Original Article

Fe₃O₄/Co₃O₄–TiO₂ S-scheme photocatalyst for degradation of organic pollutants and H₂ production under natural sunlight

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ABSTRACT

Sunlight responsible mono- and co-doped TiO₂ nanoparticles (Co₃⁺ and Fe₃⁺) were prepared via sol–gel technique. The X-ray diffraction (XRD) results showed no phase change of TiO₂ was observed after the addition of Co³⁺ and Fe³⁺ ions. Diffuse reflectance spectra (DRS) results showed a significant red-shift of the absorption edge after doping TiO₂ by Co³⁺ and Fe³⁺ and the band gap energy reduced sharply from 3.10 to 1.72 eV. X-ray photoelectron spectroscopy (XPS) results emphasized the existence of multivalent states of Co²⁺, Co³⁺, Fe²⁺ and Fe³⁺. The results of ultraviolet photoelectron spectroscopy (UPS), work function, electron spin resonance (ESR) illustrated the Fe₃O₄/Co₃O₄–TiO₂ formed of ternary hetero-junctions. The photocatalytic performance of the prepared photocatalysts was determined for photodegradation of tetracycline (TC) and phenol (Pl) and production of hydrogen. The results illustrated the existence of multivalent states of Fe and Co ions (Co²⁺, Co³⁺, Fe²⁺ and Fe³⁺) together improved the solar light absorption, inhibited the recombination of photo-generated charges and consequently enhanced the photocatalytic efficiency of TiO₂ compared with mono-doped TiO₂ (Co₃O₄/TiO₂ and Fe₃O₄/TiO₂). The sample with 5%Fe₃O₄/Co₃O₄–TiO₂ showed the highest photoactivity. The mineralization (TOC), photodegradation mechanism and reusability of prepared photocatalysts were also studied. The Fe₃O₄/Co₃O₄–TiO₂ nanoparticles showed high photostability and can be adopted as a promising materials for different environmental and H₂ production applications.

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1. Introduction

In recent years, global energy demand increased rapidly due to the rapid growing of population and industrialization and led to appearing of different environmental problems [1–6]. Several efforts have been exerted to find a sustainable and efficient clean energy source as alternative source of fossil fuels and also ecofriendly [1,7,8]. Solar energy is clean and sustainable energy and could avail for production of hydrogen from water splitting as clean energy and also environmentally friendly and for waste water treatment of different environment pollutants [5,7,9,10]. Semiconductors nanocrystals have been applied as a promising approach for production of hydrogen and for solving and controlling on the environmental pollution [11,12]. Different efforts have been exerted to improving the photocatalytic properties of photocatalysts under solar light energy [13–15]. TiO₂ is one of the most important photocatalysts which attracted enormous attention for the environmental cleanup, solar energy conversion, hydrogen production and gas sensors due to its unique properties as high photochemical stability, special optoelectronic properties, nontoxicity, low-cost and high photocatalytic activity [16–18]. However, the major drawback of utilizing TiO₂ as photocatalyst under solar light illumination is its large bandgap (3.2 eV for anatase, 3.0 eV for rutile) where only about 4%–5% of the solar energy consists of UV light as well as the fast recombination of photogenerated e⁻–h⁺ pairs which largely hindered its practical application [16,19–21]. Different strategies have been developed to overcome on these drawbacks by modification the electronic structure of TiO₂ to absorb the visible light and be able to utilize a higher portion of the solar spectrum, including decoration, doping and coupling with other metals, non-metals ions and metal oxides [22,23]. However, the doping of 3 d-transition metals into TiO₂ can lead to heterojunctions with narrow the band gap of TiO₂ due to creation of new states which effectively improves the absorption in the visible light leading high catalytic efficiency in the visible light [24].

Different mechanisms have been proposed to describe the pathway charge carriers through photocatalysts heterojunctions, type II, Schottky junctions, and Z-scheme heterostructures [25–27]. However, different limitations and disadvantages conclusions resulted during application of these mechanisms to describe the charge transfer through the heterojunctions [26,28]. Therefore, S-scheme heterojunctions mechanism has been proposed as a suitable solution for these limitations and disadvantages explanations that induced by the previous photoactive mechanisms. In this mechanism, the heterojunction composed of two or more semiconductors, coupled with each other i.e., composed of a reduction photocatalyst (RP) and an oxidation photocatalyst (OP) [27,29]. However, the powerful photogenerated electrons and holes are remain in the CB of RP and VB of OP, respectively, while the useless photogenerated electrons and holes are recombined, leading a strong redox potential [30]. The pollutants that resulted from the industrial processes such as antibiotics, dyes, pigments, inks ....etc. led to appearing of different environmental problems which caused different problems to microorganisms, aquatic environments, and human beings [31–36]. The photodegradation of organic pollutants is one of the most popular and important methods due to its advantage as effectiveness method, low cost and simplicity of operation [37–39].

