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Preparation of Nanocomposite of TiO₂ Nanoparticles and CuS Nanoflakes for Visible-Light Photocatalytic Decomposition of Nitenpyram Pesticide

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In this study, a novel TiO₂-CuS heterojunction nanocomposite was prepared from TiO₂ anatase nanoparticles and CuS nanoflakes through hydrothermal method and used, for the first time, as a visible-light photocatalyst for decomposition of agricultural insecticide Nitenpyram. Crystallinity, shape, and size of particles, and optical properties of the prepared nanocomposite were investigated using FESEM, XRD, Mott-Schottky, photoluminescence (PL), and UV-Visible spectroscopy analyses. The results indicated that the TiO₂-CuS heterojunction nanocomposite was successfully prepared and compared to the pure CuS and TiO₂ semiconductors, it exhibited a better photocatalytic performance mainly due to the improvement in optical properties (increasing the ability of visible-light absorbance) and reduction of the photoinduced electron and hole recombination rate. According to the Mott-Schottky analysis and radical scavenger tests, superoxide radical was detected as the major oxidizing agent involved in photocatalytic degradation of Nitenpyram, and a type II charge transfer pathway was suggested to improve the photocatalytic activity.

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1. INTRODUCTION

Nitenpyram is used as one of the most important commercial insecticides owing to its high insecticidal activity, suitable water solubility, and broad spectrum [1]. However, given the widespread use of insecticides in agriculture, they are frequently found in groundwater, soil, and rivers, hence recognized as a serious environmental pollution [2]. In this regard, various techniques including biodegradation with bacteria, membrane reactors, electrochemical degradation, and photocatalytic degradation have been employed to eliminate these compounds from the polluted

environment [3-7]. Among these techniques, advanced oxidation by photocatalysts is an attractive one that is mainly used for degradation of these contaminants [8,9].

TiO₂, as a popular semiconductor, has attracted considerable attention for photocatalytic decomposition of different inorganic and organic pollutants. The superiority of TiO₂ to its counterparts lies in its unique characteristics including high stability, less toxicity, low cost, and high oxidation power of the photoinduced charge carriers [10]. However, due to its wide band gap, TiO₂ has low activity under visible light. Another notable drawback is its fast recombination of the photoinduced charge carriers [11]. Therefore, To overcome these

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drawbacks, up to now, a variety of strategies have been developed namely doping with metal or nonmetal elements [12], morphology and surface engineering [13], and constructing heterojunction with other semiconductors [14]. Among these methods, heterojunction photocatalyst have attracted remarkable attention, leading to improved photocatalytic efficiency by expanding the absorption region to the visible-light range and decreasing the recombination rate of the photoinduced electron-hole pairs [15-17].

In recent decades, Copper (II) sulfide (CuS) semiconductor as a p-type semiconductor has gained considerable significance as an efficient photocatalyst for degradation of organic pollutants [13]. However, due to its narrow band gap, CuS enjoys rapid recombination of the photogenerated electron-hole pairs, hence low photocatalytic performance. To address this restriction, numerous methods have been developed to suppress the electron-hole recombination rate among which, this semiconductor is mainly used as the heterojunction composite with other semiconductors [14] such as ZnO/CuS [18], CuS/BiVO₄ [19], CuS/BaTiO₃ [20], and CuS/g-C₃N₄ [21], to name a few.

In this study, a TiO₂-CuS heterojunction nanocomposite was prepared with novel morphology from anatase TiO₂ nanoparticles, and CuS nanoflakes via hydrothermal routes and then used for the visible-light photocatalytic decomposition of Nitenpyram. Characterization of the synthesized samples was performed using FESEM, XRD, Mott-Schottky, photoluminescence (PL), and UV-Visible spectroscopy analysis.

2. MATERIALS AND METHODS

2.1. Materials

Titanium isopropoxide (Ti(OCH(CH₃)₂)₄) triethanolamine, sodium hydroxide, ethanol, Cu(NO₃)₂·3H₂O, thiourea, ethylene glycol were purchased from Merck in high purity.

