Significantly photoinduced synergy between sodium sulfite and ammonium nitrate and the mechanism study

Wen-Na Hu, Jian Liu, Wei Liu and Xian-Feng Zhang

ABSTRACT

In this paper, a significantly photoinduced synergy between ammonium nitrate and sodium sulfite via dye decolorization was first found. This study mainly aims to explore the influences of several fundamental aspects on the photoinduced synergy as well as discuss the detailed mechanisms. The dye removal efficiencies of methyl orange and methylene blue of the synergistic system are much higher than that of a single one, and they reach 96.4% and 90.7% when the illumination is 6 and 14 min, respectively. The optimum mass ratio of sodium sulfite and ammonium nitrate in the reaction system is 1:1. The reaction process of photoinduced synergy follows the first-order reaction equation. Effects of different structures of dyes, amount of sodium sulfite and initial dye concentration on the synergistic effect were investigated. The changes of UV-vis spectra in the course of photoinduced synergy were also examined. The excellent synergistic effect can owe to the simultaneous photoreduction and photooxidation reaction with respect to photoinduced hydrated electrons (e_{aq}^-) and $SO_4^{\bullet-}$ active species, respectively. This work may provide some insight into detoxifying water contaminants in practical applications as well as developing other novel photoinduced synergistic systems with high performance.

Key words | ammonium nitrate, decolorization, mechanism, sulfite, synergistic effect

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INTRODUCTION

Photocatalysis has attracted people's great attention over the past decades due to its broad application prospects in a number of significant fields of environmental pollution improvement (Jiang *et al.* 2017; Wang *et al.* 2017), hydrogen production by solar energy and biology (Qiu *et al.* 2017), manufacturing dye-sensitized solar cells (Guo *et al.* 2017; Yan *et al.* 2017), and so on. So far, a large number of photocatalysts including metal oxides (Freitag *et al.* 2015), sulfides (He *et al.* 2014), nitrides (Wang *et al.* 2014), their mixed solid solutions (Kato *et al.* 2015), and metallic or nonmetal acid salts (Meng *et al.* 2015) have been extensively used to degrade organic contaminant. At the same time, numerous attempts about modification have been developed by many researchers at home and abroad, such as noble metals deposition, doping transition metals, doping non-metallic elements, surface photosensitization and construction of composites (Li *et al.* 2015), etc., to improve the quantum efficiency and expand the scope of practical application. However, there are still some problems to be solved in their applications, because the photocatalytic performance is limited by the low quantum efficiency, poor selectivity, the instability and undesirable structure of semiconductors themselves (Bokare & Choi 2014). Therefore, great efforts are to be devoted to developing novel photocatalysts or photoinduced reaction systems with high activity and high selectivity for their applications in the field of photocatalysis.

Recently, the bis-ions coexistence system of NH_4^+ and NO_3^- (denoted as BICS hereafter) was found to present a capability for the decolorization of soluble dyes under UV or solar light irradiation in our previous report (Chen *et al.* 2011). It is a remarkable fact that the color removal by BICS is a photocatalytic reduction reaction, during which ammonium nitrate plays a photocatalyst role. The reason is that $NO_3^{\bullet}$ radicals and hydrated electrons (e_{aq}^-) are produced from NO_3^- under light illumination, and then the quick reaction of e_{aq}^- with the π bonds in chromophore of dyes leads to an immediate decolorization. From the viewpoint of practical applications, however, the decolorization efficiency of dyes is not high and it will take a long time to decolorize them completely. Hence, there is still a quite far distance from the expected goal. To improve the

decolorization efficiency and put the application into practice, construction of a new synergistic reaction system between BICS and other substrates with photoinduced property may be a good strategy. Considering the dye decolorization by BICS is a photocatalytic reduction process containing hydrated electrons (e_{aq}^-) and free radicals reactions, the selected candidate that also involves e_{aq}^- and active species in the course of reaction is of great importance to the possible synergistic effect. It was demonstrated that the photoinduced oxidation of sulfite to sulfate was a significant chemical process, during which high active species would be produced (Wang *et al.* 2009). As a consequence, it has great potential application values in sewage disposal. As a matter of fact, it was reported that the homogeneous iron–sulfite (Guo *et al.* 2013) and heterogeneous rectorite–sulfite (Shi *et al.* 2014) were the systems associated with sulfite to efficiently degrade organic pollutants. To the best of our knowledge, however, the homogeneous system consisted of ammonium nitrate and sodium sulfite possessing synergistic effect has not been reported. Therefore, it is particularly urgent and important that investigation on the key controlled factors that affect the synergistic system along with the photoinduced reaction mechanisms. This work not only provides a new idea and way for the removal of organics, but also has important guiding significance to construct other homogeneous synergistic systems.

In this work, ammonium nitrate and sodium sulfite are the respective substitute for BICS and sulfite to simplify the research work. It is first reported that the photoinduced synergistic dye removal between ammonium nitrate and sodium sulfite with its application in removal of dyes. Methyl orange (MO), sunset yellow FCF, carmine, orange G, ponceau S, naphthol green B, methylene blue (MB) and indigo were employed here to carry out the experiment. Several fundamental aspects regarding the effects of different structures of dyes, illumination time, the ratio of ammonium nitrate and sodium sulfite, the dosage of ammonium nitrate, and initial dye concentration on the dye removal efficiency are investigated. The kinetics and changes of UV-vis spectra in the process of photoreaction were researched as well. The possible reaction mechanisms of photoinduced synergy were also discussed systematically and in detail.

EXPERIMENTAL

Materials

The anhydrous sodium sulfite used in the experiments was purchased from Sinopharm Chemical Reagent Co., Ltd.

