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Structural Investigations of TiO_2/SiO_2 Nanoparticles Synthesized by Co-Precipitation: Modeling and Optimization

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Abstract- **Nanocomposite consisting of Titanium dioxide (TiO_2) and silicon dioxide (SiO_2) was prepared by the wet chemical method. The effect of process variables like concentration of precursors, rate of addition of precipitating agent and annealing temperature on lattice strain of TiO_2/SiO_2 was studied using $2^{(5-2)}$ fractional factorial design. The optimal calculated parameters of process variables like concentration of precursors1, concentration of precursor 2, drop rate and annealing temperature were found to be .1 mol/l, .4 mol/l, 6 d/min and 300^{0}C respectively. The significant effect of independent factors was analyzed using ANOVA. The Model F-value ≈ 12.16, implies the model design is significant. The correlation coefficient R^2 was 0.8455, which indicates that the observed results fitted well with model prediction. The results were shown in the form of 3D perturbation plots which shows that lattice strain is affected by concentration of precursor 1 and annealing temperature. The prepared samples were structurally characterized by X-ray diffraction (XRD) analysis and Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy indicated the presence of a limited number of Si–O–Ti bonds in TiO_2/SiO_2 binary oxides.**

Keywords—**Nanocomposites, Factorial, Binary oxides, nanocrystallites, Optimization.**

I. INTRODUCTION

The nanocomposite materials have been widely recognized as one of the promising research area. At nano scale, materials exhibit a greater surface area compared with conventional particles. Due to this enhanced surface the use of nano particles increase the availability of surface active sites. The composites of binary oxides, at nano dimensions, show excellent optical, electrical and mechanical properties [1]. Titania (TiO_2) based materials are of great interest for a wide variety of applications as air purification, self-cleaning surfaces, UV-screening of agriculture films, an opacifying agent in paint, and for UV-absorption in the form of sunscreen cosmetic products. Nano structured TiO_2 powder is not thermally stable and easily loses its surface area. Therefore, several groups have investigated titania coating on high surface area supports such as silica or alumina [2].

Incorporation of SiO_2 into the TiO_2 would reduce the particle size, increase the specific surface area, and suppress the TiO_2 phase transformation from anatase to rutile [3]. The chemical properties of titanium dioxide with silica, are intimately related to the crystallographic structure (e.g. rutile, anatase, brookite) [4-5]. The anatase form of titania/silica (TiO_2-SiO_2) composite have received considerable attention due to their unique properties, such as stability, low thermal expansion coefficient, and high refractive index, which lead to their uses in a wide variety of applications as X-ray imaging, display monitors, laser, amplifiers for fiber–optic communication [6], non-toxicity, photocatalytic property [7], catalyst support [8-12], and optoelectronic devices etc. Many synthetic approaches have been employed to prepare TiO_2/SiO_2 binary oxides as Coprecipitation process has been proved to be an efficient method to prepare ultra-fine particles dispersed in different matrices. Using this method, a control over the surface morphology, structure, texture and chemical composition can be attained by carefully monitoring the preparation parameters [13]. In this work four main processing parameters i.e concentrations of TiO_2 (X1), concentration of SiO_2 (X2), annealing temperature (X3) and drop rate (X4) are optimized using 3-level, 4-factor central composite factorial experimental design. The effect of process variables on lattice strain of TiO_2/SiO_2 is also studied using response surface methodology (RSM).

RSM is one of the most prominent statistical modeling techniques. This methodology includes various types of experimental designs such as central composite, Box-Behnken, D-optimal design, 3 level factorial, user defined, one factor, miscellaneous and historical data etc. The selection of experimental is depending on the objectives of the experiment and the number of factors to be investigated. Factorial design is one of the most popular "Response surface designs" and advantage of such methodology is to provide less experimental runs and time, thus provides more efficient optimization. In the present study author report synthesis of TiO_2-SiO_2 binary oxides and investigate the influence of variables on the structural properties of the composites.

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To the best of author's knowledge the effects of these factors are not determined and previous reports in the literature represent their different influence on the mentioned responses.

II. Experimental Design Synthesis

A. Synthesis of sample-

For the synthesis of TiO_2/SiO_2 via co-precipitation method, oxides of *titania* (.1 to .3 m mol) and silica (.1 to .3 m mol) were converted to their chloride salt by adding stoichiometric amount of hot diluted hydrochloric acid after which transparent solution was formed. The ammonia was used as precipitation agent. Then the solution of chloride salt was added to the ammonia solution at a certain rate by means of continuous stirring. The final solution was stirred for 30 minute. The mixture was centrifuged under 2000 rpm for 8 minute. The obtained precipitate was washed with distilled water three times and dried at 80^0C for 24 hours in an oven. The powdered sample was annealed at different temperatures.