In this work we prepared new ternary heterojunction Fe₂O₃/Co₃O₄–TiO₂ with S-scheme mechanism able to absorb the solar energy as available and sustainable natural energy source in treatment of waste water for removal the organic pollutants and generation of H₂ as clean energy, ecofriendly and alternative energy source. Also, study the effect of electronic states of dopants and dopants content on the structural, morphological and optical properties of TiO₂ and reflection of these changes on the photocatalytic activity of TiO₂. The photocatalytic performance of the prepared samples was investigated for degradation of TC and Pl and for H₂ production.

2. Experimental

2.1. Samples preparation

TiO₂, Co₃O₄, TiO₂, Fe₂O₃/TiO₂ and Fe₂O₃/Co₃O₄–TiO₂ nanoparticles were prepared by simplest sol–gel technique. Typically [40]: 2.0 gm of CTAB was dissolved in 30 ml of ethanol and then 12 ml of titanium (IV) isopropoxide was added with constant stirring for 1 h. Next, 0.25 gm of Co(NO₃)₂.6H₂O and definite masses of Fe(NO₃)₃.9H₂O according to the required amount of iron dopant were dissolved in 20 ml of ethanol and then transferred to the above solution with continuous stirring for 2 h. Then, 10 ml of ammonia solution was added and stirred vigorously for 0.5 h. Afterward, the solution was left in the air overnight and the resulted gel was filtered, washed with deionized water and then dried at 80 °C for 8 h. Finally, the powder was calcined at 500 °C for 3 h. Similarly Co-doped TiO₂ was prepared without addition of Fe(NO₃)₃.9H₂O and TiO₂ without addition of Fe(NO₃)₃.9H₂O and Co(NO₃)₃.6H₂O.

2.2. Characterization

The XRD patterns of the prepared photocatalysts were obtained on a PW Philips 1830. The Fourier transform infrared (FTIR) spectra were determined using a Shimadzu FTIR spectrometer. The morphology of the prepared photocatalysts was obtained using TEM using a JEOL-JEM-2100. Elemental composition study was achieved using energy dispersive X-ray (EDS) spectroscopy equipped on SEM instrument. DRS analysis was recorded on a Shimadzu spectrophotometer (UV3600, Japan). XPS analysis was performed on a Microtech electron spectrometer. The photoluminescence (PL) spectra of were obtained using JASCO F.P.–750 Model, (Japan) spectrofluorometer.

2.3. Catalytic activity measurements

2.3.1. Photodegradation of pollutants

The photocatalytic activity of the prepared samples was investigated by degradation of TC and Pl under sunlight...
illumination. The photoreactions were achieved in reactor surrounded with a cooling-water system. In this method, 0.05 g of photocatalyst powder was transfer into 50 ml of pollutant solution (Co = 10 mg·L⁻¹). The photoreactions were achieved in sunny days from 11.5 a.m. to 2.5 p.m. In the beginning, the mixture was stirred in dark for 30 min and then transfer under the sunlight illumination with continuous and stable stirring. The degradation of pollutant was checked at regular intervals by taken 2 ml of the solution and then centrifuged to separate the photocatalyst powder and the remaining concentration of pollutant determined on a Shimadzu, MPC-2200 UV–vis spectrophotometer.

To investigate the active species that played the active role in the degradation of TC and Pl, different scavengers (1 mM) were added to the reaction mixture including Na₂EDTA, benzoquinone (BQ) and isopropanol (IPA) as scavengers of h⁺, ·O₂, and ·OH, respectively [41, 42]. Also, the mineralization of the pollutants was investigated by total organic carbon (TOC) measurements using a Shimadzu-VCSN TOC analyzer. After the photodegradation, the %TOC of pollutant was estimated using the following equation:

\[
\% \text{TOC} = \left( \frac{\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}}}{\text{TOC}_{\text{initial}}} \right) \times 100 \quad (1)
\]

2.3.2. Hydrogen production

The production of H₂ from water splitting was carried out under simulated sunlight using 150 W Xe lamp equipped with UV cutoff filter (λ > 400 nm). Typically, 0.02 g of the photocatalyst powder was dispersed into 100 ml of 25 vol.% ethanol–water mixture in a Quartz reactor under magnetic stirring. Prior to start, gases in the reactor was removed by passing of N₂ gas through the reactor. The evolved H₂ gas was collected in gas bags, and were analyzed on GC-2014 (Shimadzu) equipped with a molecular sieve and Porapak Q column connected to TCD detector.