Ammonium nitrate, tert-butyl alcohol, sunset yellow FCF, carmine, orange G and ponceau S were supplied by Aladdin Industrial Corporation. Methyl orange (MO), naphthol green B, methylene blue (MB) and indigo were purchased from Shanghai Baoman Bio-Technique Co. Ltd. Ethanol was supplied by Anhui Ante Food Co. Ltd. Ammonium nitrate was dried at 70 °C in air and ground in the agate mortar before use. All chemicals were of analytically pure grade and used without further purification. Deionized water was used throughout this study.

Experimental procedure and analysis

Experiments were carried out in a photoreaction apparatus as same as our earlier report (Chen *et al.* 2011). Briefly, a 375 W medium pressure mercury lamp was purchased from Beijing Institute of Electric Light Source and laid in the chamber of annular quartz tube to use as the light source in the research work. The maximum emission wavelength of the lamp located at approximately 365 nm. The circulating cooling water passed through the inner thimble of annular tube to remove immediately the heat released from the lamp. A 500 mL unsealed beaker of 12 cm diameter was used as the reaction vessel. The temperature of the reaction solution is monitored no more than 25 °C during the experiment. Prior to the experiment, the 50 mL dye and 0.1 g sodium sulfite (ammonium nitrate) were put in the unsealed beaker, and a magnetic stir bar was used to blend the reaction solution. The distance between the light source and the surface of the reaction solution is 11 cm. The UV irradiation intensity (wavelengths below 400 nm) on the reaction solution surface is about 18,300 µW/cm^2. The schematic diagram of photoreaction apparatus is shown in Figure 1.
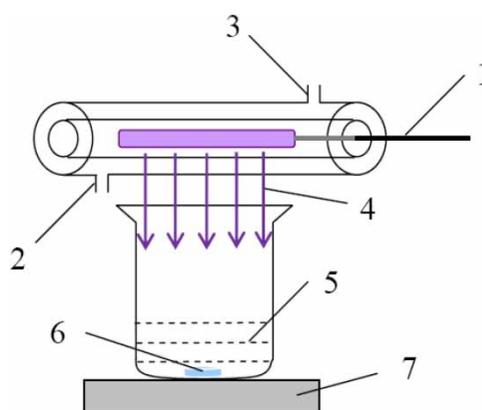

Figure 1 │ Schematic diagram of photoreaction apparatus. 1 – lamp; 2 – cooling water inlet; 3 – cooling water outlet; 4 – light; 5 – reaction solution; 6 – magnetic stir bar; 7 – magnetic stirrer.

The concentration of dyes in solution was determined spectrophotometrically. At the given time intervals, the concentration of dye was determined by a spectrophotometer from its maximum absorption at a wavelength of 464 nm for MO and 664 nm for MB with deionized water as a reference sample. The photoinduced decolorization efficiency of dyes η was calculated from the following expression:

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 is the initial concentration of dyes before illumination. The respective initial concentrations of MO and MB were 10.0 and 2.5 mg/L without special introductions. C is the concentration of dyes after the illumination time t.

RESULTS AND DISCUSSION

Effects of different dye structures on the photoinduced synergy

To account for different kinds of dyes on the synergistic effect, various dyes with different structures were employed to conduct the experiments within 2 min illumination. The concentration of sodium sulfite and ammonium nitrate is 2.0 g/L, respectively. The initial concentration (C_0) of dyes, different structures of dyes, the synergistic decolorization efficiency (η) between ammonium nitrate and sodium sulfite are listed in Table 1. For comparison, the individual color removal efficiency of dyes by ammonium nitrate (η_1) and sodium sulfite (η_2) are also shown in the table. As shown in Table 1, various dyes such as MO, sunset yellow FCF, carmine, orange G, ponceau S, naphthol green B, MB, indigo, etc., can be decolorized by sodium sulfite and ammonium nitrate, respectively. Remarkably, it is worth noting that these dyes are more easily degraded by the synergetic system consisted of sodium sulfite and ammonium nitrate. Furthermore, it is noticeable that $\eta > \eta_1 + \eta_2$, which indicates the synergistic effect for decolorization is obvious between sodium sulfite and ammonium nitrate under the experimental conditions. For example, it is known that the color removal efficiencies of MO by ammonium nitrate (η_1), sodium sulfite (η_2) and the corresponding synergistic decolorization efficiencies (η) are 2.8%, 21.7% and 41.4%, and those of MB reaches 8.4%, 13.6% and 59.0%, respectively.
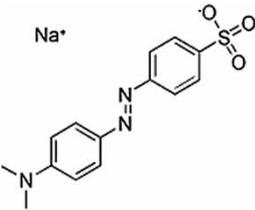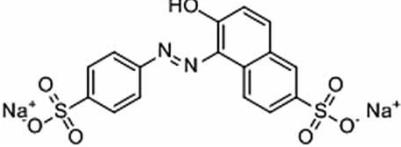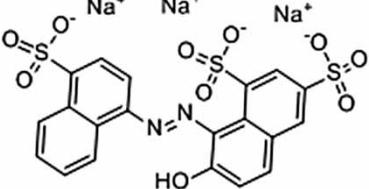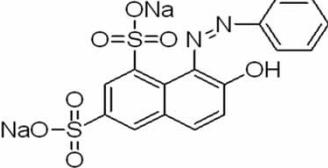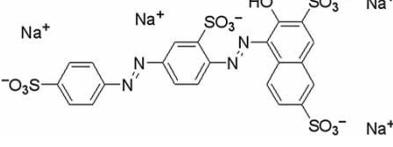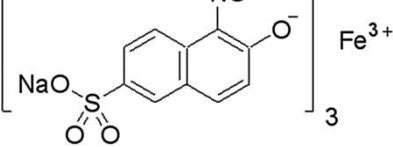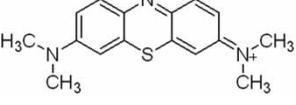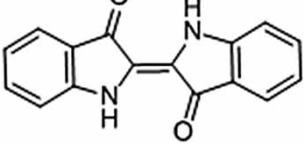
Effect of illumination time

