Safranin dye degradation by using Fe_2O_3-SnO_2 Nanocomposites under natural Sunlight

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Abstract

Metal oxide based semiconductor photocatalysts are well known for multifunctional applications. Herein, we have reported the ex-situ synthesis of Fe_2O_3-SnO_2 nanocomposite system using simple wet impregnation method. Total five semiconductor nanomaterial photocatalysts were prepared as Fe_2O_3, SnO_2, 1, 2.5 and 5% of SnO_2 over Fe_2O_3 surface. After successful synthesis of these photocatalysts its formation is checked using UV-Vis spectroscopy, FTIR and RAMAN analysis. Photocatalytic dye degradation performance is checked towards safranin dye using all the five photocatalyst systems. Resultant composite photocatalysts were not showed some impressive photocatalytic activities as compared to individuals. This above observation is may be due to the less gap between conduction band levels of both photocatalyst systems.

Keywords: *Composite, Dyes, Degradation, Photocaltalysis.*

I. Introduction

Nanostructured semiconductor materials are at the center of attraction among the scientific community due to their fascinating properties like suitable band gap, higher surface area and optical properties [1].Depending on these impressive properties they are used for extensive range of applications in various fields such as photocatalysis, sensors (gas, humidity), solar cells, optoelectronic and nano devices etc [2]. Particularly, TiO_2, ZnO, SnO_2, ZrO_2 and Fe_2O_3 nanosystems are used as a catalyst for the elimination of organic pollutants. Many complex organic pollutants when released in water sources they remained there for long period of time causing serious ill effects to aquatic life. Mainly, colored complex dyes are playing a very vital role in the water pollution since they are persistent over a long period of time ultimately, that affects the human health [2]. There exist many physical, chemical and biological treatment methods to eliminate this harmful organic dyes.

Photocatalysis is one of the very promising method as it is with very less side products and less cost in comparison to other. TiO_2 is most important and discussed photocatalytic material known till date [3]. Fe_2O_3 is a semiconducting inorganic material which is also known as Hematite or Red iron oxide which is a promising candidate in photocatalysis. Various other sulfides and oxides are used for making composites with Fe_2O_3. On the other hand, SnO_2 is also one of the best semiconducting oxide material which is mostly used for sensing, resistors, optoelectronic devices and photocatalytic applications [4].

In the present article, we have demonstrated the synthesis, characterization and photocatalytic activity of Fe_2O_3-SnO_2 nanocomposite. After successful synthesis of these photocatalysts its formation is checked using UV-Vis spectroscopy, FTIR and RAMAN analysis. Photocatalytic dye degradation performance is checked towards safranin dye using all the five photocatalyst systems [5-7]. Resultant composite photocatalysts were not showed some impressive photocatalytic activities as compared to individuals [8]. This above observation is may be due to the less gap between conduction band levels of both photocatalyst systems [9-11]. These type of nanocomposites may be useful for the removal of other organic complex dyes [12-14].

II. Experimental

II.1. Materials

Fe_2O_3 and SnO_2 nanomaterial used are as it is without any further purification ordered from LOBA chemicals.

II.1.1.Synthesis of nanocomposite photocatalyst systems

For the formation of Fe_2O_3-SnO_2 nanocomposite systems simple wet impregnation method was employed, which is discussed as below. Both the individual's catalysts were synthesized separately and used after all characterization. Take 0.5gm of Fe_2O_3 in three different beakers and add 25 mL of ethanol to each with continuous stirring. After 30 min. 1, 2.5 and 5 weight percent of SnO_2 is added with respect to Fe_2O_3 while continuous stirring. These solutions were kept under constant stirring till the ethanol evaporates completely. Lastly, the powdered composites were heated at 80 °C for 12 hours to get complete dry photocatalyst systems. Before subjected to the XRD, FTIR and Raman spectroscopy characterization these all photocatalytic systems were well mixed using mortar and pestle.