B. Characterization of sample

Complementary methods were used to characterize annealed samples. In order to determine the crystallite size, XRD patterns of samples were recorded by using a Philips X-ray powder diffractometer PW/1710 having GIXRD geometry; with Ni filter, using monochromatic CuK radiation of wavelength 1.5418Å at 50KV and 40mA. The divergence of scanning beam on the source slide was controlled with the help of 0.15mm slit. Powered samples were scanned in the range 20^0 to 80^0. Fourier transform infrared spectrometer has been used to study the IR properties of prepared samples in the Mid-IR range, 4000-400 cm-1 using Perkin- Elmer instrument.

C. Statistical method and data analysis

The study explored the four main processing parameters used in this method; TiO_2-SiO_2 was optimized using 3-level, 4-factor central composite factorial experimental design. Concentrations of TiO_2 (X1), concentration of SiO_2(X2), Annealing temperature(X3) and drop rate (X4) were used as independent variables on the basis of preliminary trials. Strain was selected as dependent variable and the effect of independent variables on Strain was studied at 3 levels i.e, low (coded value = −1), middle (coded value = 0), high (coded value = +1). The experimental design and statistical analysis of data were done using the Design Expert software.

The design determines the effect of each factor on response and also determines how the effect of each factor varies with the change in the level of the other factors, i.e. interactions [14]. If factors are interdependent (interaction between two or more factors), it means that the level of one factor changes the effect of other factors on a specific response [15]. For this study, experimental conditions for the test conducted are summarized in Table1.

TABLE 1.
Experimental Design for all independent variables, showing coded values at three level (high, medium and low) for all the independent variables (concentration of TiO_2, concentration of SiO_2, temperature and drop rate).

Factors	High level	Medium level	Low level
Con TiO_2(X1)	1	0	-1
Con SiO_2(X2)	1	0	-1
Temperature(X3)	1	0	-1
Drop rate(X4)	1	0	-1

Statistical analysis was performed using Design Expert software. In this study, the optimum operation condition for strain was obtained by analyzing the relationships between the variables and the response.

The behavior of the response surface methodology (RSM) was expressed by the following Quadratic equation [16-17].

Based on this analysis in Yahiaoui et. al. [18] and Kaladhar et. al. [19], the general equation of the second-order or quadratic model may be generated, as represented in Equation.

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum\sum_{i<j} \beta_{ij} X_i X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \epsilon$$

where Y is the expected response-strain, Xi are the encoded value for factors like as concentrations of precursors(TiO_2, SiO_2), temperature(T), and drop rate. β_0, β_i, β_{ij}, β_{jj} are constants, i is the leading coefficient for each variable, and ij is the effect of the interaction of coefficients as demonstrated by Ozbay et.al.[20], Montgomery et.al.[21], Mason et.al.[22], Raj et.al.[23] and € is the random error.

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Co-efficient of determination (R^2) was used to describe the accuracy of the model, F value (Fisher variation ratio) and probability value (Prob > F) were applied to evaluate the significance of the model terms [16,24].

III. Statistical Analysis And Modeling

The most important statistical activity is the planning of experiments in which Statistical data can be obtained. The experimental results, data for strain was evaluated using quadratic model by performing 30 runs. Quadratic factorial design is a reliable method to simplify the process of identifying the most influential preparation variable.The regression analysis was applied to develop the best-fit model using the collected data. The response Strain (Y1) was predicted by a quadratic equation shown as in Eq.(1).

$$Y=3.74478E-004+9.77778E-006*X1+2.86111E-005*X2+9.53333E-005*X3+1.22778E-005*X4++3.01250E-005*X1X2-4.12500E-005*X2X4+4.08750E-005*X3X4+4.61290E-005*(X2)^2-5.23710E-005*(X3)^2 \quad (1)$$

Where Y1 is the strain, X1 is the concentration of (TiO_2), X2 is the concentration of (SiO_2), X3 is the annealing temperature, X4 is the drop rate per minute. To evaluate the statistical significance of the quadratic model, F-test was conducted for the analysis of variance (ANOVA). The ANOVA tests results for the output strain is shown in Table 2.

