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 Nano materials are greatly influence with the conditions of synthesis such p H, temperature, solvent, and the precipitation reagents. Many elements were used for synthesized simple or complexes molecules for many applications [1[. The method of preparation influence on the product properties especially when required forming specific crystal particle with surface area phase, crystalline and size, all of it forming a surface with new chemical and physical properties [1-2]. May be the real reason for huge attentions in studied TiO2 due to shown three phases with variance in physiochemical behavior encourage to use in many applications [3] and that could be accrued when change the conditions of production to forming Rutile, Brookite and Anatase [4] .TiO2 classified as semiconductor with specific activity for the reaction which catalytic within UV-light and that influence with morphology by preparation method , which responsible in variance the activity for , anatase , rutile and brooklet [5 ].

The advantages of TiO2 has non-toxicity low cost high with corrosion resistance and amazing stability were complete with strong performance of photogenerated carrier redox [6]. the disadvantage represent by [7] limited responsibilities of TiO2 with absorbance light (UV-region only) and that absolutely reduce the activity of TiO2 causing the wide band gap and high recombination probability. Generally The ways that depended to enhance the activity of TiO2 mostly include i- adding ether species such dye sensitization or hybrid with other species such 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 significantly affects on the final product of TiO2 phase by chemical precipitation is the pH values of the solution, thus the aim of the work was 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 from VEKTON Inc., Russia and hydrogen peroxide H2O2 (40%) and sodium hydroxide were supplied from Sigma ,India . the solutions were prepared by using distills water which was prepared in lab with conductivity 3 μ S/cm.

1. Synthesis TiO2

Four samples of Titanium dioxide TiO2 were prepared from Titanyl sulfate by 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 converted white solution to 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 filtered and washed 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 change the p H to 8, 11 and 14. the synthesized TiO2 was characterized by X-ray diffraction and Raman spectroscopy.

1. 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 polymorphous and amorphous in the synthesized materials were done from the relative areas of the characterized peaks for Rutile, Brookite and Anatase phases. Figure 1 refers to the analysis spectrum by Raman spectroscopy while figure 2 and 3 refers to XRD patterns for synthesized TiO2 at different pH from TiOSO4 as precursor with H2O2 as reactant materils.

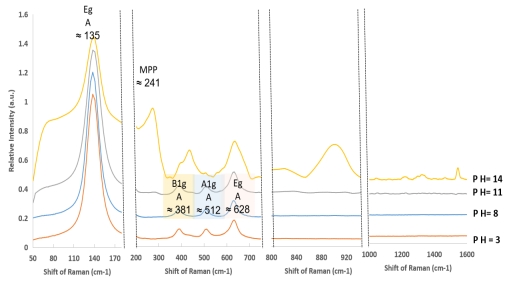


Figure 1: Raman spectroscopy for synthesized TiO2 from TiOSO4/H2O2 at different pH ( 3, 8, 11, and 14)

The correlation method for by using vibrational selection rules four active modes from predicts six Raman active modes which A1g + B1g + 2 Eg were refers 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 mode A1g+ B1g+ Eg which shown with Anatase also refers to Rutile phase [11]. In the same time the synthesized TiO2 at p H = 14 represent 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 multi photon process, thus mostly it refers to Brokit phase [ 12]. Thus the identification between Anatase and Rutile phases with Raman spectroscopy may be required more and more specific behavior to find final decision about that. The group theory and Raman polarization selection rules is not enough, although the sensitivity of Raman spectroscopy to identified symmetric groups. the limitations were representing in Raman scattering strength cannot predicate for the individual crystal lattice, and appears the second order modes in the Raman spectrum. The XRD analysis were separated in two section and plotted in Figure 1 and 2 which include direct measurement of crystalline phase TiO2 nanoparticles. Mostly The produced TiO2 nanoparticles contained three phases anatase, brookite, and rutile according to the adjusted H2O2 ratios and change the pH of the mixture which responsible on the nature of product.

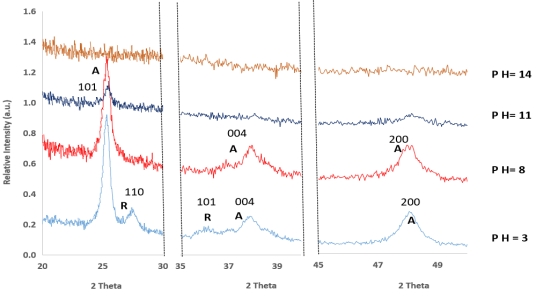


Figure 2: The XRD patterns for synthesized TiO2 from TiOSO4/H2O2 from (20o - 50o )

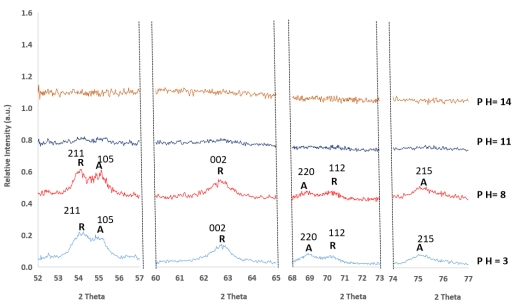


Figure 3: The XRD patterns for synthesized TiO2 from (52o - 77o )

At pH = 2 the product include two phase Anatase and Rutile with ratios (90:10) respectively after increase the p H to 8 , 11 and 14 the cases were change and variance. The behavior of precipitation with change acidity influence directly with the process of forming nuclear and orientations of it to Build compact structure with crystal structure.

When pH was 3 the amount of -OH or oxygen free radical’s ligands is higher due to reacting with H+ and enhance forming -OH which inter to dehydration reactions and occupy the corner part to gain Anatase/Rutile phase [13-14]. the XRD technique theoretically and experimentally shown high efficiency in quantitative and qualitative analysis for the atomic structure-composition of materials, due to proportional between diffraction angle and diffraction intensity which influence with set of atomic planes [ 15-16]. from Figure 2 and 3 it can be divided to three part; the first for two samples at p H 3 and 8 include two section (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 could be seen that synthesized TiO2 at pH 3 and 8 were mixture from Rutile and Anatase with maximum value for the last phase. The synthesized TiO2 at pH = 11 mostly refer to Anatase phase while increase pH to 14 the results shows noncrystalline form which may be refers to Brookite form or amorphous TiO2 [ 17-18]. The value of crystalline size D were estimated by the Scherrer formula [D = K λ/β cosθ] where K particle shape factor represent 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 shown 11.39 ,9.97 nm and 21.93 nm for the synthesized TiO2 at 3, 8, and 11 value of pH respectively. The sample which prepared at pH = 14 was shown more than 70 nm with amorphous phase and that mostly refers to Brookite phase. The XRD patterns before normalization the data witnessed increase 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 keeping the abilities for converting the all of it to Ti=O and that mostly reduce the value of particle size which probably revere with acidic media. in this section we believed that, H2O2 as source of -OH were succeed to remove SO4-2 in acidic media more than basic media which may related to play basic solution as inhibition for -OH and that weaken the activities towards remove 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 the table 1 and 2 for XRD data, there is no influence of pH at 3 and 8 or there is very limit change in intensity and width of peaks which after that witness clear change at pH 11 when most of peaks were disappear and reduce in intensity and width. Finally, the XRD patterns of synthesized TiO2 obtained at higher pH (14), there is no peaks are observed from 20o to 80o, which mostly refers to an amorphous structure.

Conclusions

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

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