II.1.2. Characterizations:

The formation of composite systems with the individuals are checked by using powder XRD (PXRD) technique (20° to 80° range, scan rate =1° /min) equipped with a monochromator and

Ni-filtered Cu Kα radiation from Bruker AXS model D-8. UV-1800, Shimadzu is used for the recording the absorbance value of dye remained solution after each reading. For the molecular identification Raman spectroscopy is used (RENISHAW inVia Raman microscope). For the identification of vibrational modes present in Fe-O and Sn-O bonds FTIR (Shimadzu, IR Affinity-1) is used.

II.1.3. Photocatalytic dye degradation study

The photocatalytic dye degradation using all the five nanocomposite systems were performed under natural sunlight using following procedure. Herein, we used Safranin dye for the first time. A 10 ppm stock solution (01 liter) of safranin dye was prepared by dissolving 10 mg of dye in 1000 mL DI water. During each degradation experiment 100 ml, 10 ppm of Safranin solutions were taken in 150 mL flask. To this solution 10 mg of photocatalyst systems were added and stirred for 30 min in dark to attend the adsorption desorption equilibrium for the solar light [15-16].

II.1.4. Photocatalytic degradation of safranin in Sunlight

On the roof top of building a safranin dye solution in a photoreactor were stirred and after fix interval of time 2 mL of samples were removed and centrifuged for 15 min at 3600-3800 rpm to separate the photocatalyst. The supernatant liquid was analyzed using UV-visible spectrophotometer (UV-1800, Shimadzu) to record the change of Safranin concentration. The absorbance value at wavelength 520 nm was used to find out the % dye degradation. The % dye degradation was calculated using equation (1).

% dye degrade = $(C_0-C_t)/C_0 \times 100$ …(1)

where, C_0 is an initial concentration of Safranin dye and C_t is the concentration of Safranin after irradiation time 't'.

III. Results and Discussions

III.1. FTIR Analysis

After complete synthesis of Fe_2O_3-SnO_2 nanocomposite systems the structural characterization was performed using FTIR analysis.

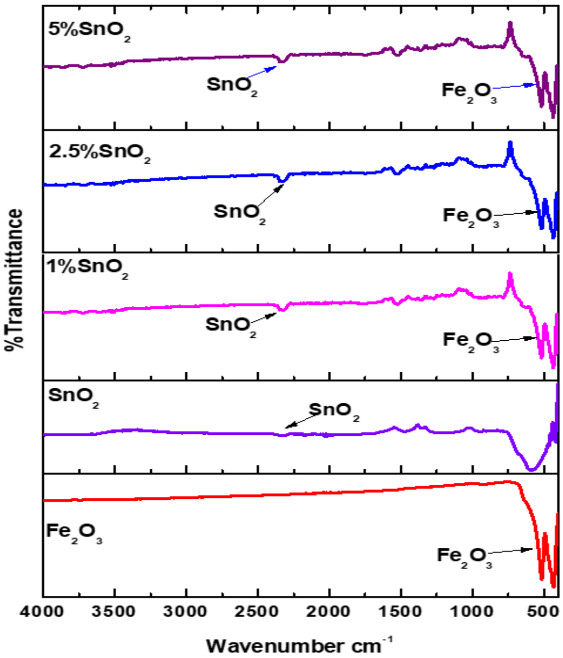

Figure 1: FTIR analysis of Fe_2O_3-SnO_2 nanocomposites

Figure 1 shows the FTIR spectrum of Fe_2O_3, SnO_2, 1, 2.5 & 5% Fe_2O_3-SnO_2 nanocomposites. From figure it is very clear that the peaks around 450 to 550 cm^{-1} are attributed to Fe_2O_3 nanostructures and no any other prominent peaks ware seen in the Fe_2O_3 spectrum. The peak responsible for SnO_2 vibration were seen at around 550 to 650 cm^{-1} the peak at around 2200 to 2250 cm^{-1} is due to the SnO_2 nanoparticles. Also, in figure, 1, 2.5 & 5% Fe_2O_3-SnO_2 nanocomposites both the peaks of Fe_2O_3 and SnO_2 were seen which conforms the formation of nanocomposite of SnO_2 over the surface of Fe_2O_3 nanoparticles [17].