3. Results and discussion

3.1. XRD analysis

The XRD patterns spectra of TiO₂, Co₃O₄–TiO₂, Fe₃O₄/TiO₂ and Fe₂O₃/Co₃O₄–TiO₂ nanoparticles are shown in Fig. 1. XRD pattern spectrum of TiO₂ shows diffraction peaks located at 25.28°, 38.75°, 48°, 55.7°, 62.04°, 68.96°, 70.4° and 75.2° indicating the presence of well crystalline of anatase structural phase (JCPDS# 21-1272) [43–45]. Also, a small peak observed at 27.5° attributes to the rutile phase. The diffraction peaks of Co₃O₄–TiO₂ and Fe₃O₄/Co₃O₄–TiO₂ nanoparticles (Fig. 1) showed the same characteristic peaks as TiO₂ and no phase change was observed after the addition process of cobalt and iron ions. This indicates that the addition of Co and Fe ions conserved the initial crystal structure of TiO₂ and enhanced the stability of the anatase phase through inhibition of anatase to rutile phase transformation [16, 46]. Further, the intensity of diffraction peaks decreased gradually with increasing the Fe₃O₄ amount and no diffraction peaks attributed to Fe₃O₄ were observed with increasing the Fe₃O₄ content up to 5 wt.%, indicating the high dispersion and incorporation of Fe ions into the TiO₂ lattice [16, 47]. However, new small peaks were detected in the sample with 10 wt.% Fe₃O₄, indicating that some of the Fe ions precipitated out on the surface of TiO₂ [48]. The small peak that appeared at 35.8° indicates to the formation of Fe₂O₄ [49, 50]. On the other hand, Fig. S1 (Supplementary information) displayed shift of anatase peaks (101) to higher angles after the addition of cobalt and iron ions into the TiO₂. This observation can be ascribed to the
shrinkage of unit cell of TiO2 after the addition of Co and Fe ions which proves the replacement and substitution of some Ti ions by Co and Fe ions due to the similar radius of Co2+ (0.61 Å) and Fe3+ (0.64 Å) to that of Ti4+ (0.68 Å) which confirmed the incorporation of Co and Fe ions in the TiO2 lattice [16, 46, 51, 52].

The crystallites size of samples were calculated using Scherer’s equation and the results were listed in Table 1. From Table 1, the crystallites size decreased gradually with increasing the Fe3O4 amount, indicating that the addition of Co and Fe ions reduced the grain growth of TiO2 due to the suppressing impact of Co and Fe ions on the crystallite growth of TiO2 causing reduction in the size of the crystals [46, 47]. In comparison, the crystals size of 5%Fe3O4/TiO2 was determined (Table 1) and the results showed that the crystals size of 5% Fe2O3/TiO2 was larger than that of 5%Fe3O4/Co3O4–TiO2 indicating the presence of Co and Fe ions together are more active in hindering the grain growth of TiO2 compared with Fe ions alone.

3.2. TEM analysis

The morphologies of TiO2, Co3O4–TiO2, Fe3O4/TiO2 and Fe3O4/Co3O4–TiO2 nanoparticles were studied as presented in Fig. 2. The images display that the samples have spherical morphology and the average particles size varying in the range from 10 to 21 nm. Also, the images shows that the particle size decreased after the addition of Co and Fe ions to the TiO2 compared with TiO2. On the other hand, the particle size of 5%Fe3O4/Co3O4–TiO2 nanoparticles (Fig. 2(b) and (c)) showed as spherical particles with size larger than that of 5%Fe3O4/Co3O4–TiO2 nanoparticles. These observations are almost the same as that observed in the XRD results.

3.3. FTIR analysis

The FTIR spectra of pure and doped TiO2 are shown in Fig. 3. In the spectra, broad peaks appeared at 3420, 1627 and 1382 cm⁻¹ attributed to the stretching and bending vibrations of –OH and adsorbed water on the samples surface [41, 53, 54]. The FTIR spectrum of pure TiO2 (Fig. 3(a)) displayed broad absorption in the region of 400–900 cm⁻¹ attributed to the stretching vibration of Ti–O and Ti–O–Ti bonds [23, 42]. In addition, the band at 1040 cm⁻¹ attributes to the bridging stretching of Ti–O–Ti bonds [23]. The FTIR spectrum of Co3O4–TiO2 (Fig. 3(b)) showed two absorption bands located at 666 and 585 cm⁻¹ attributed to the Co2+–O and Co3+–O vibrations which confirms the spinel structure of Co3O4 [55–57]. Further, Fig. 3(c)–(f) displayed that the addition of Fe3O4 led to appearance of bands at around 480, 430 and 541 cm⁻¹ could be attribute to the vibrations of Fe–O modes [38] while the band at 1060 cm⁻¹ attributed to the Ti–O–Fe [59]. Also, Fig. 3 showed that the intensity of these bands increased with increasing the Fe3O4 amount. It’s reported that, the broad absorption band between 420 and 750 cm⁻¹ indicates to the incorporation of dopants in the TiO2 lattice and formation of Metal–O–Ti bonds [60]. Compared with undoped TiO2, Fig. 3 displayed small deviation in the bands positions under 1627 cm⁻¹ after the addition of Co and Fe ions indicating the introducing of Co and Fe ions in the TiO2 lattice and formation of Ti–O–Co and Ti–O–Fe network [53, 60, 61]. On the other hand, the intensity of the band at 666 cm⁻¹ enhanced after the addition of Fe3O4 indicating the overlapping of this band with the absorption band that resulted from the Fe–O band [48, 62].

