Effects of surface modification of TiO$_2$ with ascorbic acid on photocatalytic decolorization of an azo dye reactions and mechanisms

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Abstract

The formation of surface modification on TiO$_2$, which can be easily attained by a simple addition of ascorbic acid to aqueous TiO$_2$ suspensions, uniquely affects both photocatalytic reactions and mechanisms. Surface modification results in the formation of a colored surface complex that causes red shift of the absorption threshold of TiO$_2$, enhancing utilization of the solar spectrum. The decolorization rate of methyl orange, taken as a model for recalcitrant azo-dye, was observed to be the function of surface modified TiO$_2$ used during the process. It was found that surface modified TiO$_2$ was more effective for oxidation of azo bond than pure TiO$_2$ irradiated by both UV light and solar light. Through investigating the effects of dissolved oxygen, CCl$_4$ and *tert*-butyl alcohol on the decolorization of methyl orange, the mechanisms are proposed that the superoxides ($^{\bullet}$O$_2{}^{-}$) mediated oxidation pathways are dominant for cleavage of azo bond of methyl orange on surface modified TiO$_2$ with ascorbic acid, whereas the OH radical mediated oxidation pathways are largely inhibited due to the hindered complexation of ascorbic acid on the surface of TiO$_2$. Finally, elementary charge transfer process on surface modified TiO$_2$ and the implication to photocatalytic reaction pathway are discussed.
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Keywords: TiO$_2$; Ascorbic acid; Methyl orange; Azo bond; Superoxides

1. Introduction

Azo-dye pollutants from the textile industry are an important source of environment contamination. Indeed, these effluents are toxic and mostly non-biodegradable and also resistant to destruction by physicochemical treatment methods. Removing color from wastes is often more important than other colorless organic substances, because the presence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably [1–5].

Therefore, it is necessary to find an effective method of wastewater treatment in order to remove colors from textile effluents. In the recent 20 years, TiO$_2$ is the photocatalyst that is most extensively and intensively studied, and the applications of TiO$_2$ and its modification to photocatalytic

degradation of dyes have been extensively reported [6–9]. Generally, surface modifiers can affect the TiO$_2$ characteristics by three ways: (a) by inhibiting charge recombination; (b) by exploring the wavelength response range; (c) by changing the selectivity or yield of a particular product [10]. Ascorbic acid (widely known as Vitamin C), a naturally available compound, was used as a modifier in a solid-state cell based on TiO$_2$ and CuI and has been identified that photo-excited dye molecules inject electrons into the conduction band of TiO$_2$ and holes into the valence band of CuI [10–12]. But there has yet no report about the effects of surface modification with ascorbic acid on TiO$_2$ photocatalytic oxidation (PCO) systems for azo-dye. Special attention is focused on our research aims of achieving highly reactive photocatalysts under the irradiation of UV light, as well as realizing the efficient utilization of solar light using a photocatalytic system.

In this paper, we take methyl orange as a model for recalcitrant azo-dye and investigate the effects of ascorbic acid

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on the TiO$_2$ photocatalytic decolorization of methyl orange solutions. The mechanisms are preliminarily proposed as the formation of charge transfer complexes of ascorbic acid on the TiO$_2$ surface and the superoxides mediated oxidation pathways are dominant for cleavage of azo bond.

2. Experimental

2.1. Materials and chemicals

Ascorbic acid and methyl orange (short as AA and MO below, respectively) were purchased from Shanghai Chemical Reagents Company and used without further purification. Their structures are given in Scheme 1. TiCl$_4$, *tert*-butyl alcohol (*t*-BuOH) and CCl$_4$ were obtained from Shantou Xilong Chemical Factory of Guangdong and used as received.

Preparation of nano-scale TiO$_2$ powders: nanosized TiO$_2$ was prepared by the hydrolysis method of TiCl$_4$ according to Zhang [13]. TiCl$_4$ was added dropwise and under stirring to 300 mL of water at about 0 °C. This aqueous solution was then mixed with (NH$_4$)$_2$SO$_4$ solution and placed in a temperature-controlled bath. The mixed solution was treated with 2.5 M dilute NH$_4$OH until the pH value was 7 and simultaneously stirred at high speed, and then maintained at 95 °C for 1 h. The colloidal TiO$_2$ solution was washed until free of chloride ions. The hydrous oxide was dried at 80 °C and calcined at 450 °C for 3 h at the rate of 5 °C/min.

