Synergistic effects of C, N, S, Fe-multidoped TiO₂ for photocatalytic degradation of methyl orange dye under UV and visible light irradiations

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Abstract

The aim of this work is the synthesis and characterization of C, N, S–Fe multidoped TiO₂ photocatalysts. The nanoparticles were prepared by sol–gel method and investigated by X-ray diffraction (XRD), transmission electron microscopy, UV–visible diffuse reflectance spectroscopy (DRS) and N₂ adsorption–desorption isotherm (BET). Photocatalytic activity of the photocatalysts was studied by degrading methyl orange (MO) under UV and visible light irradiations. XRD analysis illustrated that all synthesized samples present the anatase phase. CNS–0.3Fe-doped TiO₂ exhibited the highest surface area of 891 m²/g. DRS showed that Fe doping had efficiently narrowed the band gap to 2.74 eV and broaden the visible-light response region. The synthesized nanomaterials exhibited high photodegradation ability in the decomposition of MO than commercial pure TiO₂ nanoparticles Degussa P25.

Keywords Photodegradation · Sulfur · Iron · Carbon · Visible light · UV–visible

1 Introduction

The textile industry effluents are among the major environmental pollution sources, especially water pollution, which destroys the aquatic life and seriously influences the planet climate changes [1]. However, various physical and chemical techniques have been investigated to remove dye compounds such as adsorption on activated carbon, biodegradation, ozonation, and advanced oxidation processes (AOPs) such as Fenton and photo-Fenton reactions [2, 3], H₂O₂/UV processes and TiO₂ photocatalysis [4–8].

Heterogeneous photocatalysis is widely used in wastewater treatment belonging to the class of advanced oxidation processes (AOPs) and it is used as an alternative treatment method for the removal of toxic pollutants from

wastewaters then transform them into nonhazardous substances such as CO₂, H₂O [9]. Titanium dioxide (TiO₂) is among the most photomaterials extensively studied owing to the strong oxidizing power of its photogenerated holes, low cost, non-toxicity, fast oxidation rate and chemical stability [10]. It is used for various applications such as photocatalysis [11], solar cells [12]. Commercial TiO₂ Degussa P25 photocatalyst was used as a reference contains about 80% anatase and 20% rutile. The wide band gap of TiO₂ (3.2 eV anatase) limits its utilization to visible light [11, 13]. It can absorb only ultraviolet irradiation at wavelengths shorter than 385 nm for photocatalytic activity which is only 5% in the solar irradiation [14]. Hence, limiting the efficiency for solar application, the energy used from solar energy to activate TiO₂ is less than 3–5%

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[15]. Thus, the use of solar energy is important and much studied these last years. Up to date, several methods have been used for the preparation of doped TiO_2 catalysts [16, 17]. Among them, sol–gel has homogeneous and narrow particle size distribution of doping in TiO_2 materials with large surface area and proved to be an excellent photocatalyst for photocatalysis application [18].

Over the past few decades, numerous endeavors have been conducted, in order to enhance the photocatalytic activity of TiO_2 and extend its absorption from UV into the visible-light region. Several approaches; to extend the spectral response of TiO_2 from UV into the visible light region; have been studied by doping with metal ions and nonmetals to provide defect states in the band gap [19–21]. Metals and nonmetals doping have attempted to modify the optical properties of TiO_2 and decrease its band gap energy by generating new energy levels, also known as impurity states, between conduction and valence bands [22]. Nitrogen, Carbon, and sulfur are the most popular nonmetal dopants used to modify the optical properties of TiO_2 [23].

In the current research CNS–xFe doped TiO_2 nanopowders were prepared with high photocatalytic properties via simple sol gel method. The photocatalytic performances were investigated by photodegrading methyl orange dye in aqueous solution under UV and visible light irradiations.

2 Experimental

2.1 2.1. Synthesis of C, N, S–xFe– TiO_2 nanoparticles.

All chemicals were used as received without further purification and purchased from Sigma-Aldrich. An amount of thiourea reagent was dissolved in deionized water and kept in a water–ice bath. Under vigorous stirring, then titanium isopropoxide was added slowly into the aqueous solution and then iron (III) chloride was added. The solution was stirred for 12 h, aged for 24 h and then dried in air at 80 °C. Finally, the mixture was ground into a fine powder and then calcined at 500 °C for 2 h. The same synthesis without adding iron chloride was performed to prepare pure TiO_2 . The amount of iron used in this study was 0, 0.1 and 0.3 wt% (the mass percentage of iron ion in the titanium oxide powder). The commercial TiO_2 Degussa P25 powder was used as a reference without any further treatment.

