Preparation and physicochemical analysis of \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) hybrid ternary systems with enhanced photocatalytic activity under solar light irradiation

Angamuthu Muthamilarasu\textsuperscript{1}, Murugesan Sivakumar\textsuperscript{1}, Dhandapani Sakthi\textsuperscript{2}, Pullar Vadivel\textsuperscript{3}, and Santhanam Sivakumar\textsuperscript{1*}

\textsuperscript{1}Department of Chemistry, E. R. K Arts and Science College, Dharmapuri-636905, India
\textsuperscript{2}Department of Physics, E. R. K Arts and Science College Dharmapuri-636905, India
\textsuperscript{3}PG & Research Department of Chemistry, Salem Sowdeswari college, Salem-636010, India

Abstract

Various combinations of \( \text{TiO}_2 \) and \( \text{SnO}_2 \) in binary composites of \( \text{SnO}_2/\text{TiO}_2 \) and (2-10 wt. %) \( \text{Co}_3\text{O}_4 \) on \( \text{SnO}_2/\text{TiO}_2 \) of ternary composite \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) with were prepared. All the photocatalysts shows anatase crystalline phase and some of appropriate peaks of \( \text{SnO}_2 \) and \( \text{Co}_3\text{O}_4 \) peaks also present in binary and ternary systems, which is confirmed by X-Ray diffraction analysis. UV-Vis DRS indicated that all ternary composite \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) showed strong response in visible region and pure materials shows representative band positions. The molecular structure of M-O linkages (Ti-O, Co-O and Sn-O) is studied by FTIR analyses. Other physicochemical techniques such as SEM and PL also confirm the surface property and electronic excitation state. Ternary composite \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) demonstrates the highest decomposition for simultaneous degradation of reactive orange 30 (RO 30) under solar light.

Keywords: Ternary composite; \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \); \( \text{TiO}_2 \); Solar light degradation; reactive orange 30

*Corresponding author E-mail: sivabanu8494@gmail.com
1. Introduction

Water resource contamination and energy crises constitute the most important issues in the modern world. Both problems affect not only the quality of human life, but also human health, considering the availability of drinking water and energy resources, as well as increasing contamination of the environment, which is especially noticeable with regards to climate change. One of the main sources of environmental pollution is untreated industrial wastewater. Its direct release to surface water results in a serious contamination of fresh water. Photocatalytic and photoelectrocatalytic treatment with the application of sunlight offers an inexpensive and green technology for possible complete removal of refractory pollutants, such as surfactants, pharmaceuticals, pesticides, textile dyes, and heavy metals, from industrial wastewater. Furthermore, photoelectrochemical treatment of wastewater can be coupled with a simultaneous recovery of energy stored in the wastewater. This chemical energy is often wasted [1].

The demand for efficient and stable materials which can be applied as a photocatalyst or photoelectrocatalyst in wastewater treatment under visible light irradiation has increased during the last two decades. In particular, metal oxide–semiconductors have attracted great interest. Among these TiO\textsubscript{2} has found to be the most efficient waste water purifier and photocatalyst due to its high degradation efficiency, nontoxicity, and water insolubility, hydrophilicity, against photo corrosion, constancy and inexpensive obtainability [2]. Furthermore TiO\textsubscript{2} can be easily deposited on different kind of substrate like glass, steel, activated carbon, fibres, inorganic materials [2] which make it an easy to use and highly reusable photocatalyst.

However, the mass use of the TiO\textsubscript{2} as photocatalyst is restricted by its large band gap such as approximately 3.2 eV for anatase phase and [3]. This allows TiO\textsubscript{2} to work most efficiently under only UV-ray illumination. TiO\textsubscript{2} can be use only for a very small part (5\%) of solar flux incident on earth’s surface for photocatalytic activity [2]. This property can be enhanced by tuning the band gap of TiO\textsubscript{2} towards visible light region, such that it can be able to use the abundant solar spectrum incidenting on earth’s surface. Till now numerous works has been reported on modification of band structure of TiO\textsubscript{2} by adding another semiconductor with lower band gap [3].