2.2. Photolysis and analyses

All TiO$_2$ suspensions were prepared at a concentration of 1 g/L, and the initial MO concentration was fixed at 20 mg/L. AA was added as surface modifier, and the mixed suspensions were stirred in the darkness for 30 min to allow equilibrium. The pH of suspensions was adjusted with H$_2$SO$_4$ and NaOH solution to the desired values. For the photooxidation experiments in the absence of dissolved oxygen, the reactor was continuously purged with nitrogen gas during the irradiation. Photoirradiation employed a 12 W UV bactericidal lamp (Spectronics, BLE-6T365) as a light source (light intensity was 2500 μW/cm^2) or irradiation direct by solar light. The reactor was open to the ambient air (air-equilibrated case) or closed with a rubber septum under nitrogen gas (N$_2$-saturated case) and stirred magnetically during irradiation, maintaining the temperature at 30 °C. Sample aliquots were withdrawn by a 1 mL pipet intermittently during photoreaction and filtered
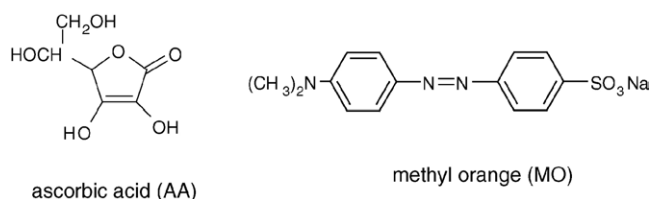
Scheme 1. Strutures of ascorbic acid and methyl orange (C.I. no. 13025).

by centrifugal filter (Beijing Medical Centrifuge Factory, LG10-2.4A) to remove TiO$_2$ particles. Quantitative analysis of MO was performed using UV–vis recording spectrophotometer (Shimadzu, UV-2501PC) at $\lambda_{max} = 464$ nm. All the experiments were triplicate. The results presented were the mean values with a total error of less than 5%.

2.3. Surface characterization

One gram per liter of suspensions containing different concentration of AA were stirred for 30 min for equilibrium, filtrated thoroughly washed with ethanol and then dried at 120 °C for 12 h. The prepared samples were in the form of KBr thin disks and characterized with FTIR spectrometer (Nicolet Avatar 360 FTIR).

The electrophoretic mobilities of TiO$_2$ particles in aqueous suspensions were measured to determine their zeta potentials as a function of pH and [AA] using a zeta potential analyzer (Brookhaven Instruments Co.) equipped with a He–Ne laser and thermostated flat board cell.

The optical absorption spectrum of pure TiO$_2$ and surface modified TiO$_2$ were recorded with a UV–vis recording spectrophotometer (Shimadzu UV-2501PC).

