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Sol-gel Synthesis & Characterization of Nanocomposites of Cu/TiO2 and Bi/TiO2Metal Oxides as Photocatalysts

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ABSTRACT

Nanocomposites of Cu/ TiO_2 and Bi/TiO_2 metal Oxides have been synthesized by Sol-Gel method. Nanosols were prepared by dissolving salts of Precursors in suitable Solvents (double distilled water , Ethanol) in the first step of synthesis . These Nanosols were converted into Gels on heating and continuous Stirring .Characterization was done by UV/VIS , FTIR , XRD ,and TGA/DTA Techniques . The Credibility of prepared samples was investigated by the degradation of a Textile Dye Rhodamine B under Solar Light irradiation. The results revealed that these Nanocomposites possess Photocatalytic activity.

Keywords: *Sol-Gel, Cu/TiO_2, Bi/TiO_2, Photochemical reaction, Nanocomposites*

1. INTRODUCTION

During recent decade, Nanotechnology has been booming in many areas of life. It is an interdisciplinary technology which includes Science, mechanics, aerospace and electronics.[3]

Both Nanoscience and Nanotechnology deals with characterization, preparation, exploitation and exploration of Nanostructures including Nano clusters, Quantum dots, Nano Crystals, Nanotubes and Nanowires. On the other hand Nanostructure involves arrays, Super lattices and assembles of individual Nano materials. [2]

A group of metal oxide nanoparticles of $TiO_{2,}$ Al_2O_3, ZnO and MgO possess photo catalytic biological species, electrical conductivity and UV absorption. Now-a-days intensive researches involving the nanoparticles of metal oxides have been focusing on antimicrobial, self-decontamination and UV blocking functions for civilian health products and military protection gears.[4]

Nanocomposites are substances which are prepared by combining two or more pure substances with distinctly different properties (might be mechanical, electric, magnetic, optical, thermal, chemical etc.) in order to create a composite material that combines the desirable properties of each other to create a multi-functional substance.

In 2007, two scientists described the synthesis & characterization of Nanosize crystalline TiO_2 and SiO_2 / TiO_2 mixed oxide particles and observed their photocatalytic activity for Rhodamine B degradation. Results showed that photodegradation of RB proceeds by psuedofirst order reaction kinetics.[1]

Nanocomposites TiO_2 / SiO_2 using Sol-gel method were reported in 2010 by K Balachandran and Co-workers. They explored structured effect on size and thermal stability of these nanocomposites. These NTSC (Nano TiO_2 / SiO_2 composite) were characterized by FTIR, XRD, SEM-EDS and TG-DTA techniques. Titania source was Titanium tetraIsopropoxide with ethanol and water, Silica source was Silicic acid.[2]

In 2002 photo catalytic detoxification of textile dye reactive blue 4 was carried out by B. Neppolian and co-workers. Reactive blue 4 dyeswere totally mineralized on irradiation with TiO_2photocatalyst. Solar light intensity was measured by Lux meter. Molecules of dye were degraded to CO_2, SO_4^{2-} and water under solar light. HPLC and COD were used to study degradation of dyes respectively. [3]

In 2003 kinetic and mechanistic investigation were performed on Titanium dioxide by Ioannis K. Konstantinou and others .Rate of decolourization of azo dyes and formation of end products was reported.

2. EXPERIMENTAL

Chemicals

Titanium tetrabutoxide (Aldrich), as a precursor of TiO_2 and Ethanol as solvent were used. $Cu(NO_3)_3$(Merck), Acetic Acid (Merck), $Bi(NO_3)_{3,}$ Double Distilled water . SDBS (sodium dodecylbenzenesulfonate) was used as surfactant.

Synthesis of Nanocomposites

Procedure

7.6 ml of Titanium tetrabutoxide (Merck) was added slowly into 8 ml of Ethanol under vigorous stirring to form solution A. Then a certain amount of copper Nitrate (2gm) was dissolved in 2ml ethanol. This solution was added in solution A drop wise. Solution was stirred continuously for 24 hours. Later surfactant was added. The resulting solution was heated up to 100^0C and stirred for evaporation. Sticky Gel was formed as viscosity and colour changed. In an oven Gel was dried at 100^0C for 3 hours. The bluish green Nanopowder was prepared. Prepared sample was subjected to heating at 400^0C in furnace. Blue coloured crystals were formed.

