

Effect of Tannic Acid on Photocatalytic Efficiency of NiFe₂O₄ and ZnO

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Abstract

ZnO, NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO photocatalysts were successfully synthesized and characterized, and they demonstrated significant photocatalytic efficiency under visible-light. The photodegradation rates of congo red (CR) are 35.7%, 19.4%, 25.5% and 91.1% over the ZnO, NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO for 180 min, respectively. The results display that the NiFe₂O₄/TA/ZnO has the most excellent photocatalytic efficiency for CR among to the other photocatalysts. Furthermore, NiFe₂O₄/TA/ZnO may be separated easily from solution by magnet because of the magnetic property of NiFe₂O₄. The considerable increment in efficiency of NiFe₂O₄/TA/ZnO can be attributed to synergistic effects between NiFe₂O₄, the tannic acid (TA) and ZnO, which extend lifetime and hinder the recombination of photogenerated charge carriers. This work presents new perspectives on the use of tannic acid based magnetic photocatalysts in wastewater treatment.

Keywords: NiFe₂O₄, tannic acid, magnetic separation, photocatalytic efficiency.

1. Introduction

Visible driven photocatalysis applied by preparing new functional materials presents new insights for wastewater treatment [1–3]. Semiconductor photocatalysts have an important potential due to it transform solar energy to chemical energy in the environmental treatment [4]. ZnO, which only absorb the light in the UV range, is one of the influent photocatalysts, because of its wide band gap energy. The strategies such as doping with noble metals and coupling of other semiconductors have been developed to activate ZnO in visible region [5–7].

After photocatalytic processes, recycling and reuse of photocatalysts are of considerable significance for the maintainable use of resources [8,9]. Recently, magnetic semiconductors such as MFe₂O₄ (M=Cu, Zn, Co, Ni) have drawn attention about recycling and reuse of photocatalysts [8]. NiFe₂O₄ is a magnetic material with narrow band gap energy, high magnetic separation and chemical stability [4,10]. However pure NiFe₂O₄ illustrates weak photocatalytic performance owing to the rapid recombination of charge carriers [10]. When their own features of ZnO and NiFe₂O₄ are taken in consideration, the combination of ZnO and NiFe₂O₄ may overcome the above mentioned problems [10,11].

Tannic acid is the form of gallotannine, which is an ester of glucose and gallic acid [12]. Nuray et al., reported that the tannin is a suitable support material for photocatalysis. Units of phenolic groups of tannic acid may interact with photoinduced electrons. Then, the electron continues to the ester ring owing to the pi bonds in the tannic acid and the unpaired electrons over the

oxygen. And finally, it leaves without splitting the ester ring. Tannic acid acts as electron scavengers in photocatalysis, delaying the recombination of the charge carriers [13].

Recently, many studies have been performed with ZnO/NiFe₂O₄ magnetic nanoparticles under visible light. However, no study has been published on the enhancing influence of the tannic acid as a modifier on photocatalytic activity of NiFe₂O₄/TA/ZnO. This study reports the preparation of magnetically separable NiFe₂O₄/TA/ZnO photocatalysts via solvothermal process and their photocatalytic efficiency for congo red (CR) decomposition. The NiFe₂O₄/TA/ZnO photocatalyst shows higher activity than ZnO and NiFe₂O₄. Under visible-light, neither ZnO alone nor NiFe₂O₄ alone is not photocatalytically active. In conclusion, this study is attributed to two basic topics. They are the synthesis of visible active NiFe₂O₄/ZnO and the delaying of recombination via TA.

2. Materials and Methods

2.1 Materials and apparatus

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Merck), Nickel(II) Chloride Hexahydrate, (NiCl₂·6H₂O, Merck), sodium hydroxide (NaOH, Merck), Iron(III) chloride hexahydrate (FeCl₃·6H₂O, Merck), ethylene glycol (C₂H₆O₂, TEKKİM), CR (commercial grade), and ethanol (Merck) were supplied.

2.2 Synthesis of photocatalysts

ZnO was synthesized by the method described in the work of Nuray et al. [14,15].

For synthesis of NiFe₂O₄ was used by solvothermal approach. In this procedure, 2 mmol FeCl₃·6H₂O and 1 mmol NiCl₂·6H₂O were dissolved in C₂H₆O₂. Then, 15 mmol sodium acetate was added to the suspension and ultrasonicated for 1 h. Then, the solution heated at 160 °C for 18 h. The acquired NiFe₂O₄ was washed, and afterwards, separated by a magnet and dried at 70 °C.