3. Results and discussion

3.1. Effects of surface modified TiO$_2$ with AA irradiated by UV light

The MO solutions were irradiated with or without the addition of AA and TiO$_2$. The results are shown in Fig. 1. The decolorization in the TiO$_2$/UV-light system is due to the oxidative cleavage of azo bond in the dye molecules, which was testified by Vinodgopal and Kamat [14]. The direct photochemical oxidation of MO solutions occurred little with the addition of AA, but occurred in the dye solu-
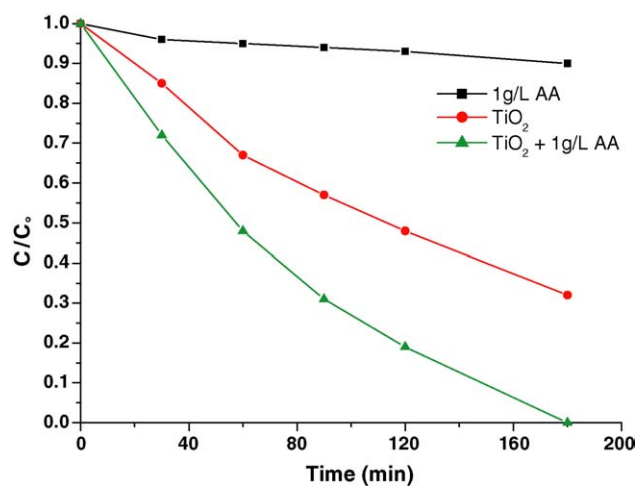
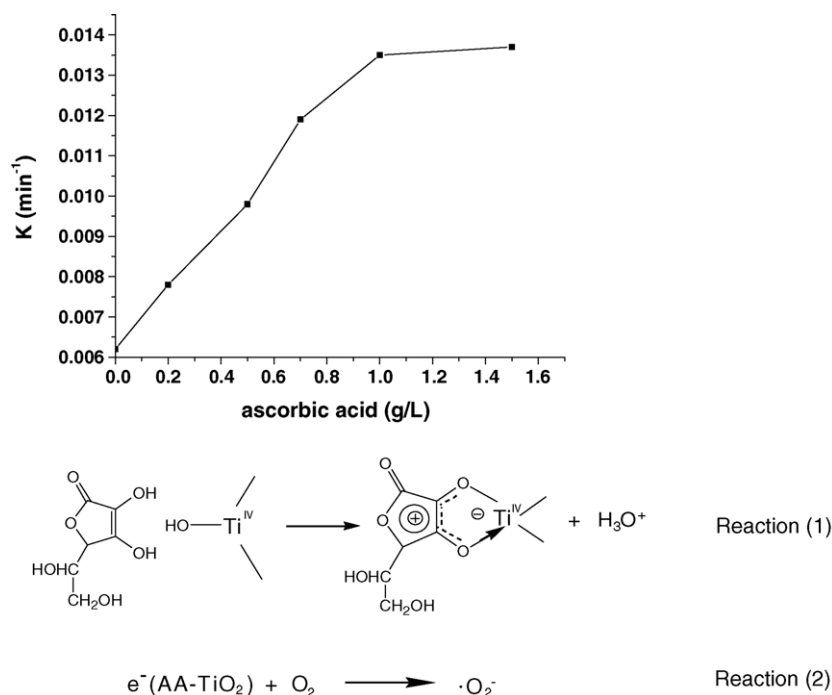Fig. 1. Photocatalytic decolorization of MO irradiated by UV light: [MO] = 20 mg/L, [TiO$_2$] = 1 g/L.

Fig. 2. Effects of AA concentration on photocatalytic decolorization of MO: [MO] = 20 mg/L, [TiO$_2$] = 1 g/L.

tions containing only TiO$_2$. It can also be seen from the figure that the color of MO was removed at the irradiation time of 3 h containing 1 g/L AA and TiO$_2$, compared with ca. 70% of MO solutions was degraded for the same experiment performed containing only TiO$_2$. When the UV lamp was switched off, only negligible reactions of ca. 0.2% can occur in the darkness. It can be concluded that AA greatly promotes the TiO$_2$ photocatalytic decolorization of MO solution.

The photocatalytic decolorization rate of MO solutions is also in accordance with first-order kinetics law during the initial stage of the reaction [15]. As shown in Fig. 2, when photocatalytic reaction containing AA and TiO$_2$, the rate was twice as large as that of the solutions containing only pure TiO$_2$, which may illustrate that the reaction rate increased as increasing AA concentration. When the mass concentration ratio of AA to TiO$_2$ was 1:1, the decolorization rate reached the maximum. This is due to the specific modification of AA binding to the surface of TiO$_2$, and this system has an important feature in that charge pairs are instantly separated into two phases, the holes on the donating AA and the electrons in the conduction band of TiO$_2$ [11] which react with O$_2$ to produce superoxides according to reactions (1) and (2). This process rather resembles visible light photosensitization of oxide surface by absorbed dye in charge transfer. The more electrons inject into the conduction band of TiO$_2$, the more superoxides are produced. The superoxides are moderate oxidants, and their standard reduction potentials [16] [E° (O$_2{}^-$/HO$_2{}^-$) = 1.0 V; E° (O$_2{}^-$/H$_2$O$_2$) = 1.7 V] are sufficient to oxidize azo bond. When the separated charge pairs occured during the photocatalytic oxidation, the AA

was oxidized and its oxidation product of dehydro-ascorbic acid (DHAA) was desorbed from the TiO$_2$ surface, but at the same time excess AA in the solution instantly was bound to the new bare surface. This process does not stop until charge transfer ceases and all of AA in the solution is completely oxidized. These viewpoints will be further discussed later in this paper.