Preparation of $Bi(NO_3)_2$

Nanocomposites

For precursor solution 10 ml of titanium tetrabutoxide was dissolved in 38 ml of absolute alcohol. Solution was stirred continuously. In another beaker added 0.5 ml of Acetic acid in 2 ml of water. 38 ml of ethanol was added into this solution. Then both solutions were mixed on a hot plate with vigorous stirring. Mixture was turned into SOL. Then solution of $Bi(NO_3)_3$ was added drop wise into this solution. Transparent colloidal suspension was formed, Stirred on hot plate for 1 hour. It was kept for aging for 2 days. Gel was formed. Resulting gel was dried at 70^0C in oven and ground to fine powder. Calcination of dried sample was done at 500^0C for 4 hours.

Characterization

The prepared sample was characterized by UV-VIS, FTIR, XRD, TGA/DTA analytical techniques.

Photo degradation of Textile Dye

Experimental

To test the performance of prepared samples of Nanocomposites degradation of a Textile Dye Rhodamine B under UV light was carried out. It was observed that samples showed photo catalytic activity under Solar light irradiation.

For the experiment a calculated quantity of catalyst (0.1) molar Sol in water was used. Five different samples of Nanocomposites were prepared. Dye solution was prepared by dissolving 30 mg /l in distilled water. For complete adsorption dye solution was kept in dark for 30 minutes. Then 10 ml Sol was added into test tubes. Samples were placed in Sunlight for UV radiations. Five test tubes containing dye solution and Nanosols were kept in Sunlight for 15 days. About 40% degradation was observed at the end of the reaction. Colour of the dye was changed due to degradation process.

Good results were obtained during April-June peak summer period. At the end samples were collected and were analyzed by UV –VIS Spectrometer.

3. RESULTS & DISCUSSIONS

Characterization of Cu-TiO_2 Nanocomposites

Nanocomposites of Cu-TiO_2 prepared by Sol-Gel method were characterized by various Analytical techniques.

UV-VIS

In UV-VIS spectrum of sample, maximum absorption was observed at 794 nm & 525 nm. As calcination temperature increases broad band emerges.

The absorption band between 600-800nm clearly suggest the increase in crystalline nature of the sample.

FTIR:

FTIR spectrum was recorded with Gel and with powder sample separately. Results have shown various bands. Fig: 1

The band at 653.90 cm^{-1} may be attributed to Cu-O Stretching. Two bands at 1650 cm^{-1} and 3642.9 cm^{-1} are due to O-H vibrations. The absorption band at 729.29 cm^{-1} is due to O-Ti-O skeleton.

Another band at 1383.6 cm^{-1} can be assigned to Organic molecules.

Bands between 2800-2900 cm^{-1} are due to organic impurities.

Table 1: FTIR results of Cu-TiO_2 Nanocomposites

Band Position	
653.90 cm^{-1}	Cu-O Stetching
1383.6 cm^{-1}	Organic molecule
792.29 cm^{-1}	O-Ti-O Vibrations
1650 & 3642.9 cm^{-1}	O-H Vibrations

XRD

Powder XRD analysis was performed. Fig: 2 exhibits XRD spectrum of the sample. Peaks are at 20=29.45, 38.93, 48.369 which shows crystalline nature of Nanocomposites.

Table 2: XRD results of Cu-TiO_2Nanocomposites

	2Ø	d
1	29,459	3,0296
2	38,939	2,3111

Average particle size calculated by Debye-Scherrer Equation is found to be 6.7 nm, & 6.9nm.

TGA/DTA/DSC:

Fig: 3 represents TGA graph of Nanocomposites material. The wt. loss is at 80-100^{0}C .It is due to dehydration process. Second wt. loss is observed at about 250^0 C which indicates decomposition of organic molecules. Third wt. loss takes place at 360^{0}C. Reaction is endothermic but becomes exothermic afterwards. Finally compound decomposes at 800^{0}C.

Table: Showing results of thermal analysis of Cu-TiO_2 Nanocomposites

S.No.	Peaks	Temperature	Wt. Loss (DTA)	Δ H
1	1	100 Ċ	4 %	+VE
2	2	250 Ċ	13 %	-VE
3	3	360 Ċ	20 %	_VE
4	4	600 Ċ	25 %	+VE
5	5	800 Ċ	40 %	+VE

Characterization of Bi-TiO_2 Nanocomposites

Bi-TiO_2 Nanocomposites prepared by SolGel method were characterized by various techniques.