In the preparation of NiFe₂O₄/TA, 0.5 g of NiFe₂O₄ nanoparticles were dispersed in 20 mL of water under ultrasonic stirring for 1 h. Subsequently, 0.25 g tannic acid was added to NiFe₂O₄ dispersion and stirred ultrasonically for 2 h. The obtained NiFe₂O₄/TA was separated with a magnet, and washed. Consequently, the nanocomposites were dried at 70 °C [16].

NiFe₂O₄/TA/ZnO was prepared by a microwave-hydrothermal method. Firstly, 0.1 g NiFe₂O₄/TA was sonicated 30 mL of DW and 4 mmol Zn(NO₃)₂·6H₂O was added into the dispersion. After that, 12.5 mmol NaOH was dropped into the dispersion and stirred 1 h. The formed suspension was treated at 170 °C for 10 min in a microwave oven. The resulting samples washed and dried at 70 °C [13].

2.3 Instrumentation

The molecular structures of nanophotocatalysts were verified by powder X-ray diffraction (XRD, PANalytical Empyrean, Netherlands). The morphologies of samples were examined by using a scanning electron microscopy (SEM, Philips XL30 SFEG). The spectral characterizations were recorded via Fourier transform infrared Shimadzu UATR Two instrument (Japan). The optical features of products were determined by a UV-visible spectrophotometer (UV-Vis, Shimadzu UV-2600PC).

2.4 Photocatalytic testing

Photocatalytic efficiency of samples were determined by decomposition of CR. Irradiation was supplied by a 128 W visible light. In degradation processes, 50 mg of nanophotocatalyst was dispersed by a stirrer in 16 ppm CR solution. Before illumination, the solutions were stirred for 30 min in the darkness to provide formation of adsorption/desorption equilibrium of CR. 5 mL of the aliquots were withdrawn at specific time intervals, separated and investigated by the UV-Vis spectroscopy in the maximum absorbance of CR. The rate of degradation was detected by the Equation (2.1): [13–15,17,18].

$$\text{degradation (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (2.1)$$

where C₀ and C demonstrate the initial and the reaction concentrations of CR.

3. Results and Discussion

3.1 Characterization of photocatalysts

Figure 1 displays the XRD profiles of the nanophotocatalysts. The XRD profile of ZnO

demonstrates apparent peaks for hexagonal ZnO (JCPDS no.79-0206). The peak values at 2θ values of 31.7, 34.4, 36.2, 47.5, 56.6, 62.9, 66.4, 67.9, 69.1, 72.6, 76.9, 81.4, 89.6° are indexed as (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) planes of the ZnO with hexagonal wurtzite structure (ICSD98-015-5780), respectively. The diffraction peaks at the 2θ values of 30.26, 35.64, 43.30, 53.83, 57.26 and 62.89° are related to (220), (311), (400), (422), (511) and (440) planes of spinel NiFe₂O₄ (JCPDS no. 54-0964), respectively. In the XRD spectra of NiFe₂O₄/TA, NiFe₂O₄ are shadowed by modifying TA, leading to the invisible of the some of the peaks of TA caused to disappear some of the NiFe₂O₄ peaks. In the XRD spectra of NiFe₂O₄/TA/ZnO, both NiFe₂O₄ and TA peaks are observed. This situation is evidence that the composite is formed [13–15,17–19].

The morphology of the products has been verified by SEM analysis. Figure 2a-d illustrates the SEM images of ZnO, NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO. As can be seen Figure 2a, ZnO has irregular nanoplate structures [14,18]. NiFe₂O₄ consists of lots of agglomerated spherical nanoparticles (Figure 2b) [10]. In Figure 2c, Tannic acid can not be observed because the surface of the TA molecule is completely covered with agglomerated NiFe₂O₄ nanoparticles. Figure 2d shows NiFe₂O₄/TA/ZnO nanostructures containing ZnO nanoplates and agglomerated spherical NiFe₂O₄ nanoparticles.