3.2. Characterization of surface modified TiO$_2$

3.2.1. FTIR spectrum studies

After surface modification with AA, surface Ti atoms formed bidentate complexes through the *ortho*-substituted hydroxyl groups of furan ring binding to AA [11], which offered increased stability with little distortion of bond angles and distances. As shown in Fig. 3, two peaks of the spectrum of pure TiO$_2$ at 1636.68 and 1384.78 cm^{-1} were assigned to the in-phase bending vibration of surface OH groups. In the spectrum of modification TiO$_2$ with different concentration of AA, there appeared three continuous peaks between 1000 and 1170 cm^{-1} due to C–O stretching vibration of Ti–O–C bidentate complexes. Their positions were slightly shifted toward higher energies after the modification, indicating increase in their electron densities for lower electronegativity of the Ti atoms. As increasing the AA dosages, the intensities of C–O stretching increased consequently, whereas the intensities of the in-phase bending of surface OH groups decreased. It was due to the more addition of AA, the more AA binding to surface OH groups of TiO$_2$ to form bidentate complexes. So the amounts of surface OH groups were decreased.
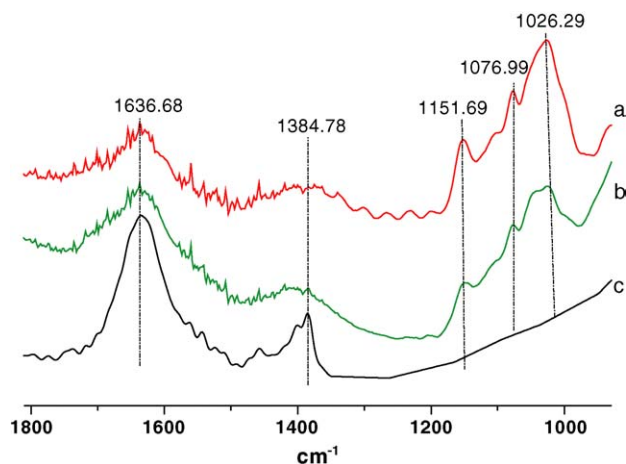
Fig. 3. Infrared spectrum of pure TiO_2 and surface modified TiO_2: (a) $TiO_2 + 1$ g/L AA, (b) $TiO_2 + 0.2$ g/L AA and (c) TiO_2.

3.2.2. Zeta potentials studies

Generally solid oxides in aqueous suspensions possess electrical charge due to the amphoteric dissociation of surface OH groups, the adsorption of H^+/OH^- ions, or metal hydroxo compounds from the hydrolysis of solid materials. The resultant surface charge is pH dependent. Fig. 4 shows the variation of zeta potentials of suspended TiO_2 particles in water as a function of pH and AA. The pH was controlled by the addition of dilute H_2SO_4 or NaOH. The measured iso-electric point was about 3.5–4, less than the literature data [17], which was related to the preparation of TiO_2. In the presence of AA, the isoelectric point was shifted to lower pH values and the positive charge on TiO_2 surface at acid pH region was much reduced since the surface $Ti–OH_2^+$ groups were replaced by $Ti–O–C$ species. This was good consistent with IR results. It was interesting to note that the isoelectric point was negative in most of the pH range in the presence of 1 g/L AA. This was due to the complexation between surface Ti (IV) sites and modifier (AA) should affect the surface
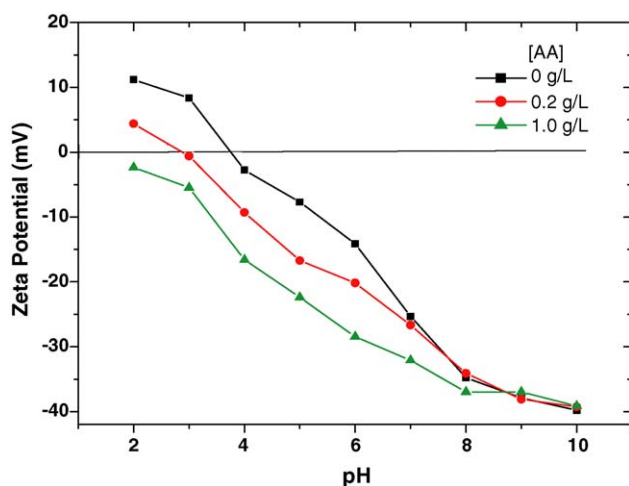