MO and MB were chosen as typical representations of the familiar dyes to investigate the impact of illumination time on the synergistic effect between ammonium nitrate and sodium sulfite. The concentration of both ammonium nitrate and sodium sulfite is 2.0 g/L. Effect of illumination time on the synergistic effect for MO and MB is illustrated in Figure 2(a) and (b), respectively. For comparison, the decolorization efficiency of dyes by single ammonium nitrate or sodium sulfite was also tested under the same conditions. The blank experiment showed that the photoinduced self-degradation efficiency of dyes was little under a short-time illumination. As seen from Figure 2(a), the color removal efficiency of the mixing solution of ammonium nitrate, sodium sulfite with MO in dark could be negligible. MO can be decolorized undoubtedly by ammonium nitrate, sodium sulfite and the synergistic system consisted of them. As for MO, all of the decolorization efficiencies improve with the increasing illumination time, but the color removal efficiency for the synergistic system enhances the most rapidly among the variation tendencies. In other words, ammonium nitrate and sodium sulfite exhibit excellent synergistic effect, and the decolorization efficiency of MO can reach up to 96.4% after 6 min illumination. As shown in Figure 2(b), similar results were found in regard to MB, although the removal efficiency of the mixing solution of ammonium nitrate, sodium sulfite with MB in the dark increased slightly. The decolorization efficiency of MB improves remarkably from 0 to 85.9% with the increasing illumination time from 0 to 6 min, and then increases slowly to 90.7% when the illumination time is 14 min. The enhanced photoinduced decolorization efficiency may be attributed to the simultaneous interaction between dyes and the cumulative e_{aq}^- as well as $SO_4^{\bullet-}$ with the gradual illumination time.

Effect of the mass ratio of ammonium nitrate and sodium sulfite

The total mass weight of ammonium nitrate and sodium sulfite with different ratios varying from 10:1, 5:1, 1:1, 1:5, to 1:10 was 0.2 g. The experiments were performed after they were dissolved in 50 mL dyes. The mass ratio of ammonium nitrate and sodium sulfite has an obvious synergistic effect on the dye removal efficiency. The result is shown in Figure 3. From Figure 3(a) and (b), it can be seen that all of the systems containing different ratios of ammonium nitrate and sodium sulfite have good photoinduced synergy.

Table 1 | Effects of different dye structures on the photoinduced synergy[a]

Entry	Dyes	C_0 (mg/L)	Structure of dyes	η_1 (%)	η_2 (%)	η (%)
1	Methyl orange (MO)	10.0		2.8	21.7	41.4
2	Sunset yellow FCF	10.0		6.3	25.8	45.3
3	Carmine	10.0		8.2	27.5	47.6
4	Orange G	10.0		7.8	6.4	20.8
5	Ponceau S	10.0		8.8	17.2	34.4
6	Naphthol green B	5.0		5.9	10.6	31.7
7	Methylene blue (MB)	5.0		8.4	13.6	59.0
8	Indigo	10.0		7.0	16.3	34.8

[a]Illumination time = 2 min; Concentration of both ammonium nitrate and sodium sulfite = 2.0 g/L.
η_1: the decolorization efficiency of dyes by ammonium nitrate.
η_2: the decolorization efficiency of dyes by sodium sulfite.
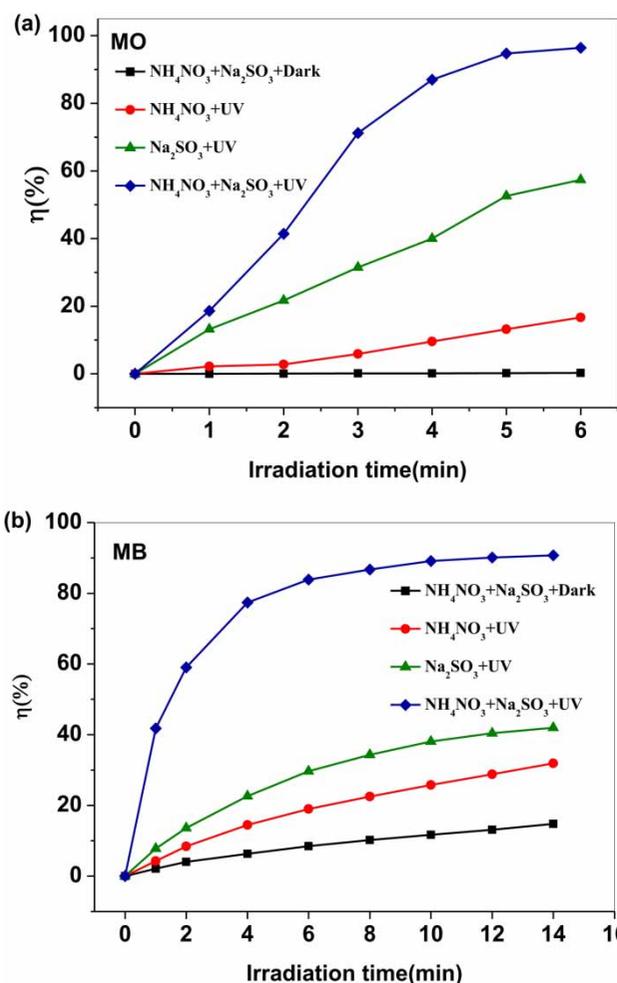η: the synergistic decolorization efficiency of dyes by sodium sulfite and ammonium nitrate.

Figure 2 │ Effect of illumination time on the photoinduced synergy for MO (a) and MB (b) decolorization.

Figure 3 │ Effect of the mass ratio of ammonium nitrate and sodium sulfite on the photoinduced synergy for MO (a) and MB (b) decolorization.

