Ternary hybrid formation and Photocatalytic activity of NiO/CuO/TiO₂ microstructure over textile azo dye under solar light irradiation

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Abstract

The photocatalytic degradation and mineralization of ReactiveOrange30 on NiO/CuO/TiO₂ ternary composites has been studied using solar light irradiation. This NiO/CuO/TiO₂ ternary composites were prepared by different mass ratios of NiO and CuO/TiO₂ (3wt% to 15wt.%) on the ethanolic dispersion and annealed at 300° C. SEM, UV- Vis DRS, PL, XRD and FTIR analysis has used to characterize the all photocatalysts. NiO/CuO/TiO₂ ternary composites demonstrate enhanced photocatalytic activity than NiO/TiO₂, CuO/TiO₂ and pure TiO₂ due to separation of photogenerated electrons and holes charges. The NiO/CuO/TiO₂ ternary composites shows good photostability and the photocatalyst retain the 94% of its initial activity in the seventh cycle, respectively.

Highlights

- The ternary NiO/CuO/TiO₂ composites show enhanced photocatalytic degradation of reactive orange 30 under solar light irradiation.
- The solar light active ternary NiO/CuO/TiO₂ composites were effectively synthesized with a simple ethanolic dispersion method.
- The highly visible acting property, fine surface morphology, photogenerated charges separation and crystalline phase of ternary NiO/CuO/TiO₂ composites good agreement with suitable physicochemical techniques.
- Ternary NiO/CuO/TiO₂ composites are stable and exhibits excellent reusability.

Introduction

Increased population and industrial activities have resulted in industrial effluent generation and pollution of water bodies, harmful to humans and aquatic life especially when they contain substances such as dyes, pesticides, heavy metals and pharmaceutical wastes [1]. The world production of dyes has increased dramatically over the past years and these azo dyes, reactive dyes, solvent dyes for instance are used by the textile, food, adhesive, cosmetics, arts, construction, paints, glass and ceramic industries extensively [2]. The release of these colored organic substances into our environment is a source of aesthetic pollution and is detrimental to the environmental ecosystems.

High chemical stability and low biodegradability of these organic pollutants have necessitated the search for suitable treatment methods that can easily break down inherent chemical components. Techniques such as adsorption, biodegradation, ozonation and photo-Fenton processes have been adopted in treating dyes and pesticides pollutants [3]. However, these methods have been reported to be ineffective in the treatment of polluted water bodies [4]. Recent studies have been focused on the use of advanced oxidation processes such as photocatalysis for the removal of dyes and pesticides from wastewaters [5].

Titanium Dioxide semiconductor has been widely investigated in waste water treatment using photocatalytic and sonocatalytic process [6, 7]. As catalyst, TiO_2 has several advantages such as low cost, and nontoxic [8]. However single metal TiO_2 has several drawbacks that reduce its efficiencies. High rate recombination of electron and holes of TiO_2 is the main problem in waste water treatment [9]. The second problem is the difficulty of TiO_2 to separate from the aqueous solution. Therefore we need to find an effective method to enhance the efficiency of TiO_2 as a catalyst for water treatment. The couple metal oxide is one of the most common solutions for enhancing the degradation efficiency of TiO_2 .

Coupled metal oxide has an ability to reduce recombination of electron-hole pairs so it could enhance the degradation efficiency [10, 11]. TiO_2 has coupled with many materials such as CuO , CeO_2 and many others [12]. Among other materials, CuO has been proved to be able to enhance the degradation efficiency compared to single TiO_2 metal oxide. Suitable band edge between n-type TiO_2 and p-type CuO semiconductors facilitates electron and holes to transfer easily between TiO_2 and CuO and vice versa [13].

NiO is chief and cheap semiconducting oxides, which has been mostly consumed in photocatalytic applications. The reason is efficiently suppress the electron-hole recombination and enhance the degradation kinetics by composing with ZnO because of the difference in band gap energy [14]. ZnO-NiO composite is one of the most important photocatalytic systems, which has attracted a lot of interest. Some researchers indicated the development of properties and efficiency of these materials by compositing [15,16].