III.2. X-ray diffraction analysis

Figure 2 depicts the powdered XRD patterns of Fe_2O_3, SnO_2, 1, 2.5 and 5% of Fe_2O_3-SnO_2 nanocomposites.

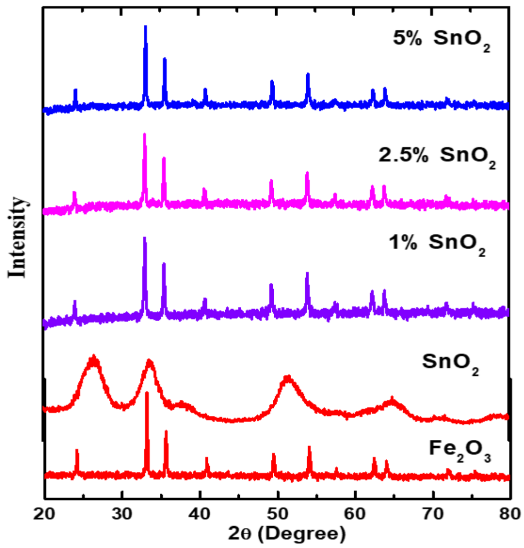

Figure 2. Powdered XRD of Fe_2O_3-SnO_2 nanocomposites

Form figure it is very clear that Fe_2O_3 and SnO_2 showed resemblance with earlier reports. In 1, 2.5 & 5% of Fe_2O_3-SnO_2 nanocomposites all the peaks attribute to only Fe_2O_3 nanostructure and no any prominent peaks for SnO_2 were seen this might be due to the very less percentage of SnO_2 used formation on nanocomposite hence not detected in the XRD analysis [18].

III.3. RAMAN analysis

Raman spectrum of Fe_2O_3-SnO_2 nanocomposites were shown in figure 3. The Raman shift at around 1300 cm^{-1} is attributed to the Fe_2O_3 nanostructure and the spectrum for 1, 2.5 & 5% are fore the Fe_2O_3-SnO_2 nanocomposite. From figure it is very clear that, the peak at around 650 cm^{-1} is because of SnO_2 nanoparticles (marked using * in the diagram). As the concentration of SnO_2 is increasing over the surface of Fe_2O_3 nanoparticle the intensity of SnO_2 peak is also increases as shown in the Figure [19]. For more clarification, the SnO2 peak is highlighted in zoom.

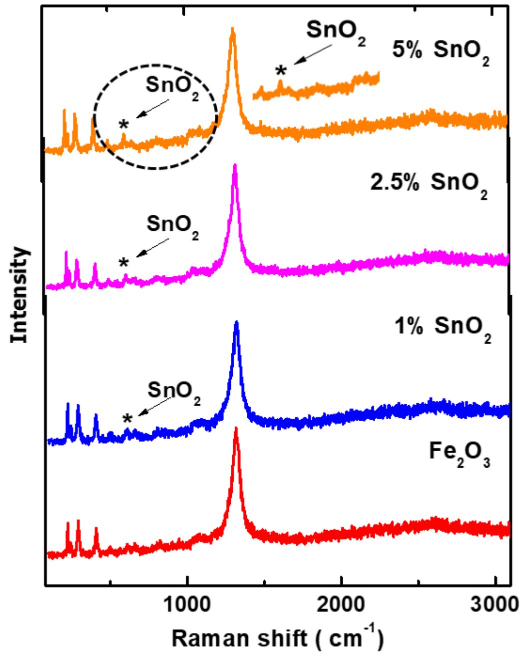

Figure 3. Raman analysis of Fe_2O_3-SnO_2 nanocomposites

III.4. Photocatalytic Safranin dye degradation

Photocatalytic activity of Fe_2O_3, SnO_2 and 1, 2.5 and 5% of Fe_2O_3-SnO_2 nanocomposites were checked in absence of light, without any of the above catalyst and also in presence of all five catalysts. The graph of absorbance studies for all the five photocatalytic systems were showed in figure 4.

From Figure 4 it can be seen that as the time passes the absorbance intensity decreases with different rates depending on the photocatalysts.