UV-VIS

UV-VIS Spectrum was recorded with diluted solution of Sol with water. Fig: 4 shows absorption peaks at 792 nm, 532nm, 462 nm respectively. It is clear that in combination with Bi catalyst increase in absorption wavelength is observed. The spectrum shifts towards visible region.

FTIR

FTIR spectrum was recorded with Sol of the sample. Fig: 5 show absorption bands at different positions. The absorption band at 1652 cm $^{-1}$ is due to bending vibrations of O-H group. Another band at 867cm^{-1} is due to O-Ti-O vibrations .The absorption band at 653.77cm^{-1} is due to Bi^{+3} cation. Other weak bands at 2397cm^{-1} and 1915cm^{-1} are due to organic impurities.

Table; 1 FTIR results of Bi- TiO_2Nanocomposites

	Band position	Result
1	1652cm^{-1}	Bending vibration of O-H
2	2397 -1915cm^{-1}	Organic impurities
3	867cm^{-1}	O-Ti-O vibrations
4	653.7cm^{-1}	Bi^{+3} cation

XRD

XRD analysis was performed after calcination of the sample. Fig: 6 shows XRD pattern of Nanomaterial. Major peaks at 29.3^0 ,38.8^0, 47.6^0 , 54.9^0 show crystalline nature of the sample . Average particle size calculated by Debye - Scherrer equation was found to be 6.7nm & 6.9 nm.

Table; 2 showing XRD results of Bi-TiO2 Nanocomposit

	2Ø	d
1	29,362	3,0394
2	38,841	2,3168
3	47,640	1,9073
4	54,932	1,6701

TGA/DTA/DSC

Thermal Analysis was performed with TGA SDT TA USA at 100-1000^0 C. Fig: 7 exhibits TGA/DTA/DSC graphs of the sample. It shows that a rapid wt. loss occurs from 200^{0}C-250^{0}C due To volatilization of physically adsorbed water. About 4% wt. loss is observed. Second wt. loss occurs at 300-400^{0}C due to carbonization & burning of organic groups in the compound. This process is accompanied by heat evolution. It is evident from exothermic peaks detected by DSC curves.

Finally major wt. loss is seen at 700^{0}C due to decomposition of the compound. About 33% wt. loss is observed.

Table: Showing results of thermal analysis of Bi-TiO2Nanocomposites

S.No.	Peaks	Temperature	Wt. Loss (DTA)	Δ H
1	1	100 Ċ	4 %	-VE
2	2	250 Ċ	8 %	-VE
3	3	360 Ċ	10 %	_VE
4	4	660 Ċ	25 %	+VE
5	5	700 Ċ	33 %	+VE

Results & Discussions

Fig: 8 - 9 show spectra obtained after UV-VIS analysis. It is clear that absorption maximum of Rhodamine B was shifted to lower wavelength region due to disappearance of colour. The Abs.max for Rh B without catalyst was recorded and found to be 547nm. After degradation spectra showed Blue shift.

Table 1. Showing results of UV-VIS Analysis.

Sr. No.	Type of Catalyst	Wave Length	Absorbance
1	Dye solution only	547 nm	2.553
2	Bi/TiO_2	533 nm ,438 nm	1.848 , 1.955
3	Cu/TiO_2	499 nm	0.238

4. CONCLUSION

Following Conclusions have been drawn from Experimental Studies.

The Nanomaterial (Nanopowder, Nanocomposites, Nanoparticles) was successfully synthesized by Sol-Gel method and it was characterized by various Analytical Techniques. Results showed that prepared samples contain expected chemical compositions. It was observed that amorphous compounds were converted to crystalline form on heat treatment.

Particle size of samples calculated by Debye-Scherrer equation was in Nanoscale range.

Performance of Nanocomposites was tested by the Degradation of Textile dye Rhodamine B under Solar Light irradiation.

To examine extent of degradation samples were analysed by UV-VIS spectroscopy.

Results have shown that Absorbance maximum of Rhodamine has been shifted to blue region due to degradation process.

So it is concluded that these prepared Nanocomposites have photo catalytic activity under Solar light irradiation.