In recent years, more and more researchers have interested to the fabricating of ternary composites. In the whole ternary catalytic reaction process, photo-generated carriers can be transferred in multiple steps through the induction mechanism to achieve the purpose of electron and hole separation, thereby achieving photocatalytic activity beyond the binary catalytic system [17, 18]. And an increasing number of ternary photocatalytic materials have been reported, such as $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3/\text{BiOBr}$ [19], $\text{Ag}_3\text{PO}_4/\text{TiO}_2/\text{Fe}_3\text{O}_4$ [20], $\text{Bi}_2\text{WO}_6/\text{Ag}_2\text{S}/\text{ZnS}$ [21], and $\text{V}_2\text{O}_5/\text{BiVO}_4/\text{TiO}_2$ [22].

Based on the above background conversation, incorporated using first row transition metal oxides coupled on TiO_2 semiconductor, $\text{NiO}/\text{CuO}/\text{TiO}_2$ ternary composites were fabricated by a simple dispersion method. The $\text{NiO}/\text{CuO}/\text{TiO}_2$ ternary composites exhibit much higher photocatalytic activity and excellent cycling performance for removal of Reactive Orange 30 in water under solar light irradiation.

Experimental Work

This work deals with the process of preparation of catalyst, characterization techniques and the experimental set-up used for the carrying out the photocatalytic degradation process.

Chemicals used

Reactive Orange30 a widely used in textile dye with dichloroquinoxaline group and azo group supplied by Vexentdyeaux India Pvt. Ltd, Mumbai (Minimum dye content 70%) were used for photocatalytic degradation studies.

Chemical formula: $C_{29}H_{13}Cl_2N_5O_{13}S_4Na_4$

Molecular weight: 930.56

Water solubility: 70g/L at 293k

λ_{max} :422 nm

Titanium tetrachloride (99.5%), oxalic acid dehydrate (GR), ethanol (LR), Copper acetate (GR) and Nickel chloride (GR) were supplied by Merck India Pvt. Ltd; dye solutions for photocatalytic studies were prepared in double distilled water. Sodium hydroxide and hydrochloric acid (both AR grade from Qualigens) were used for modifying the pH of the solutions. Potassium dichromate (AR), Silver sulphate (GR), mercury sulphate (GR) 99% Ferroin (GR) and Sulphuric acid were used for COD analysis. 2-propanol, oxalic acid and ascorbic acid used as scavengers in deduction of active species measurement.

Synthesis of anatase TiO_2

In the typical synthesis of TiO_2 , 5mL of $TiCl_4$ 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 calcinaied at 450°C for 4 h to obtain crystalline TiO_2 .

Preparation of CuO microstructure

CuO microstructure was synthesized by using micelle surfactant method. In typical synthesis 0.005 mol metal salts (Copper source) has been dissolved into 100 mL distilled water, which reacts with 0.01 mol of NaOH solution to produce nickel hydroxide precipitate. Then aqueous micelle solution of CTAB was added to the above solution, and it was further refluxed for 12 hours at 75°C. The supernatant was then decanted, and the solid residue was washed three times with water, dried in air at 100°C for 10 hours, and calcined in muffle furnace at different temperature, 600°C for 5 hours.

Nickel oxide synthesis

For the synthesis of Nickel oxide, firstly 0.005 mol nickel nitrate was dissolved in 100 ml distilled water. 2.50 g citric acid was dissolved and stirred in 50 ml water in a separate beaker. The dissolved Citric acid was slowly added to the solution of nickel nitrate. After homogenization of the solution, aqueous ammonia was added drop wise awaiting the pH reached to 8. The solution was slowly heated up to 70 °C

and it was allowed to be evaporated. Then it was placed in an oven at 100 °C for upto water drying. The obtained gel was calcined in the furnace at 500 °C for 5 h.

Preparation of CuO/TiO₂ binary composites

In the preparation of 4wt % CuO/TiO₂ binary composites, 0.04 g of CuO 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 0.96 g of TiO₂ was added, and the stirring was continued to overnight and then the suspension was dried and subsequently annealed at 300°C for 3 hours in a muffle furnace. The same procedure used for synthesis of further heterojunction photocatalysts (4wt% CuO/TiO₂, 8wt% CuO/TiO₂, 12wt% CuO/TiO₂, 16wt% CuO/TiO₂ and 20wt % CuO/TiO₂ binary composites) and were labelled as CuT4, CuT8, CuT12, CuT16 and CuT 20 respectively.