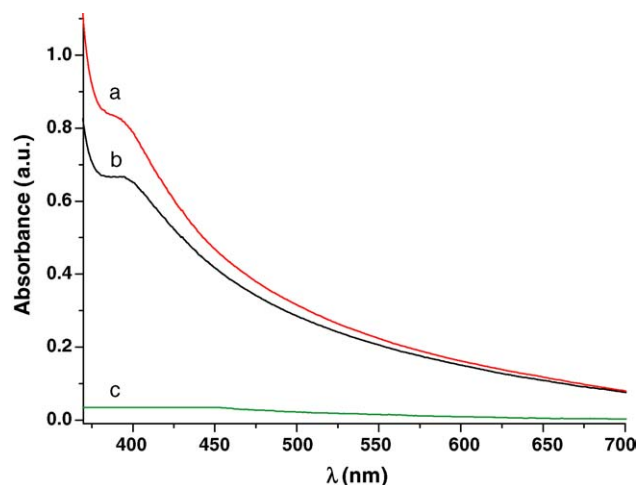Fig. 4. Zeta potentials of TiO_2 in aqueous suspensions ($[TiO_2] = 2$ mg/L) as a function of pH and [AA].

Fig. 5. Effects of the addition of AA on absorption spectrum of TiO_2 aqueous suspensions (optical path length: 1 cm): (a) 0.1 g/L $TiO_2 + 1$ g/L AA, (b) 0.1 g/L $TiO_2 + 0.2$ g/L AA and (c) 1 g/L AA.

charge density and consequently the zeta potentials. It is of advantage to separate the TiO_2 particles from the dye solutions in practical applications, since the less aggregated TiO_2 sol should be formed away from the isoelectric point range.

3.2.3. UV–vis spectrum studies

Due to this specific binding of AA to the surface of TiO_2, the optical properties of TiO_2 consequently change. In contrast, AA failed to produce the absorption above 350 nm since it had no chromophores of its own, but the absorption threshold of modification TiO_2 shifted toward the red region of spectrum up to ca. 600 nm and the broad maximum at ca. 400 nm (Fig. 5). As increasing AA concentration, both of absorption intensity and red shift increased. Moser et al. [18] had reported that the bands in the visible observed in the presence of salicylate or catechol corresponded to ligand-to-metal charge transfer. Light promoted electrons transfer from the modifier to the conduction band of TiO_2 and decreased ionization potential of the electrons donor. Thus, the surface modified TiO_2 exhibiting a significant red shift is ascribed to the crystalline environment of the metal.

In order to prove UV–vis absorption spectroscopic results, the photocatalytic decolorization experiments of MO solutions were performed in the solar light. From Fig. 6, it can be definitely seen that the decolorization rate of MO greatly increased with AA under the solar light irradiation, which indicated that the modified TiO_2 certainly expands the wavelength response range.