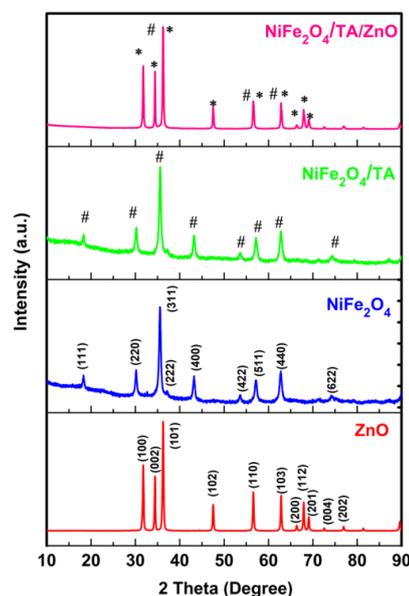


Figure 1. XRD patterns of the photocatalysts.

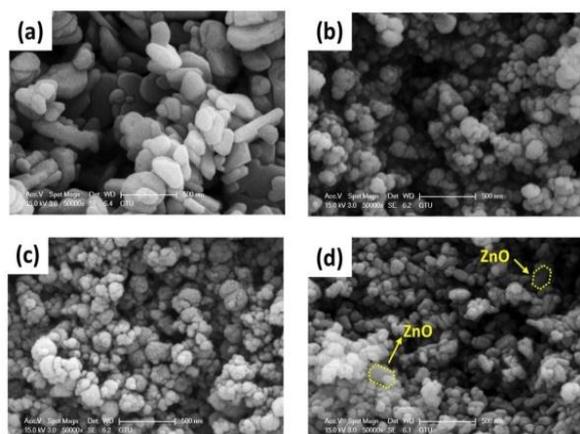


Figure 2. SEM images of (a) ZnO, (b) NiFe₂O₄, (c) NiFe₂O₄/TA and (d) NiFe₂O₄/TA/ZnO.

The optical features of the photocatalysts were examined by UV-visible diffuse reflectance spectra and band gap energies of them were displayed in Figure 3. As shown in Figure 3, the band gap energies of ZnO, NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO correspond to visible region. With modifying TA and ZnO, band gap energy of NiFe₂O₄ is replacing to the left. UV-DRS datas are described the Kubelka-Munk (K-M) relation $(F(R)) = (1-R)^2/2R$. In here, R is the reflection of the product [15]. The band gap energies of ZnO, NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO are detected 3.24 eV, 1.88 eV, 2.13 eV and 2.63 eV, respectively.

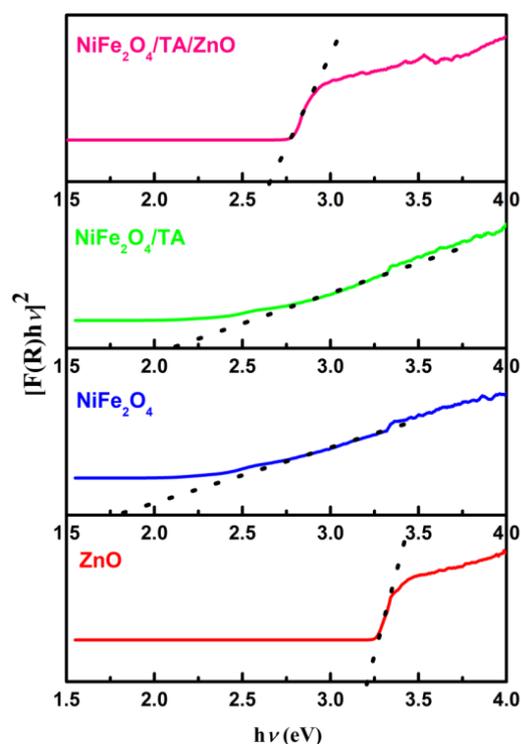


Figure 3. The K-M function versus $h\nu$ curves of the products for band gap energy detection.

FT-IR spectra of the products are demonstrated in Figure 4. The band at 440 cm⁻¹ corresponds to Zn-O stretching

vibrations (Figure 4a). As can be illustrated in Figure 4b-d, the peaks at 580 cm⁻¹ and 440 cm⁻¹ exhibit Fe-O and Ni-O bond, respectively. The peaks around 1626-1440 cm⁻¹, 1200 and 1050 cm⁻¹ are imputed to C=C-C vibrations in the aromatic carbon, C-OH stretching vibrations and C-O vibrations in the epoxy groups for tannic acid, respectively [20]. The peak at 3435 cm⁻¹ corresponds to -OH vibrations of the water molecule [20].