2.2 Evaluation of photocatalytic activity

The irradiation was performed using two lamps (6 W) UV and visible lights. Under visible irradiation, short wavelength components (< 420 nm) of the light were cut

off using a glass filter before the output of light source to remove UV light and admit only visible light to enter into the reactor. All the experiments were carried out using 10 ppm of methyl orange dye and 0.5 g/L of catalyst. Before the photoreaction, the suspension was stirred in dark for 45 min to make sure that the mixture had achieved adsorption/desorption equilibrium, then 2 ml of the solution was taken from the reactor at a constant time. The suspension was filtered through 0.2 μm pore-size microporous then the concentration of the solutions was analyzed in a UV–Vis spectrophotometer.

2.3 Characterizations

In the present work, a simple sol–gel method was adopted to prepare CNS–xFe– TiO_2 nanoparticles. The powders were characterized by X ray diffraction (XRD) patterns (Philips X'pert pro MPD model X-ray diffractometer using Cu K α radiation as the X-ray source). The optical properties are measured by optical reflectance at room temperature using Lemda-950 Perkin Elmer and Biochrom Libra S12 UV/Vis Spectrophotometer. The morphology was observed on a transmission electron microscopy (TEM, Tecnai G2 Spirit 120 kV). Adsorption isotherms were measured using a Micromeritics 3Flex 3500 physisorption instrument, equipped with a thermostatic vapor source.

3 Results and discussion

Figure 1 represents the diffractograms of multidoped TiO_2 photocatalysts using different Fe content. Further observation shows that the peak intensities decrease and become wider, indicating the formation of smaller TiO_2

Fig. 1 X-ray powder diffraction spectra of pure TiO_2 and doped TiO_2 samples calcined at 500 °C

crystallites [24]. TiO₂ Degussa P25 composed of 75–80% anatase and 20–25% rutile was used as a reference [25]. Furthermore, no crystalline phases assigned to iron or iron oxide were detected by XRD in any of samples, which could be ascribed to the good dispersion of metal ions on TiO₂ or because of the very low dopant amount in the samples or it might be because Fe³⁺ ions substituted Ti⁴⁺ ions and were inserted into the crystal lattice of TiO₂ during sol gel process [26]. It has been observed that doped photocatalysts presented well-crystallized anatase phase and show a trace amount of rutile. Indeed, brookite peaks are absent, which would clearly show that doping inhibits the anatase to rutile transformation and anatase to brookite phase transformation.

Furthermore, the increase of Fe doping ratio produces negligible enlarged lattice parameters. A slight decrease and angle shift in (101) diffraction peak of TiO₂ might be derived because of the similarity of ionic radius between Fe³⁺ and Ti⁴⁺, proving that Fe³⁺ has successfully been doped into the TiO₂ lattice [27] or by the introduction of nonmetal which could inhibit the growth of TiO₂ crystallites. Trevisan et al. [28] have proved that N doping with single element does not enhance the photocatalytic performance of TiO₂ as using multi-elements co-doping of C and N. The crystallite sizes of as-prepared samples were calculated by measuring the full width at half maximum of anatase peak using the Scherrer equation (Table 1).

$$D = 0.94\lambda / \beta \cos\theta$$

where **D** is the crystallite diameter, **λ** is the wavelength of X-ray CuKα, **β** is the full width at half maximum of (101) peak and **θ** is the half angle of the diffraction peak on the 2θ scale [29]. The average grain size determined by using the Scherrer formula was estimated to be 8 nm. Nevertheless, doped TiO₂ photocatalysts have almost the same crystallite size, which indicates that Fe doping has no influence on the particle size. This result reveals that doping with C, N, and S decrease the crystallite size of TiO₂. Furthermore, when nonmetal are incorporated into the crystal lattice of TiO₂, some extent deformation has been introduced into crystal structure of TiO₂ [30] or it could be assigned to the synergistic effects that C, N, and S play in the growth of TiO₂ crystallites. Our further study reveals

that the modification of iron decreases the grain size and not by the contribution of C and N, which indicates that the modification of S-doping decreases the grain size of materials.

Transmission electron microscopy (TEM) images showed the morphology of TiO₂ doped using different amounts of iron. TEM images of pure TiO₂ and multidoped TiO₂ are illustrated in Fig. 2a–d. The images reveal spherical particles with smooth surface; otherwise, some aggregates of few particles and slight agglomeration are also shown. It has been noticed a uniform morphology to that observed in undoped TiO₂. The particle size distribution of particles ranges between 8–9 nm and show good homogeneity of particles.