SnO\textsubscript{2} has extensively used in dye-sensitized solar cells, Li-ion battery solar cells, solid-state gas sensors, photo electrochemical material, photocatalysis, etc. as it has unique photoelectronic properties, nontoxicity, and chemical stability, prominently it is widely used as photocatalyst, however the flower like SnO\textsubscript{2} exhibited greater photocatalytic performance [4-6]. As discussed in earlier, the wider band gap of SnO\textsubscript{2} leads to the faster photo recombination rate resulting ineffective for photocatalysis.

Co\textsubscript{3}O\textsubscript{4}, an excellent mixed-valence compound and p-type semiconductor, has been used in electrochemistry, sensor and catalyst [7]. Several studies presented that Co\textsubscript{3}O\textsubscript{4} effectively degraded organic contaminants in aqueous environment under excitation of incident visible light [8, 9]. Co\textsubscript{3}O\textsubscript{4} and Co based metal tittannate has been also coupled with other photocatalysts to further improves their photocatalytic activity [10-12]. The presence of Co\textsubscript{3}O\textsubscript{4}, for example, in the Co\textsubscript{3}O\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} heterojunction, prevented the recombination of photo-induced charges resulting in significant improvement of photocatalytic ability of the Bi\textsubscript{2}WO\textsubscript{6} [13].

[14] S. Vadivel et. al., were confirmed the CoTi\textsubscript{3}O\textsubscript{6}/Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} ternary nanostructures shows excellent degradation ability when compared with binary Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}, CoTi\textsubscript{3}O\textsubscript{6}/TiO\textsubscript{2} and pure TiO\textsubscript{2}. The highly porous ternary TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4}/Ni photocatalyst successfully synthesized via photo reduction method by [15] Tao Li et.al.,. This ternary composites enhances the hydrogen production activity. This article was suitable evidence for Co\textsubscript{3}O\textsubscript{4} based ternary composites also shows better photocatalytic properties.

Based on the above background discussion, Co\textsubscript{3}O\textsubscript{4}/SnO\textsubscript{2}/TiO\textsubscript{2} ternary composites were fabricated by a simple dispersion method and which is tested photocatalytic dye degradation activity. The fabricated ternary composites analysed physicochemical techniques.

2. Materials and methods

2.1 Materials

Titanium tetrachloride (99.5\%), Cobalt acetate (GR), oxalic acid dehydrate (GR), ethanol (LR) stannous chloride (GR) and aqueous ammonia (GR) were used for the preparation of the photocatalyst. The
dye, reactive blue 4 (Molecular Weight: 683.41, λmax: 598 nm, abbreviation: RB 4) are commercial grade were obtained from Vexent Dyeaux India Pvt. Ltd. Sodium hydroxide and Hydrochloric acid were purchased from LobaChemie for adjusting the pH of the dye solutions. Potassium dichromate (AR), Silver sulphate (GR), Mercury sulphate (GR) 99% Ferroin (GR) and Sulphuric acid were used for COD analysis. Double distilled deionised water was used for the preparation of dye solutions.

2.2 Methods

2.2.1 Synthesis of anatase TiO₂

Anatase TiO₂ was synthesized from TiCl₄ as reported in literature [16]. In the typical synthesis of TiO₂, 5 mL of TiCl₄ was added into 50 mL of ice cold distilled water with stirring for 2 h and a clear solution was obtained after stirring, then to that solution, aqueous ammonia was added drop wise till the formation of a gel. The gel solution was washed repeatedly with distilled water to remove the entire chloride ions in the solutions and then it was kept for drying at 100°C to remove part of the absorbed water. The dry gel was milled and calcinated at 450°C for 4 h to obtain crystalline anatase TiO₂.

2.2.2 Synthesis of Co₃O₄

In the preparation of Co₃O₄, 10 g of Cobalt acetate dissolved in 100 ml distilled water was converted in to cobalt hydroxide by slowly adding 1 M NaOH solution with vigorous stirring. The obtained Cobalt hydroxide was washed with double distilled water and dried in hot air oven at 100°C to remove water and then solid obtained was ground in a pestle mortar and calcined at 550°C for 4 hours.