2.2. Synthesis of TiO₂ Nanoparticles

To prepare TiO₂-anatase nanoparticles, 7 mL of (Ti(OCH(CH₃)₂)₄) and 14 mL of triethanolamine were dispersed in 30 mL water. Then, followed by increasing the pH of the solution up to 10 with 1 M sodium hydroxide solution, the final solution was stirred for 12 hours. The resulting gel was subjected to the hydrothermal process in a Teflon-lined autoclave for 24 hours at the temperature of 140 °C. The precipitated nanoparticle was extracted by centrifuging and followed by washing with water and ethanol for several times, it was dried at 60 °C.

2.3. Synthesis of CuS Nanoflakes

To prepare CuS nanoflakes, Cu(NO₃)₂·3H₂O as a

precursor was dissolved in 15 mL of distilled water and in another beaker, 3 mmol of thiourea was dissolved in 15 mL of ethylene glycol. Next, the contents of these solutions were mixed together under ultrasonication. Then, the final mix was subjected to the hydrothermal process in a Teflon-lined autoclave for 12 hours at the temperature of 150 °C. The resultant nanoflakes were separated out by centrifuging and after washing with ethanol and deionized water for several times, they were dried at 60 °C.

2.4. Synthesis of TiO₂-CuS Nanocomposite

In a typical process, for synthesis of the TiO₂-CuS heterojunction nanocomposite, 0.5 g of anatase TiO₂ nanoparticles was mixed with 0.5 g of CuS nanoflakes and dispersed in 100 mL water by ultrasonication for 60 min. Then, the final suspension was transformed into a 150 mL Teflon lined stainless autoclave and subjected to the hydrothermal process for 20 h at the temperature of 180 °C. At the end of the process, the resulting nanocomposite was separated using a centrifuge, washed several times with deionized ethanol and water, and dried in a vacuum oven at 60 °C.

2.5. Photocatalytic Activity

For better evaluation of the photocatalytic performance of the fabricated samples, photocatalytic decomposition of Nitenpyram was done under 570 W Xenon lamp illumination. In this experiment, the reaction solution containing 0.05 g of the dispersed photocatalyst, 3 mg of Nitenpyram, and 100 mL of deionized water was mixed and kept in a dark under-stirring condition to develop adsorption-desorption equilibrium prior to irradiation. Then, the obtained suspension was irradiated with the visible light. After the time intervals, Degradation Percentage (DP) of Nitenpyram was analyzed using CARY 100 Bio VARIAN UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSION

The crystallinity of the prepared samples were examined based on X-Ray Diffraction (XRD) analysis on X'Pert MPD diffractometer using Cu K α line radiation. The XRD patterns are illustrated in Figure 1.

For CuS nanoflakes, the peaks at $2\theta = 27.61^\circ$, 29.41° , 31.81° , 32.61° , 48.01° , and 52.81° can be indexed to the diffractions from (101), (102), (103), (006), (110), and (108) lattice planes, respectively, corresponding to the CuS hexagonal (covellite) structure (JCPDS 006-0464) [22].

For TiO₂ nanoparticles, the major diffraction peaks positioned at $2\theta = 25.3^\circ$, 37.6° , 47.9° , 54.5° , and 62.5° can be indexed to the diffraction from (101), (004), (200), (105), and (204) lattice planes of the anatase titanium dioxide phase (JCPDS #21-1272), respectively [23]. In

the XRD spectrum of the TiO₂-CuS heterojunction nanocomposite, the diffraction peaks of CuS and TiO₂ are vividly observed, indicating the successful preparation of the heterojunction nanocomposite. The existence of sharp diffraction peaks confirms the high crystallinity of the synthesized samples.

