanium dioxide as polymorphous and amorphous in the synthesized materials was done from the relative areas of the characterized peaks of the Rutile, Brookite and Anatase phases. Figure 1 refers to the analysis spectrum by Raman spectroscopy, while Figures 2 and 3 refer to XRD patterns for synthesizing TiO2 at different pHs from TiOSO4 as precursor to H2O2 as reactant materials.



Figure 1: Raman spectroscopy for synthesized TiO2 from TiOSO4/H2O2 at different pH ( 3, 8, 11, and 14)

The correlation method for using vibrational selection rules four active modes predicts six Raman active modes, which, A1g +  B1g + 2 Eg, refer to anatase TiO2 phase and that were very clear in the three synthesized TiO2 at p H = 3 , 8, and 11[10]. The three active modes, A1g+ B1g+ Eg, which are shown with Anatase, also refer to Rutile phase [11]. At the same time, the synthesized TiO2 at p H = 14 is represented by four peaks at 137, 439,642 and 917 cm-1 refers to AIg mode and the mode at 241 cm-1 can be related to the multi-photon process. Thus, mostly it refers to Brokit phase [12].   Thus, the identification between Anatase and Rutile phases with Raman spectroscopy may require more and more specific behavior to find final decision about that. The group theory and Raman polarization selection rules are not enough. Despite the sensitivity of Raman spectroscopy to identifying symmetric groups, the limitations represented in Raman scattering strength cannot predicate for the individual crystal lattices, and appear to be second order modes in the Raman spectrum. The XRD analysis was separated into two sections and plotted in Figure 1 and 2 which include direct measurement of crystalline phase TiO2 nanoparticles.  Mostly, the produced TiO2 nanoparticles contain three phases: anatases, brookite, and rutile according to the adjusted H2O2 ratios and change the pH of the mixture, which is responsible for the nature of the product.

 

Figure 2: The XRD patterns for synthesized TiO2 from TiOSO4/H2O2 from (20o - 50o )



Figure 3: The XRD patterns for synthesized TiO2 from (52o - 77o )

 At pH = 2, the product includes two phases, Anatase and Rutile with ratios (90:10) respectively after increasing the p H to 8, 11 and 14, the cases were changed and varied. The behavior of precipitation with changing acidity directly influences the process of forming nuclear and orientations of it to build a compact structure with crystal structure.

  When pH is 3, the amount of -OH or oxygen-free radical ligands is higher due to reacting with H+ and enhancing forming -OH which inter into dehydration reactions and occupy the corner part to gain Anatase/Rutile phase [13-14]. The XRD technique has theoretically and experimentally shown high efficiency in quantitative and qualitative analysis of the atomic structure-composition of materials, due to proportional between diffraction angle and diffraction intensity which influence the set of atomic planes [ 15-16]. From Figure 2 and 3 it can be divided into three parts; the first for the two samples at p H 3 and 8 includes two sections (I) peaks at 25.7, 38.3, 48.2, 55.2, 63.1, and 74.9 which can be related to Anatase phase. (ii) the second section at 28.1/28.3 , 36.3 , 54.3/54.4, 62.9/61.1 and 70.4/70.3 ca be due to Rutial phase.

Table 1; The peaks summary from (2theta =20o-50o ) to synthesized TiO2 at pH= 3, 8, 11 and 14

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **TiO2 sample** | **A** | **R** | **R** | **A** | **A** |
| **p H /3** | **25.2s** | **28.1s** | **36.3w** | **38.2s** | **48.3s** |
| **p H/ 8** | **25.4s** | **28.3vw** | **-** | **38.2s** | **48.3s** |
| **p H/ 11** | **25.7w** | **-** | **-** | **38.4vw** | **48.6vw** |
| **p H/ 14** | **-** | **-** | **-** | **-** | **-** |

From table 1 it can be seen that synthesized TiO2 at pH 3 and 8 was a mixture of Rutile and Anatase with the maximum value for the last phase. The synthesized TiO2 at pH =  11 mostly refers to the Anatase phase, while increasing pH to 14 the results show a noncrystalline form which may refer to the Brookite form or amorphous TiO2 [17-18]. The values of crystalline size D were estimated by the Scherrer formula [D = K λ/β cosθ], where the K particle shape factor is represented by K with wavelength λ of incident X-ray light, causing peaks θ with characteristic is full width at half maximum β=FWHM [19-21]. The results showed 11.39, 9.97 nm  and 21.93 nm for the synthesized TiO2 at 3, 8, and 11 values of pH, respectively. The sample which was prepared at pH = 14 was shown to be more than 70 nm with an amorphous phase and that mostly refers to the Brookite phase. The XRD patterns before normalization of the data witnessed an increase in the intensity of peaks with increasing particle size. Thus, the arrangement of particle size with intensity was as shown:TiO2 (p H= 11) > TiO2 (p H= 3) > TiO2 (p H= 8)

 Table 2; Summary for peaks starting with (2theta =50o ) to (2theta=80o)of synthesized TiO2 at pH= 3, 8, 11 and 14

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **TiO2 sample** | **R** | **A** | **R** | **A** | **R** | **A** |
| **p H /3** | **54.3m** | **55.2w** | **62.9m** | **68.8w** | **70.4w** | **75.2w** |
| **p H/ 8** | **54.4s** | **55.3m** | **61.1m** | **68.8w** | **70.3 w** | **75.3 m** |
| **p H/ 11** | **-** | **-** | **-** | **-** | **-** | **-** |
| **p H/ 14** | **-** | **-** | **-** | **-** | **-** | **-** |

The temperature of calcination was enough to prevent losing most of OH with maintaining the ability to convert all of it to Ti=O and that mostly reduces the value of particle size, which probably revere with acidic media. In this section, we believed that H2O2 as a source of -OH were succeeding in removing SO4-2 in acidic media more than basic media, which may be related to play basic solutions such as the inhibition of -OH and that weakened the activities towards removing the SO4-2. The XRD analysis showed that at pH = 3, predominates in character for a crystalline analysis phase with a minority for rutile phases and that were reported in Table 1 and 2. According to Table 1 and 2 for XRD data, there is no influence of pH at 3 and 8 or there is very limited change in the intensity and width of peaks, which after that witness clear changes at pH 11 when most of the peaks disappear and reduce in intensity and width. Finally, the XRD patterns of synthesized TiO2 were obtained at higher pH (14), there are no peaks observed from 20o to 80o, which mostly refers to an amorphous structure.

Conclusions

Chemical deposition of TiOSO4 with H2O2 at room temperature is a simple synthetic method to prepare TiO2 in different forms after changing the p H of the solution. The pH parameters play important roles to creating specific types of crystalline and that was analyzed by Raman spectroscopy and XRD analysis.  The TiO2 sample obtained at pH = 3 was a mixture between Anatase and Rutial, which changed after variance the acidity to 8 and 11 to reduce the Anatase form to increase Rutile, then at pH =14 mostly converted to amorphous TiO2. Thus, we believed that ‘’ the change in acidity represents the best way for synthesizing TiO2/P25 -Degussa with higher activity’, because this method succeeded in creating the desired combination of crystal structure.

AI disclaimer

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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