2.2.3 Synthesis of SnO₂ microstructure

For the synthesis of SnO₂ microstructre, first 0.5 molar SnCl₂·5H₂O (solution A) were dissolved in 50 ml of deionized water. In the second step, already prepared 1 M NaOH solution was adding dropwise in solution A with constant stirring at 70°C upto form a white color gel. In the third step, obtained gel was subjected to filtration and washing. After filtration, the white precipitate was allowed to dry at 85°C upto no more water molecule and then ground to a powder. The prepared samples were then annealed at 450°C to obtain the uniform granules of SnO₂ microstructure.

2.2.4 Formation of SnO₂/TiO₂ heterojunction composites

Synthesized pure anatase TiO₂ was used to fabricate the SnO₂/TiO₂ heterojunction composites structure with SnO₂ microstructure. For the preparation of 3 wt% SnO₂/TiO₂ heterojunction composites, 0.03 g of SnO₂ microstructure was first added to 40 ml of ethanol, to that 0.2750 g of oxalic acid was added and the mixture was stirred in a magnetic stirrer to form a homogeneous suspension. To that suspension, 0.97 g of anatase TiO₂ was added and the stirring was continued for 12 hours. Then the suspension was dried and subsequently annealed at 300°C for 3 hr in a muffle furnace. The final product obtained was labeled as SNT 3. Similarly, 6, 9, 12 and 15 wt% of SnO₂/TiO₂ heterojunction composites were prepared by varying SnO₂ and TiO₂ ratios and were labeled as SNT 6, SNT 9, SNT 12 and SNT 15 respectively.

2.2.5 Preparation of ternary composite photocatalysts

In the preparation of 2 wt% Co₃O₄/SnO₂/TiO₂ ternary composites, 0.02 g of Co₃O₄ was first dispersed in 40 ml of ethanol, to that suspension, 0.2750 g of oxalic acid was added, and the mixture was stirred in a magnetic stirrer to form a homogeneous suspension. To that suspension 0.99 g of SnO₂/TiO₂ heterojunction composites was added, and the stirring was continued for 12 hours. Next step the suspension was dried and subsequently annealed at 300°C for 3 hours in a muffle furnace. The Co₃O₄/SnO₂/TiO₂ ternary composites with 4, 6, 8 and 10 wt % of Co₃O₄ were prepared by varying Co₃O₄ and SnO₂/TiO₂ heterojunction ratios as in a same method.

2.2.6 Evaluation of Photocatalytic Activity

The photocatalytic studies were carried out under natural solar light on plain sky atmosphere days during the period of February to May-2021. In a typical experiment, 50 ml of Reactive Orange 30 solution were taken in 250-ml glass beaker with 50 mg of photocatalyst added and saturated with oxygen by aerated with an air-pump unto 1 hour to attain adsorption equilibrium. Then the dye solution (Model pollutant) was set aside in direct sunlight with continuous aeration and the concentration/absorbance of the dye remains was measured gradual interval time by measuring its light absorbance at the visible λmax by using a Elico UV-Visible spectrophotometer. In order to avoid the difference in results due to oscillation in the intensity of the sunlight, a set of experiments have
been carried out simultaneously. For pH studies the pH of the dye solutions were modified to different pH such as 3, 5, 7, 9 and 12 by using 0.1M HCl and NaOH solution. For concentration studies, the degradation of dye solution of various concentrations at pH 3 were treated using the photocatalyst and the efficiency of the catalyst was calculated from the percentage of degradation of the dye solution.

The percentage of degradation was calculated using the following relations,

\[
\text{% of Degradation} = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

Where \( C_0 \) is the initial concentration of the dye solution, \( C \) – the concentration of the dye remains after degradation.