3.4. XPS analysis

Figure 4 displays the full range survey XPS spectra of 10% Fe3O4/Co3O4–TiO2 nanoparticles are displayed in Fig. 4. The main peaks indicates to existence of Ti, Fe, Co, C and O elements detected at 458.37 (Ti2p), 712.21 (Fe2p), 783.04 (Co2p), 287.19 (C1s) and 530.2 eV (O1s) as shown in Fig. 4(a). From Fig. 4(b), the high-resolution scan of Ti2p region spectrum showed the presence of main doublet composed of two peaks at 458.13 eV and 464.2 eV assigned to Ti 2p3/2 and Ti 2p1/2, respectively, which arise from spin–orbit splitting and existence of Ti4+ in the TiO2 lattice [63, 64]. Also, two peaks appeared at 457.68 eV and 463.38 eV assigned to Ti 2p3/2 and Ti 2p1/2 indicating the formation of Ti4+ [65]. Another peak appeared at 459.48 eV assigned to the formation of M–Ti–O (M = Fe or Co ions) which indicate to incorporation of Mn+ into the lattice of TiO2 [22, 66, 67]. The high-resolution spectrum of Fe 2p (Fig. 4(c)) shows peaks appeared at 710.74 eV with its satellite at 717.66 eV and 713.5 eV with its satellite at 720.53 eV attributed to 2p3/2 and Fe 2p1/2, respectively [58, 68]. Also, another peaks appeared at 724.07 and 726.85 eV (satellite), attributed to Fe 2p1/2 [69]. Another satellite peaks appeared at 730.25 and 733.95 eV attributed to valence interband transitions. These results indicate to the existence of Fe2+ and Fe3+ oxides [47]. The high-resolution spectrum of Co2p (Fig. 4(d)) displayed peaks appeared at binding energy around 780.53 and 792.43 eV with two satellite peaks at 786.12 and 801.22 eV, respectively, indicating the existence of Co3+ oxidation states while the peaks at 782.85 and 796.78 eV with two satellite peaks at 788.9 and 803.89 eV, respectively, verifying the existence of Co3+ oxidation states in the sample [70–72]. It was reported that the presence of Co3+ species in the sample generates more anionic defects, producing excess surface oxygen which in turn improves the photocatalytic activity [72]. On the other hand, Co3+ can incorporate in the TiO2 lattice due to the ionic radius Co3+ is 0.65 Å which nearly has the same ionic radius as that of Ti4+ (0.68 Å) [73]. The O 1s

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Crystallite size D (nm)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>18.5</td>
<td>3.10</td>
</tr>
<tr>
<td>2% Co3O4–TiO2</td>
<td>16.7</td>
<td>2.53</td>
</tr>
<tr>
<td>2% Fe3O4/Co3O4–TiO2</td>
<td>14.6</td>
<td>2.32</td>
</tr>
<tr>
<td>5% Fe3O4/Co3O4–TiO2</td>
<td>13.4</td>
<td>1.85</td>
</tr>
<tr>
<td>10% Fe3O4/Co3O4–TiO2</td>
<td>11.6</td>
<td>1.72</td>
</tr>
<tr>
<td>5% Fe3O4/TiO2</td>
<td>15.2</td>
<td>2.10</td>
</tr>
</tbody>
</table>
XPS spectrum exhibited peaks at 529.06, 529.22, 529.50, and 529.71 eV assigned to lattice oxygen while the peak at 531.5 eV assigned to oxygen defect sites and surface oxygen [24,66,70].