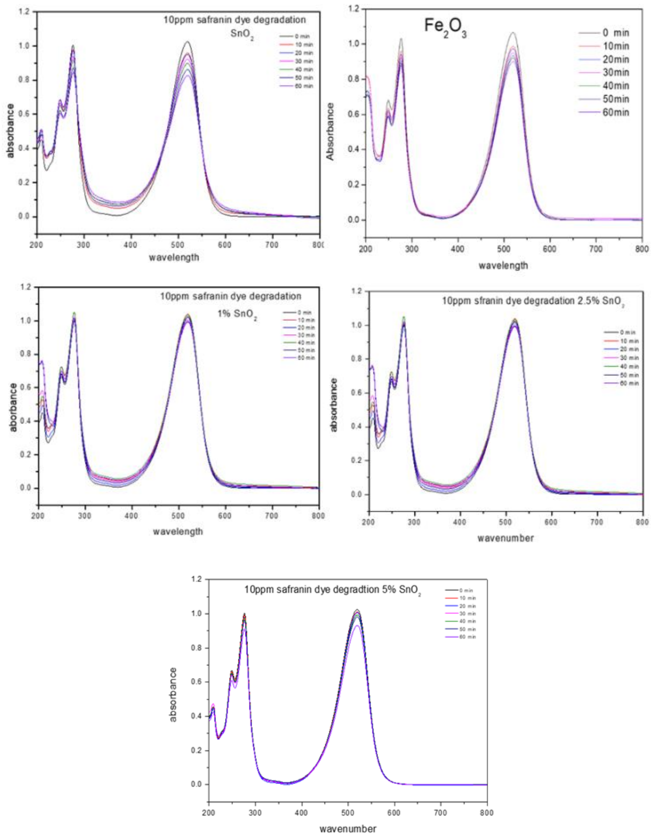

Figure 4: Absorbance graphs of Fe_2O_3, SnO_2 1, 2.5 and 5% of SnO_2 over Fe_2O_3 nanocomposite

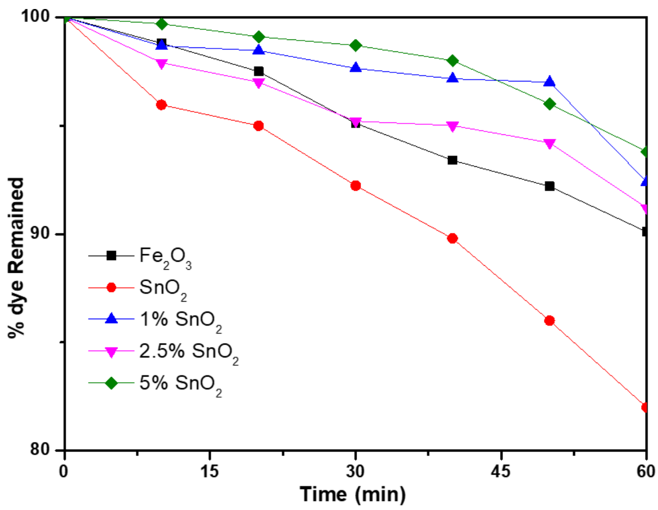

Figure 5. Percent Safranin dye degradation

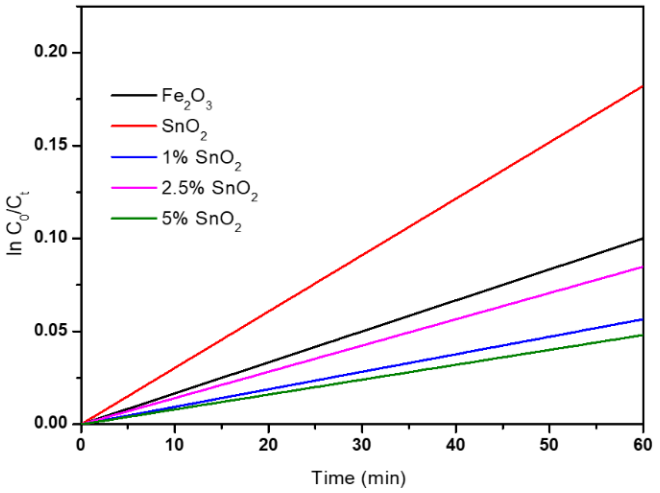

Figure 6. Rate of Safranin dye degradation

Depending on these absorbance graphs, we also calculated and plotted the percentage of Safranin dye degradation as functions of irradiation of 60 time as shown in the figure 5.

