Enhancement of TiO_2 activity under visible light by N,S codoping for Pb(II) removal from water

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Abstract

This paper deals with a systematic study on the co-doping N,S on TiO_2 photocatalyst to improve its activity under visible light on the removal of Pb(II) from the aqueous media. The co-doping TiO_2 by N,S atoms was conducted in an autoclave by one-step hydrothermal of TiO_2 mixed with nitric and sulfuric acids as the sources of N and S, respectively. The mole ratio of TiO_2:nitric acid:sulfuric acid was varied as 1:1:0.5, 1:1:1, and 1:1:1.5 to find the best ratio toward the activity. The co-doped photocatalysts obtained were characterized by specular reflectance UV/Vis (SRUV), X-ray diffraction (XRD), and fourier transform infrared (FTIR) instruments. A batch experiment was carried out for oxidation of Pb(II), driven by a combination of visible light and TiO_2-N,S photocatalyst. The research results attribute that co-doping N,S into TiO_2 has remarkably narrowed the gap in the TiO_2 structure, emerging in the visible region. It was also proven that the co-doped in TiO_2 can considerably enhance its activity in the removal of Pb(II) under visible light, and the highest activity was owned by TiO_2-N,S (1:1:1). Furthermore, the most effective removal of Pb(II) 10 mg/L (98%) could be reached by employing 500 mg L^{-1} of the TiO_2-N,S (1:1:1) dose, 45 min of the time, and the solution pH at 7. The Pb(II) removed is due to the photo-oxidation induced by OH radicals to form the handleable PbO_2.

Keywords: Co-doping, N-S dopant, TiO_2, Photocatalytic removal, Pb(II)

Introduction

Oxidation of various organic pollutants on a solar-powered semiconductor photocatalyst provides a clean and environmentally friendly process [1]. Among the existing semiconductor materials, titanium dioxide (TiO_2) is a very active, low cost, and non-toxic photocatalyst. TiO_2 with a wide gap assigned by Eg 3.20 eV can only be activated under UV light [2–16], and consequently, it is less active under visible light exposure. This deficiency restricts the application of TiO_2 photocatalyst under low cost sunlight, which is mostly composed of visible light [2, 8, 11]. The enhancement of TiO_2 activity under visible light by mono-doping [2–6, 9, 10] and co-doping [7, 8, 11–16] has been proven to be the most successful strategy. By doping process, the gap can be narrowed

and thus decreasing the Eg of TiO$_2$ [2–8, 10, 11, 13–15], emerging in the visible radiation. Thereby, the visible response and the activity of organic pollutant degradation of the doped TiO$_2$ under visible light exposure are considerably enhanced [2, 3, 5, 9–11, 13]. Besides, the improvement of the photodegradation of various organic pollutants underdoped TiO$_2$ is also contributed by the ability of the dopant in suppressing the recombination of electrons (e$^-$) and holes (h$^+$) photogenerated by TiO$_2$ during UV irradiation [5, 9, 15], as presented as Eqs. (1) and (2).

$$TiO_2 + h\nu \rightarrow TiO_2\left(e^- + h^+\right) \tag{1}$$

$$TiO_2\left(e^- + h^+\right) \rightarrow TiO_2 + heat \tag{2}$$

Compared to metal elemental dopants, the non-metals are more interesting due to their smaller size allowing them to be inserted into the TiO$_2$ crystal lattice facilely [2, 4, 9–11]. Furthermore, among the non-metal dopants, nitrogen has attracted extensive interest as it can be easily introduced into the TiO$_2$ structure, due to its atomic size, which is comparable with that of oxygen, its low ionization energy, and high stability [2–4, 15]. In accordance, N-doped TiO$_2$ demonstrates significant photocatalytic activity under visible light irradiation [2–4]. It was also reported that increasing the dopant loaded has improved the photodegradation of organic pollutants, but the further increase was found to show the opposite effect [2, 5, 8–11, 15]. This unexpected trend is generated by the turning role of the dopant from preventing becomes servicing recombination [5, 6, 11, 15]. Consequently, the fast recombination may proceed that declines the effectiveness of the photocatalytic organic degradation.

For solving such drawback, co-doping TiO$_2$ with two different non-metal elements has received intensive attention [6, 7, 11–16], as with low loading co-dopants can deliver a significant effect on increasing the photocatalytic degradation of various organic pollutants under visible light [2, 15]. Moreover, some studies have also proven that co-doped TiO$_2$ showed higher activity than the corresponding mono-doped [8, 11, 15].