### 2.2.7 Characterization

X-ray powder diffraction (XRD) patterns of the photocatalysts were recorded on a Philips X’pert-MPD diffractometer in the 2θ range 20–80° using Cu-Kα radiation. The data were collected with a step of 0.028 (2θ) at room temperature. The phase structure of the products was determined by comparing the experimental X-ray powder patterns to the standard compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). The crystallite sizes were calculated from the peak width using the Scherrer equation. The surface morphologies and particle size were observed by Scanning Electron Microscopy (JEOL.JSM-6360LV). UV-Visible diffuse reflectance spectra were acquired by a Perkin-Elmer Lambda 35 spectrometer. BaSO4 was used as the reflectance standard. The photoluminescence emission spectra of the samples were measured at room temperature using Perkin-Elmer LS 55 Luminescence spectrophotometer. Fourier transform infrared spectra of the samples were measured on an IR Prestige-21 spectrometer (Shimadzu). For this, the samples were formed into pellets with KBr.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of the ternary photocatalysts

The synthetic procedures for the formation of the \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) ternary composites are illustrated in representative method. \( \text{Co}_3\text{O}_4 \) microstructure was first synthesized, and then \( \text{SnO}_2/\text{TiO}_2 \) hybrids were fabricated by a simple ethonalic dispersion reaction. Using solar light irradiation on a \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) ternary composite was finally degrading the reactive azo dye solution.

#### 3.1.1 Molecular structure analysis

FT-IR analysis as very important and fundamental tool for interprets essential functional groups of photocatalysts. Figure 1 shows FT-IR results of fabricated sample owing to the stretching and bending vibrations in between the range of 400-4000 cm\(^{-1}\). The bands for oxalic acid were totally disappeared after annealing of \( \text{Co}_3\text{O}_4/\text{SnO}_2/\text{TiO}_2 \) ternary composite at 300°C. This is the additional proof for all ternary composites contains only metal element without any organic matter. Specifically, the CO stretching band of

![FT-IR spectrum of 8wt% Co₃O₄/SnO₂/TiO₂ ternary composite](image-url)
appears at about 1600 cm\(^{-1}\), was totally disappeared [17]. The band appears at 672 cm\(^{-1}\) due to vibrations of the [18] M-O (Ti-O, Co-O and Sn-O) bond and can be observed in all samples after the calcinations. The most intense band was the typical vibration of the Ti-O-Ti bond at 551 cm\(^{-1}\).

3.1.2 Crystalline phase analysis

The XRD patterns of developed binary (Co\(_3\)O\(_4\)/TiO\(_2\) and SnO\(_2\)/TiO\(_2\)) and ternary Co\(_3\)O\(_4\)/SnO\(_2\)/TiO\(_2\), as well as the single samples (TiO\(_2\), Co\(_3\)O\(_4\) and SnO\(_2\)) were shown in Figure 2.

The diffraction peaks of TiO\(_2\) were consistent with the values in the standard card (JCPDS, no. 21-1272). The diffraction peaks at 2\(\theta\) value of 25.3\(^{\circ}\), 37.8\(^{\circ}\), 48.1\(^{\circ}\) and 54.9\(^{\circ}\) of anatase TiO\(_2\), indicating that only anatase TiO\(_2\) formed in this case. The diffraction peaks appeared at 2\(\theta\) = 36.9\(^{\circ}\), 38.6\(^{\circ}\), 44.9\(^{\circ}\), 55.8\(^{\circ}\) and 59.5\(^{\circ}\) are assigned of spinal based cubic Co\(_3\)O\(_4\), which is also exactly matches with JCPDS card no. 43-1003. The crystallinity of the SnO\(_2\) is clearly evident by the sharper diffraction peaks at respective diffraction angles which can be readily indexed for its rutile tetragonal structure of the pure SnO\(_2\) powder. The obtained rutile phase is comparable with the standard JCPDS data (Card No. 88-0287). The sample exhibited only the tetragonal phase and the major peaks appear at 2\(\theta\) = 26.9\(^{\circ}\), 34.3\(^{\circ}\), 521\(^{\circ}\) and 62.1\(^{\circ}\). The XRD patterns of the Co\(_3\)O\(_4\)/TiO\(_2\) binary composite sample are similar
to those of the TiO$_2$, but very weaker with respective of the Co$_3$O$_4$ amounts. However, SnO$_2$ coupled TiO$_2$ heterojunction composites pronounced the less reflections of anatase TiO$_2$ phase with some major characteristic peaks of SnO$_2$. In the case of 8wt% Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites, new much weaker diffraction peaks are found at 26.8°, 33.73° and 36.89° which can be ascribed to the planes of SnO$_2$ and Co$_3$O$_4$. The results can be attributed to the relatively low diffraction intensity caused by the minimal content of SnO$_2$ and Co$_3$O$_4$. No impurity phase was observed in the ternary XRD pattern. Thus, it could be confirmed that the ternary hybrid composites present a three-phase composition.