These Nanocomposites can be used for waste water treatment, Cancertreatment, as antimicrobial agent, Catalyst in chemical reactions, etc.

Acknowledgement

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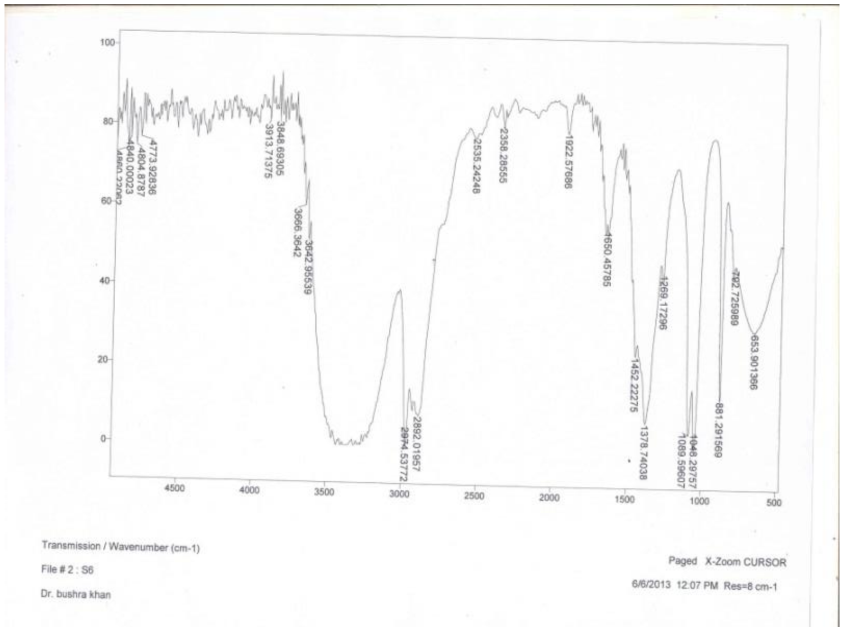