Synthesis of NiO/CuO/TiO₂ ternary composites

The typical preparation of NiO/CuO/TiO₂ ternary composites is as follows: firstly, 0.98g as-prepared CuO/TiO₂ binary composite are dispersed in 40 ml CH₃CH₂OH and stirred for 1 h. Then, 0.02 g NiO powder is added into the above solution and again stirred upto 12 h. After volatilization of the CH₃CH₂OH, dark greenish powder is obtained after drying at 80 °C in the air. The whitedark greenish powder is the NiO/CuO/TiO₂ ternary composites. Further, NiO/CuO/TiO₂ ternary composites prepared with various weight ratio of NiO and CuO/TiO₂, these ternary composites labeled as 0NCT, 2NCT, 4NCT, 6NCT, 8NCT, 10NCT and 12NCT.

Photocatalytic degradation of NiO/CuO/TiO₂ ternary composites

All the photocatalytic experiments were performed under natural sunlight on clear sky days during the period of October to december-2020. In a typical experiment, 50 ml of dye solution (concentration 50 mg l⁻¹) was taken with 50 mg of photocatalyst in a 250 ml glass beaker. Then the dye solution was kept in direct sunlight with continuous aeration and the concentration of the dye remains was measured periodically by measuring its light absorbance at the visible λ_{max} by using Elico SL- 171 Visible spectrophotometer. In order to avoid the variation in results due to fluctuation in the intensity of the sunlight, a set of experiments have been carried out simultaneously. The active species from photocatalytic mechanism were detected by using in the same procedure in presence of scavengers.

Characterization of Photocatalyst

X-ray powder diffraction (XRD) patterns of the photocatalysts were recorded on a Philips X'pert-MPD diffractometer in the 2 θ range 20°–80° using Cu K α radiation. The data were collected with a step of 0.028 (2 θ) 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

Scherer equation. The surface morphologies and particle size were observed by Scanning Electron Microscopy (JEOL.JSM-6360LV). The optical properties of the synthesized catalysts were measured by using UV–Vis DRS spectrophotometer (Shimadzu, UV-3600) with BaSO₄ as the background. The photoluminescence emission spectra of the samples were measured at room temperature via 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.

Results And Discussion

Crystalline properties analysis

The XRD patterns of pure TiO₂, CuO, NiO and binary 16wt % CuO/TiO₂, and 3,6,12wt% ratio of NiO/CuO/TiO₂ composites are shown in **Figure 1**. The pure materials diffraction peaks in **Fig. 1** agree with the standard patterns for cubic NiO in Joint Committee on Powder Diffraction Standards (JCPDS) card no. 01-071-1179, anatase-phase TiO₂ (JCPDS card no. 78-2486), and monoclinic CuO (JCPDS card no. 89-5895), respectively. The XRD patterns of the CuO/TiO₂ binary composite seem to show the major diffraction peak located in the fundamental TiO₂ pattern, it represents some amounts of CuO coupled with TiO₂.

In the case of NiO/CuO/TiO₂ ternary composites, new much weaker diffraction peaks are found at representative areas which can be ascribed to the planes of CuO and NiO. The results can be attributed to the relatively low diffraction intensity caused by the minimal content of CuO and NiO.

The morphology and microstructure analysis

The morphology and microstructure of the composite samples were characterized by SEM. **Fig. 2a–e** depict the SEM images of anatase TiO₂, 16wt % CuO/TiO₂, ternary 6, 9, 12 wt% of NiO/CuO/TiO₂ composites.

The anatase TiO₂ appears to have highly agglomerated particles as shown in **Fig. 2a**. The CuO/TiO₂ binary powder after being irregular shaped grains and were agglomerated in the morphology (**Fig. 2d**). **Fig. 2c** is the SEM image of 6wt% ternary NiO/CuO/TiO₂ composites. No more difference in morphology can be predicted compared with the CuO/TiO₂ composites. A representative SEM image of 9wt% of NiO/CuO/TiO₂ composites and 12 wt% of NiO/CuO/TiO₂ composites is shown in **Fig. 2d& e**, showing some of CuO and NiO particles strongly adherent on the broad surface of TiO₂, because of two different shaped particles in micrometer size.

FTIR spectrum of photocatalyst

The FTIR spectrum of as prepared samples such as TiO_2 and 12 wt% of NiO/CuO/TiO_2 composites was shown in **Figure 3**. The prepared TiO_2 photocatalyst reveals the presence of some absorption bands in the ranges from 400 cm^{-1} to 4000 cm^{-1} .