3.1.3 Surface morphology analysis

Scanning electron microscopic technique is used for the determination of morphologies and dispersion of the photocatalyst. The scanning electron micrograph of pure TiO$_2$, 8 wt% Co$_3$O$_4$/TiO$_2$, 12 wt% SnO$_2$/TiO$_2$ were shown in the Figure 3 (a, b and c). These morphologies consist of irregular agglomerated particles and were in the form of bulky particles. Figure 3 (d) and (e) shows the images of the Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites photocatalyst. Further the formation of ternary composites, it shows different morphologies compared to binary and pure TiO$_2$ photocatalysts. In the Co$_3$O$_4$/SnO$_2$/TiO$_2$ morphology indicate Co$_3$O$_4$ and SnO$_2$ growing in the platform of TiO$_2$. From these results, Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary photocatalyst has been shows suitable surface morphology for photocatalytic degradation of reactive dyes. The reason is form of small size irregular particles and highly dispersed Co$_3$O$_4$ on the SnO$_2$/TiO$_2$ ternary photocatalyst.

3.1.4 Crystalline nature Analysis

The TEM analysis for the examination of the size and morphology of the prepared Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites is displayed in Figure 4. A honeycomb structure with irregular-shaped grains embedded was observed in the TEM image of Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites (Fig. 4a). A mixture of spherical and elongated spherical grains was observed for the Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites. The domination of TiO$_2$ along with Co$_3$O$_4$ and SnO$_2$ in the Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites is thus well confirmed. The particles sizes are in the range of 100 nm.

Figure 3 SEM images of TiO$_2$, 8 wt % Co$_3$O$_4$/TiO$_2$, 12 wt % SnO$_2$/TiO$_2$, 8 wt % Co$_3$O$_4$/SnO$_2$/TiO$_2$ and 10 wt % Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites
Moreover, the selected area electron diffraction (SAED) pattern of $\text{Co}_3\text{O}_4$/SnO$_2$/TiO$_2$ ternary composites (Fig. 4b) reveals a ring-like pattern, indicating the low crystalline nature of $\text{Co}_3\text{O}_4$/SnO$_2$/TiO$_2$ ternary composites. Meanwhile, characteristic diffraction rings of anatase TiO$_2$ are displayed by the SAED patterns, which is consistent with the XRD pattern of $\text{Co}_3\text{O}_4$/SnO$_2$/TiO$_2$ ternary composites in Figure 2. Hence, some lattice fringes or diffraction rings related to SnO$_2$ and Co$_3$O$_4$ can be observed due to its low crystalline feature.

Figure 4 a) TEM and 4b) SAED pattern of Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites

Figure 5 UV-visible DRS spectra pure TiO$_2$, Co$_3$O$_4$, SnO$_2$, 8 wt% Co$_3$O$_4$/TiO$_2$ 12 wt% SnO$_2$/TiO$_2$ binary composites, 8 wt% Co$_3$O$_4$/SnO$_2$/TiO$_2$ and 10 wt% Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites
3.1.5 Optical properties analysis

The visible-light absorption property plays a serious role in determining the visible photocatalytic behavior of a photocatalyst. The optical properties of the binary SnO₂/TiO₂ and Co₃O₄/TiO₂ composites and Co₃O₄/SnO₂/TiO₂ ternary composites were investigated by ultraviolet-visible diffuse reflectance spectroscopy in the wavelength range from 200 to 800 nm and the results are shown in Figure 5.