3.3. Photocatalytic mechanisms of the TiO_2 suspensions with AA

Although OH radicals mediated pathway are generally deemed to dominant in most TiO_2 photocatalytic oxidation reactions [19–23], superoxides have been recently proposed as a main photocatalytic oxidants in photocatalytic oxida-
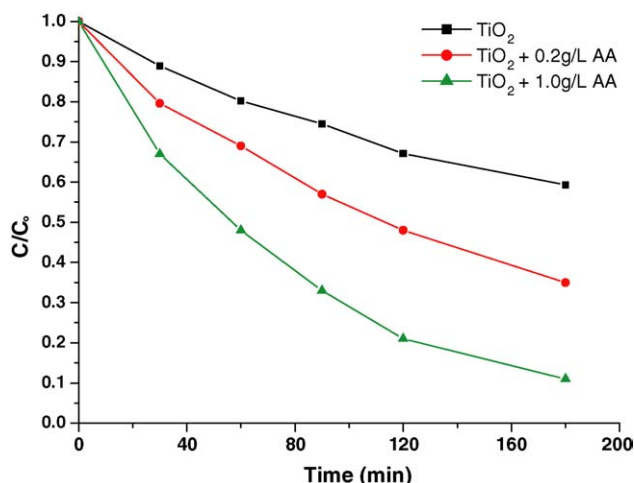
Fig. 6. Photocatalytic decolorization of MO irradiated by solar light: $[MO] = 20\,mg/L$, $[TiO_2] = 1\,g/L$.

Fig. 7. Effects of electron acceptors (O_2 or excess CCl_4) and t-BuOH addition on photocatalytic decolorization of MO irradiated by UV light: $[MO] = 20\,mg/L$, $[TiO_2] = 1\,g/L$, $[AA] = 1\,g/L$, $[t$-BuOH$] = 0.5\,M$.

tion of some metal ions and azo-dye [24–30]. As for surface modification of TiO_2 with AA, it is not clear which one is the key oxidant for cleavage of azo bond of MO among $^{\bullet}O_2{}^{-}$, $HO_2{}^{\bullet}$ and $OH^{\bullet}$ radicals. In order to figure out this problem, we investigated the effects of dissolved oxygen, CCl_4 and $tert$-butyl alcohol in the modified TiO_2 suspensions irradiated by UV light. As shown in Fig. 7, the compare of curves of TiO_2/AA and TiO_2/AA/t-BuOH shows that the OH radicals should not be responsible for MO decolorization since the addition of 0.5 M t-BuOH (OH radical scavenger, t-BuOH $+$ $^{\bullet}OH \rightarrow t$-BuOH$(-H)^{\cdot} + H_2O$) did not reduce the rate of MO decolorization. Furthermore, the decolorization rates of MO were faster in the air-equilibrated suspensions than in the N_2-saturated suspensions, which could explain in a way that dissolved oxygen should be essential for MO decolorization. The role of oxygen is universally regarded as a conduction band electrons scavenger to inhibit fast charge pair recombination. But in the N_2-saturated suspensions, instead of dissolved oxygen the addition of excess CCl_4, which is known to accept conduction band electrons on TiO_2
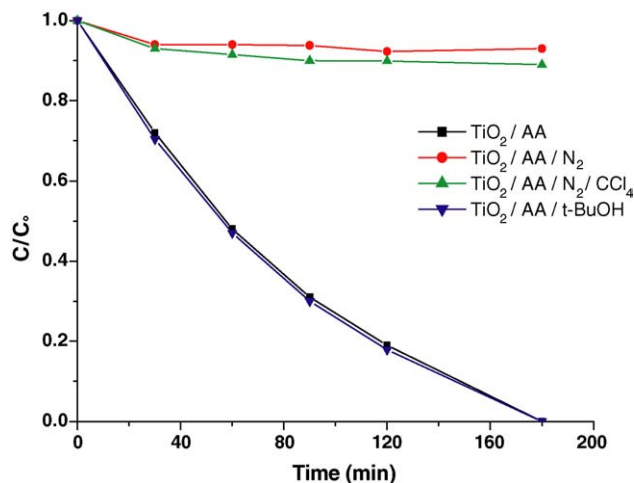
($CCl_4 + e_{cb}{}^{-} \rightarrow {}^{\bullet}CCl_3 + Cl^{-}$), had little assist on the photocatalytic decolorization rate. Therefore, the role of O_2 could not only be as a conduction band electrons scavenger but more important as a precursor of main oxidant. Zhao and co-workers [31] suggested that the position of dye molecule with the largest frontier electron densities was first attacked by superoxides, on the basis of molecular orbital calculations by frontier electron densities and point charges on all the individual atoms of the dye. This is correlated with our results of experiments. Since the more electronegativity of the N atom than the C atom, the azo bond of MO molecule has the largest frontier electron densities and theoretically it should be first cleaved. But as we known, the cleavage of N=N bond is difficult, and maybe the cleavage between the N atoms and the phenyl groups may be partially occurred.

