

Visible light responsive TiO₂ modification with nonmetal elements

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Developing visible light responsive (VLR) TiO₂ photocatalysts is essential and attractive for the consideration of solar energy utilization. A large amount of work have shown TiO₂ modified with several nonmetal elements having VLR performance, although according to DFT calculation, Asahi denied the VLR properties of fluorine, carbon, etc. in doping TiO₂. Therefore, the origins of VLR activity desire further delicate discussion. In this mini-review, several strategies for VLR TiO₂ modification have been introduced, including N doping or B/N codoping, surface modification with sensitizing matter such as carbonaceous or other organic substances, surface alkoxy modification via a ligand-to-metal charge transfer (LMCT) process, and enhanced dye sensitization by fluorine modification. Besides doping, there are much more approaches to fabricate VLR TiO₂ modified with nonmetal elements. However, it is still in demand to explore new methods to obtain more stable and efficient VLR TiO₂ for practical application.

Keywords visible light, modified, doping, TiO₂, photocatalysis, sensitization, ligand-to-metal charge transfer

1 Introduction

Exploitation of low carbon or carbon free new energy is crucial for sustainable development of humankind. A large number of studies have been focused on solar energy because of its being abundant, accessible, renewable and free of carbon. Semiconductor photocatalysis is a promising approach to chemical conversion of solar energy for environmental cleanup, electrical generation, and water splitting for hydrogen energy [1]. TiO₂ is one of the most popular photocatalysts because of its advantages of stability, activity and low cost. However, its wide band gap (3.2 eV for

anatase) restricts that TiO₂ can be active only in the range of ultraviolet light, which accounts for only 3%–5% of solar energy [2]. Developing a visible light responsive (VLR) photocatalyst is obviously meaningful for practical applications.

VLR TiO₂ has been regarded as the second generation of TiO₂ photocatalysts [3] and attracted much attention recently. Since the exciting work of Asahi [4], who has reported a VLR nitrogen doped TiO₂ and provided detailed theoretic analyses on nonmetal ions doped TiO₂, there is a large number of work on nonmetal doped TiO₂ involving almost all nonmetal elements except the inert gas elements. Although Asahi denied the effective VLR activity of doped TiO₂ with such elements as carbon, fluorine, sulfur, etc., there are still observations on the photocatalytic activity under visible light for so-called doped TiO₂. The components, structures and physiochemical properties of “doped” TiO₂ are always varied with source materials and synthesis methods. Therefore confused results on the visible light performance would be found when less attention has been paid on their essential components and structures. Moreover, it is more accurate in most cases using the nomenclature of “modification” instead of “doping”. In this mini-review, we would like to give comprehensive results of visible light responsible TiO₂ modified with nonmetal elements.

2 Doped TiO₂ with nonmetal elements

In the description of “doped” TiO₂, hetero-atoms, except Ti and O, should enter into the crystal lattice of TiO₂, presenting as replacing sites of Ti or O or the interstice of the lattice. Two requirements for VLR activity of doped TiO₂ have been proposed by Asahi, which are i) doping should introduce states in the band gap of TiO₂ and ii) the states in the gap should overlap sufficiently with the band states of TiO₂ [4]. The former is to make sure that the doped TiO₂ has visible light absorption properties and the latter is to ensure the efficiency by favoring the charge transfer and separation in the lifetime.

Nitrogen doped TiO₂ is regarded as the best suitable VLR nonmetal doped TiO₂. Various methods have been reported for the syntheses of nitrogen doped TiO₂, which can be classified into dry methods and wet methods. Dry methods include sputtering TiO₂ target in an N₂(40%)/Ar gas mixture as described in the initiated work of Asahi [4], or sputtering a Ti metal under a N₂O/Ar gas mixture [5], annealing TiO₂ powder or films under NH₃ flow [6], ion implantation of TiO₂ single crystal with N₂⁺/Ar⁺ mixtures [7], pulsed laser deposition (PLD) using TiN target in nitrogen/oxygen mixture [8], and growing N-doped TiO₂ homoepitaxially on

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TiO₂(110) rutile using plasma-assisted molecular beam epitaxy (PAMBE) [9], etc. However, most of these dry methods require special equipments, so they cannot be suitable for scaled-up production. Much more attention has been put on the wet methods, which include nitriding the transparent colloid TiO₂ nanocrystal to TiO_{2-x}N_x with amine compounds (such as triethylamine or hydrazine) [10,11], hydrolyzing or post-treating the titanium precursor with aqueous ammonia solution [12–15], homogeneous precipitation in hexamethylenetetramine-titanium trichloride mixed solution followed by solvothermal process [16], microemulsion-hydrothermal method using triethylamine, urea, thiourea, and hydrazine hydrate as nitrogen sources [17], and high energy ball milling of P25 titania-5% Hexamethylenetetramine mixture followed by calcinations [18], etc.