SnO₂/TiO₂ shows low absorption than synthesized TiO₂ in visible region; Co₃O₄/TiO₂ also shows better absorbance band in the visible region such as 386 nm to 566 nm. These results reveal that increases the visible light activity of the TiO₂ photocatalyst. The ternary Co₃O₄/SnO₂/TiO₂ ternary composites largely shift to in the range of visible light absorption (372 to 652 nm). In comparison with the undoped-TiO₂ and Co₃O₄/TiO₂ binary system the Co₃O₄/SnO₂/TiO₂ ternary composites showed a red shift in absorption edge, indicating that the Co₃O₄, and SnO₂ coating of TiO₂. This result is advantageous to broaden the response region of Co₃O₄/SnO₂/TiO₂ ternary composites to visible light and to use solar light as light source in the degradation of dye wastewater [19, 20].

3.1.5 Electron-hole charge separation analysis

The luminescence (PL) measurements were performed using an excitation wavelength of 360 nm to investigate the lifetime and separation of photo-induced electron-hole pairs in TiO₂. The PL spectrum of selective photocatalyst was shown in Figure 6.

![PL spectra](image)

Figure 6 PL spectra pure TiO₂, 12 wt% SnO₂/TiO₂ binary composite, 8 wt% Co₃O₄/SnO₂/TiO₂ and 10 wt% Co₃O₄/SnO₂/TiO₂ ternary composites

From the PL data, there was close link between the PL intensity and the recombination process of photo-generated electron-hole pairs of the photocatalyst. Generally, a higher value of PL peak intensity indicates the rapid recombination of the photo-generated electron-hole pairs of the catalyst, while a lower value indicates the higher separation of photo-generated electron-hole pairs [21]. The PL spectra of TiO₂ represented a peak at 525 nm, indicating the surface and irradiative electron-hole recombination of the below conduction band and valance band. The emission peak intensity of Co₃O₄/SnO₂/TiO₂ ternary composites is lower than those of TiO₂, binary SnO₂/TiO₂ composites, which indicates that the, lower recombination rate photogenerated electron-holes while, formation Co₃O₄/SnO₂/TiO₂ ternary composites.

3.2 Photocatalytic Studies

3.2.1 Photodegradability of Reactive Orange 30

Photocatalytic activity towards the degradation of RO 30 and photostability is widely used in many industrial fields such as textiles, plastics, paper, coatings and rubber. The discharge of dyes into water has received global concern because of their overall environmental hazards.

According to the adsorption-desorption behavior results of photocatalysts without light irradiation, after 30 min adsorption, there is almost no change in the concentration of dye, which indicates that the adsorption-desorption behavior reached an equilibrium. Figure 7 (a) showed the variations of the characteristic absorption of RO 30 (= 430 nm) under visible light irradiation by using Co₃O₄/SnO₂/TiO₂ ternary composites as photocatalyst. The characteristic absorption of RO 30 reduces gradually with prolonging the irradiation time, and the characteristic absorption of RO 30 is hardly observed after every 10 min under solar light irradiation. RO 30 can only be slightly degraded under solar light irradiation without catalysts, indicating that RO 30 is a stable molecule and that the photolysis mechanism can be ignored. For a comparison, the plots of RO 30 dye degradation using TiO₂, Co₃O₄ and SnO₂ were included. TiO₂ could degrade less than 81% of the dye after 120 min of visible light irradiation due to this poor visible light absorption capability and larger band gap energy. Co₃O₄ and SnO₂ have shown the very poor
photocatalytic activity with the degradation efficiency of about 32% and 47% respectively. It is interesting that when TiO$_2$ is combined with Co$_3$O$_4$ or SnO$_2$, the photocatalytic activity is increased. The degradation rate of Co$_3$O$_4$/TiO$_2$ and SnO$_2$/TiO$_2$ was 99% and 96% within 120 min, respectively. The improved photocatalytic activity could be attributed to the formation of the heterojunction as well as the higher surface area. When Co$_3$O$_4$ were deposited on the surface of SnO$_2$/TiO$_2$, the photocatalytic activity enhanced (100% within 100 min).

This result further indicated that the formation of Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites greatly enhanced the photocatalytic activity since the ternary composite had a similar surface area with the binary composites.