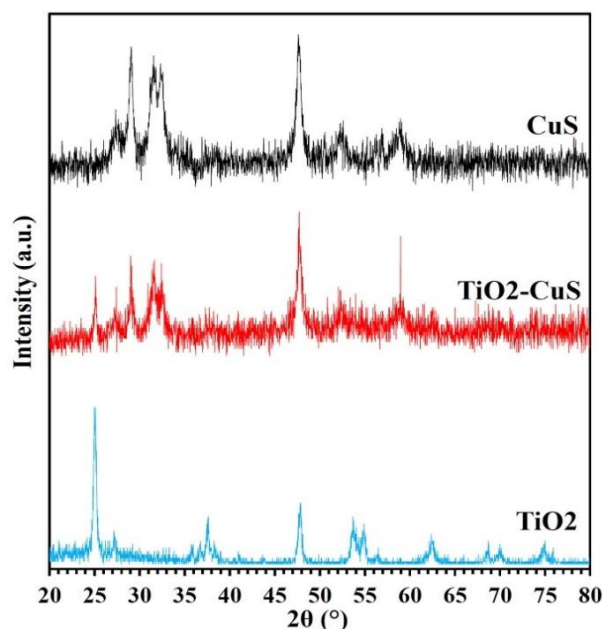


Figure 1. XRD patterns of the prepared samples

Once FE-SEM analysis is carried out on Tescan MIRA 3 FESEM, obtaining information about the size and morphology of the nanostructures that make up the nanocomposite is made possible. The FE-SEM results for the prepared TiO₂-CuS nanocomposite are shown in Figure 2a where the TiO₂ nanoparticles of about 40 nm in size and CuS nanoflakes of about 20 nm in thickness can be identified. To confirm the presence of TiO₂ and CuS compounds in the TiO₂-CuS nanocomposite, EDS analysis was carried out on the TiO₂-CuS sample to identify the elemental composition and confirm the presence of CuS and TiO₂ in this sample. The peaks of Ti, S, O, and Cu elements are vividly observed in the EDS spectrum of TiO₂-CuS sample in Figure 2b, confirming the successful preparation of the TiO₂-CuS heterojunction.

The optical properties of the prepared samples were examined through UV-Vis Diffuse Reflectance Spectroscopy (UV-DRS) on Shimadzu UV-2550 UV-vis spectrophotometer. Figure 3 demonstrate the obtained UV-Vis diffuse reflectance spectra of the samples according to which, the absorption edge of the TiO₂-CuS heterojunction shows a red-shift, compared to the bare TiO₂; hence, composition of the TiO₂ with CuS can improve the visible-light capture efficiency of TiO₂. The band gap energy (E_g) of the samples was obtained based

on the Kubelka–Munk model [24]. As seen in Figure 3b, the obtained value of E_g for TiO₂ is 3.2 eV while the value of E_g for TiO₂-CuS heterojunction sample is 2.7 eV, confirming the remarkable effect of heterojunction interface formation on the E_g of TiO₂ reduction which in turn enhances its visible-light photocatalytic performance.

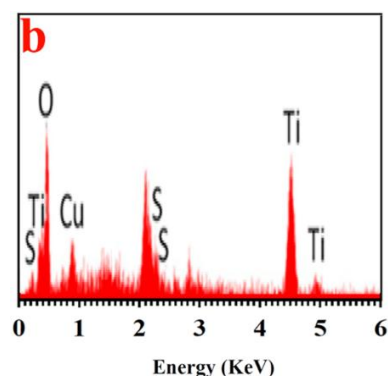
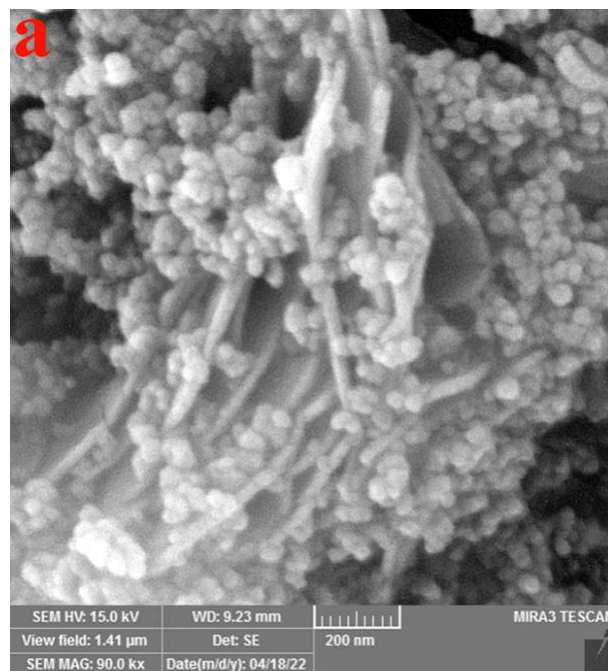


Figure 2. FE-SEM image (a) and EDS spectrum (b) of TiO₂-CuS nanocomposite

PL spectroscopy can be used for predicting the separation of charge carriers on the prepared samples. A decrease in the PL intensity can be attributed to the reduction in the charge carriers' recombination rate, thus resulting in the enhancement of the photocatalytic activity [25]. The emission PL spectra of the obtained samples were derived from Varian Cary-Eclipse 500 fluorescence spectrometer at the excitation wavelength of 300 nm.