3.5. UV–vis spectroscopy

Figure 5 shows the optical absorption spectra of TiO₂, Co₃O₄, Fe₃O₄/TiO₂, Fe₃O₄/Co₃O₄–TiO₂ nanoparticles. Undoped TiO₂ displayed an absorbance just below 410 nm resulted due to its band gap excitation [23]. The spectra of the doped TiO₂ samples showed a redshift of absorption edge to higher wavelengths indicate that the addition of Co and Fe ions led to a decrease in the band gap of TiO₂. This resulted due to introduce of additional energy levels in the bandgap of TiO₂ [74]. Also, Fig. 5 showed the intensity of visible-light absorption gradually increased with increasing the Fe₃O₄ amount. Moreover, the doped TiO₂ samples showed new absorption thresholds appeared at 426 and 526 nm indicating the creation of oxygen vacancies and formation and d–d spin forbidden transition of Co⁴⁺ and Fe³⁺ [51,75]. Another new absorption bands appeared at 670 and 745 nm may be resulted due to the splitting of electrons states in the d-orbital of Co²⁺, showing the d–d transition, and charge transfer transition from oxygen to Co²⁺ [24,51,55]. These results emphasized the incorporation of Co and Fe ions into the TiO₂ lattice [48,60].

The band gap energy (Eg) of the prepared samples was estimated using Tauc’s equation as shown in Fig. S2. The calculated values of Eg are listed in Table 1. Form Table 1, the Eg of TiO₂ reduced sharply after the addition of Co and Fe ions. Furthermore, the Eg of TiO₂ decreased gradually with increasing the Fe₃O₄ amount. The enhancing of visible light absorption and the narrowing of Eg of TiO₂ after the addition of Co and Fe ions could be ascribed to the creation of new energy levels in the band gap of TiO₂ and following the
excitation of d-electrons of Co and Fe oxides to the valence or conduction band of TiO₂ or d–d transition among the Fe ions [47,74,76].

It is remarkable to note that, the E₉ of 5% Fe₃O₄/Co₃O₄–TiO₂ is much lower and the absorption in the visible region is much higher than that of the 5% Fe₃O₄/TiO₂. This demonstrates that the co-doping of TiO₂ with Co and Fe ions enhanced the separation and inhibited the recombination of photogenerated charges and decreased the band gap width of TiO₂ and consequently, improved the photocatalytic properties of TiO₂ under visible light irradiation [77].

3.6. Photoluminescence (PL)

Photoluminescence (PL) is a suitable technique to investigate the recombination rate of photogenerated e⁻–h⁺ pairs and consequently, knowing extent of the photocatalyst efficiency. The PL emission spectra of pure TiO₂, Co₃O₄–TiO₂, Fe₃O₄/TiO₂, and Fe₃O₄/Co₃O₄–TiO₂ samples were recorded at 325 nm excitation wavelength, as displayed in Fig. 6. The samples displayed three emission peaks appeared at 410, 461 and 520 nm. The emission peak at 410 nm ascribed to the free excitation emission of the band gap [78], while the peaks at 461 and 520 nm are probably arising from the defect centers associated with oxygen vacancies with one and two trapped electrons, respectively [24,78]. As shown in Fig. 6, all of the doped TiO₂ have lower PL intensity compared to pure TiO₂ indicating the role of dopants in inhibition the recombination of e⁻–h⁺ pairs. In addition, the PL intensity suppressed effectively with increasing the Fe₃O₄ amount and 5% Fe₃O₄/Co₃O₄–TiO₂ showed the lowest PL intensity implying that the 5 wt.% of Fe₃O₄ is an optimal doping amount. In contrast, by increasing the Fe₃O₄ amount to 10 wt.%, the PL intensity increased which demonstrated that the suppression of the recombination depends strongly on the amount of Fe₃O₄.

For identifying the role of Co ions in the retardation of recombination, the results of PL spectra (Fig. 6) illustrated that the PL intensity of 5% Fe₃O₄/Co₃O₄–TiO₂ is significantly lower than that of 5% Fe₃O₄/TiO₂ which has Fe ions only, indicating the synergistic effect between Co and Fe ions played important role in reducing the recombination e⁻–h⁺ pairs and consequently enhancing the photocatalytic activity of TiO₂. The role of Co ions in enhancing the separation of e⁻–h⁺ pairs maybe resulted due to the ability of Co ions to trap the conduction electrons of TiO₂ effectively due to its high reduction potential (Co³⁺ + e = Co²⁺, E₀ = +1.81 V) and can induce p-type conductivity onto the TiO₂ leading formation of p–n junction which facilitated the migration of the holes toward the photocatalyst surface [79].