TABLE 2.
Showing 30 run based on the trail of software (all possible combinations of independent variables (i.e effect of process variables on Strain)).

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A:con v205	B:con sio2	C:temperature	D:drp	strain
		m/l	m/l	^{o}c	r/m	---
17	1	-1	0	0	0	0.000352
28	2	0	-1	0	0	0.000389
29	3	0	0	-1	0	0.00047
3	4	-1	1	-1	-1	0.00031
24	5	0	0	0	1	0.000366
21	6	0	0	-1	0	0.00024
22	7	0	0	1	0	0.00035
10	8	1	-1	-1	1	0.000216
15	9	-1	1	1	1	0.000405
1	10	-1	-1	-1	-1	0.000235
6	11	1	-1	1	-1	0.000248
2	12	1	-1	-1	-1	0.000256
20	13	0	1	0	0	0.000401
9	14	-1	-1	-1	1	0.000235
16	15	1	1	1	1	0.000571
11	16	-1	1	-1	1	0.00027
30	17	0	0	0	0	0.000368
8	18	1	1	1	-1	0.00056
23	19	0	0	0	-1	0.000375
4	20	1	1	-1	-1	0.00039
18	21	1	0	0	0	0.00034
14	22	1	-1	1	1	0.000568
7	23	-1	1	1	-1	0.000459
27	24	1	-1	0	0	0.000375
5	25	-1	-1	1	-1	0.0004
25	26	0	0	0	0	0.000389
13	27	-1	-1	1	1	0.000565
19	28	0	-1	0	0	0.000386
12	29	1	1	-1	1	0.000258
26	30	-1	0	1	0	0.000375

TABLE 3.
The ANOVA results. In this Transform is chosen as Power and Lambda comes out to be equal to 1and constant is 0.

ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2.612E-007	9	2.902E-008	12.16	< 0.0001	significant
A-con TiO_2	*1.721E-009*	*1*	*1.721E-009*	*0.72*	*0.4058*	
B-con sio2	*1.473E-008*	*1*	*1.473E-008*	*6.17*	*0.0219*	
C-temperature	*1.636E-007*	*1*	*1.636E-007*	*68.56*	*< 0.0001*	
D-drp	*2.713E-009*	*1*	*2.713E-009*	*1.14*	*0.2990*	
AB	*1.452E-008*	*1*	*1.452E-008*	*6.08*	*0.0228*	
BD	*2.722E-008*	*1*	*2.722E-008*	*11.41*	*0.0030*	
CD	*2.673E-008*	*1*	*2.673E-008*	*11.20*	*0.0032*	
B^2	*7.329E-009*	*1*	*7.329E-009*	*3.07*	*0.0950*	
C^2	*9.447E-009*	*1*	*9.447E-009*	*3.96*	*0.0605*	
Residual	4.773E-008	20	2.386E-009			
Lack of Fit	*4.050E-008*	*15*	*2.700E-009*	*1.87*	*0.2532*	*not significant*
Pure Error	*7.223E-009*	*5*	*1.445E-009*			
Cor Total	3.089E-007	29				

D. Result and discussion-

Table 3 and Table 4 show the ANOVA test results. Coefficient of determination (R^2), adjusted R^2 and predicted R^2 values were used to evaluate the fitness of the model. Adjusted R^2, which adjusts for the number of explanatory terms in a model relative to the number of data points. It is modification of R^2 [25]. However, a regression model predicts the responses for new observations is presnted by, the predicted R^2 [26]. The residual error to the pure error from triplicated experimental design points are compared by the lack of fit [26,27]. In model, the p-value for lack-of-fit is 0.2532, which is greater than 0.0010, indicating that the lack-of-fit is not significant relative to the pure error. However, a model with reasonable R^2 value is acceptable with significant lack-of-fit [27-29]. The Model F-value of 12.16 implies the model is significant. Values of "Prob > F" less than 0.0001 indicate model terms are significant. The "Pred R-Squared" of 0.5724 is in reasonable agreement with the "Adj R-Squared" of 0.7760; i.e. the difference 0.2036. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable; ratio of 12.692 indicates an adequate signal. This model can be used to navigate the design space. The red line was produced by the software based on the externally studentized to define outliers, as shown in the diagnostics plots outlier exists in the plot indicating that the model is consistent with all the data. All the externally studentized residual were randomly scattered across the graph and furthermore, there is no significant distribution pattern for all the diagnostics plots. The residuals are normally distributed if the points on the plot follow a straight line [30]. The probability plot of the studentized residuals is to check for normality of residuals. Studentized residuals versus predicted values are to check for constant error. Externally Studentized residuals to look for outliers, i.e. influential values, and three-dimensional surface plot Fig.5 and Fig.6 provide a better visualization of the statistically significant factors derived from the statistical analysis.