The synergistic decolorization efficiencies of MO and MB improve remarkably with increasing ratio of ammonium nitrate and sodium sulfite, although at the higher ratios, e.g. 5:1 and 10:1, the synergistic removal efficiency decreases, suggesting that the optimal ratio of ammonium nitrate and sodium sulfite is 1:1. When the ratio is smaller or larger than 1:1, the system prevents the active radicals from producing, which implies the synergistic effect will become lower. This result also noticeably indicates that both ammonium nitrate and sodium sulfite play a vital role in enhancing the photoinduced synergy. That is to say, only ammonium nitrate and sodium sulfite have an appropriate ratio, the wonderful photoinduced synergistic effect can be highlighted. Based on the above results, it demonstrates that the photoinduced synergistic effect indeed exists between ammonium nitrate and sodium sulfite, and the initial design is correct in the present study.
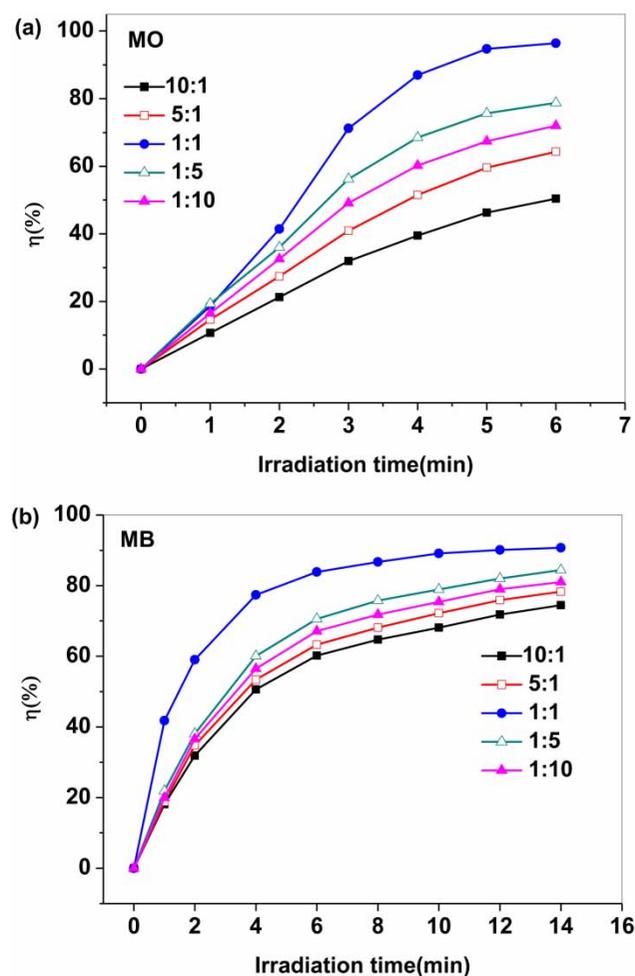
Effect of sodium sulfite concentration

The illumination time was 2 min. The mass ratio of ammonium nitrate and sodium sulfite was fixed at 1:1. Effect of dosage of sodium sulfite (or ammonium nitrate) on the photoinduced decolorization efficiency of MO and MB are depicted in Figure 4. It is evidently seen that the synergistic degradation efficiency of MO changes extraordinarily from 17.2% to 58.3% and that of MB enhances quickly from 39.5% to 67.6%, as the sodium sulfite dosage increases from 0.5 to 4.0 g/L. While the concentration is beyond 4.0 g/L, a relatively smaller enhancement of the removal efficiency is observed. When the sodium sulfite concentration is 8.0 g/L, the photoinduced decolorization efficiency of MO and MB is 65.4% and 72.4%, respectively. Hence, the suitable amount of sodium sulfite is 4.0 g/L for the fading of the MO and MB in this study. It is known to all that NO_3^- and SO_3^{2-}
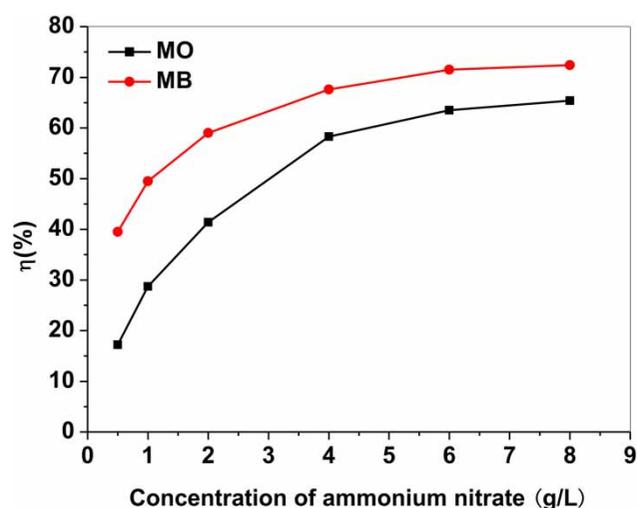
Figure 4 │ Effect of sodium sulfite concentration on the photoinduced synergy.

contain the nitrogen to oxygen double bond (–N = O–) and the sulphur to oxygen double bond (–S = O–), respectively, which conduces they are only excited by UV light. The increasing amount of sodium sulfite will improve the quantity of photons absorbed, which favors the synergistic effect and results in the enhanced decolorization efficiency. Similar results were observed in our earlier report (Liu *et al.* 2013).