3.7. Photocatalytic activity measurements

3.7.1. Photodegradation of TC and Pl

The photocatalytic activity of TiO₂, Co₃O₄–TiO₂, Fe₃O₄/Co₃O₄–TiO₂ and Fe₃O₄/TiO₂ nanoparticles were investigated by degradation of TC and Pl under sunlight illumination as shown in Fig. 7. The results showed that the photodegradation of TC and Pl enhanced significantly after the addition of Co and Fe ions to TiO₂. In addition, Fig. 7 displayed that the photodegradation of both two pollutants increased gradually with increasing the Fe₃O₄ amount and the 5% Fe₃O₄/Co₃O₄–TiO₂ showed the highest activity with nearly 100% of degradation compared with other contents of Fe₃O₄. The enhancing in the photocatalytic activity of TiO₂ after the addition of Co₂O₄ and Fe₂O₃ ascribed to the dual role trappers of Fe²⁺ and Fe³⁺ (Eqs. (1) and (2)) and Co²⁺ and Co³⁺ (Eqs. (4) and (5)) which acted as electrons and holes trappers which in turn firmly inhibited the recombination process of e⁻–h⁺ and extended their lifetimes of e⁻–h⁺ [74,80–82]. However, when the Fe₃O₄ amount exceeded 5 wt.%, the photocatalytic
efficiency of Co$_3$O$_4$–TiO$_2$ was decreased indicating the Fe$^{3+}$ at higher concentrations acted as a recombination center of photogenerated e$^-$–h$^+$ pairs [80,83]. Moreover, increasing the Fe$_3$O$_4$ amount promoted the aggregation or formation of multilayers of Fe$_3$O$_4$ on the surface of Co$_3$O$_4$–TiO$_2$ which in turn shielded the light to arrival into the Co$_3$O$_4$–TiO$_2$ surface and consequently, reduced of the number of photogenerated charge carriers [23].
Fe$^{3+} + e^- \rightarrow Fe^{2+}$  \hspace{1cm} (2)

Fe$^{2+} + h_v^+ \rightarrow Fe^{3+}$  \hspace{1cm} (3)

Co$^{3+} + e_{CB} \rightarrow Co^{2+}$  \hspace{1cm} (4)

Co$^{2+} + h_v^+ \rightarrow Co^{3+}$  \hspace{1cm} (5)

For comparison, Fig. 7 showed the photocatalytic activity of 5%Fe$_3$O$_4$/Co$_3$O$_4$−TiO$_2$ is much higher than that of 5%Fe$_3$O$_4$/TiO$_2$ (without Co ions) for degradation of TC and Pl. The enhancing in the photocatalytic performance of TiO$_2$ after doped with double metal (5%Fe$_3$O$_4$/Co$_3$O$_4$−TiO$_2$) compared with the single doped TiO$_2$ (Co$_3$O$_4$−TiO$_2$ and 5%Fe$_3$O$_4$/TiO$_2$) resulted from the synergistic effect between Co and Fe ions which played important role in inhibiting the recombination rate of $e^-−h^+$ pairs which in turn enhanced the photoactivity of TiO$_2$. In addition, the existence of anatase and rutile phase together, Ti$^{3+}$ and oxygen vacancies played together in enhancing the photocatalytic activity of TiO$_2$ [84].

The photodegradation kinetics of TC and Pl were investigated using the Langmuir–Hinshelwood first-order kinetic model according to the following formula [85]: $\ln \left( \frac{C_0}{C_t} \right) = kt$. Fig. S3 showed the kinetic curves of TC and Pl degradation and
the calculated degradation kinetics parameters were listed in Table 2. The results indicated that the photodegradation of TC and Pl follows the pseudo first-order kinetics. Also, Table 2 displays that the photodegradation rate $k$ increased with increasing Fe$_3$O$_4$ amount and the 5% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$ showed the highest photodegradation rate.

The mineralization of TC and Pl was evaluated by TOC analysis at different intervals of irradiation time over 5% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$ as shown in Fig. S4. After 100 min, the degradation results were 100% of both TC and Pl while the % TOC removal efficiencies for TC and Pl were 67.4% and 85.6%, respectively after 180 min. However, increasing the irradiation time to 240 min, the %TOC reached 100% for TC and Pl indicating the complete mineralization of TC and Pl into CO$_2$ and H$_2$O. The results above demonstrate that the 5% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$ showed the highest photocatalytic activity and both TC and Pl can be mineralized effectively and completely.

To compare the photocatalytic performance of our samples with other photocatalysts, Table 1S shows that the 5% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$ showed excellent photocatalytic performance compared with other literatures for photodegradation.

![Photodegradation efficiency of undoped and doped TiO$_2$ nanoparticles.](image)

**Table 2 – Correlation coefficients and rate constants for TC and Pl photodegradation.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>TC</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.007</td>
<td>0.99552</td>
</tr>
<tr>
<td>2% Co$_3$O$_4$–TiO$_2$</td>
<td>0.01794</td>
<td>0.99571</td>
</tr>
<tr>
<td>2% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$</td>
<td>0.02407</td>
<td>0.99905</td>
</tr>
<tr>
<td>5% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$</td>
<td>0.03447</td>
<td>0.9984</td>
</tr>
<tr>
<td>10% Fe$_3$O$_4$/Co$_3$O$_4$–TiO$_2$</td>
<td>0.0096</td>
<td>0.99698</td>
</tr>
<tr>
<td>5% Fe$_3$O$_4$/TiO$_2$</td>
<td>0.01311</td>
<td>0.98837</td>
</tr>
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</table>
of organic pollutants and for H2 production under sunlight illumination [13,86–89].