TABLE 4.
Showing the values of co efficent of R_{squ}(ANOVA test result) by software.

Std. Dev.	4.885E-005	R-Squared	0.8455
Mean	3.707E-004	Adj R-Squared	0.7760
C.V. %	13.18	Pred R-Squared	0.5724
PRESS	1.321E-007	Adeq Precision	12.692

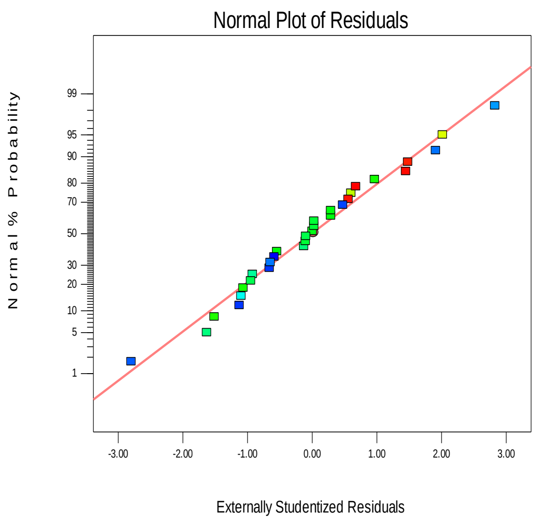

Figure 1. Normal plot of Residuals (Externally Studentized Residual)

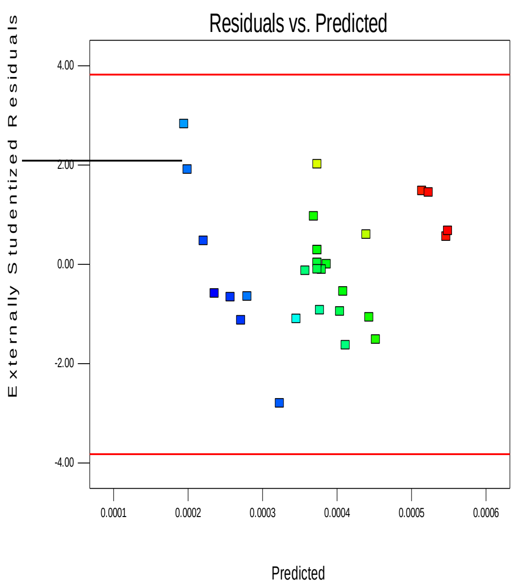

Figure 2. Residuals Vs. Predicted(Externally Studentized Residuals)

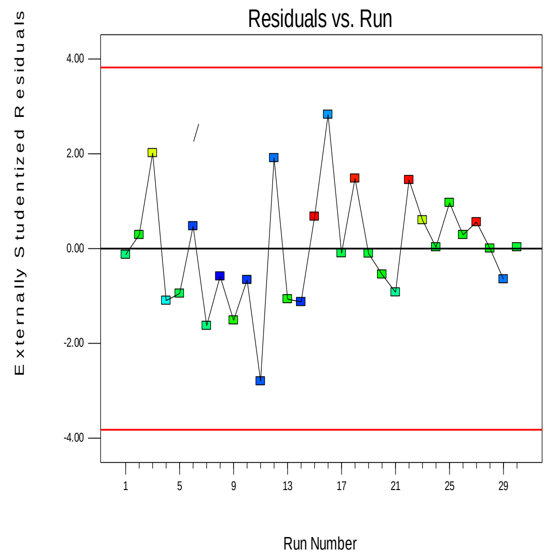

Figure 3. Residual Vs. Run(Externally Studentized Residuals).