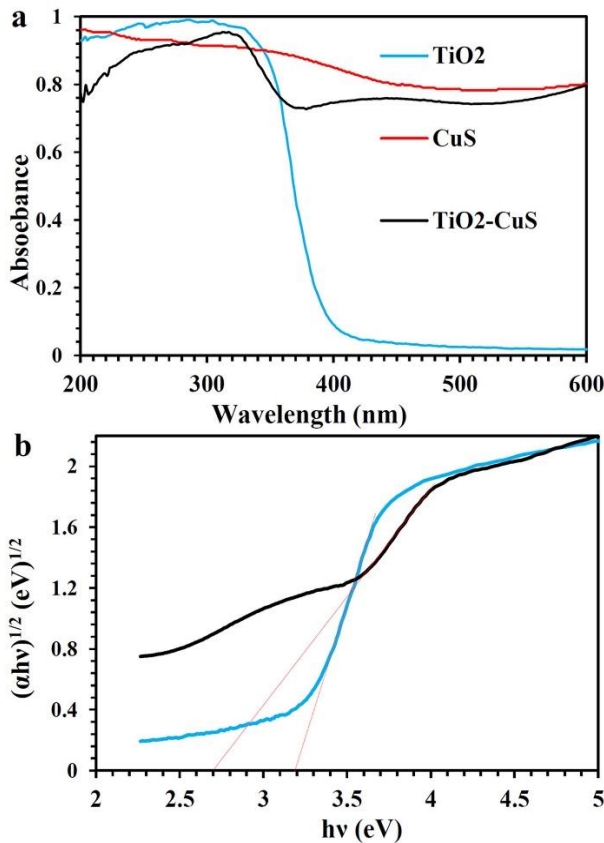


Figure 3. (a) UV-Visible DRS spectra and (b) the $h\nu$ vs $(\alpha h\nu)^{1/2}$ plots for the estimation of E_g

As shown in Figure 4, the PL emission intensity of the TiO₂-CuS heterojunction nanocomposite followed a decreasing trend, compared to the bare TiO₂ sample. Such decrease in the PL emission intensity can be attributed to the suppressed recombination rate of photoinduced charge carriers. In this regard, due to the decreased recombination rate of the charge carriers on the TiO₂-CuS heterojunction, this sample exhibited enhanced photocatalytic performance.

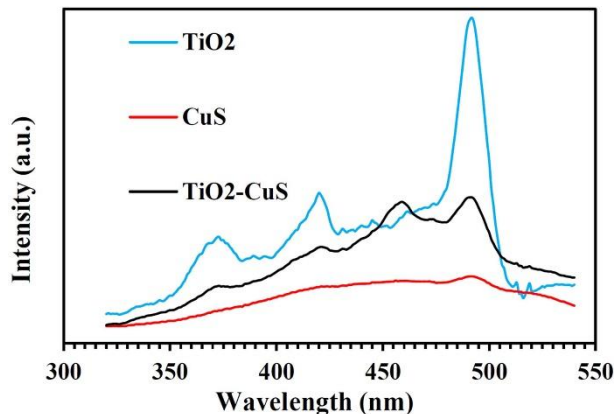


Figure 4. Photoluminescence spectra of the TiO₂, CuS, and TiO₂-CuS samples

The flat-band potential (E_{FB}), conduction band potential (E_C), and valance band potential (E_V) of the TiO₂ and CuS samples were estimated based on Mott-Schottky test, as shown in Figure 5. The positive slope of the linear part of the Mott-Schottky curve of TiO₂ sample reveals that this sample is an n-type semiconductor. However, the negative slope of linear part of the Mott-Schottky curves of CuS sample, indicating that CuS is a p-type semiconductor [26,27]. As observed in Figures 5a and 5b, E_{FB} values of CuS and TiO₂ were measured as approximately +0.5 V and -0.63 V (vs. Ag/AgCl) (+0.7 V and -0.43 V vs. NHE), respectively. As reported in the literature, for n-type semiconductor, the value of E_{FB} is 0.1 V lower than E_C and for p-type semiconductor, it is about ~ 0.1 eV higher than E_V [26]. As a result, the E_C value of the CuS and TiO₂ samples are equal to about +0.8 and -0.53 eV vs. NHE, respectively. In addition, the E_V value of the CuS and TiO₂ samples was estimated based on $E_V = E_C + E_g$ and consequently, the E_V value of these samples were obtained as 2.67 and 3.4 eV vs. NHE, respectively.