In the FTIR spectrum a wide band from 400 to 650 cm^{-1} was observed that corresponds to the metal-oxygen bond [23,24]. The absorption band at 632 cm^{-1} corresponds to Ti-O stretching vibration. The signal at 1630 cm^{-1} is associated with the molecular H_2O (H-O-H) bending frequency. The characteristic bands in a range of $500\text{--}750\text{ cm}^{-1}$, were considered as the stretching frequency of Ti-O Ni-O and Cu-O bond and were observed in the NiO/CuO/TiO_2 composites. There is no peak at 2900 cm^{-1} for NiO/CuO/TiO_2 composites, regarding C-H stretching band, which means all organic compounds were removed from the samples after calcinations. The broad peaks around 3396 cm^{-1} and sharp peaks at 1630 cm^{-1} are associated with the stretching and bending vibration of surface adsorbed water and hydroxyl groups of all the samples. The surface hydroxyl groups play an important role in the photocatalytic process, as these groups can be trapped by the holes generated under sunlight irradiation to form hydroxyl radicals which can suppress electron-hole recombination, hence increase the photocatalytic efficiency.

Optical properties photocatalysts

The visible-light absorption property plays a serious role in determining the visible photocatalytic behavior of a photocatalyst.

The optical properties of the pure TiO_2 , CuO, NiO and binary 16wt % CuO/TiO_2 , 9 wt % NiO/TiO_2 and ternary 3,6 and 6wt% NiO/CuO/TiO_2 composites were investigated by ultraviolet-visible diffuse reflectance spectroscopy in the wavelength range from 200 to 800 nm and the results are shown in **Fig. 4**. Interestingly, it can be observed that there is a clear red-shift in the absorption of the ternary NiO/CuO/TiO_2 composites in comparison with that for CuO/TiO_2 and NiO/TiO_2 . The ternary NiO/CuO/TiO_2 composites showed stronger and broader absorption in the visible-light region. Diffuse reflectance spectroscopy (DRS) analysis which based on Kubelka-Munk which obtained from absorbing material is expressed as follows: $f(R) = (1-R)^2/2R = K/S$

Where, R is the absolute reflectance of the samples and F(R) is the so-called Kubelka function.

The band gap energy is estimated by the formula $\lambda_g = 1239.8/E_g$, where λ_g is band gap wavelength and E_g is the band gap energy. The calculated band gap energies were found to be 3.19, 1.56, 3.1, 3.4 and TiO_2 , CuO, NiO respectively. In comparison with the undoped- TiO_2 and CuO/TiO_2 binary system the ternary NiO/CuO/TiO_2 composites showed a red shift in absorption edge, indicating that the NiO and CuO coating of TiO_2 .

Photoluminescence spectra

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 TiO_2 . The photoluminescence (PL) spectra of pure TiO_2 , 16 wt% CuO/TiO_2 , 9 wt% $\text{NiO}/\text{CuO}/\text{TiO}_2$ and 12% $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites are displayed in **Figure 5**.

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 [25].

The PL spectra of TiO_2 represented a peak at 594 nm, indicating the surface and irradiative electron-hole recombination of the below conduction band and valance band. After incorporating NiO on the CuO/TiO_2 surface, the PL emission intensity is significantly reduced, indicating lower charge carrier recombination. Furthermore, a significant PL quenching was observed when NiO was added to CuO/TiO_2 composites. Indeed, the effect of NiO on the charge carrier separation was phenomenal and also revealed that TiO_2 hindered or suppressed electron-hole pair recombination, which improved photocatalytic activity.

Photocatalytic Studies

Photodegradability of Reactive Orange 30

The photocatalytic activity of the pure TiO_2 , CuO/TiO_2 and $\text{NiO}/\text{CuO}/\text{TiO}_2$ ternary composites was evaluated in the photodegradation of Reactive Orange 30 (RO 30) at room temperature, under solar light were shown in **Figure 6 (a)**.