3.7.2. Hydrogen production

Figure 8 shows that the photocatalytic performance of pure and doped TiO2 was enhanced significantly after doping of TiO2 with Co and Fe ions. No appreciable H2 was detected in case of pure TiO2 while the 5% Fe3O4/TiO2 gave very small amount of H2 compared with 5% Fe3O4/Co3O4–TiO2 after 5 h. On the other hand, the 5% Fe3O4/Co3O4–TiO2 showed the highest activity towards H2 production compared with other content of Fe3O4 with 2890 μmol g−1. Fig. S5 showed the effect of sacrificial agent on the mount of H2 production where the amount of generated H2 increased after the addition of sacrificial agent compared with that without using sacrificial agent. Based on these results, the synergistic effect between Co and Fe ions enhanced the photocatalytic activity of TiO2 significantly.

3.7.2.1. Photocatalytic mechanism. To understand the role of active radicals in the photodegradation of TC and Pl over 5% Fe3O4/Co3O4–TiO2 nanoparticles, different scavengers were used as shown in Fig. S6. Based on the results, the photodegradation of both TC and Pl are greatly suppressed after the addition of IPA and BQ scavengers where the photodegradation efficiencies were 15.8% and 22.5% of TC and 31.4% and 25.3% of Pl after 1 h, respectively. On the other hand, the addition of Na2EDTA (h+ scavenger) was accompanied by slight retardation with 50.2% and 59.8% for TC and Pl, respectively, after 1 h of photoreaction. According to these results, O2·− and HO• are the primary active species in the photodegradation of TC and Pl while h+ played a less important role.

In addition, the active species in photocatalysts was determined using electron spin resonance (ESR). As displayed in Fig. S7, no noticeable signals of both DMPO−•O2− and DMPO−•OH adducts were detected in the 5% Fe3O4/Co3O4–TiO2 nanoparticles under dark condition. However, under sunlight illumination, quadruple signal with an intensity ratio of 1:2:2:1 for DMPO−•OH adduct is detected indicating that •OH radicals were generated during the photocatalytic reaction (Fig. S7). Similarly, the spectrum of DMPO−•O2− showed four characteristic peaks with intensity ratio of 1:1:1:1 under sunlight illumination. According to these results, O2·− and HO• are the active species in the photodegradation of Pl and TC.

The work function of the TiO2, Fe3O4 and Co3O4 were determined using ultraviolet photoelectron spectroscopy (UPS) as shown in Fig. S8. The work function was determined by the following equation: \( \Phi = h \nu - E_{\text{cutoff}} \), where \( \Phi \), \( h \nu \), and \( E_{\text{cutoff}} \) are the work function, incoming photon energy from the He I source (21.21 eV), and the secondary electron cutoff energy, respectively. The calculated work function for the TiO2, Fe3O4 and Co3O4 are 5.67, 5.20 and 5.17 eV which indicates that the TiO2 has the highest work function compared with Fe3O4 and Co3O4.

On the basis of these results above, the mechanism of the photodegradation of TC and Pl under sunlight irradiation is proposed according of S-scheme heterojunction as shown in Scheme 1 [27,28,30]. Ternary heterojunction was formed when Fe3O4 and Co3O4 entities were put into contact with TiO2, electron transfer occurred at the interface from Fe3O4 and Co3O4 to TiO2, because the work function of TiO2 is larger than that of Fe3O4 and Co3O4, leading formation of electron depletion layer near the interface of Fe3O4 and Co3O4 and electrons accumulation layer in the TiO2 [30]. Under sunlight illumination, the photogenerated electrons in the CB of TiO2 recombined with the photogenerated holes in the VB of Fe3O4 and Co3O4 driven by the internal electric field, which in turn prevented the recombination of the powerful photogenerated electrons in CB of Fe3O4 and Co3O4 and the photogenerated

![Fig. 8 – Photocatalytic activity for H2 production over undoped and doped TiO2.](image-url)
holes in VB of TiO₂ leading enhancing the photodegradation of PL and TC and for H₂ production [90]. The photogenerated electrons in CB of Fe₃O₄ and Co₃O₄ react with oxygen molecules on the surface of photocatalysts to generate superoxide radical -O₂⁻ (Eqs. (6) and (7)), while the photogenerated holes react with hydroxyl groups and water molecules on the surface of catalyst to produced OH radicals (Eq. (8)) [47,83]. and these electrons and holes migrate to the surface of photocatalyst to initiate the photodegradation of TC and PI (Eqs.(9) and (10)) [87]. The mechanism of H₂ evolution also is displayed in Scheme 1. In this mechanism, the photogenerated holes reacted with H₂O and produced OH radicals (Eq. (8)). The resulted OH radicals attract the sacrificial agent molecules (ethanol) and produced H⁺ (Eq. (11)). The resulted H⁺ ions were reduced by the photogenerated electrons and finally resulted H₂ (Eq. (12)).