Fig: 1 FTIR Spectrum of Cu/TiO_2Nanocomposites

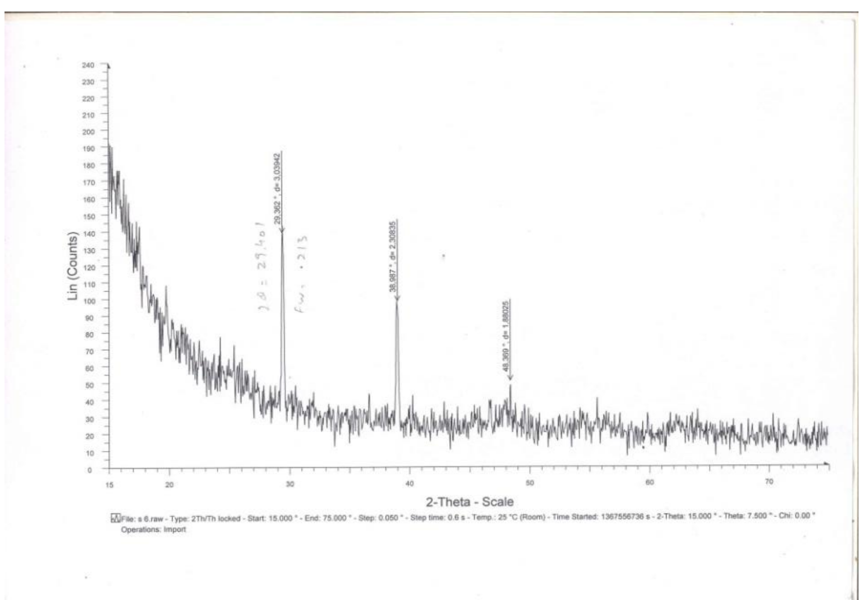

Fig: 2 XRD Spectrum of Cu/TiO_2Nanocomposites

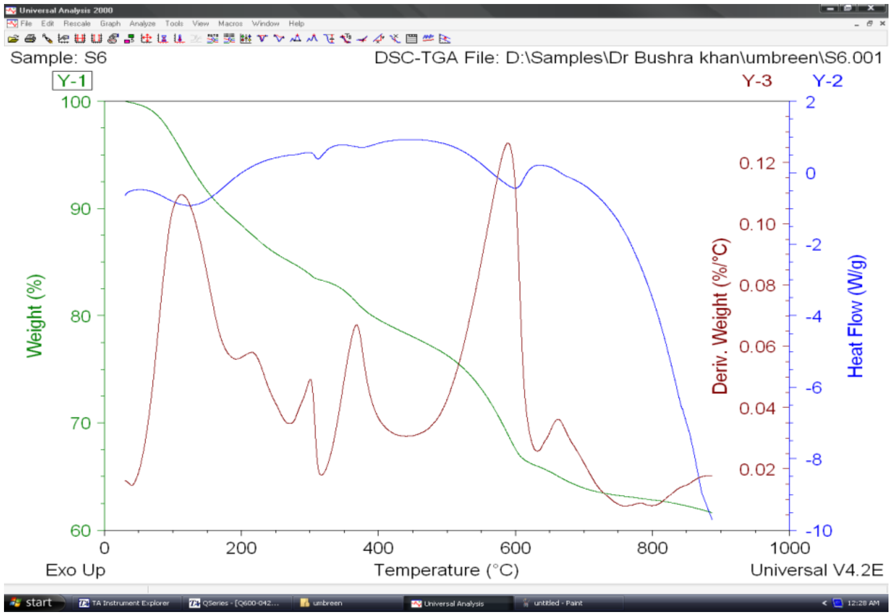

Fig: 3 TGA/DTA of Cu/TiO_2Nanocomposites