All these experiments were done in presence of natural sunlight around 12 noon to 1 PM in day light in order to get maximum light intensity. For Fe_2O_3 and SnO_2 around 10% and 18% of dye degraded respectively. As the concentration of SnO_2 is increases the rate of degradation was expected to increase, but surprisingly we have not seen any improvement in the rate of degradation. Along with this we also explored the Safranin dye degradation experiments without light (in the dark) and without any of the above photocatalyst semiconductor catalyst. In the dark no Safranin dye degradation found which supports the mechanism of photocatalytic experiments [20-21]. Figure 6 gives the idea about rates of Safranin dye degradation against the time. For the 1, 2.5 and 5% of the SnO_2 over the surface of Fe_2O_3 rates are almost same. This proves that the 1 to 5% weight is might not be sufficient for the enhancement of activity.

Conclusions

Ex-situ synthesis of Fe_2O_3-SnO_2 nanocomposite system using simple wet impregnation method is reported. All five photocatalysts systems were prepared as Fe_2O_3, SnO_2, 1, 2.5 and 5% of SnO_2 over Fe_2O_3 surface. After successful synthesis of these photocatalysts its formation is checked using UV-Vis spectroscopy, FTIR and RAMAN analysis. Photocatalytic dye degradation performance is checked towards safranin dye using all the five photocatalyst systems. This above observation is may be due to the less gap between conduction band levels of both photocatalyst systems. Resultant composite photocatalysts were not showed some impressive photocatalytic activities as compared to individuals. These types of hybrid nanosystems can also be utilized for the number of applications.

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Conflict of Interest. There is no any conflict of interest.

References

[1] A. A. Ali, I.S. Ahmed, E.M. Elfiky. Auto-combustion Synthesis and Characterization of Iron Oxide Nanoparticles (α-Fe2O3) for Removal of Lead Ions from Aqueous Solution. Journal of inorganic and oragametallic polymers. 31, 384–396, 2021.

[2] V. V. Pham, M. Cao, V. Le. Insight into the photocatalytic mechanism of tin dioxide/polyaniline nanocomposites for NO degradation under solar light. Journal of Nanomaterials, 2016, 1-8, 2016.

[3] D. Zhao., W. Xiang. Nanoparticles assembled SnO2 nanosheet photocatalysts for wastewater purification. Materials Letters, 210, 354-357, 2018.

[4] R. Mithun Prakash, C. Ningaraju, K. Gayathri, Y.N. Teja, M. Aslam Manthrammel, Mohd. Shkir, S. AlFaify, M. Sakar, One-step solution auto-combustion process for the rapid synthesis of crystalline phase iron oxide nanoparticles with improved magnetic and photocatalytic properties. Advanced Powder Technology, 33, 0921-8831,2022.

[5] S. Pandit, S. Bhalerao, U. Aher, G. Adhav, V. Pandit, Amberlyst A-15: Reusable catalyst for the synthesis of 2, 4, 5-trisubstituted and 1, 2, 4, 5-tetrasubstituted-1H-imidazoles under MW irradiation. Journal of Chemical Science. 123, 421-426, 2011.

[6] G. Kumbhar, V. Pandit, S. Deshmukh, J. Ambekar, S. Arbuj, S. Rane. Synthesis of hierarchical zno nanostructure and its photocatalytic performance study . Journal of Nanoengineering and Nanomanufacturing. 3, 227-231, 2015.

[7] V. Pandit, S. Arbuj, Y. Pandit, S. Naik, S. Rane, U. Mulik, S. Gosavi, B. Kale. Solar Light driven Dye Degradation using novel Organo-Inorganic (6, 13-Pentacenequinone-TiO2) Nanocomposite. RSC Advance. 5, 10326- 1033, 2015.