Considering the advantages of using N dopant, as presented above, the double elemental dopants of N combined with C [7, 12], with P [11], as well as with S dopants [13–16] have been intensively studied. Due to the pronoun effect shown by double dopants of N and S in the improving photodegradation under visible light exposure, co-doping with N and S is growing of interest [13–16]. Several studies have investigated the co-doping TiO$_2$ with N-S atoms for accelerating the degradation of residual anti-inflammatory drug [13], antibiotic residual [14], p-chlorophenol [15], and phenol [16] in the presence of the visible light, and high results have been obtained.

To the best of our knowledge, the co-doped TiO$_2$-N,S has not been examined for oxidation of hazardous heavy metals such as Pb (II). The heavy metal become an environmental concern due to its characters including wider disposal sources, rapid accumulative in biotic tissues, and high hazard for human health [17–23]. To prevent the dangerous effect of Pb(II) ion on the ecosystem and humans, an effective detoxification method is urgently required to treat the corresponding wastewater before reaching the environment. Removal of Pb(II) ions from water has been frequently performed by adsorption techniques [17–19]. Unfortunately, at the end of the process, the adsorbent saturated with Pb(II) can generate undesired hazardous solid waste, which creates a new problem in the environment. The most suitable method is believed to be oxidation

of Pb(II) resulting from the less toxic and handleable PbO_2 [20–23]. The effective Pb(II) oxidation can be obtained through the photo-Fenton process [20] and photocatalysis over TiO_2 photocatalyst under UV illumination [20–23].

However, detoxification of Pb(II) by using N,S-coped TiO_2 in the presence of visible light so far is untraceable in the literature. The application of the N,S co-doped TiO_2 for photo-oxidation of Pb(II) in the solution contributes plausibly a novelty in Pb(II) remediation as well as the application of TiO_2-N,S photocatalyst. Under the circumstance, in the present research, photooxidation of Pb(II) over TiO_2-N,S photocatalyst under visible light irradiation is addressed.

Concerning the co-doping N,S into TiO_2, urea, and thiourea are the most employed as the sources of the N and S dopants [2, 3, 9, 10, 13, 14, 16] and other organic compounds [2, 11, 12]. However, using organic amine for N and S dopant sources can inevitably lead to organic residues on the photocatalyst surface [4, 5] that can decrease the activity of the photocatalyst. To avoid such weaknesses, in this paper, nitric and sulfuric acids are proposed as the simple inorganic N and S dopant sources respectively, into the TiO_2 structure. The co-doping is performed in one step suggesting a fast and practice process. Furthermore, to reach the maximum Pb(II) photo-oxidation result, the influences of some important parameters controlling the effectiveness of Pb(II) oxidation such as dopant amount in the photocatalyst, photocatalyst mass, irradiation time, and solution pH are also evaluated.

Methods
Materials
The main materials used were TiO_2 (Degussa P25), HNO_3 (65%), H_2SO_4 (95–97%), and $Pb(NO_2)_3$, which were purchased from E. Merck company and used without any purification.

Co-doping of TiO_2 by N and S atoms
The co-doping TiO_2 with N and S elements was employed by a pressured hydrothermal technique in the autoclave [24]. Powder of TiO_2 about 0.8 g was suspended in 20 mL of a mixture of distilled water (10 mL) and ethanol (10 mL), followed by stirring for 30 min to make a good suspension. Into the suspension, 20 mL of HNO_3 5 M and 20 mL of H_2SO_4 5 M were added, accompanied by stirring for 30 min to get a homogenous mixture. The mixture was then put in the autoclave and heated at a constant temperature of 150°C for 6 h. After that, the co-doped TiO_2 photocatalyst was collected and washed with deionized water three times to remove the weakly adsorbed species. Then, the photocatalyst was dried at 110°C and continued with calcination at 400°C for 2 h. The quantities of TiO_2, HNO_3, and H_2SO_4 introduced would give a mole ratio of Ti:N:S = 1:1:1. This as-prepared photocatalyst was coded as TiO_2-N,S(1:1:1).

The same procedure was copied for processes by addition of HNO_3 and H_2SO_4 with the same concentration (5M) but different volume, giving mole ratio of Ti:N:S = 1:1:1.5 and 1:1:0.5, as well as by using single HNO_3 and H_2SO_4 with the same volume (20 mL) and concentration (5 M). The photocatalyst samples prepared were given codes as TiO_2-N,S(1:1:1.5), TiO_2-N,S(1:1:0.5), TiO_2-N(1:1), and TiO_2-S(1:1), respectively.

