

Review of N and Metal co-Doped TiO₂ for Water Purification under Visible Light Irradiation

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Abstract: In recent years, heterogeneous photocatalysis as one of the advanced oxidation processes (AOPs) has gained wide attention in water purification due to its effectiveness in degrading and mineralizing of the organic compounds assisted with the solar UV and visible-light spectrum. Currently, a wide range of related materials have been developed, amongst which TiO₂-based photocatalysts appear to be more popular materials used in heterogeneous photocatalysis processes. However, the use of the bare TiO₂ phases presents some drawbacks and various attempts have been carried out by introduction of non-metals and metals into the TiO₂ bulk to successfully cause the red shift of the absorption onset of TiO₂ to the visible region and enhance the photocatalytic activity. This paper presents an overview on principle of photocatalytic oxidation process. Particular emphasis is given to different strategies to modify N doped TiO₂ with metal for the enhancement of its photocatalytic efficiency in degradation of various toxic organic compounds such as phenols and dyes, predominant in wastewater effluents.

Key words: heterogeneous photocatalysis, TiO₂, water purification, visible light irradiation, advanced oxidation processes

1. Introduction

In order to ensure water supplies will not dwindle, recycling of wastewater effluent is recognized to be a strategic approach in alleviating water shortage [1]. However, toxic organic compounds such as pesticides, dyes, phenols and the associated environmental hazards are discharged into the aquatic environment through various anthropogenic inputs. Despite their low concentration, the presence of these contaminants is still a major concern over public health and a major obstacle to water recycling due to their bio-recalcitrant and acute toxicity [2]. The method of “advanced oxidation processes” (AOPs) appears to become the focus of intense interest when the process can be driven by solar UV or visible light. Among AOPs, TiO₂ is generally considered to be one of the important evergreen photocatalyst due to its desirable physical and chemical properties against photochemical corrosion, efficient photocatalytic activity, high photostability, low cost and toxicity [3]. In nature, titanium dioxide (TiO₂) exists as three different polymorphs that are anatase, rutile and brookite. Among three common TiO₂ crystalline forms, anatase is the most commonly used form in photocatalysis.

Unfortunately, the use of the bare TiO₂ phases presents some drawbacks that limit its application as a general tool, such as low quantum efficiency in the visible region [4], high recombination rate for the photo produced electron-hole pairs and low transfer rate between photoelectron and oxygen molecule. The threshold wavelength corresponding to the band-gap energy of 3.2eV is at near ultraviolet radiation (387nm) for bare TiO₂, as a consequence, only 5% energy of the solar spectrum can be utilized [5]. Therefore, it's imperative to develop efficient photo catalysts which are more competitive against these drawbacks in this field and enhance photocatalytic efficiency, particularly under visible-light irradiation.

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In last years, various attempts have been carried out by introduction of non-metals, such as carbon [6], nitrogen [7], sulfur [8], fluorine [9], iodine [10] and boron [11] into the TiO₂ bulk to successfully cause the red shift of the absorption onset of TiO₂ to the visible region and enhance the photocatalytic activity. Among these elements, nitrogen was thought as the most effective substitution doping nonmetal due to a similar size to oxygen atom as well as low ionization energy, consequently, it can be easily introduced into TiO₂ lattice and substitute O, this results in exhibiting higher photocatalytic activity [12].

Besides nonmetal doped TiO₂ systems, metals for example, Ag [8], Pt [13], Fe [14], W [15], La [16], Eu [17] are another kind of efficient dopant which can facilitate to separate the photogenerated electron-hole pairs resulting in enhancement of photocatalytic activity for both oxidation and reduction.

Apart from doping TiO₂ with a single metal or nonmetal, there are several efforts that combine the two approaches, which have been reported that could result in inducing synergistic effects and higher visible-light responses as compared to the TiO₂ doped with single element [18].

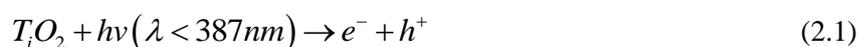
To the best of our knowledge, there have been few researches focusing on reviews of the respective advantages of nonmetal and metal co-doping TiO₂. This paper aims to review and summarize recent research on the modification of N-doped TiO₂ with metal under visible light aimed at enhancing the degradation efficiency of toxic organic compounds in wastewater.