Although N-doped TiO₂ synthesized via different approaches showed excellent VLR activities, the accurate species of nitrogen and the origin of the VLR activity are still under dispute. According to the binding energy of N_{1s}, the proposed structure of nitrogen could be shown in Table 1. It was found that the nitrogen could appear as NO_x, NH_x or other nitroxide species, forming either diamagnetic (N_b⁻) or paramagnetic (N_b[•]) bulk centers [19]. From the results of density functional theory (DFT) calculation, the substitutional nitrogen for oxygen in the anatase TiO₂ would not result in an obvious narrow-down of band gap through mixing of N_{2p} with O_{2p} states, but would bring out three new N_{2p} bands in the band gap, which induce a VLR performance of N-doped

Table 1 Relationship between nitrogen species and XPS binding energy of N_{1s}

| Binding energy/eV | Species |
|-------------------|---|
| 396–397 | N-Ti-N, nitride |
| 399 | O-Ti-N (substitutional) or Ti-O-N-Ti (interstitial) |
| 399–401 | N-N, N-O, N-C or adsorbed N ₂ |
| 407–408 | Nitrate, nitrite compounds |

TiO₂ [20, 21], as plotted in Fig. 1. However, the oxidation power of holes in N-doped TiO₂ decreased under visible illumination, that is, N-doped TiO₂ failed to catalyze the oxidation of formate ions [22]. Besides the dopant level in the band gap, the oxygen vacancies [12] or color centers [23] have also been regarded as the origin of VLR properties.

There are synergistic effects for VLR activity when codoping TiO₂ with two kinds of nonmetal elements or with both nonmetal and metal elements. Normally, one dopant contributes to the VLR properties and the other dopant (or surface modified specie) favors the charge carriers separation. Liu et al. observed the synergic effect of B/N doping mesoporous TiO₂, and they considered the high level of B dopant was necessary, and the O-Ti-B-N surface structure contributed to the VLR activity [24]. Li et al. reported a twist-like helix tungsten–nitrogen codoped titania via a one-pot method: hydrolysis TiCl₄ with ammonia in water solution in the presence of glacial acetic acid and ammonium tungstate [25]. Zhao et al. synthesized efficient Ni₂O₃/TiO_{2-x}B_x by a modified sol-gel method to incorporate B and modify with Ni₂O₃ [26]. Codoped S/N [27, 28], N/Si [29], F/N [30], N/Ag [31] having synergic effects were also reported. However, further work is needed to explain the relationship between the micro structures and components for the synergic effects of codoped TiO₂, and their photocatalytic performance, besides focusing on the VLR activities.

3 Surface modification with sensitizing matter

The origins of VLR performance of modified TiO₂ are more complicated than the exclusive “doping”. It is known that dye pollutants can be photodegraded over TiO₂ dispersion under visible light irradiation through a self-photosensitized oxidative transformation pathway [32,33]. More cathodic potential of excited states of dyes than the conduction band of

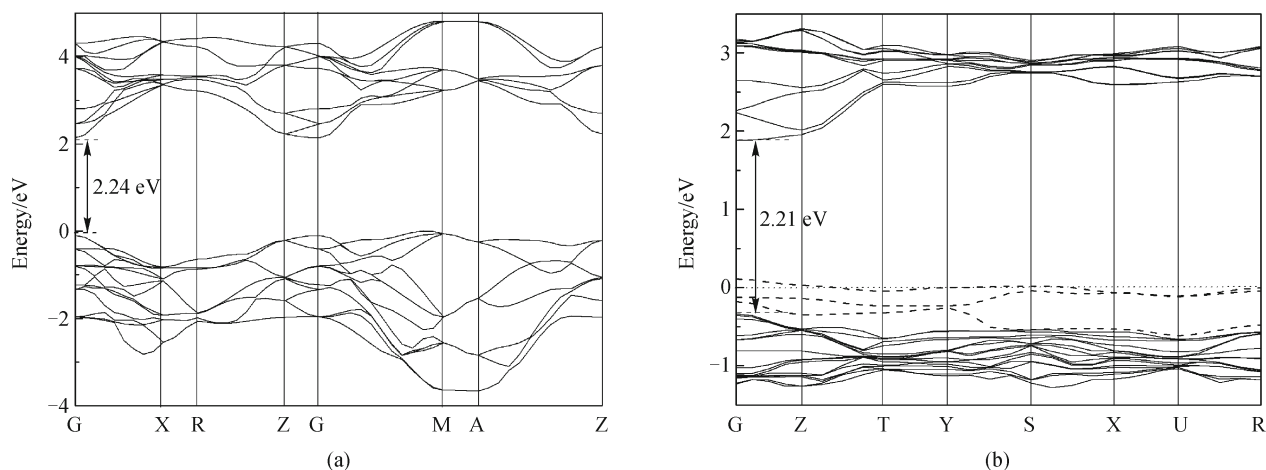


Figure 1 Calculated energy band structure of: (a) TiO₂ and (b) N-doped TiO₂ along the symmetry lines of the first Brillouin zone [21]

TiO₂ and a better adsorption of substrates over TiO₂ particles are required for the thermodynamic and dynamic feasible electron transfer, and the initiation of the transformation and degradation. Therefore, when dye pollutants are used for photocatalytic activity tests, comparison experiments should be carefully prepared. Moreover, the colorless pollutants can be degraded via the photoassisted degradation of dye sensitization. This also provided a hint that the VLR TiO₂ can be obtained through a surface sensitized pathway.

3.1 Surface sensitized with carbonaceous substance

Since the work of Khan [34], carbon modified TiO₂ has attracted much attention due to its outstanding VLR activity. According to the existing formation of carbon, there are three types of carbon modified TiO₂. The widely accepted one is carbon doped TiO₂, in which the carbon substitutes oxygen or titanium or presents as interstitial species in the lattice. The second one could be considered as carbonaceous substance on the surface of TiO₂. Such carbon modified TiO₂ as, the carbon-coated Ti_nO_{2n-1} by heat treatment of TiO₂ and poly (vinyl alcohol) in inert atmosphere [35], the coke containing titanium dioxide via acid-catalyzed sol-gel process [36], the surface hybridization of TiO₂ with graphite-like carbon layer [37], etc. can be classified into this type. The third is the TiO₂ loaded activated carbon, which is not a VLR photocatalyst. Because it is difficult to determine the accurate species of carbon and the carbonaceous substances were varied with the synthesis methods, there is controversy on the origin of VLR activity of carbon modified TiO₂. Moreover, according to the theory calculations and experimental results, the doped carbon should not be the main reason of the VLR activity.