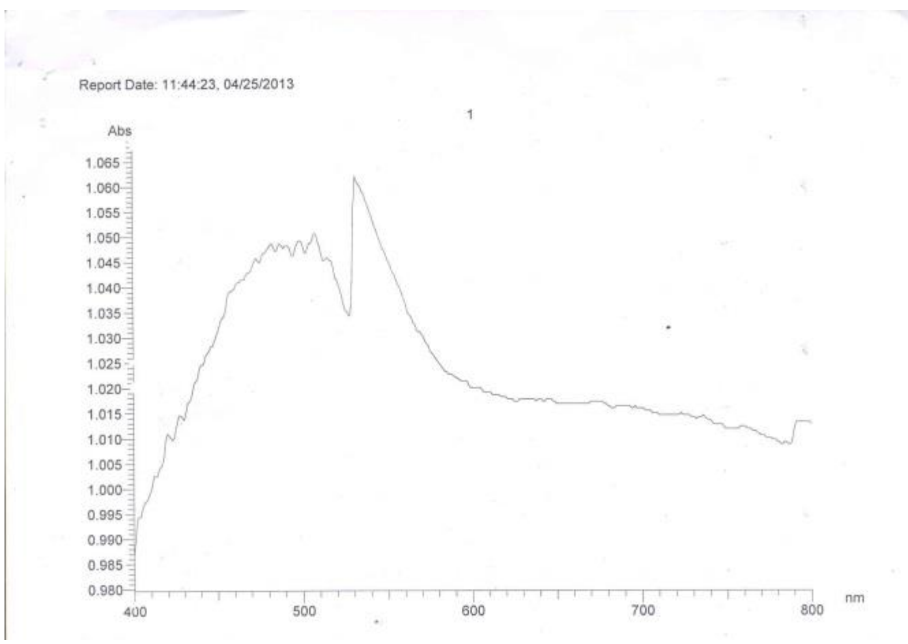

Fig: 4 UV Spectrum of Bi/TiO_2Nanocomposites

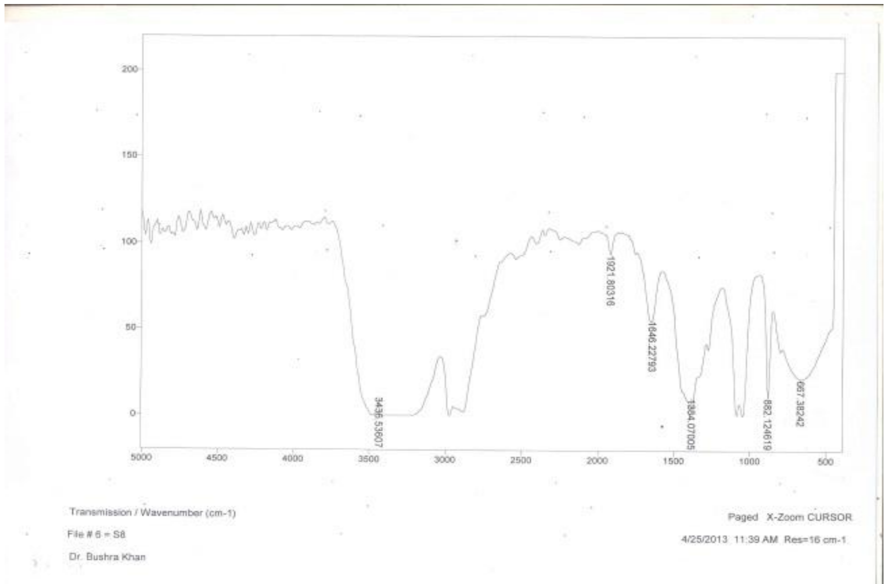

Fig: 5 FTIR Spectrum of Bi/TiO2Nanocomposites

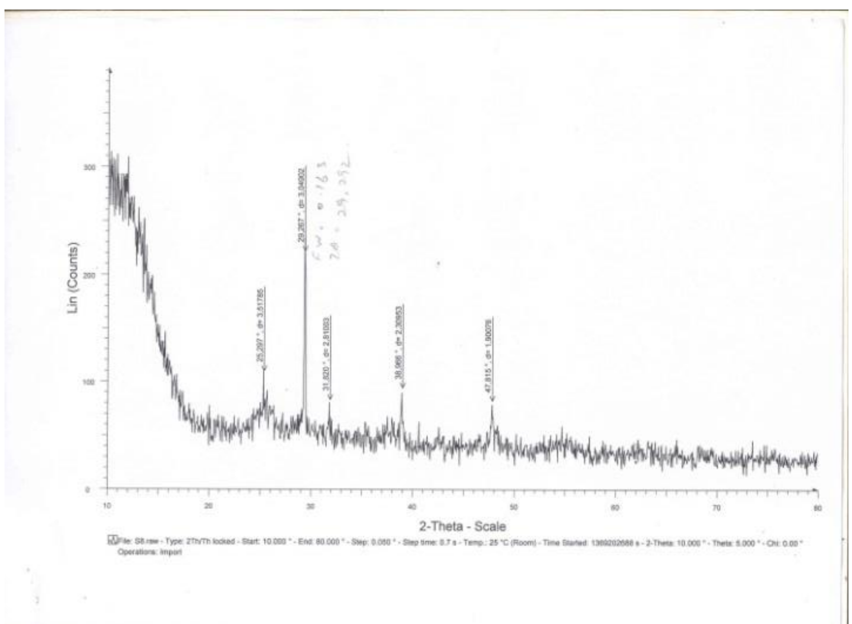

Fig: 6 XRD Spectrum of Bi/TiO2Nanocomposites