2. Principle of Photocatalytic Oxidation Process

2.1. Electronic processes in TiO₂ photocatalysis

In the photocatalytic oxidation process, photoreactions occur when the photocatalyst, usually a semiconductor, in the presence of sufficiently energetic light source, produces reactive oxidizing species (ROS) which can destroy organic pollutants.

When titanium dioxide is exposed to visible light or UV radiation, there will exist two situations. If the energy of the incident light is equivalent to or greater than the band gap energy of the semiconductor, the absorption of a photon promotes an electron from the valence band (VB) to the conduction band (CB), as a result, leading to the generation of a positive hole (h⁺) in the VB and an electron (e⁻) in the CB (Eq. (2.1)).



Otherwise, the illumination of the photocatalytic surface with energy lower can not excite an electron and results in energy dissipation in the forms of heat.

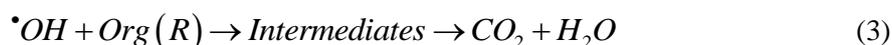
Excited state electrons and holes can be trapped as Ti³⁺ and O⁻ defect sites in the TiO₂ lattice, or migrate to the catalyst surface. As both of them are in metastable surface states, it's easy for them to react with electron donors and electron acceptors adsorbed on the semiconductor surface.

The positive hole which is a powerful oxidizing agent with high redox oxidizing potential can rapidly react with surface bound organic pollutants (Org), water or hydroxylions (OH⁻) to form extremely reactive hydroxyl radicals (•OH) (Eq. (2.2)) that subsequently attack a wide range of organic species, ultimately leading to complete mineralization of these substances and producing final degradation products such as CO₂ and H₂O [19]. The oxidative and reductive reaction can be represented by the following steps:

Oxidative reaction:



Reductive reaction:



On the contrary, oxygen molecule (O₂) as an efficient electron acceptor is reduced by the electron in the CB to produce reactive superoxide radical anions (O₂•⁻) that can enter into a chain reaction to yield a host of reactive oxygen species (ROS) such as HO₂• and H₂O₂, which eventually could convert to •OH radicals [20].

Finally, these radicals formed during this reaction can also play an important role in totally mineralization of organic pollutants in the photocatalytic reaction.

2.2. Recombination

In competition with charge transfer to absorbed organic pollutants, recombination of photogenerated charge carriers may occur either on the surface or in the bulk, that is, the excited electron reverts to the valence band without reacting with adsorbed species, liberating input energy as light or heat (Eq. (2.5)).



Moreover, electron accumulation occurs when the reduction process of oxygen and the oxidation of pollutants do not advance simultaneously, leading to the increase of charge carriers recombination and an inefficient photocatalytic oxidation [21].

Therefore, it is of paramount importance to suppress the combination and promote separation of the electron-hole pair for enhancing chemical conversion efficiency.

2.3. Evaluation of photocatalytic activity

According to the principles of photocatalytic reaction, organic pollutants are destroyed mainly on the surface of a semiconductor by reactive oxidizing species (ROS), so to some extent, the higher adsorption of organic compounds on the photocatalyst surface leads to a more efficient reaction.

Generally, the Langmuire-Hinshelwood (L-H) model which relates the rate of surface-catalyzed reaction to the surface covered by the substrate is the most commonly applied to explain heterogeneous photocatalysis, relate the rate of surface-catalyzed reactions to the surface covered by the substrate. The model equation can be expressed as follows [22]:

$$\frac{1}{r} = \frac{1}{k_r K_{ads} C} + \frac{1}{k_r} \quad (5)$$

where r is the reaction rate for the oxidation of reactant ($\text{mgL}^{-1}\text{min}^{-1}$), k_r is Langmuir-Hinshelwood reaction rate constant ($\text{mgL}^{-1}\text{min}^{-1}$), K_{ads} is a constant of adsorption equilibrium (L mg^{-1}), C is the substrate concentration (mgL^{-1}).

At low substrate concentration, that is, the initial substrate concentration C_0 is a millimolar solution (C_0 is small), the equation can be simplified to a first-order pattern demonstrating the relationship of C and t :

$$\ln \left[\frac{C_0}{C} \right] = k_{obs} t \quad \text{or} \quad C = C_0 \exp(-k_{obs} t) \quad (6)$$

where C_0 is the initial concentration of substrate in water, C is the residual concentration of pollutant at the reaction time t , furthermore, in the light of the equation, a plot of $\ln(C_0/C)$ versus time represents a straight line, the apparent first-order rate constant k_{obs} is the slope of which upon linear regression [23].