The process of hydrolysis and polycondensation of alkoxy titanate has always been discussed based on the presumption that the titanium containing precursor is hydrolyzed completely. However, by controlling the ratio of titanium and water and stirring time, an incomplete hydrolysis can be obtained to hold carbonaceous residues in the polycondensed network [38]. Fig. 2 is the ¹³C NMR spectrum of a xerogel obtained from tetrabutyl titanate. The signals at 62.9, 34.5, 18.7 and 12.9 ppm correspond to the four carbons from hydrolysis product of 1-butanol, while the signals at 76.7 to 79.6 ppm are attributed to the first carbon connecting with oxygen in the -Ti-(O-C₄H₉) group. This indicates that in the amorphous xerogel, there are considerable amount of adsorbed 1-butanol and tetrabutyl groups at the terminal of the titania network. Further calcining the xerogel at 350°C in an oxygen deficient reactor resulted in a carbon modified TiO₂ with efficient VLR activity. In the Raman spectrum, the emerged two peaks around 1582 and 1100 cm⁻¹ indicates the existence of amorphous carbons with some degrees of

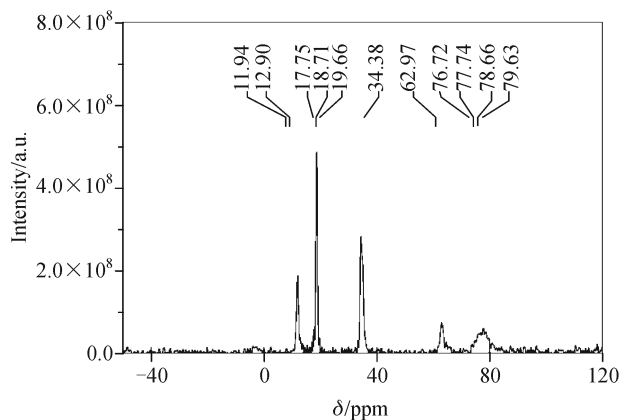


Figure 2 NMR spectrum of the sample S0 (xerogel) [38]

graphitic ordering. C_{1s} binding energy from XPS measurement suggests the existence of two kinds of carbon: interstitial doping carbon in the crystal lattice and carbonaceous substance coating on the surface. The former contributed to the slightly band gap narrowing, however, the latter played a principal role for the efficient VLR activity by serving as the sensitizer.

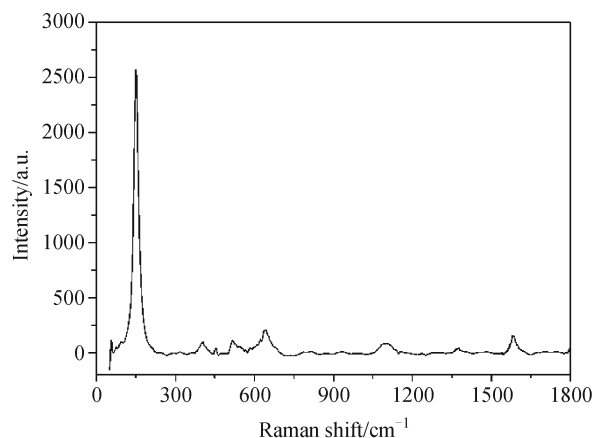


Figure 3 Raman spectra of carbon modified S350 [38]

3.2 Surface sensitized with organic substances

Kisch et al. observed that TiO₂-N obtained with urea as the nitrogen source is quite different from that of NH₃, because the former has the activity for the visible light mineralization of formic acid [39]. According to the XPS measurements, the N1s binding energy of the modified TiO₂ is 399.2 and 400.5 eV, corresponding to the data for carbon nitrides (399–400 eV, C = N-C), similar graphite-like phases (400.6 eV, N-C_{sp2}), and polycyanogen (399.0 eV, 400.5 eV, (-C = N-)x). In combination with the comparison tests, a new mechanism has been proposed. During the calcinations of titania and urea,

the VLR condensation products of melamine, which is formed from urea by titania catalyzed, come into being and covalently attach to the titania surface, as shown in Scheme 1. Another work from Wang et al. showed that the metal-free carbon nitride g-C₃N₄, whose estimated band gap is 2.7 eV, has an activity for water splitting under visible light [40]. This provided an important support for the VLR photocatalytic activity of condensation triazine derivative.

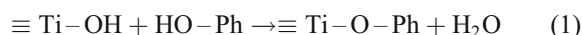
Calcinations titania with urea is an efficient and facile method to produce VLR TiO₂ thin film [41]. A titania nanoflower film has been prepared by directly oxidizing the titanium metal in hydrogen peroxide solution (Sample S-A) and subsequently treating it hydrothermally at 150°C in water (Sample S-C). The surface modification of the film was carried out by simultaneously calcining one piece of titania film (4 cm×4 cm) and 1 g urea in a connected reactor with two components [41]. The obtained TiO₂ film (S-M) showed a mixture crystal phase of anatase and rutile, held the nanoflower structure (Fig. 4), and exhibited an enhanced VLR activity for MO degradation.