The data obtained from the degradation studies were analysed with the Langmuir–Hinshelwood kinetic model:

$$r_s = \frac{kKc}{1 + KC}$$

where $r_s$ is the specific degradation reaction rate the dye (mg l$^{-1}$ min$^{-1}$), $C$ the concentration of the dye (mg l$^{-1}$), $k$ the reaction rate constant (min$^{-1}$) and $K$ is the dye adsorption constant. When the concentration ($C$) is small enough, the above equation can be simplified in an apparent first-order equation:

$$-\ln \left( \frac{C}{C_0} \right) = k_{app} t$$

Where $C_0$ is the initial concentration (mg l$^{-1}$), $C$ is the concentration of the dye after (t) minutes of illumination. The data obtained from the degradation of RO 30 fits well the apparent first order kinetics (Figure 7 (b)) and their rate constant values are given in the Table 1. The electrons in the conduction band can be transferred to surface adsorbed oxygen molecules and form superoxide anions, which can further transform to OH$^-$ and initiate the degradation of RO 30.

### Table 1 kinetics of degradation of reactive orange 30

<table>
<thead>
<tr>
<th>S.No</th>
<th>Photocatalysts</th>
<th>Kinetics parameters</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO$_2$</td>
<td>0.0082</td>
<td>0.9950</td>
</tr>
<tr>
<td>2</td>
<td>SNT 12</td>
<td>0.0134</td>
<td>0.9921</td>
</tr>
<tr>
<td>3</td>
<td>CoT 8</td>
<td>0.0191</td>
<td>0.9913</td>
</tr>
<tr>
<td>4</td>
<td>CST 2</td>
<td>0.0234</td>
<td>0.9898</td>
</tr>
<tr>
<td>5</td>
<td>CST 8</td>
<td>0.0152</td>
<td>0.9912</td>
</tr>
<tr>
<td>6</td>
<td>CST 10</td>
<td>0.0113</td>
<td>0.9921</td>
</tr>
<tr>
<td>7</td>
<td>SnO$_2$</td>
<td>0.0046</td>
<td>0.9985</td>
</tr>
<tr>
<td>8</td>
<td>Co$_3$O$_4$</td>
<td>0.0032</td>
<td>0.9980</td>
</tr>
</tbody>
</table>

#### 3.2.2 Reusability Test

It is worth pointing out that the stability of the photocatalyst is a crucial but difficult task owing to the leakage of the individual components for the photocatalytic applications in aqueous solution.

To confirm the possibility of recycling of the obtained photocatalysts, five recycling experiments were performed with Co$_3$O$_4$/SnO$_2$/TiO$_2$ ternary composites in the photocatalytic degradation of RO 30.
After each photocatalytic experiment, the ternary composite was recovered by washing with distilled water three times, drying at 100 °C for 24 h. The composite was recovered by washing with distilled water three times, drying at 100 °C for 24 h, and then fresh RO 30 solution was added. As shown in Fig. 8, no apparent deactivation of the photocatalyst was observed after five consecutive runs. Therefore, the as-prepared Co3O4/SnO2/TiO2 ternary composites showed an excellent catalytic stability, performing as genuine heterogeneous visible-light-driven photocatalysts for the treatment of organic contaminants in wastewater.

3.2.3 Photocatalytic dye degradation mechanism of Co3O4/SnO2/TiO2 ternary composites

The enhanced photocatalytic efficiency of Co3O4/SnO2/TiO2 ternary composites can be attributed to two mean factors such as the superior visible light absorbance and efficient charge separation and charge transfer by various pathways as proposed in Figure 9.

To understand the electrons-holes separation mechanism, the valence band (VB) and conduction band (CB) potentials of synthesized Co3O4, SnO2, and TiO2 should be confirmed. The VB and CB edge potentials of a semiconductor photocatalysts can be calculated from generalized equations [22]. To investigate the improved photocatalytic activity, we proposed a mechanism in Figure 9 in which we suggest the formation of possible pathway in the coupled Co3O4/SnO2/TiO2 ternary composites. In photocatalytic pathway, we assume the presence of TiO2 between Co3O4 and SnO2. From band potential arrangement, we find that the CB of Co3O4 is moderately negative than TiO2 whereas VB of Co3O4 is more positive than TiO2.