\[
\begin{align*}
\text{Fe}^{2+} + O_2 &\rightarrow \text{Fe}^{3+} + O_2^{-} &\text{(6)} \\
\text{Co}^{2+} + O_2 &\rightarrow \text{Co}^{3+} + O_2^{-} &\text{(7)} \\
H_2O + h^+ &\rightarrow O^+ + H^+ &\text{(8)} \\
O_2^{-} + \text{Organic pollutants} &\rightarrow CO_2 + H_2O &\text{(9)} \\
O_2^{-} + \text{Organic pollutants} &\rightarrow CO_2 + H_2O &\text{(10)} \\
C_2H_5OH + OH^- &\rightarrow 6H^+ + 6CO_2 &\text{(11)} \\
6H^+ + 2e^- &\rightarrow H_2 &\text{(12)}
\end{align*}
\]

3.7.3. Reusability study
The reusability and stability of the prepared samples were investigated. The repetitive experiments were carried out under the same experimental conduction. After each cycle, the catalyst was separated and washed with distilled water several times and then ethanol and finally dried at 100 °C for 8 h. Fig. S9 show the photodegradation results of TC and PI over 5%Fe₃O₄/Co₃O₄–TiO₂ after five cycles. Slight decrease in the photocatalytic activity was observed after five cycles, indicating the stability of Fe₃O₄/Co₃O₄–TiO₂ nanoparticles. The sample that used for investigation the reusability (5%Fe₃O₄/Co₃O₄–TiO₂) was characterized by XRD and TEM analysis before and after five cycles to investigate the effect of reused times on the photocatalyst structure. Fig. S10 showed no changes in the structure and morphology of photocatalyst after five cycles compared with fresh sample, indicating the high stability of prepared photocatalyst. Based on these results, the photocatalyst displayed high stability and can be reused several times in photocatalytic reactions without significant changes in its structure which makes these photocatalysts applicable materials for treatment of waste water and for H₂ production.

4. Conclusion

New ternary heterojunction Fe₃O₄/Co₃O₄–TiO₂ with S-scheme mechanism under solar-light-driven were prepared successfully via sol–gel method. The obtained XRD results showed no phase change of TiO₂ was observed after the addition of Co³⁺.
played an important role in inhibiting the recombination of TC and Pl to CO₂ and H₂O and the degradation kinetics of TiO₂ samples. XPS results emphasized the complete degradation of Fe and Co ions (Fe²⁺, Fe³⁺, Co²⁺, Co³⁺, Fe²⁺, and Fe³⁺) which played important role in inhibition the recombination of e⁻—h⁺ as illustrated from PL results and enhanced the photocatalytic activity of TiO₂. The photodegradation of TC and Pl and for H₂ production enhanced significantly after doped TiO₂ by Co⁵⁺ and Fe⁷⁺ together compared with pure mono-doped samples. %TOC results emphasized the complete degradation of TC and Pl to CO₂ and H₂O and the degradation kinetics obeyed the pseudo-first order. The scavenging results showed that the ·OH and ·O₂⁻ radicals were the active species for degradation of TC and Pl. The formation of ternary heterojunction enhanced the sunlight absorption, prevent the recombination of photogenerated charges and enhanced the photocatalytic performance greatly.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2022.07.078.

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and Fe⁷⁺ ions. DRS results displayed that the absorption of visible light was enhanced significantly after doping TiO₂ by Co⁶⁺ and Fe⁷⁺ and the Eg was reduced sharply from 3.10 to 1.72 eV. XPS results emphasized the existence of multivalent states of Fe and Co ions (Co²⁺, Co³⁺, Fe²⁺ and Fe³⁺) which played important role in inhibition the recombination of e⁻—h⁺ as illustrated from PL results and enhanced the photocatalytic activity of TiO₂. The photodegradation of TC and Pl and for H₂ production enhanced significantly after doped TiO₂ by Co⁵⁺ and Fe⁷⁺ together compared with pure mono-doped samples. %TOC results emphasized the complete degradation of TC and Pl to CO₂ and H₂O and the degradation kinetics obeyed the pseudo-first order. The scavenging results showed that the ·OH and ·O₂⁻ radicals were the active species for degradation of TC and Pl. The formation of ternary heterojunction enhanced the sunlight absorption, prevent the recombination of photogenerated charges and enhanced the photocatalytic performance greatly.

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