Characterization

The effect of co-doping on the crystallinity of TiO_2 was followed by using an X-ray diffractometer of 6000X Shimadzu with Cu K radiation. The XRD patterns were recorded from 4–40° of the 2 theta angles. The absorption edge and band gap energy of the samples were measured using a UV/visible spectrophotometer equipped with a Specular reflectance accessory of the UV-1800 series. The SRUV spectra were taken from 300–800 nm of the wavelength. Infrared spectra (IR) with the wavenumber of 4000–400 cm^{-1} were recorded on a Shimadzu Prestige 21 Infrared spectrophotometer that was used to evaluate the success of the N,S doping. The determination of Pb(II) concentration in the solution from the photooxidation process was carried out by using 3110 Perkin-Elmer flame Atomic Absorption Spectrophotometry elemental analysis.

Photocatalytic removal of Pb(II) from water under visible irradiation

In this typical process, 25 mg of the co-doped photocatalyst mixed with 50 mL of a solution containing Pb(II) 10 mg/L was stirred to get a homogenous mixture. The mixture was placed in a container glass, and the container was put in the photo-process apparatus equipped with 4 visible lamps (TL-D Intensity @20 W, 2000 lm/m^2). Then, the visible lamps were turned on, and the mixture was magnetically stirred for 30 min. After the desired time, the solution in the container was filtered under 41 Whatman filter paper to collect the solution containing the Pb(II) residue. The concentration of Pb(II) ions left in the solution was analyzed by using AAS based on the respective standard curve. The removed Pb(II) (in %) from the solution was calculated by the following equation:

$$\frac{Co - C}{Co} \ x \ 100\% \qquad\qquad\qquad (3)$$

where Co is the initial amount of Pb(II) (mg) and C represents the amount of Pb(II) left in the solution (mg).

The same procedure proceeded with various mole ratios of Ti:N:S, photocatalyst masses, irradiation time, and solution pH, as well as by using mono-S-doped and N-doped photocatalyst as a comparison.
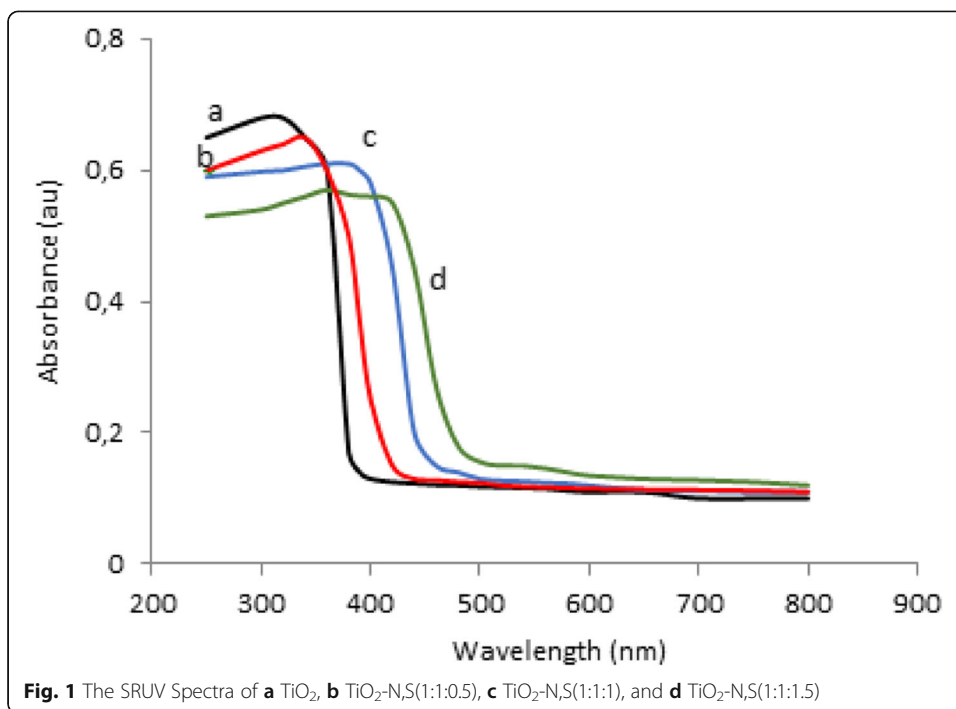
Result and discussion

Characterization of The N,S Co-doped TiO_2

SRUV spectra

The SRUV spectra of the co-doped TiO_2 along with un-doped photocatalysts are exhibited in Fig. 1. By taking the intersection of the absorbance at the respective wavelength, the maximal absorbance can be obtained. From the maximal absorbance, the band gap energies of the photocatalyst can be calculated, and the calculation results are presented in Table 1.