Although efficient VLR TiO₂ can be obtained through forming carbonaceous or organic sensitizer from the simple hydrolysis of organic titanate compounds or using pyrolysis carbon nitride compounds, the reduction and degradation of

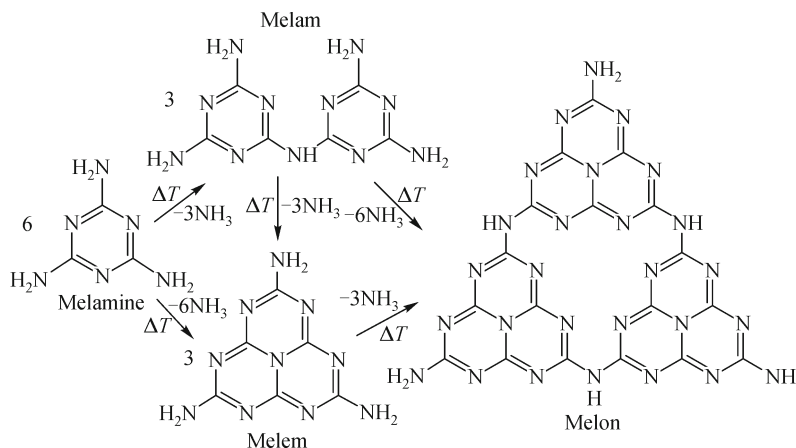
the surface sensitizer during the photocatalytic reaction would result in a decrease of VLR activity. Therefore the stability of such VLR TiO₂ is poor. This surface sensitized VLR TiO₂ with carbonaceous substance offers an implication: When using organic compounds as the source materials, one should carefully determine the presence and the role of the carbonaceous residues.

4 Alkoxy-derived VLR TiO₂

It was found that the complex formation between some colorless molecules and the surface of TiO₂ could lead to visible light absorption via a ligand-to-metal charge transfer (LMCT) process. Choi et al. reported that the phenolic compounds can be photocatalytic degraded over pure TiO₂ under visible light irradiation by the surface complex mediated path [42]. The probable phenolate linkage structure is shown in Eq. (1).



A novel alkoxy-derived TiO₂ with VLR activity can be attributed to a similar LMCT process [43]. To avoid carbon doping, the whole modification process is carried out at low temperature. A precursor, light yellow hydrosol of TiO₂ was



Scheme 1 Condensation products of melamine produced at 350°C–500°C in the absence of titania [39].

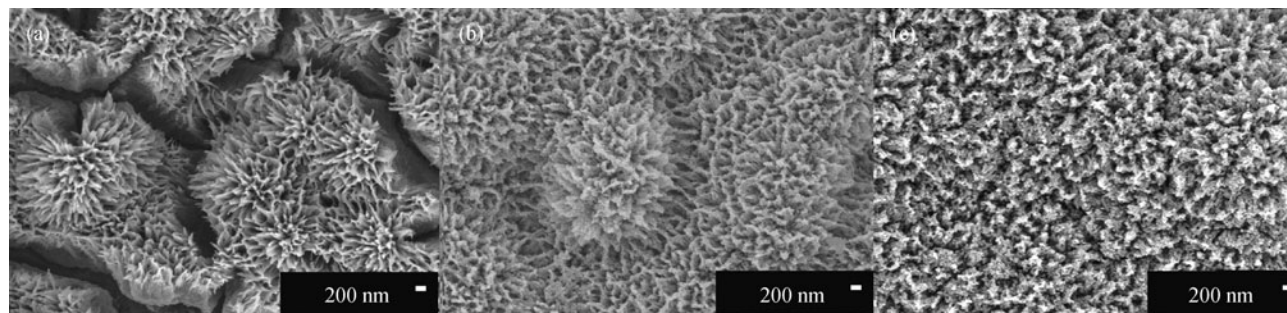


Figure 4 Surface morphology of the samples (a) S-A; (b) S-C; (c) S-M [41]

obtained by dropwise adding tetrabutyl titanate into a nitric acid solution under vigorous stirring. After ageing for 12 h, the sol was treated under refluxing at 120°C for 12 h, and dried at 80°C to obtain the sample RH-80. The directly dried sample (H-80) and the hydrothermal treated sample (AH-80) have also been prepared for comparison. As shown in Fig. 5, direct drying of the aged-sol (H-80) achieved an appreciable VLR activity for MO degradation, and further refluxing (RH-80) resulted in a surprising efficient VLR photocatalyst. According to the results of IR spectra in Fig. 6, it was interesting to note the intensity of the absorption peak at 1380 cm⁻¹, which is considered to be the sign of alkoxy groups, corresponding well to the visible light degradation

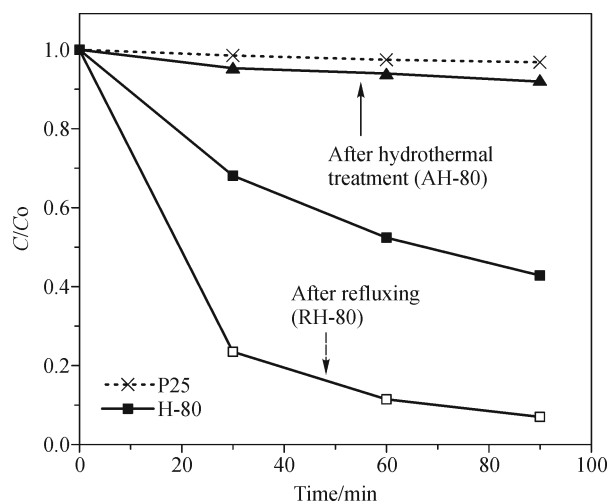


Figure 5 Photodegradation of MO on different TiO₂ samples under visible light ($\lambda > 400$ nm) [43]