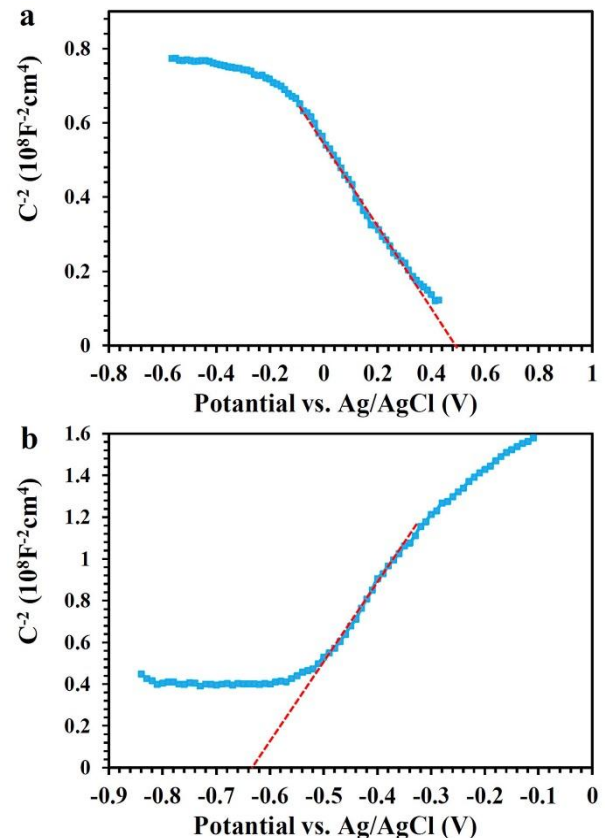


Figure 5. Mott-Schottky (MS) plots of (a) CuS and (b) TiO₂ samples

The photocatalytic activities of the fabricated photocatalysts were evaluated by comparing the photocatalytic decomposition of Nitenpyram over the

synthesized samples under visible-light illumination. As shown in Figure 6, in the case of the absence of photocatalyst (Blank), no degradation of Nitenpyram is reported, confirming the stability of this insecticide under visible-light illumination. However, remarkable degradation was observed in the presence of TiO₂, CuS, and TiO₂-CuS heterojunction nanocomposite, and about 52%, 24%, and 100% of Nitenpyram was decomposed in 60 min of irradiation, respectively. Due to the improvement in the visible-light capturing and also the retarded recombination rates of electron-hole pairs on the TiO₂-CuS heterojunction samples, this sample shows remarkably enhanced photocatalytic performance.

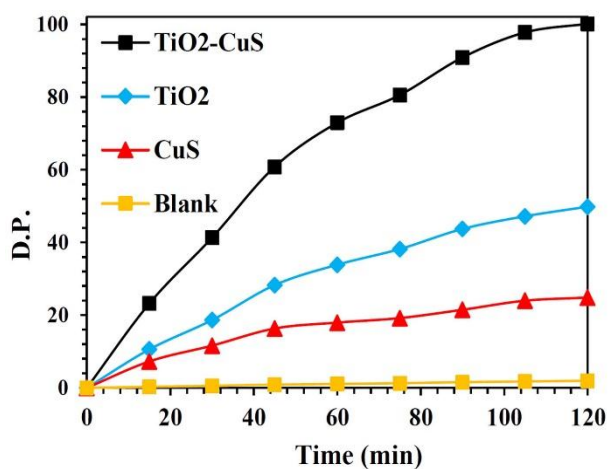


Figure 6. Visible-light photocatalytic degradation of Nitenpyram by using the synthesized samples

To further evaluate the roles of superoxide radical ($O_2^{\cdot-}$), hydroxyl radical (OH^{\cdot}), and hole on the photocatalytic decomposition of Nitenpyram on the TiO₂-CuS nanocomposite, benzoquinone (BQ), tert-Butyl alcohol (t-BUOH), and Ethylenediaminetetraacetic acid (EDTA) were added to the reaction solution as the scavengers of these species, respectively [28]. As demonstrated in Figure 7, the highest reduction in the photocatalytic efficiency was witnessed in the presence of BQ, confirming the major role of superoxide radicals during the photocatalytic decomposition of Nitenpyram. Of note, the photocatalytic degradation was also retarded in the presence of t-BUOH. Therefore, hydroxyl and superoxide radicals are the major oxidizing species responsible for photocatalytic activity of TiO₂-CuS nanocomposite under visible-light illumination.