Data in the Table 1 indicates that by co-doping, the absorption of the photocatalyst shifts significantly into a longer wavelength, entering the visible region. The shifts are due to the considerable decrease of the band gap energy, resulting from narrowing the gap, which is synergically created by the two dopant (N and S) atoms. Further, the decreasing band gap energy is observable in more effective when the amount of dopant S is enlarged giving larger narrowing the gap. This data provides evidence of the success

Fig. 1 The SRUV Spectra of **a** TiO_2, **b** TiO_2-N,S(1:1:0.5), **c** TiO_2-N,S(1:1:1), and **d** TiO_2-N,S(1:1:1.5)

of co-doping. The decrease of Eg and absorption shift allow TiO_2 to be highly responsive under visible irradiation. Similar findings have also been frequently reported [2, 5, 8–10, 15].

XRD data

Figure 2 displays the XRD patterns of un-doped TiO_2 along with the co-doped TiO_2-N,S samples. The XRD pattern of TiO_2 is characterized by peaks appearing at 25.091, 37.651, 48.021, 53.891, 55.071, 62.381, 68.701, 70.041, and 75.001 of the 2θ under Cu-Kα that well fit with those of the standard anatase phase of TiO_2 recorded by JCPDS card number of 01-071-1167 [2].

Similar patterns of the co-doped photocatalyst samples to the pattern of the undoped TiO_2 are also clearly observed. The difference that appeared in the intensities of the doped photocatalyst is lower than the intensities of the undoped one. With the increase of the amount of S in the co-doped photocatalyst, the intensities are seen to be considerably decreased. The lowering intensities imply the crystallinity deforms partially, due to the insertion of the atom dopants in the crystal lattice [2, 10]. The more amount of S dopant produces, more S inserted into the lattice leading to higher deformation of the crystal. This alteration of the intensities is good proof of the success of the N,S co-doping in TiO_2. Other studies have also obtained the same trend [2, 5, 8, 11].