3. Modified N Doped TiO₂ with Metal

3.1. Photocatalytic activity of modified N-doped TiO₂

Recently, many reports about using various strategies to synthesize the co-doped TiO₂ with nitrogen and metal elements such as noble metal, rare earth metal and transition metal as the modification substances, have been published, which was shown in Table 1. And it had already been proved that the prepared photocatalysts demonstrated more excellent photocatalytic activities for decomposition of enormous organic pollutants in wastewater than doping with N or single metal in the visible light region, further confirming that this combinative method is a promising way of improving the activity. Fig. 1 contrasted the degradation efficiencies of different pollutants in water by pure TiO₂, metal doped TiO₂, N-TiO₂ and metal and nitrogen co-doped TiO₂ under visible light.

The high photocatalytic activity of the co-doped samples is probably due to narrowing the band gap [24], or the formation of localized mid-gap states [25] or generating oxygen vacancies [26] by N doping and reducing the recombination rate of charge carriers by metal doping, as well as the synergistic effect caused by co-doped these two elements.

As shown in Fig. 1, the removal efficiencies of contaminants were by pure TiO₂ under visible light irradiation rather low. This is because the energy of visible light is lower than the band gap energy of TiO₂, photoreactions and reactive oxidizing species could not be activated and produced [34].

Table 1: Modified N-TiO₂ photocatalysts and the preparation method and the model pollutants used for testing the photocatalytic activity

| Type of catalyst | Catalyst dosage | Precursors and modification methods | Reaction conditions and degradation of organic pollutants | Reference |
|---|----------------------|--|---|-----------|
| MWCNT/N, Pd co-doped TiO ₂ (0.5% MWCNT) N, Pd co-doped TiO ₂ (0.5% Pd) | 1 gL ⁻¹ | The photocatalyst was prepared by using MWCNTs synthesized using the nebulised-spray-pyrolysis method followed by acid functionalisation, Ti(OC ₃ H ₇) ₄ , Pd(NH ₃) ₂ Cl ₂ , and NH ₃ as precursors and calcination for 2h at 500 °C. | Degradation of Eosin Yellow (EY), 99.55 and 99.3% in 2h under simulated solar radiation ($\lambda > 450\text{nm}$) with the light intensity of 1000 Wm ⁻² at 25 °C, respectively. | [27] |
| Gd, N/TNT | 0.2 gL ⁻¹ | The catalyst was prepared by a hydrothermal method and then co-doped with Gd ³⁺ and N through ion-exchanging with H ⁺ using TiO ₂ powders, Gd(NO ₃) ₃ and NH ₄ Cl as the precursors and calcination at 300 °C. | Degradation of 2.5 × 10 ⁻⁵ mol/L rhodamine B, over 70% (1:1 Gd, N/TNT, 1:2 Gd, N/TNT, and 2:1 Gd, N/TNT), the maximum rate was 81.4% achieved by 1:1 Gd, N/TNT, in 2h under visible light irradiation using the xenon lamp (350W) with 400nm cutoff filter. while the photo-degradation of Rhodamine B for pure TNT was only 34%. | [28] |
| Y-N-TiO ₂ | 1 gL ⁻¹ | The catalyst was synthesized by a sol-gel method by using titanium n-butoxide (Ti(OBu) ₄) urea and Y(NO ₃) ₃ · 6H ₂ O as precursors and calcination at 500 °C in air for 2 h. | 0.05 at.% Y-N-TiO ₂ showed the best photocatalytic performance for degrading 10mg/L methylene blue (MB) solution than that of pure and other codoped (with different amount of Y) samples, about 48% in 3h using a 500W long-arc xenon lamp as the light source. | [29] |
| Mn-N-TiO ₂ | 1 gL ⁻¹ | The catalyst was prepared by the hydrothermal synthesis method using titanium tetrachloride (TiCl ₄), ammonia and MnSO ₄ powder as precursors and calcination under a dry flow of air at 573–873K for 2h. | Among the synthesized samples, 0.4mol% Mn-N-TiO ₂ calcined at 673K exhibited the highest photocatalytic efficiency. The RhB conversion reached 95.3% after the reaction for 180min. under visible light irradiation using a 500-W Xe lamp with a UV cut-filter ($\lambda > 400\text{ nm}$) as visible light source. | [30] |
| Zn-N-TiO ₂ | 1 gL ⁻¹ | The catalyst was prepared by the sol-gel method using zinc acetate, urea and titanium n-butoxide (Ti(OBu) ₄) as the precursors and calcination at 500 °C under air for 2h. | Among the synthesized samples, (Zn,N)-codoped (with 1 at.% Zn) TiO ₂ demonstrated the highest photocatalytic efficiency for degradation of 10mg/L methylene blue (MB) and the degradation rate is 85% in 3h using a 500W long-arc xenon lamp as the light source. | [31] |
| Bi-N-TiO ₂ | 1 gL ⁻¹ | The catalyst was prepared via anneal at 500 °C for 2 h after a simple sol-gel combined hydrothermal method using titanium n-butoxide (TTBO), BiCl ₃ and KSCN as the precursors. | Among the synthesized samples, Bi-N-TiO ₂ demonstrated the highest photocatalytic efficiency for degradation of 10 mg/L acid orange (AO7), 86.42% in 6h under visible light irradiation using a 500 W Halogen lamp with a glass optical cutoff filter (cutoff $\lambda < 400\text{ nm}$), at the same time, the insulation film to filter out $\lambda > 750\text{ nm}$. | [32] |
| Fe-N-TiO ₂ | Not available | The catalyst was prepared via sol-gel method loaded on low-density polyethylene loaded on (LDPE) film with dimension of 50mm × 100mm × 0.125mm using the tetrabutyl titanate, urea and ferric nitrite (Fe(NO ₃) ₃ · 3H ₂ O) as the precursors and annealed at 500 °C in the furnace for 3 h. | Among the synthesized samples, Fe-N-TiO ₂ demonstrates an obviously higher catalytic activity for degradation of DPA solution, 80% in 90min under visible irradiation using a 500W Xe lamp with the irradiation below 400 nm removed by 2M NaNO ₂ solution. | [33] |