Effect of initial dye concentration

As shown in Figure 5, the photoinduced decolorization efficiencies of dyes diminish with their initial concentration. As for MO, the photoinduced removal efficiency is 57.6% as the initial concentration is 5 mg/L, while that is 20.2% corresponding to 25 mg/L. With regard to MB removal, its efficiency is 59.0% and 22.8% when the respective original concentration is 2.5 and 12.5 mg/L. The decolorization occurs mediated by
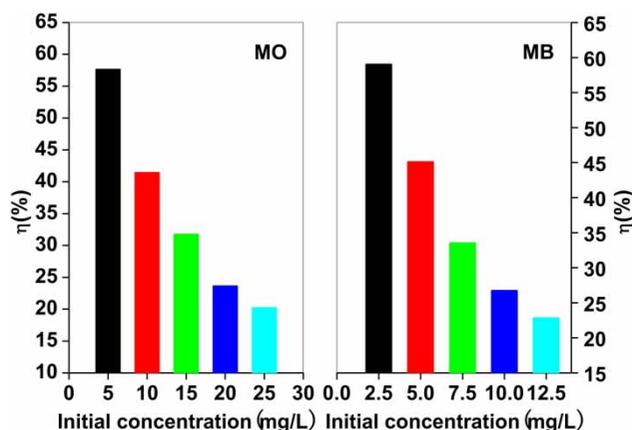

Figure 5 │ Effect of initial dye concentration on the photoinduced synergy.

the direct reaction between sulfate radical ($SO_4^{\bullet-}$) and the dye (see section on Proposed reaction mechanisms in the present study). When both sodium sulfite and ammonium nitrate have unchanging concentration with consequently constant active species available for photoreaction, the synergistic effect tends to decrease with the increasing initial concentration of dyes. The same result was reported in previous study involved sulfite oxidation process (Wang *et al.* 2009).

Reaction kinetics

According to the method to determine the degradation kinetics for organic pollutants in previous report (Liu *et al.* 2013), we attempted to obtain linear function for dye removal using several usual kinetics equations. Then the first-order reaction kinetics was established by making a linear plot of $\ln(C_0/C)$ against illumination time. The kinetics for the decolorization of MO and MB are shown in Figure 6. As shown in Figure 6(a), the
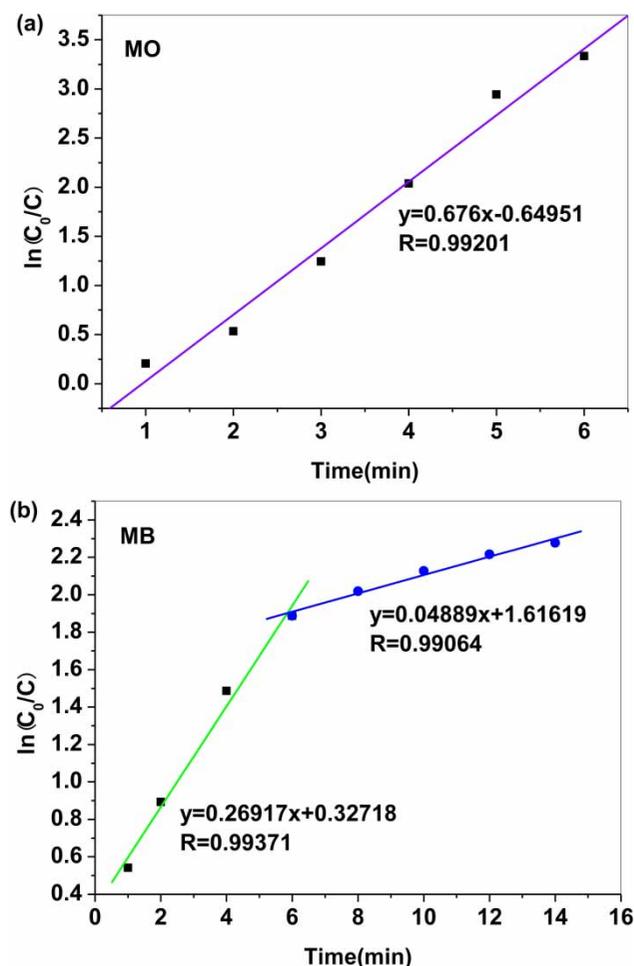

Figure 6 │ Kinetics of photoinduced synergy for the decolorization of MO (a) and MB (b).

first order kinetics equation for MO removal is y = 0.676x-0.64951 with the corresponding correlation coefficient of 0.99201. While there are two linear regions in Figure 6(b) for the photoinduced decolorization of MB, namely, when the illumination time is 0–6 min and 6–14 min, the corresponding linear equation is y = 0.26917x + 0.32718 and y = 0.04889x + 1.61619, respectively. The related coefficient of linear fitting in the plane figure is quite good to be 0.99371 and 0.99064, respectively. From Figure 6, it also can be seen that the two apparent reaction rate constants for photoinduced decolorization of MB are 0.26917 min^{-1} and 0.04889 min^{-1}, respectively, and that of MO is 0.676 min^{-1}. The above analysis reflects indirectly that the reaction of ammonium nitrate, sodium sulfite with dyes is independent, but they influence each other during the reaction process, namely, one ongoing reaction will give rise to the quick response of another reaction and facilitate it.