Table 1 The effect of co-doping on the decreasing Eg

Photocatalyst	TiO₂	TiO₂-N,S (1:1:0.5)	TiO₂-N,S (1:1:1)	TiO₂-N,S (1:1:1.5)
Wavelength (nm)	387	420	460	490
Eg (eV)	3.20	2.95	2.69	2.53
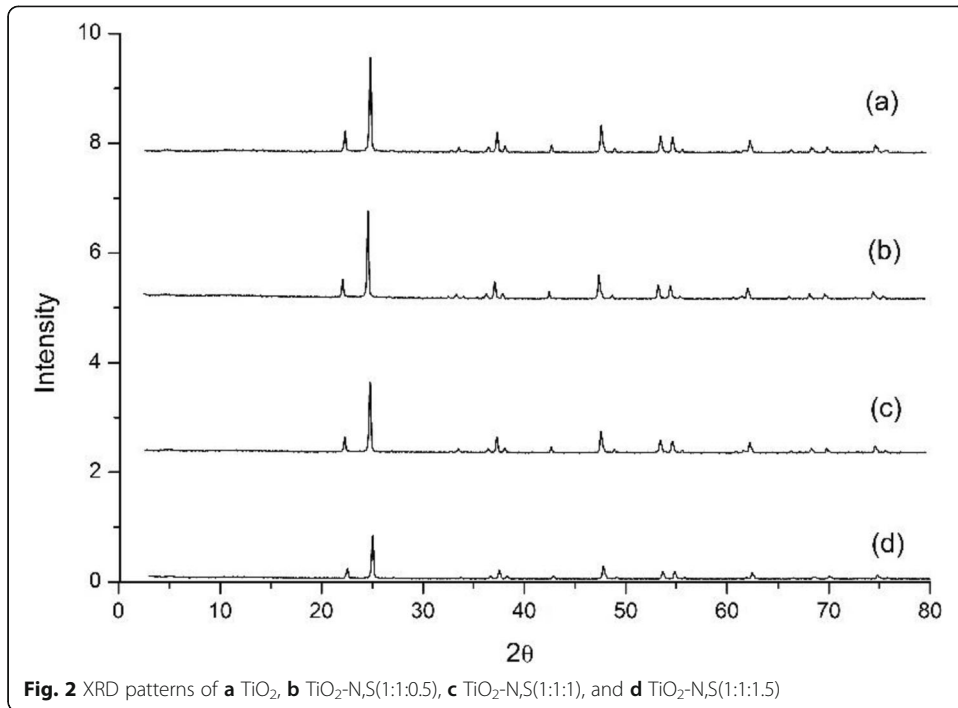
Fig. 2 XRD patterns of **a** TiO$_2$, **b** TiO$_2$-N,S(1:1:0.5), **c** TiO$_2$-N,S(1:1:1), and **d** TiO$_2$-N,S(1:1:1.5)
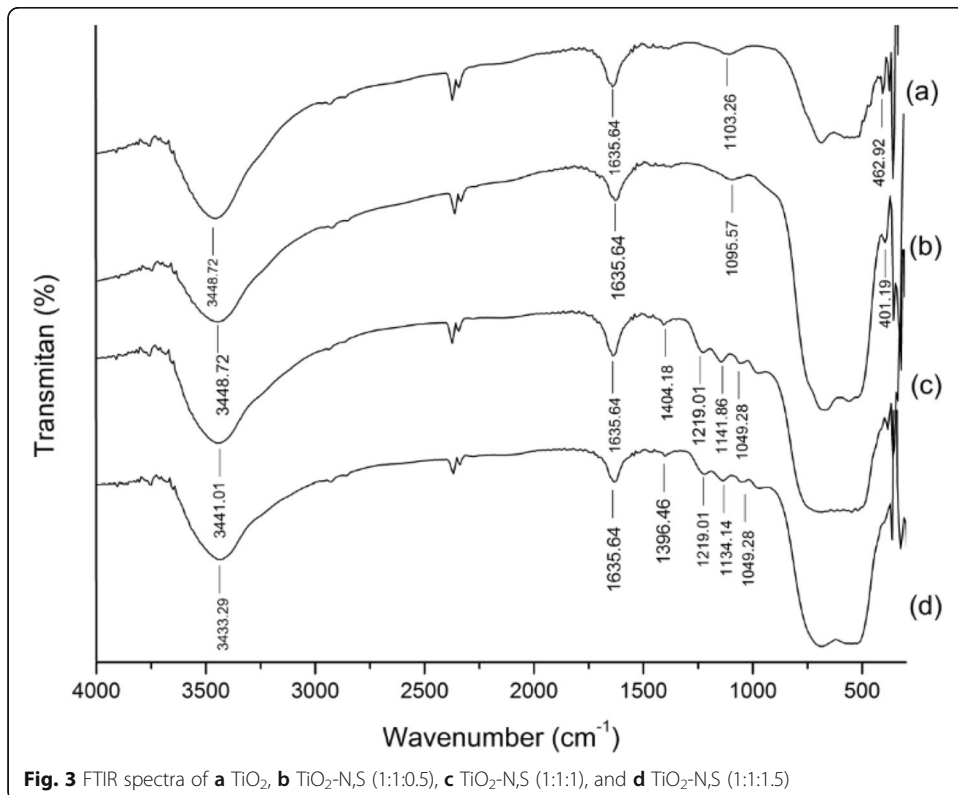
Fig. 3 FTIR spectra of **a** TiO$_2$, **b** TiO$_2$-N,S (1:1:0.5), **c** TiO$_2$-N,S (1:1:1), and **d** TiO$_2$-N,S (1:1:1.5)
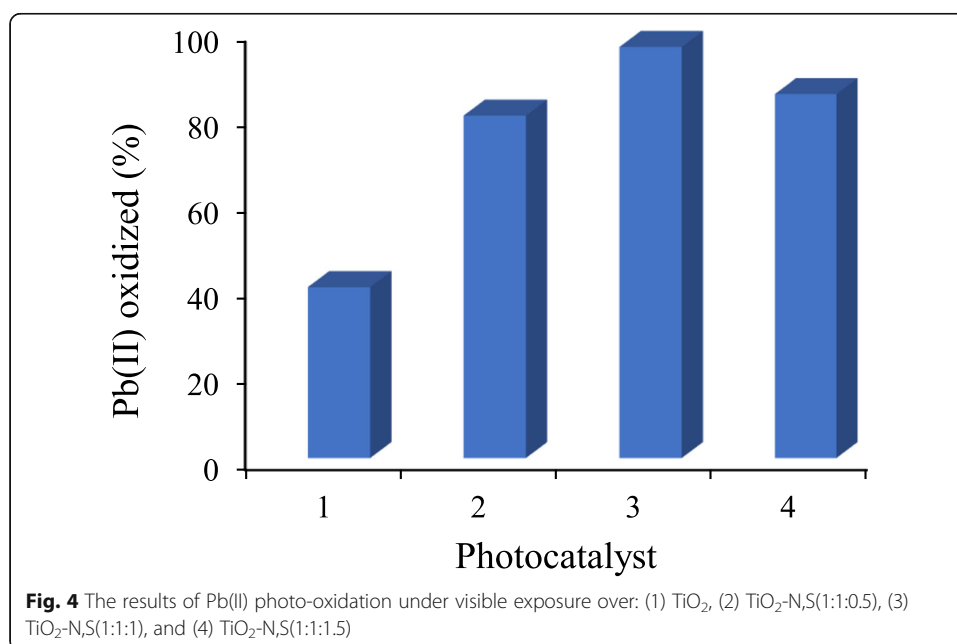
FTIR data