The one-electron reduction of dissolved oxygen by conduction band electrons is kinetically sluggish in water. However, we found that the increase of photocatalytic decolorization rate in the presence of surface modifier could be
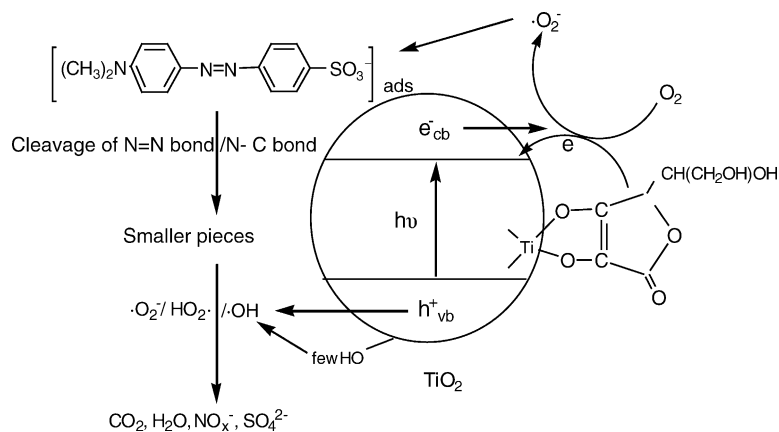
Scheme 2. Schematic illustration of MO photooxidation pathway in surface modified TiO_2 with AA.

confirmed with all above experiments. Based on our and other results, a reaction pathway of the photocatalytic decolorization MO for cleavage of azo bond in TiO_2 suspensions can be suggested as schematically shown in Scheme 2. It illustrates the photocatalytic decolorization rate markedly increases under the conditions that could enhance the generation of superoxides and summarizes the elementary charge transfer processes occurring on the surface modified TiO_2 with AA. The free OH radicals will also be generated from the valence band hole or the surface-bound OH radicals, but they are largely inhibited due to the hindered complexation of AA on the surface of TiO_2 and not main photocatalytic oxidants for cleavage of azo bond. According to this scheme, the first step of photocatalytic mechanism on the surface modified TiO_2 is that AA formed bidentate complexes through the *ortho*-substituted hydroxyl groups of furan ring; The second step involves the electrons of AA transfer to conduction band of TiO_2 and then superoxides are formed acceleratively through the one-electron reduction of dissolved oxygen by conduction band electrons; The third step is superoxides attack MO and then complete photocatalytic oxidation cleavage of azo bond (N=N bond or partially N−C bond); At the last step, smaller pieces are further completely photocatalytic oxidized to CO_2, H_2O, NO_x^- and SO_4^{2-} by $^\bullet O_2^-$, $HO_2^\bullet$ or few $OH^\bullet$ radicals.

4. Conclusions

We have investigated a new type of surface modified TiO_2 photocatalyst with AA, which forms charge-transfer bidentate complexes and expands the wavelength response range and Suitable amount of AA addition in the TiO_2 suspensions greatly enhances the MO photocatalytic decolorization rate of cleavage of azo bond, irradiated by both UV light and solar light. AA complexation on TiO_2 surface behaves as sites where charge transfer accumulates. The more free electrons on the modified TiO_2 surface that react with O_2 generate more superoxides and result in more efficient oxidations. In this work, we focus on only the MO photocatalytic decolorization of cleavage of azo bond on surface modified TiO_2, which seems to have no universality. However, we aim mainly to remove color from waste by testing the feasibility of enhancing photocatalytic decolorization rate with AA and expanding the wavelength response range. Further studies on all photocatalytic process of MO and other dyes will be summarized in our next study.

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