Changes of UV-vis spectra

UV-vis absorption spectroscopy measurements were carried out using a HITACHI U-3900 UV-VIS spectrophotometer. The amount of both sodium sulfite and ammonium nitrate used was 2.0 g/L. The absorption spectra changes of MO and MB solution in the process of photoinduced synergy at given minutes are shown in Figure 7. As shown in Figure 7(a), the spectrum of MO exhibits a maximum absorption peak at 464 nm in the visible region. And that MO can be decolorized by the system consisted of ammonium nitrate and sodium sulfite, pure ammonium nitrate, and pure sodium sulfite. Nevertheless, compared to the inserted plot in Figure 7(a), it is conspicuous that the decolorization efficiency of MO by the synergistic system is far greater than that by pure ammonium nitrate and pure sodium sulfite, because of the favorable generation of photoinduced synergistic effect in the system. There is still a strong absorption intensity of MO at 464 nm by employing single ammonium nitrate or sodium sulfite after 6 min irradiation, while almost no absorption peak can be seen by using the photoinduced synergistic system under the same conditions. The results are in good agreement with the removal efficiency of MO investigated in section on Effect of illumination time in this article. Similarly, Figure 7(b) shows absorption spectral changes of MB during the fading process. It is clearly seen that there are two main absorption peaks at 664 nm and 610 nm for MB, corresponding to the characteristic structure of its monomer and dimer, respectively (Morgounova *et al.* 2013). The decolorization efficiency of MB at 664 nm increases rapidly at the beginning
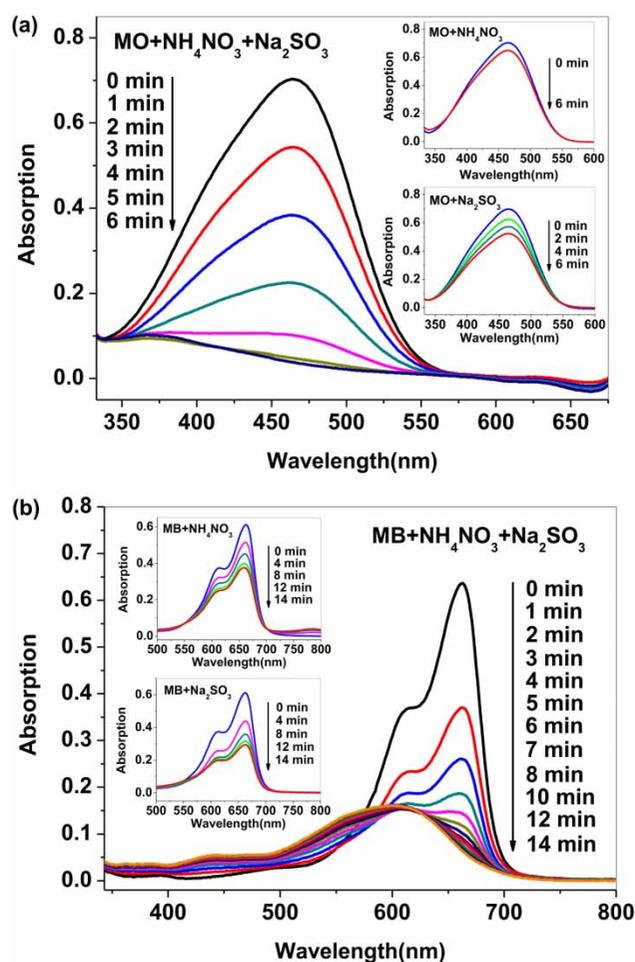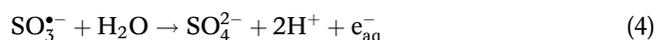

Figure 7 │ UV-vis absorption spectra changes of MO (a) and MB (b) in the process of photoinduced synergy.

of 6 min. And then with the illumination time increasing from 6 to 14 min, the absorption intensity of dimer has almost no change, which causes the removal efficiency of MB at 664 nm improved slightly. The same results are also verified in Figure 2. These results once again demonstrated the evidence between sodium sulfite and ammonium by decolorization of dyes.
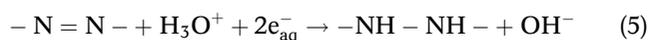
Proposed reaction mechanisms

Based on the above results, it is known that sodium sulfite and ammonium nitrate participate in the chemical reaction simultaneously. Under UV light illumination, the $NO_3^{\bullet}$, $SO_3^{\bullet-}$ radicals and hydrated electrons (e_{aq}^-) are produced. These electron-transfer steps are as follows (Tacconi *et al.* 2000):

$$NO_3^- + h\nu \rightarrow NO_3^{\bullet} + e_{aq}^- \tag{2}$$

$$SO_3^{2-} + h\nu \rightarrow SO_3^{\bullet-} + e_{aq}^- \tag{3}$$

$$SO_3^{\bullet-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + e_{aq}^- \tag{4}$$
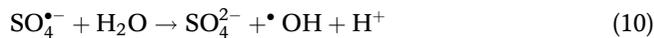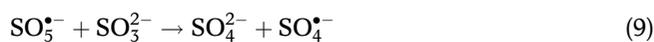
As shown in Equations (2)–(4), 1 mol SO_3^{2-} and NO_3^- can generate 2 mol and 1 mol hydrated electron under the experimental conditions, respectively. After introducing sodium sulfite, the abundant hydrated electrons in the system accelerate the migration of e_{aq}^- to the surface of dye molecules and are helpful to improve the photoreduction reaction rate as well. Because it was demonstrated that the dye removal by ammonium nitrate was a photoreduction reaction, in which the hydrated electrons (e_{aq}^-) reacts immediately with the chromophore and results in the quick decolorization (Chen *et al.* 2011). The overall reaction for MO decolorization can be expressed as Equation (5) according to some related reactions in the literature (Földváiry & Wojnáirovits 2009), which is similar to MB removal. Furthermore, the ammonium nitrate served as a photocatalyst and it was proposed that NO_3^- and NH_4^+ transformed themselves into each other, as shown in Equations (6) and (7).

$$-N = N- + H_3O^+ + 2e_{aq}^- \rightarrow -NH-NH- + OH^- \tag{5}$$

$$NH_4^+ + 2NO_3^{\bullet} \rightarrow 3NO_2^{\bullet} + 3H^{\bullet} + H^+ \tag{6}$$

$$NO_2^{\bullet} + OH^- \rightarrow NO_3^- + H^{\bullet} \tag{7}$$

At the same time, according to the reported result (Chen *et al.* 2012), it is known that $SO_3^{\bullet-}$ anion radicals are not stable, which can react very rapidly with O_2 and generates $SO_5^{\bullet-}$ and $SO_4^{\bullet-}$ radicals, as shown in Equations (8)–(10). Consequently, they not only produce $SO_5^{\bullet-}$, $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals but also react with molecular oxygen in the system, promoting the decolorization efficiency of dyes enhanced greatly. The fading of MB first increases rapidly before 6 min, implying unstable $SO_3^{\bullet-}$ transforms to other more active species. With the increasing illumination time from 6 to 14 min, the decolorization efficiency of MB improves slightly, indicating that oxygen depletion prevents the transformation of $SO_3^{\bullet-}$ to $SO_5^{\bullet-}$, even less the generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$ active radicals. These demonstrate the correctness of experimental results in sections on Effect of illumination time and Changes of UV-vis spectra in this paper. Similar results were also reported (Shi *et al.* 2014).