Surface area is one of the most important factors influencing the photocatalytic performance of TiO₂. Surface area (*S*_{BET}) of as-prepared photocatalysts were determined from the N₂ adsorption–desorption isotherms using the Brunauer–Emmett–Teller method. Figure 3 shows nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution plots of TiO₂. N₂ adsorption–desorption isotherms exhibit typical type IV isotherms and type H1 hysteresis loops according to the IUPAC classification, implying mesoporous structures [31]. The crystallite sizes were estimated to be 8 nm. Nevertheless, the surface area is not greatly affected by the crystallites size.

The specific surface areas of CNS–xFe–TiO₂; 0, 0.1 and 0.3% of iron was found to be 373.5 m²/g, 103.7 m²/g and 891.5 m²/g, respectively. By increasing iron amount, the BET specific surface area of the as-prepared nanoparticles is the smallest one. Consequently, the high specific surface area of CNS–0.3Fe–TiO₂ (891.5 m²/g) could be assigned to the incorporation of Fe-doping into the matrix of TiO₂. However, Fe-doping has a major role in stabilizing the mesoporous textural properties of the photocatalyst rather than N, C and S doping. The pore size distribution of 0.1% is irregular and exhibits a decrease in the specific surface area which can probably be attributed to the inhibitory effect that iron plays in the distribution of the pore size and the specific surface area compared with that of 0 and 0.3% of Fe. Table 1 summarizes the surface area, the pore volume,

Table 1 Crystallite sizes, BET surface area, pore volume and pore size of samples

Photocatalysts	Crystallite size (nm) from XRD	Surface area (m ² /g)	Pore volume (cm ³ /g)		Pore size (nm)	
			<i>V</i> _{BJH-A}	<i>V</i> _{BJH-D}	<i>S</i> _{BJH-A}	<i>S</i> _{BJH-D}
TiO ₂ P25	20.161	46.5824	0.0848	0.0817	8.9247	9.5465
CNS–0Fe–TiO ₂	8.555	373.5174	0.7059	0.7208	6.8316	5.9181
CNS–0.1Fe–TiO ₂	8.433	103.7035	0.1633	0.1653	5.938	5.1352
CNS–0.3Fe–TiO ₂	8.493	891.4979	1.2945	1.1306	5.415	4.5777

Fig. 2 Transmission electron microscopy images of pure TiO_2 and S-0.1Fe- TiO_2 calcined at 500°C . **a** TiO_2 P25, **b** CNS-0 Fe- TiO_2 , **c** CNS-0.1Fe- TiO_2 and **d** CNS-0.3Fe- TiO_2

Fig. 3 N_2 adsorption-desorption isotherms and the pore size distribution calculated from BJH method

and the pore size calculated using BJH equation from the adsorption branch of the isotherm. The BJH pore size distributions of multidoped TiO_2 were relatively broad and extended to higher pore size range (Table 1). It was observed that all samples exhibited a narrow pore size distribution.

The band gap energy of multidoped TiO_2 and Degussa TiO_2 P25 was observed from diffuse reflectance spectrometer (DRS) as shown in Fig. 4. The samples were analyzed in the range of 200–800 nm. The band gap energies (E_g values) of all samples are thus estimated from the plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$). The intercept of the tangent to the x-axis which gives a good approximation of the band gap energies for TiO_2 powders were illustrated in Fig. 4. The optical band gap energy of the samples is listed in Table 2. It was observed that absorption was significantly enhanced with increasing content of iron. The catalysts shift towards longer wavelengths region, whereas the band gap decreased from 3.09 to 2.74 eV. This result could be ascribed to the synergistic absorption effect of the formation of chemical bonding with C, N, S-doping and Fe [32]. The absorption edge of 0.3 wt% of Fe doped TiO_2 nanoparticles appeared at about 452 nm, corresponding to the band gap energy of about 2.74 eV.

However, the strongest absorption might be attributed to synergistic effects of nitrogen, carbon and sulfur. A noticeable decrease in the band gap energy was observed by increasing iron concentration. However, it is ascribed to the presence of iron in TiO_2 which does not change the position of the valence band and the conduction band of TiO_2 [33, 34], but it creates new energy

Table 2 Band gap energies and absorption edges of prepared pure TiO_2 and CNS-xFe- TiO_2 calculated from DRS spectra

Photocatalysts	Band gap energy (eV)	Absorption edge (nm)
TiO_2 P25	3.26	380
CNS-0Fe- TiO_2	3.09	401
CNS-0.1Fe- TiO_2	2.93	423
CNS-0.3Fe- TiO_2	2.74	452

levels in the band gap. Further, the electron migrates from the valence band into the conduction band owing to the lower excitation energy level [35].