Several characteristic peaks belonging to TiO_2 are notable in the FTIR spectra as seen in Fig. 3. The characteristic peaks of TiO_2 appearance at 700–500 cm^{-1} of the wavenumbers belonged to the O–Ti–O bond. The other peaks also appear at about 3400 and 1630 cm^{-1} associated with O–H from water adsorbed on the TiO_2 surface [9, 10, 15]. The spectra of all TiO_2-N,S samples are similar to that of TiO_2, with several new peaks at about 1390–1405, 1219, 1134–1140, and 1049 cm^{-1} of the wavenumbers. Further, the intensities of the new peaks are seen sharper as the enlargement of the S content. The peak appearing at 1396–1404 cm^{-1} was related to NO vibration. The additional peaks observed at 1049 cm^{-1} is attributable to S–O–bond that of at 1134–1140 and 1219 cm^{-1} correspond to S=O from sulfate [9, 10, 15]. The absorbance of S-O and S=O vibrations are notable only in the co-doped TiO_2 with higher S content, and the absorbance is insignificant in TiO_2-N,S with the lowest S content. Further, the absorbance of S–O and S=O vibrations are sharper with an increase in the amount of the S doped. It is assigned that with the small sulfuric acid concentration, the S doping is undetectable, and by introducing higher concentration doping N and S have been successfully proceeded [9, 10, 15].

Photocatalytic activity of the co-doped TiO_2 in the temoval of Pb(II) under visible light
Influence of co-doping

It is observable in Fig. 4 that co-doping promotes higher removal of Pb(II) under visible light compared to the undoped. Moreover, increasing the amount of S doped in co-doped TiO_2 has improved the removal, but the opposite effect is seen when the amount of S dopant is further enlarged. The improvement of the photo-oxidation in the presence of the co-doped under visible light illumination is promoted by narrowing the gap or reducing the Eg, allowing TiO_2 to be responsive by visible light. In addition, the dopant atoms can also service

Fig. 4 The results of Pb(II) photo-oxidation under visible exposure over: (1) TiO_2, (2) TiO_2-N,S(1:1:0.5), (3) TiO_2-N,S(1:1:1), and (4) TiO_2-N,S(1:1:1.5)

separation of the photogenerated electrons and hole by capturing the electrons [5, 11, 12, 14], which detains the recombination. In contrast, when the S dopant is in excessive amount, the role of the dopant switches into the recombination center [5, 6, 11, 15], which accelerates the recombination, and thus diminishes the Pb(II) removal.

The Pb(II) ion removal from the aqueous media under visible light and in the presence of TiO_2-N.S can be stimulated by 3 possible reactions. The first reaction is precipitation of Pb^{2+} with ^-OH anionic into $Pb(OH)_2$, written as reaction (4), that can only occur at pH higher than 7. The photocatalytic reaction was conducted at pH 5, suggesting that no precipitation of $Pb(OH)_2$ occurs.

$$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2 \tag{4}$$

The second possibility is the reduction of Pb^{2+} induced by electrons released by TiO_2 during light irradiation into Pb^0 following reaction (5) [22]. Since the standard reduction potential is a negative value suggesting that the reduction is impossible thermodynamically [20, 21].

$$Pb^{2+} + 2\,e^- \rightarrow Pb^0 \qquad E^o = -0.13\text{ V} \tag{5}$$

The last possible reaction is oxidation by hole (h^+) with oxidation potential as much as 3.5 V, exhibiting a strong oxidizing agent. In addition to the hole, OH radical also acts as a strong oxidizing agent with 2.8 V of the oxidation potential. The oxidation of Pb^{2+} with OH radicals to be $Pb(IV)O_2$ is represented by reactions (6) and (7).