efficiency of MO (RH-80 > H-80 > AH-80). To determine the role of the alkoxy group in the VLR activity, the sample RH-80 has been heat treated at 240°C and 300°C. A similar positive correlation between the activity and the intensity of the absorption at 1380 cm⁻¹ has been obtained again (Fig. 7). The retained alkoxy groups induce visible light absorption through electron transfer from the alkyl-linked oxygen to the Ti (IV) metal site, so as to initiate the photocatalytic process, as described in Scheme 2. Moreover, the extra addition of butanol to the pure TiO₂ (P25) or washed precursor during refluxing also helps for the alkoxy group surface modification and induces VLR performance. The presence of HNO₃ also favors the retaining of alkoxy group. The process of LMCT did provide a new insight into the modified TiO₂ with VLR activity.

5 Enhanced dye sensitization by fluorine modification

The surface properties of TiO₂, such as surface hydroxyl group, acidity, electrostatic characteristic, surface states, etc., strongly influence the adsorption of substrates and the surface electronic structure of TiO₂, thereby play a principal role in the degradation pathway of substrates. In some cases, modifying with nonmetal elements would change such surface properties of TiO₂ and induce the photocatalytic degradation of substrates under visible light. According to the DFT theory, doping TiO₂ with fluorine cannot decrease the band gap because the impurity energy originated from fluorine is below the valence band of TiO₂. However, recently, several

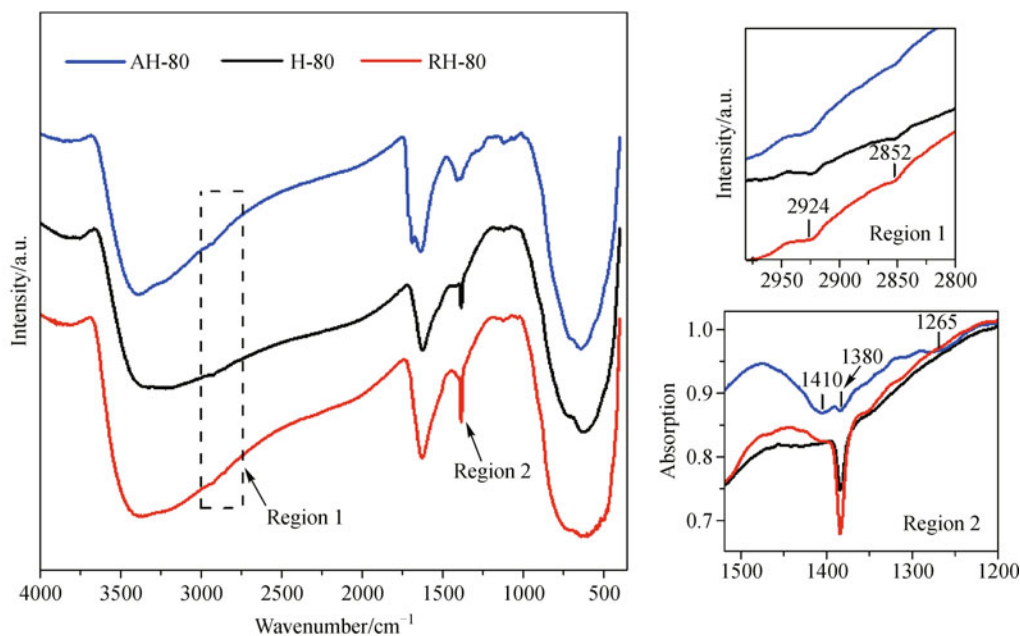


Figure 6 IR spectra of different TiO₂ samples, with two magnified regions at: (I) 2980–2800 cm⁻¹ and (II) 1515–1200 cm⁻¹ [43]

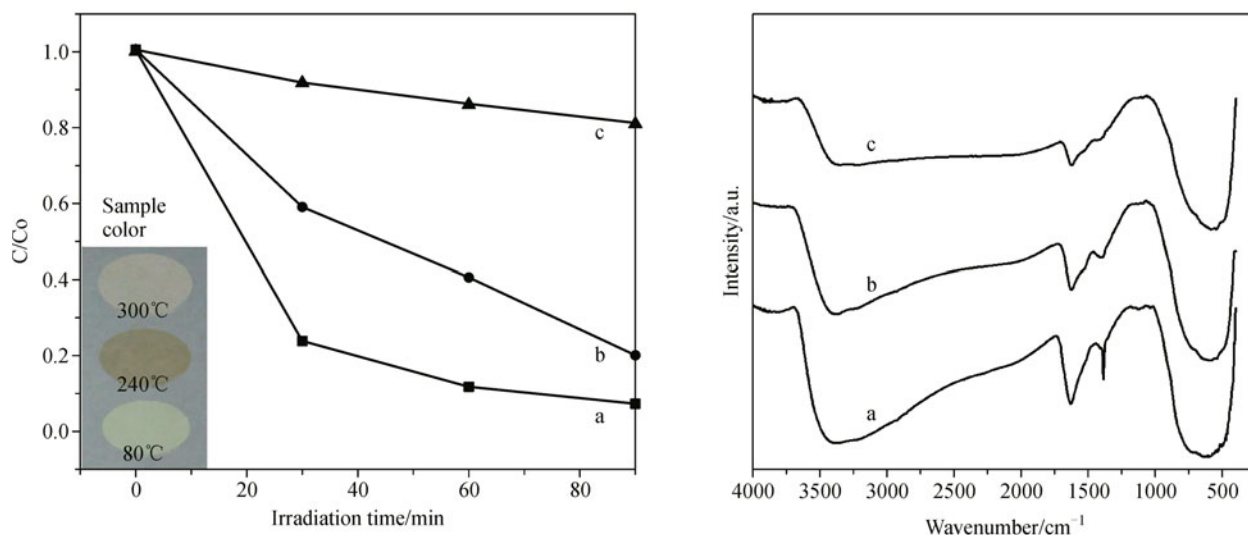
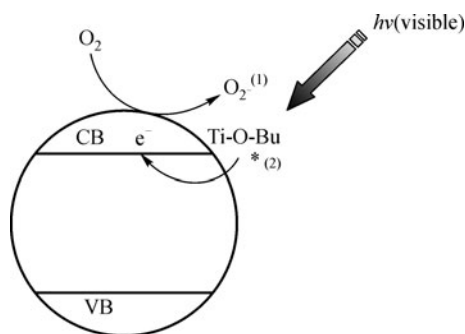