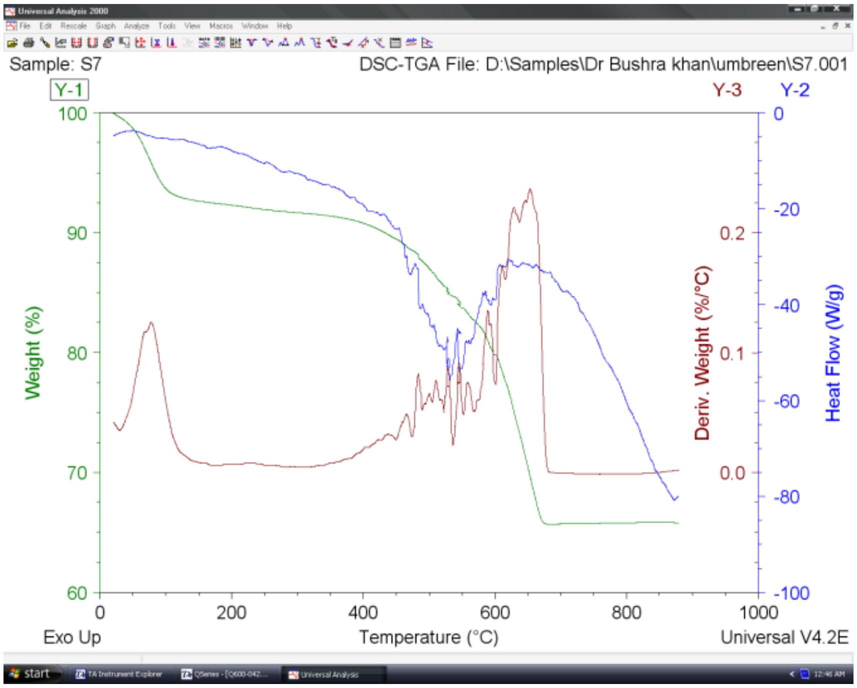

Fig: 7 TGA/DTA of Bi/TiO_2Nanocomposites

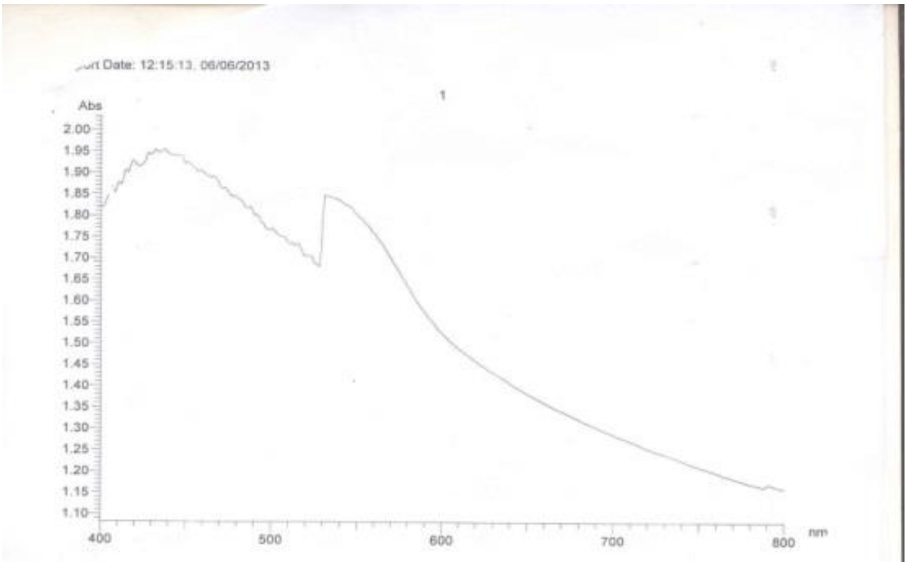

Fig: 8 UV Spectrum of Sample

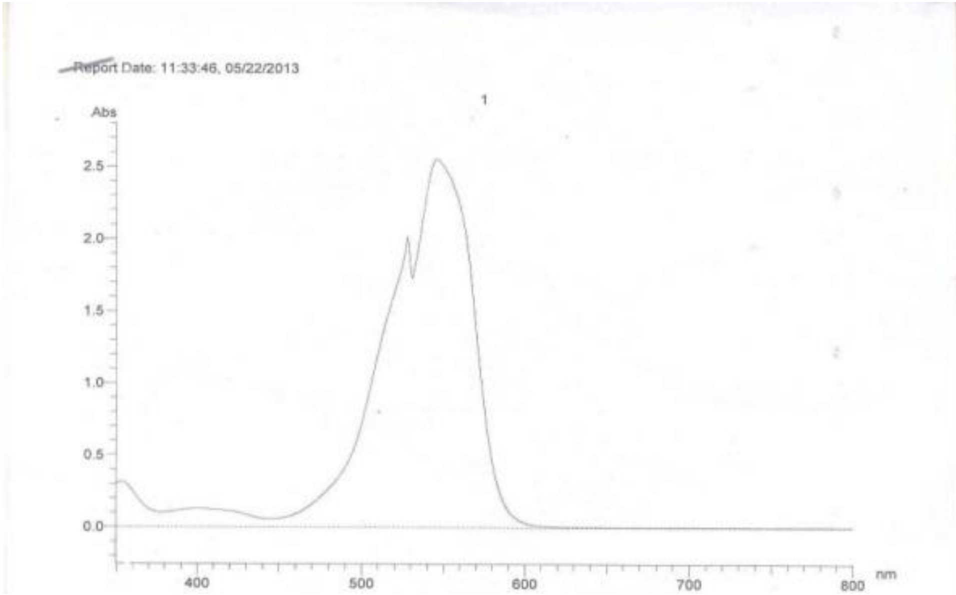

Fig: 9 UV Spectrum of Rhodamine