$$SO_3^{\bullet-} + O_2 \rightarrow SO_5^{\bullet-} \tag{8}$$

$$SO_5^{\bullet-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} \tag{9}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \tag{10}$$

To further clarify the photoinduced reaction mechanism, quenching experiments were performed by using tert-butyl alcohol (TBA) and ethanol (EtOH) as the scavengers to identify $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals, respectively (Chen *et al.* 2012). As shown in Figure 8, the removal efficiency of MO is 41.4% without scavengers, while it decreases to 3.9% and 36.8%, respectively, after adding EtOH and TBA. It indicates that $SO_4^{\bullet-}$ is the main radicals in the synergetic system, while $^{\bullet}OH$ plays a minor role in the photoreaction process. The same conclusions were drawn for decolorization of MB. The additional experiment of total organic carbon (TOC) measurement was also conducted. With respect to MO, the TOC values was 15.6 mg/L before illumination, while it was only 0.58 mg/L after 6 min illumination, indicating that the mineralization of the organic dyes was satisfactory.

In short, the active species in the dye removal are e_{aq}^- and $SO_4^{\bullet-}$. In comparison with ammonium nitrate, the redundant e_{aq}^- origin from UV light induced SO_3^{2-} and the reaction of $SO_3^{\bullet-}$ with H_2O, which urges the photoreduction decolorization reaction is improved. Furthermore, the main active species $SO_4^{\bullet-}$ is a very strong oxidant and can react with dye molecule and reduction products. The synergistic effect finds expression in the significantly enhanced decolorization efficiency of dyes as a consequence. Both photoreduction reaction and photooxidation reaction are proceeded in the synergistic system. The proposed mechanism for dye removal by the synergistic system formed of ammonium nitrate and sodium sulfite is shown in Figure 9.
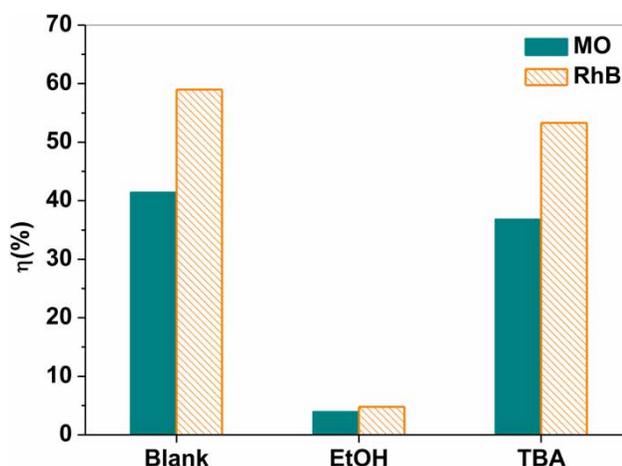

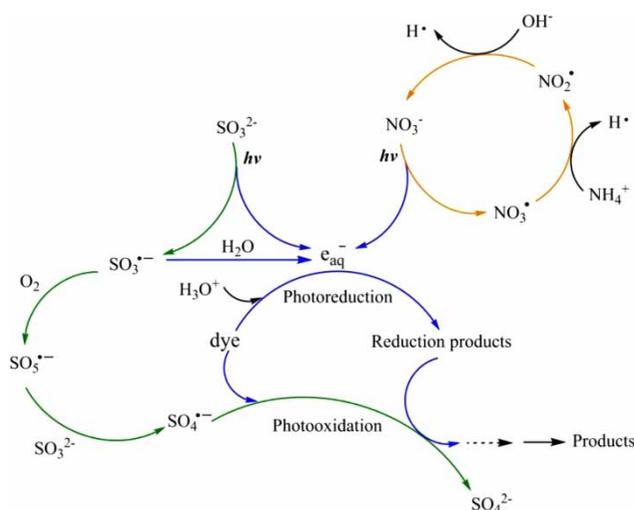**Figure 8** │ Effects of EtOH and TBA on the photoinduced synergy.

Figure 9 | Proposed mechanism for the photoinduced synergistic system between sodium sulfite and ammonium nitrate.

CONCLUSIONS

There exists a significant photoinduced synergy between sodium sulfite and ammonium nitrate via decolorization of dyes. The synergistic decolorization efficiencies of MO and MB in the system were much higher than that of a single one, and they reach 96.4% and 90.7% when the illumination is 6 and 14 min, respectively. The optimum mass ratio of sodium sulfite and ammonium nitrate in the reaction system is 1:1. The suitable amount of or sodium sulfite is 4.0 g/L. The photoinduced synergy for dyes decolorization decreases with the increasing initial concentration of dyes. The reaction process of photoinduced synergy obeys the first-order kinetics. The photogenerated hydrated electrons and $SO_4^{\bullet-}$ radicals in the system contribute to the greatly enhanced photoinduced synergy. The synergistic system is expected to be a good candidate for use in removal of organics. This work may provide some insight into the design of other novel photoinduced synergistic systems with high activity and high selectivity.

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REFERENCES

Bokare, A. D. & Choi, W. 2014 Review of iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes. *J. Hazard. Mater.* **275** (2), 121–135.

Chen, S. F., Liu, W., Zhang, H. Y. & Yu, X. L. 2011 Photocatalytic decolorization of soluble dyes by a bis-ions coexistence system of NH_4^+ and NO_3^- with high photoreduction ability. *J. Hazard. Mater.* **186** (2–3), 1687–1695.