The photocatalytic activity of undoped TiO_2 and CNS-xFe- TiO_2 with different amounts of Fe doping (0, 0.1 and 0.3 wt %) were evaluated to degrade methyl orange solution under UV and visible light irradiations. Methyl orange (MO) was selected as a model pollutant due to its chemical contaminant in industrial wastewater and cannot be photodegraded in the absence of photocatalysts under light irradiation [36]. In the current work, we compared the degradation rates of as-prepared photocatalysts with the most photoactive commercially available TiO_2 Degussa P25. Experimental results revealed that the degradation rate using CNS-xFe- TiO_2 powders is better than using TiO_2 P25 nanopowders under UV and visible light irradiations. It has been observed that the photocatalytic activity was greatly influenced by Fe^{3+} doping. The linear relationship between $\ln(C/C_0)$ and time (Figs. 5 and 6) demonstrated that photocatalytic degradation of MO followed pseudo-first-order kinetics:

Fig. 4 Plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for different catalysts. **a** TiO_2 P25, **b** CNS-0 Fe- TiO_2 , **c** CNS-0.1Fe- TiO_2 and **d** CNS-0.3Fe- TiO_2

Fig. 5 Plots of $\ln(C/C_0)$ versus time for methyl orange dye (MO) degradation under visible light. **a** TiO_2 P25, **b** CNS-0.3Fe- TiO_2 , **c** CNS-0Fe- TiO_2 and **d** CNS-0.1Fe- TiO_2

Fig. 6 Plots of $\ln(C/C_0)$ versus time for methyl orange dye (MO) degradation under UV light. **a** TiO_2 P25, **b** CNS-0Fe- TiO_2 , **c** CNS-0.3Fe- TiO_2 and **d** CNS-0.1Fe- TiO_2

$$\ln(C/C_0) = -Kt$$

t is the reaction time and k is the reaction rate constant. Figures 5 and 6 present the plots of pseudo-first order kinetic for the degradation of methyl orange solution on the catalysts under UV and visible light irradiations. It was observed that dopant concentrations could have an effect on the separation rate of electron-hole pairs. However, there is an optimum dopant concentration for nanoparticles under visible light irradiation [37]. CNS-0.1Fe- TiO_2 nanoparticles present the optimum concentration; it exhibits a maximum degradation compared to the other concentrations. Fe^{3+} can play as both electron and hole traps to decrease the recombination rate of e^-/h^+ pairs

photogenerated on the surface of the catalysts [38]. It could be assigned to the formation of Fe^{2+} and Fe^{4+} ions [39], which are less stable compared to Fe^{3+} ions (due to half-filled 5d stable electronic configuration) [40]. Thus, the trapped charges can be easily released back to form stable Fe^{3+} ions [41]. This leads to the generation of OH radical and O_2 anion and increases the photocatalytic performance.

Cong et al. [42] have reported that Fe^{3+} dopant could insert $\text{Fe}^{3+}/\text{Fe}^{2+}$ impurity level below the conduction band, while above the valence band of TiO_2 , $\text{Fe}^{4+}/\text{Fe}^{3+}$ impurity level could be introduced [43]. This leads to the increase of light absorption in visible light regions, which plays a significant role in photocatalytic performance enhancement.

Table 3 Kinetic parameters of doped and undoped TiO₂ under UV and visible light

	TiO ₂ P25	CNS-0Fe-TiO ₂	CNS-0.1Fe-TiO ₂	CNS-0.3Fe-TiO ₂
$K \times 10^{-3} \text{ (min}^{-1}\text{) (UV)}$	33.8	35.9	46.4	40.2
$K \times 10^{-3} \text{ (min}^{-1}\text{) (visible)}$	0.5	1.2	1.5	0.9

A higher Fe/TiO₂ weight ratio can strongly affects its photocatalytic activity. Nevertheless, when the concentration of Fe³⁺ ions exceeds the optimum, it acts as a recombination center for the photogenerated electrons and holes in the surface [44]. Nevertheless, it reduces the overall quantum efficiency [45], leading to a decrease of photocatalytic activity. When recombination occurs, the excited electron falls back into the valence band without reacting with adsorbed species [46]. Instead, it includes new energy levels between the conduction and the valence band of TiO₂ [47]. Kinetic values for the degradation of methyl orange on TiO₂ were listed in Table 3.

4 Conclusions

The photocatalytic degradation of MO was carried out under visible light and UV-visible irradiations. Iron dopant does not affect the crystallite size of TiO₂. However, they inhibited any phase transformation to rutile or brookite and promoted the TiO₂ anatase phase. Under UV light irradiation, Fe³⁺ ions decrease the recombination of photogenerated electrons and holes and consequently, the photocatalytic activity was enhanced. The optical study has presented a decrease in the band gap energies and an increase in the absorption edge wavelength by the formation of impurity levels between the conduction and valence band of TiO₂. Doped TiO₂ have much higher photocatalytic activity than commercial pure TiO₂ nanoparticles Degussa P-25.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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