Figure 7 Visible light degradation of MO on TiO₂ samples (a) RH-80, (b) RH-240, (c) RH-300 (with the photos of sample color) and IR spectra of different TiO₂ samples (a) RH-80, (b) RH-240 and (c) RH-300 [43]



Scheme 2 Proposed visible light-induced photocatalytic mechanism on alkoxy-modified TiO₂ surface [43]

researchers have confirmed the VLR performance of F-doped TiO₂. Li et al. prepared an efficient VLR F-doped TiO₂ by spray pyrolysis of an aqueous solution of H₂TiF₆. According to the results of photoluminescence they thought the F-doping had created two kinds of surface oxygen vacancies contributing to the visible light excitation and initiating the surface photocatalytic reaction [44]. Wang et al. prepared the surface-fluorinated TiO₂ via an HF etching method and observed the altered adsorption modes of Rhodamine B over the catalyst surface, and found the downward shift of flatband potential [45]. The changed flatband potential after fluorine modification makes it more feasible and easier to inject electrons from the excited state of the dyes to the conduction band, which has been considered to be the main reason for the VLR activity of fluorine modified TiO₂.

We prepared a fluorine-modified TiO₂ by a refluxing method at low temperature [46]. Firstly, the amorphous precursor was obtained by the hydrolysis and precipitation of

Ti(OBu)₄ in the water. The precursor was washed with a large amount of water to remove impurities. NaF and the precursor were added into water, and the solution was stirred for 12 h to achieve a fluorine adsorption equilibrium. Then the precipitation was separated, washed and dispersed into a nitric acid solution and refluxed for 12 h at 120°C to obtain fluorine modified TiO₂ with improved crystallinity. It was found that introducing fluorine in the refluxing process inhibited the growth of brookite phase, as shown in Fig. 8. The as prepared

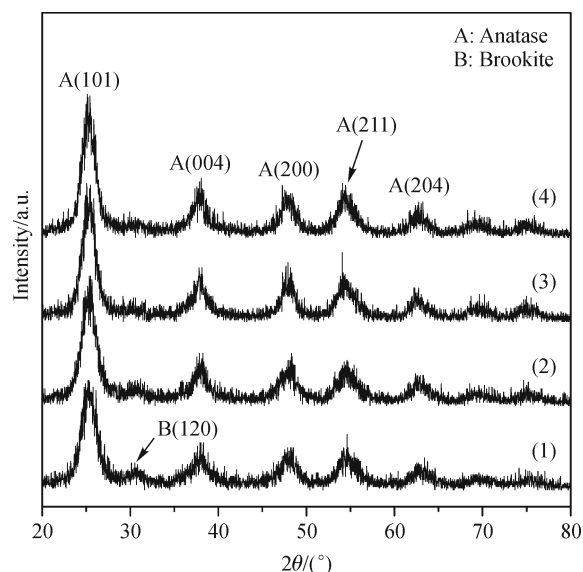


Figure 8 XRD patterns of different F-TiO₂ samples: (1) TF0; (2) TF0.1; (3) TF0.5; (4) TF2. (The different *x* value in TF*x* (*x* = 0, 0.1, 0.5, 2) represents the molar ratio of F/Ti in the synthetic process) [46]