The changes in the RO 30 dye concentration with and without the catalysts (Fig. 10) showed a slight decrement under visible-light irradiation. After 90 min, about 25%, 36%, 59%, 79.7% and 86.6%, of the RO 30 was degraded by the pure CuO , NiO , TiO_2 , CuO/TiO_2 , and $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites, respectively. The CuO/TiO_2 binary composite exhibited better degradation efficiency due to the synergistic effect resulting from the simultaneous presence of both CuO and TiO_2 phases [1]. The lowest degradation efficiency of pure TiO_2 is mainly because it could not be excited for photocatalytic reaction under visible light. The extended photoresponse and effective separation of the electron-hole pairs are responsible for the enhanced photocatalytic behavior of the CuO/TiO_2 composite. In the $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites, NiO acts as the prime absorber of visible light and can be easily excited to produce electron-hole pairs. However, its degradation efficiency is low due to its lowest bandgap value, which allows easy recombination of electrons and holes. The low degradation efficiency observed for pure TiO_2 may be due to its poor visible-light harvesting ability. These demerits are tackled when they are synthesized as a composite. The enrichment in the RO 30 degradation using ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ heterojunction is most likely due to the existence of heterojunctions between NiO, TiO_2 and CuO , which efficiently prevent charge-carrier recombination than those in binary CuO/TiO_2 heterojunction. In addition, this development may be due to

the larger surface area of the ternary NiO/CuTiO₃/ZnO heterojunction compared to those of the binary CuTiO₃/ZnO heterojunction.

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 ($\text{mg l}^{-1} \text{min}^{-1}$), 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:

$$r_s = kKc = K_{app} C \left(= -\frac{dc}{dt} \right)$$

After integration, we will get

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

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 RB 5 fits well the apparent first order kinetics (**Figure 7**) 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 $\text{OH}^{\bullet}$ and initiate the degradation of RO 30.

The enhanced sunlight photocatalytic efficiency of $\text{CeO}_2/\text{FeTiO}_3/\text{TiO}_2$ 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 8**.

To understand the electrons-holes separation mechanism, the valence band (VB) and conduction band (CB) potentials of synthesized NiO, CuO, and TiO_2 should be confirmed. The VB and CB edge potentials of a semiconductor photocatalysts can be calculated from generalized equations. To investigate the improved photocatalytic activity, we proposed a mechanism in **Fig. 8**, which we suggest the formation of possible pathway in the coupled NiO/CuO/ TiO_2 composites. In photocatalytic pathway, we assume the presence of TiO_2 between CuO and NiO. From **Figure 8**, we find that the CB of TiO_2 is more negative than NiO whereas VB of TiO_2 is more negative than NiO. Furthermore, the CB of CuO is too positive than that of

TiO₂. In addition with VB of TiO₂ is positive than that of CuO. Hence photoinduced electrons (e⁻) in CB of TiO₂ can transfer to the CB of NiO and the photoinduced electrons (e⁻) in CB of TiO₂ cannot transfer to the CB of CuO, because the conduction band potential is too low than that of TiO₂. Simultaneously, the generated holes (h⁺) can transfer from the VB of TiO₂ to the VB of CuO, and then not holes move from NiO of VB to TiO₂ VB. From the dye degradation pathway, the photogenerated charges (e⁻ and h⁺) are highly separated. Hence the photocatalytic degradation process highly enhanced.

Role of Reactive Species

Figure 9 shows the photocatalytic degradation results in the presence of different scavengers under solar light irradiation. When BQ was added to the photocatalyst mixed composition, a dramatic change in the photocatalytic activity was observed compared with the absence of scavenger, confirming that the dissolved oxygen (O₂²⁻), has a main source on the photodegradation process under sunlight irradiation.

However, a some of different change in the photocatalytic activity was observed upon the addition of 2P as a ·OH scavenger, which indicates that the O₂²⁻ and ·OH are the main reactive species in the NiO/CuO/TiO₂ composites [2]. The degradation efficiency of RO 30 decreased slightly upon in presence of AO compared with the without scavenger, which indicated the photogenerated holes are not the main active species for degradation of RO 30.

Stability and Reusability

In order to evaluate the stability of ternary CuO/CuO/TiO₂ composites during photocatalytic reaction, cycling experiments were also carried out by repeated degradation of RO 30 for seven times under solar light irradiation.

As shown in **Fig. 10**, the photocatalytic activity of ternary NiO/CuO/TiO₂ composites is high even with third cycles. Further, the degradation rate was slight decrease, which could be due to the loss and catalytic poisoning of the photocatalyst during the recycling experiments.

Effect of Oxidants on initial dye concentrations

From mechanistic and application point of view, one must realize the importance of photocatalytic reaction rate on the initial concentration of organic dyes.