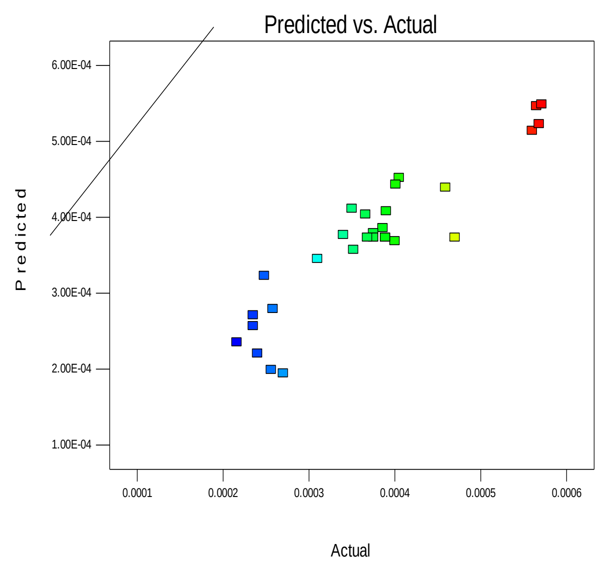

Figure 4. Predicted Vs. Actual

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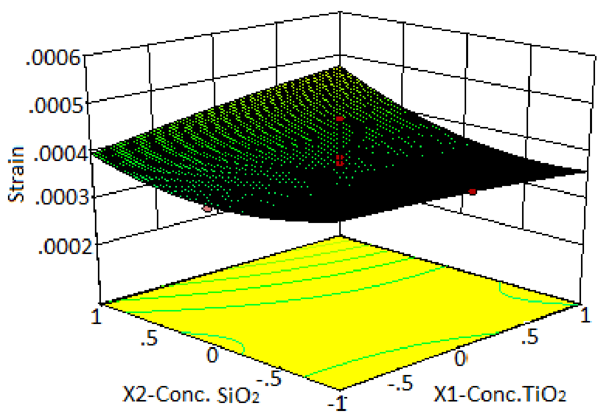

Figure 5. Three-dimensional surface plot by response surface methodology for combined effect of concentration of TiO_2 and concentration of SiO_2 on strain.

In fig.5 plot gives us the combined optimal effect on Strain. In plot maximum value of Strain is 0.00047, for this all the precursors shows their mid values. Now From collecting data from optimal conditions, When concentration of TiO_2 and concentration of SiO_2 are low but Temperature is high Strain=0.000565, Both concentrations are at their mid values but temperature is at lowest point Strain =0.000389.

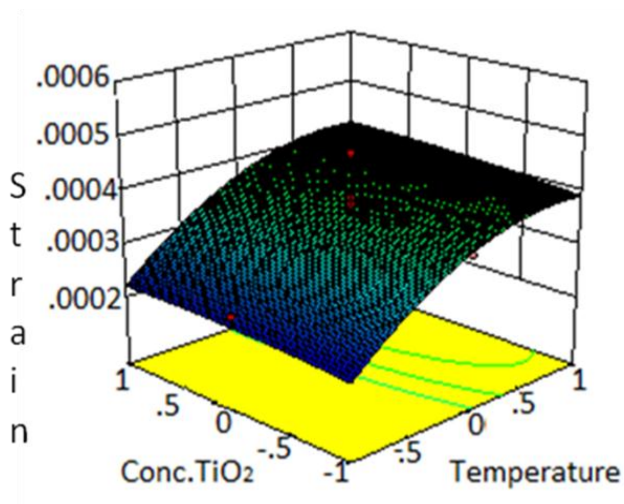

Figure 6. Three-dimensional surface plot by response surface methodology for combiend effect of temperature and concentration of TiO_2 on strain.

When concentration of TiO_2 and temperature are at lowest point but concentration of SiO_2 is at highest point, Strain=0.00031. Both concentrations(TiO_2-SiO_2) are at their highest point but temperature is lowest point, Strain is 0.00039. We can say as conentration of TiO_2 increases strain values also increases and similarly as concentration of SiO_2 increases strain also increases. But the effect is not as much effective as we can see in the case of Annealing temperature. In fig.6 plot shows the graphical strain values generated from 30 optimum points. At the best point with maximum strain is 0.000405, the optimum temperature found to be maximum (1), concentration of TiO_2(-1), concentration of SiO_2(1) and the drop rate(1) are also maximum. For obtaining value of strain i.e. 0.000571 all precursours are at their maximum point. And when all prameters are decreased to their mid values accept temperature, which is at low value, strain is at its lowest value i.e. 0.00024. Now concentration of TiO_2 and temperature are at lowest value, concentration of SiO_2 and drop rate are at their highest value. These conditions don't show more variation in Strain value. We can conclude that annealing temperature is showing positive effect as compare to the concentration of TiO_2, concentration of SiO_2 and drop rate.

E Characterization of optimal samples

In this part, the properties of optimum samples (sample of run 8) were evaluated. The structural properties of the sample were investigated by XRD. X-ray crystallography is a tool used for identifying the atomic and molecular structure of crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions.