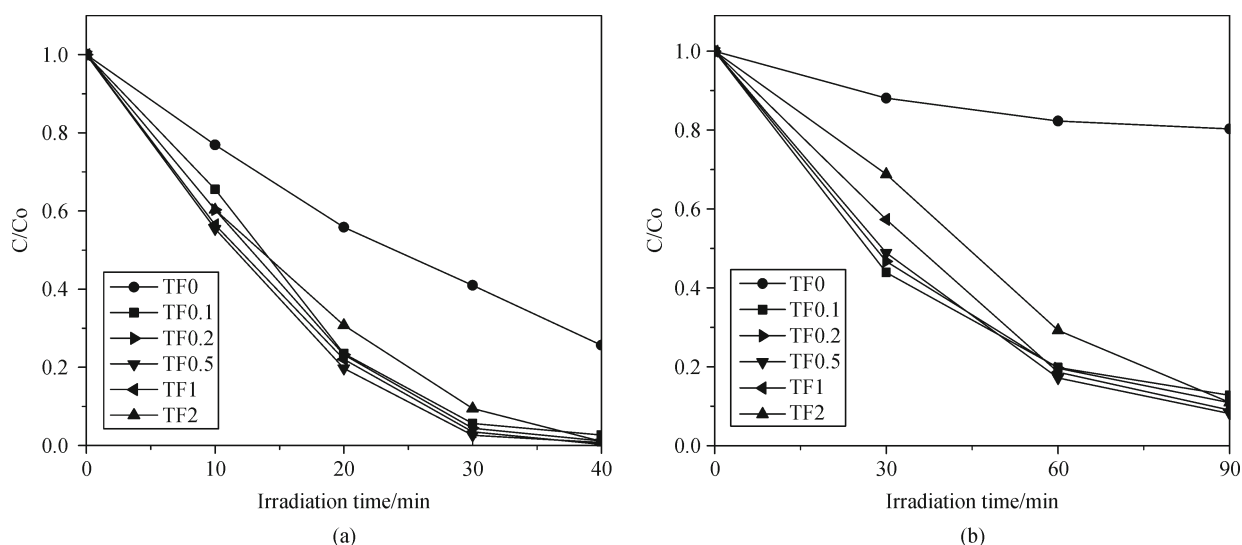


Figure 9 Methyl orange (MO) degradation on different F- TiO_2 samples (a) under UV-visible light; (b) under visible light (catalyst dosage: 1 g/L; initial MO concentration: (a) 20 mg/L, (b) 10 mg/L) [46]

fluorine modified TiO_2 (FT) showed an improved activity for methyl orange (MO) degradation under the full spectrum irradiation (Fig. 9a). Moreover, the introduction of fluorine produced an efficient VLR activity (Fig. 9b): more than fourfold of MO reduction over the FT samples compared with the unmodified TiO_2 under visible light irradiation. In fact, it should be noticed that there is no obviously infrared shifted absorption for the FT samples from the UV-Vis diffusive reflection spectra (DRS) results (Fig. 10). This suggested that the band gap narrowing is not the origin of the VLR activity of fluorine modified TiO_2 . Another piece of evidence is that phenol degradation under visible light was not improved over the TF sample. Therefore, the VLR activity of FT for dye degradation must be originated from an enhanced sensitization effect of substrates.

The presence of fluorine in the sample can be determined from IR spectra and XPS analyses. A shoulder peak at 899 cm^{-1} in the IR spectrum of TF0.5 is attributed to the stretching vibration of Ti-F bond. It indicates that fluorine has been bonded with titanium ions, which could be the chemically adsorbed species on the surface or the doped species in the crystal lattice of TiO_2 .

To further explore the origination of VLR activity, two kinds of post treatments have been done: washed with alkaline solution and heat treated at 200°C to 400°C . The VLR activity of the treated samples decreased significantly, as shown in Table 2. In the F1s region of XPS measurements, there are two peaks, a stronger one at 684.5 eV and a weaker one at 690.6 eV. Normally, the former one can be attributed to the substitution of the surface hydroxyl groups with adsorbed fluorine, which can be supported by the decreased content of hydroxyl groups from the O_{1s} binding energy at 531.7 eV.

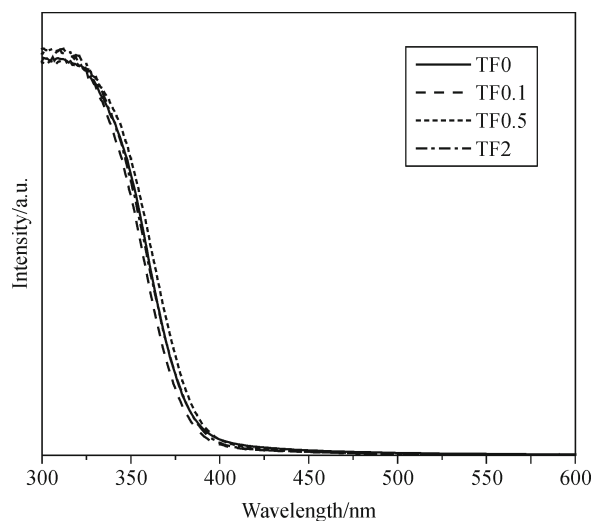


Figure 10 UV-Vis DRS of different F- TiO_2 samples [46]

Table 2 The changes of visible light degradation of MO on sample TF2 after treatment with different methods [46]

| | Treatment method | Degradation rate ^a |
|--------------------------|------------------|-------------------------------|
| Effect of alkaline wash | water-washed | 89.0% |
| | NaOH-washed | 7.2% |
| Effect of heat treatment | untreated | 89.0% |
| | 200°C-treated | 24.8% |
| | 300°C-treated | 20.8% |
| | 400°C-treated | 8.1% |

^a The data is the degradation rate of MO after 90 min under visible light irradiation ($\lambda > 400\text{ nm}$).