When the dye concentration was high, then it was absorb the bulk amount of photons, thus preventing the same to be absorbed by the photocatalyst surface. Hence, the production of oxidizing species like ·OH and O₂^{·-} obviously gets forbidden. Another problem is that more dye molecules are adsorbed on the photocatalyst surface when the dye concentration in the solution was high. This high surface coverage of photocatalyst by the dye molecules also reduces its photocatalytic activity. This screening of photons by

dye molecules can be reduced by carrying out the degradation in the presence of green oxidant such as H_2O_2 .

This oxidant produces highly reactive free radicals which can react with the dye molecules and reduces their concentration. The effect of concentration of RO 30 solution on photocatalytic efficiency of ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites was studied by varying dye concentration from 25 to 150 mg/L and results obtained were shown in **Fig.11**. The results show that the only less than 50% of the dye was photocatalytically degraded by ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites when the dye concentration above 50 mg /L. However, the ternary system shows high efficiency for the degradation of dye in the presence of H_2O_2 (10mM) [30]. Thus, it is clear that the photocatalyst in presence of H_2O_2 was able to degrade the dye solution completely below 125 mg/L on light irradiation for 120 min, whereas ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites was able to degrade the dye solution up to 50 mg/L concentration only.

Conclusion

In summary, a NiO and CuO photocatalysts along with anatase TiO_2 were prepared by 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 ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ photocatalysts. The obtained moderated image has a mixture of fine powder morphologies. UV-Vis DRS analysis reveals that the NiO and CuO photocatalysts displays a apparent visible light absorption in the range of red region. Furthermore, PL study shows that the obtained ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites have a low intensity peak. Such result may favor the capture of photoinduced electrons and inhibit charge carriers recombination. The resultant superior optical properties of ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites should enhance the degradation of RO 30 compared to the bare and binary composites (TiO_2 , CuO/TiO_2 and NiO/TiO_2) under solar light irradiation. Moreover, the active species experiments (scavenging activity) exposed that the main active species such as O_2^{2-} and $\cdot\text{OH}$. Reuse experiments indicate the reusability and stability of ternary $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites. This study introduces a potential new family of novel solar active photocatalysts for degradation of reactive dyes.

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Tables

Table 1 kinetic plot of degradation of RO 30

S.No	NiO/CuO/TiO ₂ ternary composites		
	Photocatalysts	k/min ⁻¹	R ²
1	TiO ₂	0.0082	0.9900
2	16 CT	0.0134	0.9913
3	12NT	0.0087	0.9890
4	9NCT	0.0097	0.9944
5	12 NCT	0.0154	0.9961
6	15 NCT	0.0207	0.9902
7	NiO	0.0046	0.9985
8	CuO	0.0032	0.9980

Figures

Figure 1

XRD Pattern of pure TiO₂, CuO, NiO and binary 16 wt % CuO/TiO₂, and ternary 6,9,12 wt% of NiO/CuO/TiO₂ composites

Figure 2

SEM images of TiO_2 , CuO , NiO and binary 16 wt % CuO/TiO_2 , and ternary 6,9,12 wt% of $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites

Figure 3

FTIR spectrum of TiO_2 and 12 wt% of $\text{NiO}/\text{CuO}/\text{TiO}_2$ composites

Figure 4

UV-visible DRS spectra of pure TiO_2 , CeO_2 , FeTiO_3 and binary 5 wt % $\text{CeO}_2/\text{TiO}_2$, 9 wt % $\text{FeTiO}_3/\text{TiO}_2$ and ternary 8 wt% $\text{CeO}_2/\text{FeTiO}_3/\text{TiO}_2$ composites

Figure 5

PL spectra pure TiO₂, 16 wt% CuO/TiO₂, 9 wt% NiO/CuO/TiO₂ and 12% NiO/CuO/TiO₂ composites

Figure 6

Degradation of RO 30 over NiO/CuO/TiO₂ ternary composites (initial concentration C₀ = 50 mg/l)

Figure 7

Kinetics of RO 30 over NiO/CuO/TiO₂ ternary composites (initial concentration C₀ = 50 mg/l)

Figure 8

Photoelectron injection mechanisms proposed on NiO/CuO/TiO₂ ternary composites

Figure 9

Effect of different scavengers on degradation of RO 30 in the presence of NiO/CuO/TiO₂ ternary composites under solar light irradiation

Figure 10

Stability test of ternary NiO/CuO/TiO₂ composites for seven cycles,

Figure 11

Effect of oxidants in initial concentrations

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