[8] V. Pandit, S. Arbuj, U. Mulik, B. Kale. Novel functionality of organic 6, 13-pentacenequinone as a photocatalyst for hydrogen production under solar light. Environmental Science & Technology. 7, 4178-4183, 2014.

[9] V. U. Pandit, S. S. Arbuj, R. R. Hawaldar, P. V. Kshirsagar, J. D. Ambekar, U. P. Mulik, S. W. Gosavi, B. B. Kale. Hierarchical CdS nanostructure by Lawesson's reagent and its enhanced photocatalytic hydrogen production
.RSC advances. 5, 13715-13721, 2015.

[10] L. Klaai, D. Hammiche, A. Boukerrou, V. Pandit. Thermal and structural analyses of extracted cellulose from olive husk. Materials Today: Proceedings, (2021) https://doi.org/10.1016/j.matpr.2021.10.

[11] A.S. Somwanshi, S.S. Pandit, R.D. Ghogare, V. Pandit, and A.D. Gholap. Effecient catalyst for Knoevenagel condensattion of Aryl Aldehydes with Meldrum’s Acid. International journal of Chemistry Physics Science, 7, 92, 2018.

[12] V. Pandit, S. Arbuj, R. Hawaldar, P. Kshirsagar, U. Mulik, S. Gosavi, C. Park, B. Kale. In situ preparation of a novel organo-inorganic 6, 13-pentacenequinone–TiO_2 coupled semiconductor nanosystem: a new visible light active photocatalyst for hydrogen generation. Journal of Material Chemistry, 3, 4338-4344, 2015.

[13] V. Jawale, G. Gugale, M. Chaskar, S. Pandit, R. Pawar, S. Suryawanshi, V. Pandit, G. Umarji, S. Arbuj. Two-and three-dimensional zinc oxide nanostructures and its photocatalytic dye degradation performance study. Journal of Material research. 36, 1573-1583, 2021.

[14] K. A. Nevase, S. S. Arbuj, V. U. Pandit, J. D Ambekar, S. B. Rane. Synthesis, characterization and photocatalytic activity of tungsten oxide nanostructures. Journal of Nanoengineerng and Nanomanufacturing. 5, 221-226,2015.

[15] V. Jawale, A. Al-fahdawi, S. Pandit, G. Dawange, G. Gugale, M. Chaskar, D. Hammiche, S. Arbuj, V. Pandit. 6, 13-pentacenequinone/zinc oxide nanocomposites for organic dye degradation. Materials Today: Proceedings. (2021) https://doi.org/10.1016/j.matpr.2021.10.098.

[16] S. Pandit, R. Shaikh, V. Pandit . Synthesis of 5-unsubstituted-3, 4-dihydropyridine-2-(1h)-ones using nbs as a catalyst under solvent free conditions. Rasayan Journal of Organic . 4, 907-911,2009.

[17] Dhanesh Gawari, Vikram Pandit, Niteen Jawale, Pramod Kamble. Layered MoS2 for photocatalytic dye degradation.Materials Today: Proceedings, 53, 10-14, 2022.

[18] Shrikant Barkade, Sunil Sable, Varsha Ashtekar, Vikram Pandit. Removal of lead and copper from wastewater using Bael fruit shell as an adsorbent. Materials Today: Proceedings, 53, 65-70, 2022.

[19] Pradeep Kate, Vikram Pandit, Vivekanand Jawale, Madhusudan Bachute. L-Proline catalyzed one-pot three-component synthesis and evaluation for biological activities of tetrahydrobenzo [b] pyran: evaluation by green chemistry metrics. Journal of Chemical Sciences, 134, 1-11, 2022.

[20] Vikram Pandit. Synthesis of metal sulfides using Lawesson's reagent for photocatalytic hydrogen production. Materials Today: Proceedings, 53, 6-9,2022.

[21] Vikram Pandit. Hydrogen as a Clean Energy Source .Energy Efficiency, IntechOpen, (2021) DOI: 10.5772/intechopen.101536.