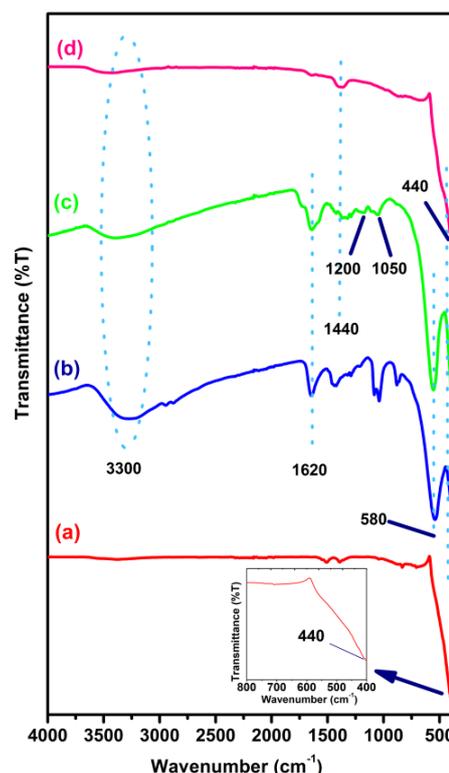


Figure 4. FT-IR spectra of (a) ZnO, (b) NiFe₂O₄, (c) NiFe₂O₄/TA and (d) NiFe₂O₄/TA/ZnO.

3.2 Photocatalytic testing

The photocatalytic efficiency of products have been examined via the CR degradation under visible light and the results are exhibited in Figure 5. As can be illustrated in Figure 5a, the degradation rates of ZnO, NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO, 35.7%, 19.4%, 25.5% and 91.1%, respectively, within 180 min. When the photocatalytic efficiencies of ZnO, NiFe₂O₄ and NiFe₂O₄/TA are compared, it is observed that TA is an enhancing effect on the performance of NiFe₂O₄. The results demonstrated that NiFe₂O₄/TA/ZnO exhibited much superior photocatalytic efficiency than ZnO, NiFe₂O₄ and NiFe₂O₄/TA. NiFe₂O₄ displays weak photocatalytic efficiency owing to rapid recombination of charge carriers. Since band gap energy of ZnO is wide, it is not very active in visible region. With TA modification, efficiency of NiFe₂O₄ has been enhanced. To determine the reaction kinetics of the degradation of CR on photocatalysts, the apparent rate constants were calculated by the pseudo-first-order kinetics [4,19].

$$\ln(C_0/C) = kt \quad (3.1)$$

where k represents for the first-order rate constant. From the Figure 5b, determined the rate constants of photocatalysts are shown in Table 1. When the k values of products are compared, NiFe₂O₄/TA/ZnO exhibited the higher degradation rate constant than the others.

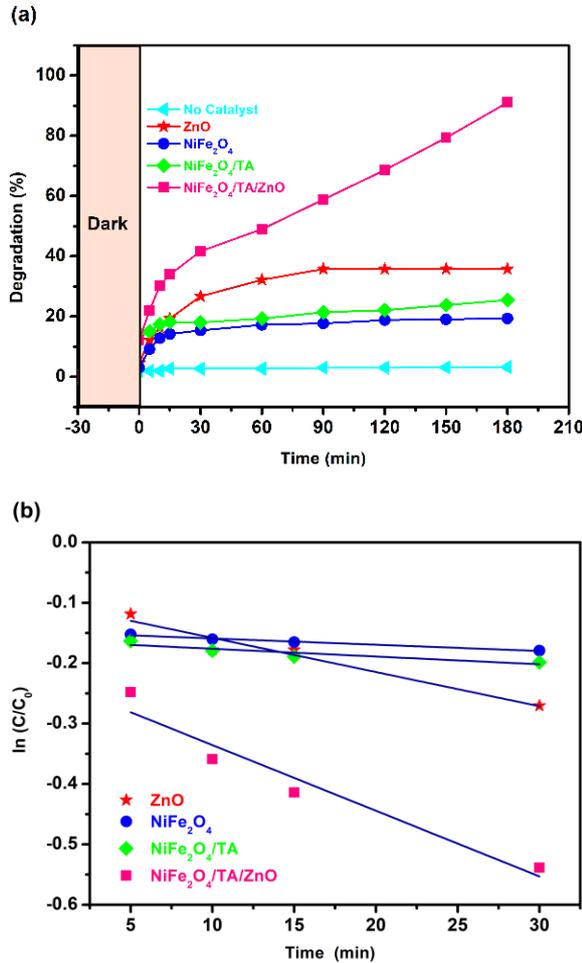


Figure 5. (a) The photodegradation of CR in existence of different nanophotocatalysts. (b) First order kinetics.