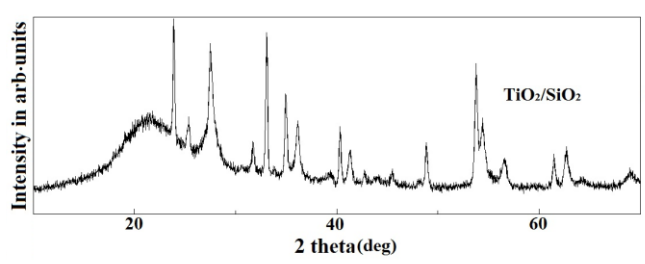

Figure7. XRD for optimal sample of TiO_2/ SiO_2

The corresponding pattern can be seen in Fig. 7. This figure shows diffraction peaks at 2θ ~ 23.880 (110), 27.480 (110), 31.700 (111), 33.060 (112), 34.940 (110), 36.060 (101), 40.320 (120), 41.240 (111), 48.340 (200), 53.760 (231), 54.200 (211), 54.420 (120), 55.460 (211), 61.440 (130), 62.660 (204).

In this sample 2θ at ~ 23.880, 27.480, 33.060, 34.940, 36.060, 40.320, 41.240, 54.200, 56.550 shows TiO_2 having tetragonal structure [JCPDS file no. 841284]. Peak at 2θ ~ 31.700 shows orthorhombic structure of TiO_2 [JCPDS file no. 841750]. There is a broad peak at 2θ =25.31◦, corresponding to the anatase crystalline structure of titanium dioxide. The presence of broad peak indicating the presence of SiO_2 stabilizes the composites by reducing its crystallization temperature [31]. It is also worth to mention here that addition of silica into the titania sol did not have an impact on the crystalline structure of titanium dioxide [32].

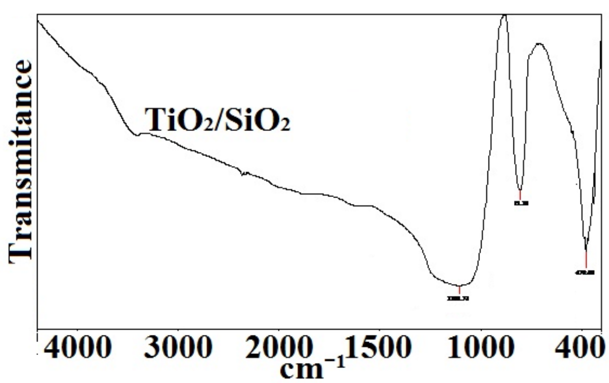

Figure8. FTIR for optimal sample of TiO_2/ SiO_2

Fig. 8 shows the FTIR spectrum of optimal sample.Fourier transform infrared spectroscopy is a technique which enables us to identify the organic, inorganic materials and specially the presence of impurity phase in natural or synthesized materials. In Fig. 8 peaks at 1098.87 cm-1 & 797.74 cm-1 corresponds to asymmetric and symmetric vibrations of Si-O-Si linkage. The band at around 476.53 cm-1 can be attribute to the Ti-O and Si-O vibrations, implying the formation of TiO_2 and SiO_2 [33-34]. The peaks at 1103.73 cm-1 and 805.16 cm-1 attribute to the asymmetric and symmetric Si-O-Si stretching vibrations [35].

IV. CONCLUSION

The statistical analysis recognized consolidating flow rate of adding the metal ions to the alkaline solution as the most consequential factor affecting the particle size. By controlling the drop rate of adding the metal ions to the alkaline solution, the actual control of the nucleation and growth steps was possible. XRD study reveals the size of nanocrystallite is in the range of 28-39 nm. Establishing Ti—O—Si and Si—O—Si linkages in the synthesized nanocomposite was demonstrated using the FTIR pattern.

FTIR spectrum of samples analyzed the functional group and characteristic bond of the used precursors The presence of anatase crystalline structure in synthesised nanoparticles was confirmed using the XRD patterns. Data were analyzed using Design Expert software. The significant effects of independent factors were analyzed using ANOVA. The Model F-value of 12.16 (for strain) implies the model is significant. The correlation coefficient of determination R^2 was 0.8455 for strain indicating that the observed results fitted well with the model prediction, and the effect was also reported in the form of 3D perturbation plots. From 3D plot we concluded that strain is strongly affected by concentration change in SiO_2, temperature and drop rate.

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