However, the latter one has been considered to result from the doped fluorine replacing the oxygen in the crystal lattice. It cannot be acceptable as the binding energy was much higher

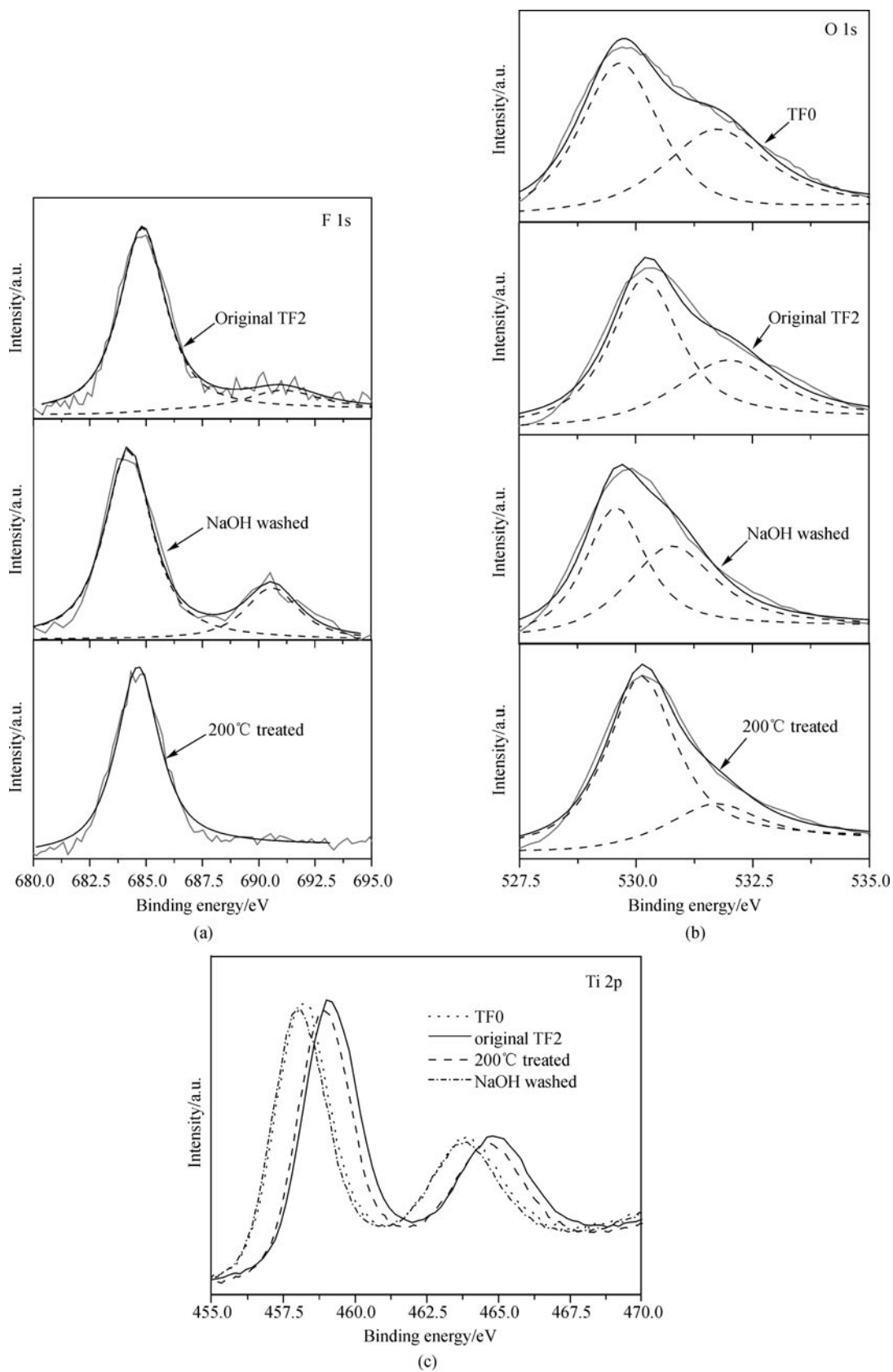


Figure 11 Changes in XPS spectra on sample TF2 before and after further treatment (compared to sample TF0): (a) F 1s; (b) O 1s; (c) Ti 2p [46]

even than that of 684.9 eV for TiF_4 . Due to the small covalent radius of fluorine, it is more reasonable to think that the fluorine ions enter the crystal lattice as interstitial species without bonding with other atoms. Therefore, the fluorine shows a high F_{1s} binding energy. It can be observed that washing with NaOH solution would decrease the surface adsorbed fluorine, but heat treating would make the interstitial fluorine escape off from the crystal lattice and convert into the adsorbed species. Because the two post-treatments decreased the VLR activity significantly, it suggested that both the surface adsorbed and the interstitial fluorine synergistically contribute to the VLR activity of the fluorine modified TiO_2 .

6 Conclusions and prospects

TiO_2 modified with nonmetals is an effective method to extend the absorption to visible range. However, the well documented nonmetals doped TiO_2 provided confused results on the origins of VLR activity. Nitrogen doped TiO_2 introducing three new impure N_{2p} bands in the gap contributes to the VLR performance and results in a lower oxidation power of visible light excited holes. Besides the story of doping, recent work has suggested that surface modification with sensitizing matter such as carbonaceous or organic substances is another important reason for the VLR properties. In addition, surface modification with alkoxy groups can also induce a VLR activity via a ligand-to-metal charge transfer process. The above cases have implied that if organic substances got involved at relatively low temperatures in the synthesis process, attention should be paid to the carbonaceous residues, which could serve as effective sensitizers. Moreover, surface modification can change the surface properties of TiO_2 , and in turn, alter the interaction between substrates and TiO_2 , thus resulting in an enhanced dye sensitization for its degradation under visible light. Fluorine modification TiO_2 is as such, in which a synergic effect of interstitials fluorine and surface adsorbed fluorine help in the enhanced dye sensitization and degradation.

Although there are various strategies for VLR TiO_2 by modifying with nonmetal elements, the as-prepared VLR TiO_2 still have some shortcomings such as instability upon prolonged irradiation or low efficiency for practical application. Developing novel heterojunctions by modifying TiO_2 with stable carbon matters could be a promising way to obtain desirable VLR TiO_2 photocatalysts.

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