$$h^+ + ^{\boxtimes}OH \rightarrow OH \tag{6}$$

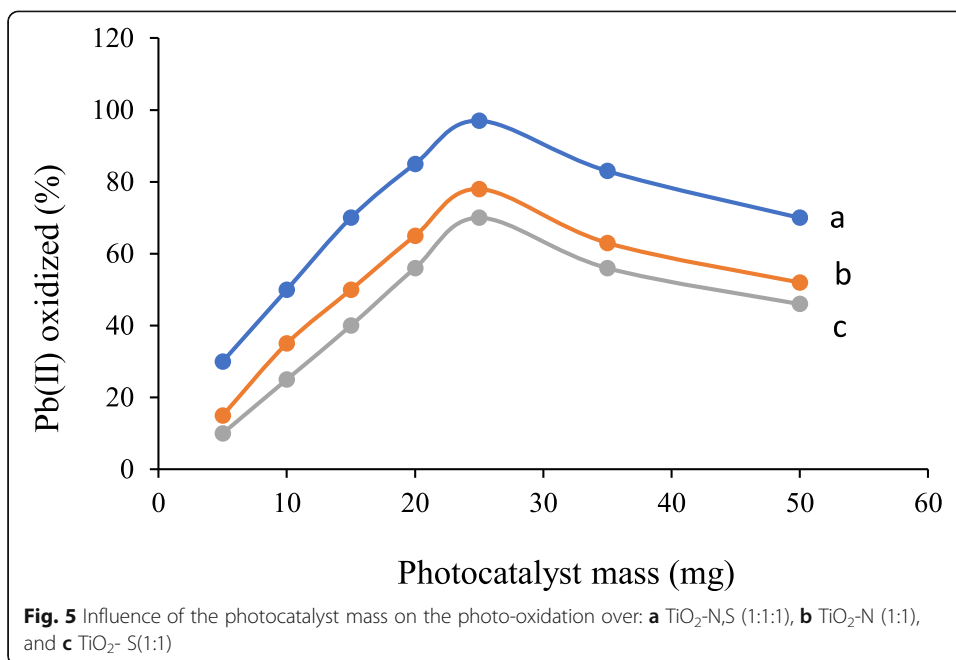$$Pb^{2+} + 2\,OH \rightarrow PbO_2 + 2H^+ \tag{7}$$

It is known that the standard reduction potential of Pb(IV)/Pb(II) is -0.67 V [21], implying that the reduction is unlikely to proceed. Hence, it is obvious that photooxidation of Pb(II) is more favorable. The more possible oxidation of Pb(II) is in agreement with the study reported [23] that Pb(II) could be oxidized by chlorine and was accelerated by Mn(VII).
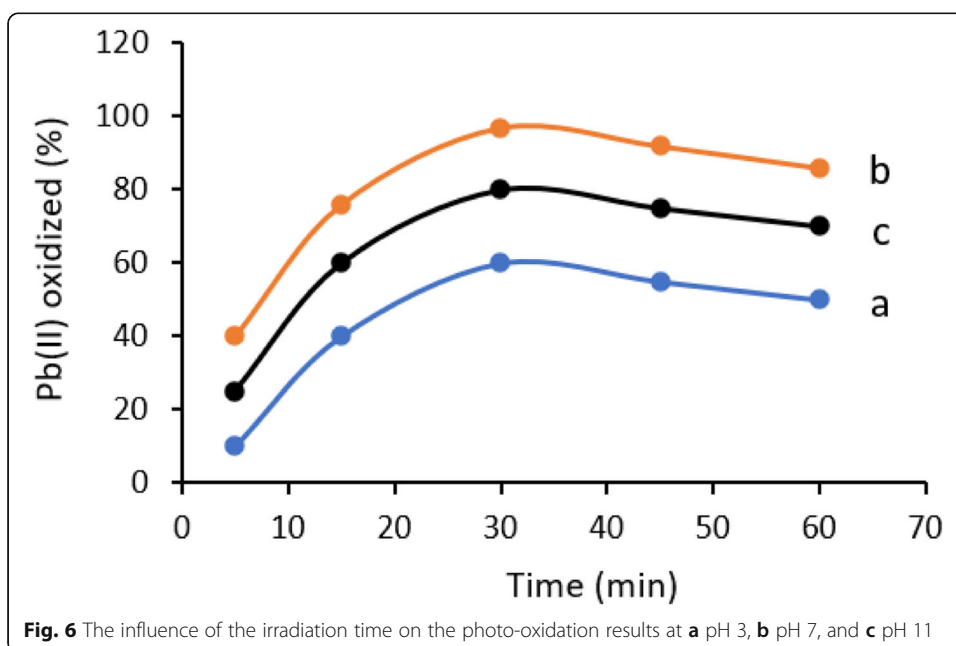
Influence of photocatalyst mass
The photocatalytic removal of Pb(II) is significantly controlled by photocatalyst mass, as displayed in Fig. 5. Notably, the effectiveness of the Pb(II) removal enhances sharply with the enlargement of the photocatalyst mass, but the oxidation is detrimental when the mass is in excess. With the higher photocatalyst mass, more OH radicals can be provided. Also, enhancing the photocatalyst mass can enlarge the active surface of the photocatalyst that improve the Pb(II) adsorption to be oxidized by OH radicals. The more number of OH radicals and Pb(II) adsorbed is beneficial to accelerate the photooxidation that reaches the maximum result.