Table 1. k values of CR photodegradation in the existence of the samples.

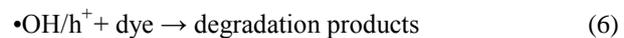
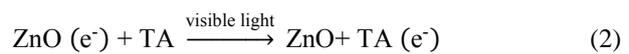
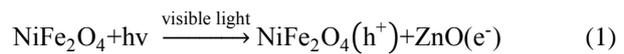
Samples	k (min ⁻¹)
ZnO	5.66×10^{-3}
NiFe ₂ O ₄	1.04×10^{-3}
NiFe ₂ O ₄ /TA	1.28×10^{-3}
NiFe ₂ O ₄ /TA/ZnO	10.8×10^{-3}

Thanks to the molecular structure of tannic acid, phenolic groups may interact with photoinduced electrons and then the unpaired electrons in phenolic groups are delocalized over the aromatic ring, this results in resonance formation. Thus, TA acts as an electron capture. Since the electrons amassed on the CB of

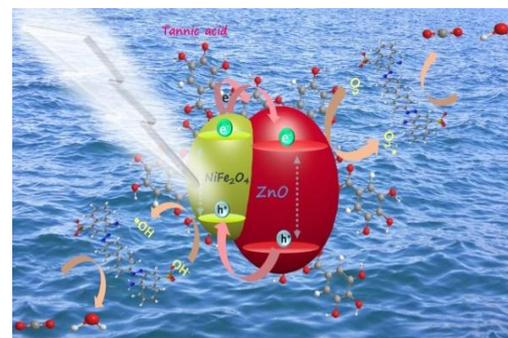
NiFe₂O₄ transfer to TA, recombination of charge carriers are greatly inhibited [13].

3.3. Photocatalytic mechanism

According the photodegradation datas, suggested a photocatalysis mechanism of NiFe₂O₄/TA/ZnO was indicated in Scheme 1. Under visible light, in the valence band (VB) of NiFe₂O₄ will be induced to the CB and then photogenerated electrons can migrated TA and ZnO. The reason why excited electrons are transferred from the CB potential of NiFe₂O₄ to the CB potential of ZnO, the CB potential of NiFe₂O₄ is more negative (-0.60 eV) than that of the ZnO (-0.12 eV). Similarly, the VB potential of NiFe₂O₄ (1.00 eV) is more negative than that of the ZnO (3.00 eV). So, the photogenerated electrons in NiFe₂O₄ are flown to TA and ZnO. In the meantime, the photogenerated holes are transferred from ZnO to NiFe₂O₄ [4,19]. The adsorbed oxygen molecules serve as the electron trapping to produce superoxide radicals. The holes will interact with H₂O to fabricated hydroxyl radicals. As a result, these strong radicals will attack to the CR and degrade to carbondioxide and water [4,13,19]. The proposal degradation mechanism of CR is demonstrated as follows:



Consequently, the enhanced photocatalytic efficiency of NiFe₂O₄, with the deposition of TA and ZnO may be clarified in three paths: (1) accelerating the separation of charge carriers, (2) improving the specific surface field, and (3) advancing the visible light usage capacity.



Scheme 1. Schematic representation of photocatalytic degradation for CR via NiFe₂O₄/TA/ZnO.

4. Conclusions

In conclusion, a magnetically separable NiFe₂O₄, NiFe₂O₄/TA and NiFe₂O₄/TA/ZnO were prepared by solvothermal method. NiFe₂O₄/TA/ZnO nanocomposites

exhibited advanced photocatalytic performance compared to the other photocatalysts. The advanced photocatalytic efficiency is related to the synergistic relationship between NiFe₂O₄, ZnO and TA. The narrow band gap energy and magnetically separable of NiFe₂O₄ and the enhanced electron transfer capability of TA positively impressed photodegradation process. It is hoped that the NiFe₂O₄/TA/ZnO will be an ideal photocatalyst for decomposition of contaminants with visible light.

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