Figure 8 shows the schematic diagram of the band alignment and type II charge carriers transfer mechanism for the photocatalytic performance of the TiO₂-CuS heterojunction during the visible-light illumination of the heterojunction photocatalyst. When light is irradiated onto this sample, the electron-hole pairs are generated in these semiconductors.

The photo-induced electron on the CB of CuS migrates to the CB of TiO₂ and at the same time, the hole on the VB of TiO₂ migrates to the VB of CuS [29]. Consequently, recombination of charge carriers considerably decreased, and the lifetime of the photogenerated electrons and holes remarkably increased. As a result, more OH^{\cdot} and $O_2^{\cdot-}$ radicals were produced, and the oxidizing power of the photogenerated holes and electrons was enhanced, hence photocatalytic efficiency improvement.

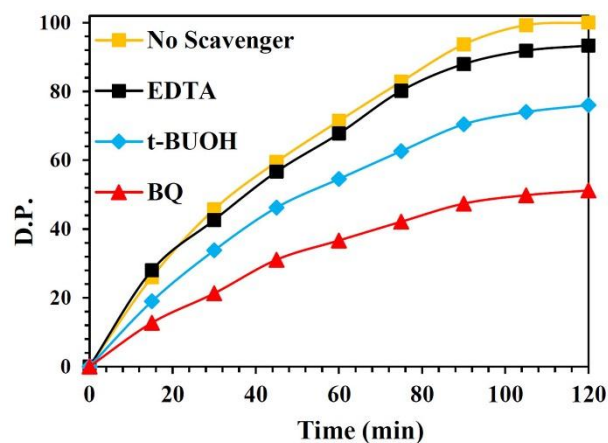


Figure 7. Activities of TiO₂-CuS nanocomposite for the visible-light photocatalytic decomposition of Nitenpyram in existence of various scavengers

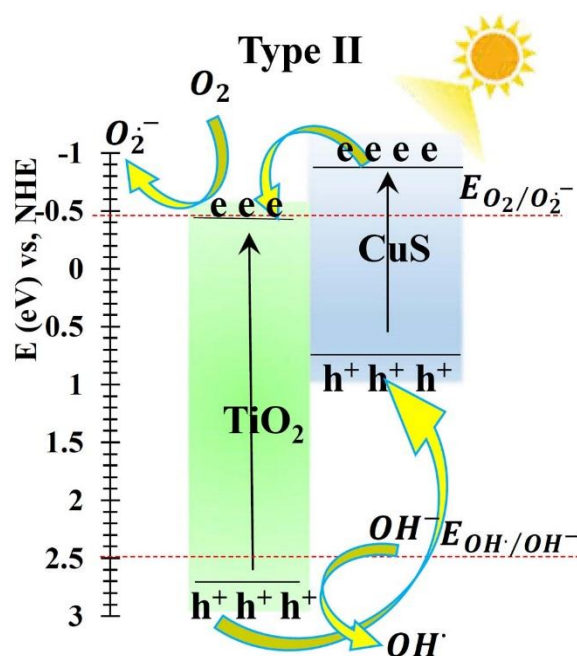


Figure 8. Type II mechanism for the photocatalytic performance of TiO₂-CuS nanocomposite

4. CONCLUSION

In the present research, a novel type II heterojunction nanocomposite was synthesized through one-step hydrothermal method from TiO₂ nanoparticles and CuS nanoflakes and then used as a visible-light photocatalyst for decomposition of Nitenpyram insecticide. Based on the obtained results, TiO₂-CuS heterojunction nanocomposite exhibited the best photocatalytic performance owing to a decrease in the electron-hole recombination rate and an increasing in the visible-light capturing. According to the results from Mott-Schottky tests and radical trapping experiments, a type II charge transfer mechanism was proposed for the degradation of Nitenpyram, and superoxide radicals were recognized as the major oxidizing agents involved in the degradation reaction.

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