The photocatalyst mass exceeding the optimum level (35 mg) can escalate significantly the turbidity, which hinders the penetration of the light. Consequently, the number of OH radicals formed may be declined and thus diminish photooxidation. A study also obtained similar results [10, 15].

Fig. 5 Influence of the photocatalyst mass on the photo-oxidation over: **a** TiO$_2$-N,S (1:1:1), **b** TiO$_2$-N (1:1), and **c** TiO$_2$- S(1:1)

Moreover, the figure also demonstrates that co-doping results in higher oxidation compared to the mono-doped. It is evidence that co-doping can noticeably increase the visible responsive of TiO$_2$ and effectively prevent the recombination, due to the synergic effect of the double dopants [8, 11–14]. The higher photooxidation of Pb(II) shown by TiO$_2$-N over that of TiO$_2$-S implies that the effect of doping N is more effective than S dopant. This trend was also reported as well [6].

Fig. 6 The influence of the irradiation time on the photo-oxidation results at **a** pH 3, **b** pH 7, and **c** pH 11

Influence of the irradiation time

Figure 6 demonstrates a sharp incremental of the Pb(II) photooxidation as the extending time up to 30 min, but there is a negative effect with the longer time than 30 min. Prolonging time of the irradiation facilitates TiO_2 to provide more OH radicals and also allows OH radicals to contact with Pb^{2+} effectively. With the longer than 30 min, the solid of PbO_2 resulting from the oxidation may be formed in a larger amount [9, 10, 15, 20], which can cover the surface of the photocatalyst. In accordance, the formation of OH radicals is fewer, and thus, the photooxidation of Pb(II) declines. Some studies have also found a similar trend [9, 10, 15, 20].

Influence of pH solution

The photooxidation effectiveness with the alteration pH can also be seen in Fig. 6. Increasing pH up to 7 exhibits an elevation of the effectiveness, but the contrary effect is seen at pH higher than 7. At lower pH, the surface of TiO_2 is protonated to be positive charge [8, 10, 11, 21], presented as reaction (7), that prevents providing OH radicals, and Pb(II) exists prominently as Pb^{2+} [19–21]. The same charges of the photocatalyst surface and Pb(II) ions restrict the adsorption of Pb^{2+} on the surface of TiO_2. The fewer OH radicals and low Pb^{2+} adsorption explain the low photooxidation of Pb^{2+} by OH radicals on the surface of the photocatalyst. At higher pH, the protonation should decrease or quiet, allowing TiO_2 to form OH radicals maximally and to adsorb Pb^{2+} effectively, which is beneficial in the high photooxidation. When the pH is climbed up to basic condition (pH 9), the most surface of TiO_2 is in the negative forms, as seen in reaction 6 [11, 21], that is to form OH radicals. In such pH Pb(II) precipitates as $Pb(OH)_2$ [19, 21]. These conditions are certainly adverse for Pb^{2+} photooxidation by OH radicals.

Conclusions

It is evidence that N and S atoms from HNO_3 and H_2SO_4, respectively, have been successfully co-doped into TiO_2. The co-doping N,S into TiO_2 has significantly decreased the Eg from 3.2 eV into 2.53–2.95 eV depending on the dopant loaded and thereby noticeably improves the photocatalytic removal of Pb(II) under visible light. Furthermore, the effectiveness of Pb(II) photooxidation is found to be considerably directed by the fraction of dopants, and the optimum mole fraction of the dopants are Ti:N:S = 1:1:1. Additionally, by applying 0.5 g/L of the TiO_2-N,S (1:1:1) photocatalyst dose in 45 min of time and pH 7, the highest removal of 10 mg/L Pb(II) could be achieved that is approximately 98%. The removal of Pb(II) from the aqueous is due to the photocatalytic oxidation induced by OH radicals to form handleable PbO_2.

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Availability of data and materials

The data used and/or analyzed during the conduct of this study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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