Furthermore, the CB of SnO2 is slightly positive than that of TiO2 but VB of TiO2 is more negative than that of SnO2. Hence photoinduced electrons (e-) in CB of Co3O4 can transfer to the CB of TiO2 and the photoinduced electrons (e-) in CB of TiO2 can transfer to the CB of SnO2. Simultaneously, the generated holes (h+) can transfer from the VB of TiO2 to the VB of Co3O4, and then not holes move from VB of SnO2 to VB of TiO2. From the dye degradation pathway, the photogenerated charges (e- and h+) are highly separated. Hence the photocatalytic degradation process highly enhanced.

3.2.4 Free radicals and holes trapping experiments

In order to understand the photocatalysis mechanism of the Co3O4/SnO2/TiO2 ternary composites, the active species generated during the process of ternary composites photocatalyzed RO 30 degradation are identified by free radical and hole trapping experiments[23]. Three different quenchers (Scavengers), t-BuOH (OH•), AO (h+) and BQ (O2•-) respectively. The method was similar to the above photocatalytic activity test. Figure 10 displayed the influence of various scavengers on the visible light photocatalytic activity of Co3O4/SnO2/TiO2 ternary composites towards the degradation of RO 30. Compared with scavenger-free system, when 10 ml of added, the degradation rate of RO 30 was hardly inhibited, indicating the absence of O2•- radical species. However, after the addition of same amount of t-BuOH, 1 mM of BQ as a scavenger for O2•- radical species was the photocatalytic activity for the degradation rate was decelerated drastically (from 99% to 30.8 %),
the degradation of Co separation. The further enhancement in the charge transfer and recombination photoinduced electrons and inhibit charge carriers intensity peak.

As for the AO photocatalysis system, the degradation rate was inhibited to some extent, indicating h⁺ was another active species that was responsible for the degradation of RO 30. Moreover, it is well known that, holes can be adsorbed on the surface of the photocatalyst and can interact with hydroxyl radicals or water molecules to generate OH•. The above results indicated that O₂⁻ and OH• is the most important oxidizing species during the RO 30 photocatalytic process, and that h⁺ in the solution is not the main active species.

4. Conclusion

In this paper, Co₃O₄/SnO₂/TiO₂ ternary composites was effectively synthesized with a simple ethanolic dispersion method followed by annealing at 300 °C for 3 hr. PXRD and FT-IR studies were confirming the formation of the Co₃O₄/SnO₂/TiO₂ ternary composites. The obtained moderated image has a mixture of fine powder morphologies. UV-Vis DRS analysis reveals that the Co₃O₄/SnO₂/TiO₂ ternary composites display an apparent visible light absorption in the range of ~ 400-700 nm. Furthermore, PL study shows that the obtained Co₃O₄/SnO₂/TiO₂ ternary composites have a low intensity peak. Such result may favor the capture of photoinduced electrons and inhibit charge carriers recombination. Furthermore, the energy band positions of Co₃O₄, SnO₂ and TiO₂ are well-matched leading to further enhancement in the charge transfer and separation. The resultant superior optical properties of Co₃O₄/SnO₂/TiO₂ ternary composites should enhance the degradation of RO 30 compared to the bare and binary composites (TiO₂, Co₃O₄/TiO₂ and SnO₂/TiO₂) under solar light irradiation. Moreover, the active spices experiments (trapping experiment) exposed that the main active species such as O₂⁻ and •OH. Reuse experiments indicate the reusability and stability of Co₃O₄/SnO₂/TiO₂ ternary composites. This study introduces a potential new family of novel solar active photocatalysts for degradation of reactive dyes.

References

[11]. Nguyen TH, Doan VT, Nguyen MK, Pham TT, Tran TMH, Nguyen HTV, Nguyen VN, Dinh Trinh T, Thanh DP, Nguyen TTT, Nguyen LMT,