Chen, L., Peng, X., Liu, J., Li, J. & Wu, F. 2012 Decolorization of orange II in aqueous solution by an Fe(II)/sulfite system: replacement of persulfate. *Ind. Eng. Chem. Res.* **51**, 13632–13638.

Földváíry, C. M. & Wojnáírovits, L. 2009 Role of reactive intermediates in the radiolytic degradation of Acid Red 1 in aqueous solution. *Radiat. Phys. Chem.* **78** (1), 13–18.

Freitag, J., Domínguez, A., Niehaus, T. A., Hülsewig, A., Dillert, R., Frauenheim, T. & Bahnemann, D. W. 2015 Nitrogen(II) oxide charge transfer complexes on TiO_2: a new source for visible-light activity. *J. Phys. Chem. C* **119** (9), 4488–4501.

Guo, Y., Lou, X., Fang, C., Xiao, D., Wang, Z. & Liu, J. 2013 A novel photo-sulfite system: towards simultaneous transformations of inorganic and organic pollutants. *Environ. Sci. Technol.* **47** (19), 11174–11181.

Guo, D. P., Xiao, S. Q., Fan, K. & Yu, J. G. 2017 Hierarchical TiO_2 submicrorods improve the photovoltaic performance of dye-sensitized solar cells. *ACS Sustainable Chem. Eng.* **5** (2), 1315–1321.

He, M., Lu, Z. Y., Zhou, W. C., Chen, T. T., Shi, W. D., Che, G. B., Huo, P. W., Zhu, Z., Zhao, X. X. & Yan, Y. S. 2014 A novel CdS photocatalyst based on magnetic fly ash cenospheres as the carrier: performance and mechanism. *RSC Adv.* **4** (104), 60148–60157.

Jiang, W. J., Zhu, Y. F., Zhu, G. X., Zhang, Z. J., Chen, X. J. & Yao, W. Q. 2017 Three-dimensional photocatalysts with a network structure. *J. Mater. Chem. A* **5** (12), 5661–5679.

Kato, T., Hakari, Y., Ikeda, S., Jia, Q. X., Iwase, A. & Kudo, A. 2015 Utilization of metal sulfide material of $(CuGa)_{1-x}Zn_{2x}S_2$ solid solution with visible light response in photocatalytic and photoelectrochemical solar water splitting systems. *J. Phys. Chem. Lett.* **6** (6), 1042–1047.

Li, G. S., Lian, Z. C., Li, X., Xu, Y. Y., Wang, W. C., Zhang, D. Q., Tian, F. H. & Li, H. X. 2015 Ionothermal synthesis of black Ti^{3+}-doped single-crystal TiO_2 as an active photocatalyst for pollutant degradation and H_2 generation. *J. Mater. Chem. A* **3** (7), 3748–3756.

Liu, W., Wang, M. L., Xu, C. X., Chen, S. F. & Fu, X. L. 2013 Significantly enhanced visible-light photocatalytic activity of g-C_3N_4 via ZnO modification and the mechanism study. *J. Mol. Catal. A: Chem.* **368–369** (1), 9–15.

Meng, F. K., Cushing, S. K., Li, J. T., Hao, S. M. & Wu, N. Q. 2015 Enhancement of solar hydrogen generation by synergistic interaction of $La_2Ti_2O_7$ photocatalyst with plasmonic gold nanoparticles and reduced graphene oxide nanosheets. *ACS Catal.* **5** (3), 1949–1955.

Morgounova, E., Shao, Q., Hackel, B. J., Thomas, D. D. & Ashkenazi, S. 2013 Photoacoustic lifetime contrast between methylene blue monomers and self-quenched dimers as a

model for dual-labeled activatable probes. *J. Biomed. Opt.* **18** (5), 056004-1–056004-8.

Qiu, B. C., Zhu, Q. H., Xing, M. Y. & Zhang, J. L. 2017 A robust and efficient catalyst of $Cd_xZn_{1-x}Se$ motivated by CoP for photocatalytic hydrogen evolution under sunlight irradiation. *Chem. Commun.* **53** (5), 897–900.

Shi, W., Cheng, Q., Zhang, P., Ding, Y., Dong, H. J., Duan, L., Li, X. X. & Xu, A. H. 2014 Catalytic decolorization of methyl orange by the rectorite–sulfite system. *Catal. Commun.* **56** (56), 32–35.

Tacconi, N. R. D., Maja Mrkic, A. & Rajeshwar, K. 2000 Photoelectrochemical oxidation of aqueous sulfite on Ni – TiO_2 composite film electrodes. *Langmuir* **16** (16), 8426–8431.

Wang, L., Ma, Y., Hao, J. & Zhao, Y. 2009 Mechanism and kinetics of sulfite oxidation in the presence of ethanol. *Ind. Eng. Chem. Res.* **48** (9), 4307–4311.

Wang, J. J., Feng, J. Y., Zhang, L., Li, Z. S. & Zou, Z. G. 2014 Role of oxygen impurity on the mechanical stability and atomic cohesion of Ta_3N_5 semiconductor photocatalyst. *Phys. Chem. Chem. Phys.* **16** (29), 15375–15380.

Wang, Y., Zhang, L. N., Zhang, X. Y., Zhang, Z. Z., Tong, Y. C., Li, F. Y., Wu, J. C.-S. & Wang, X. X. 2017 Openmouthed β-SiC hollow-sphere with highly photocatalytic activity for reduction of CO_2 with H_2O. *Appl. Catal. B: Environ.* **206**, 158–167.

Yan, Y., Shi, W. D., Yuan, Z., He, S. G., Li, D. M., Meng, Q. B., Ji, H. W., Chen, C. C., Ma, W. H. & Zhao, J. C. 2017 The formation of Ti–H species at interface is lethal to the efficiency of TiO_2-based dye-sensitized devices. *J. Am. Chem. Soc.* **139** (5), 2083–2089.