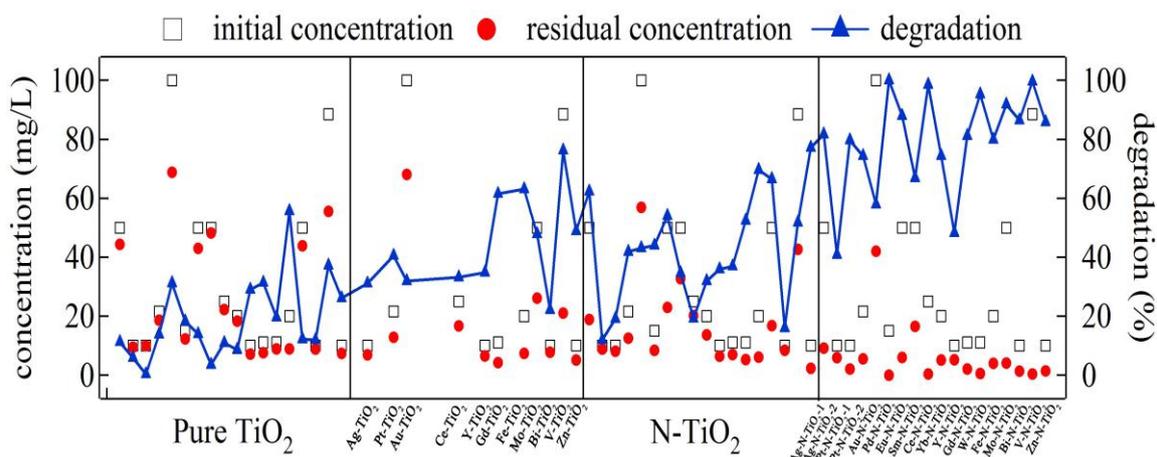


Fig. 1: Photodegradation of contaminants under visible light using pure TiO₂, metal doped TiO₂, N-TiO₂ and metal and nitrogen co-doped TiO₂

Doping metal into TiO₂ is an efficient method to improve the catalyzer activity due to suppressing the recombination of photogenerated charge carriers, since electrons could be trapped by metal atoms [35]. N-TiO₂ containing substitutional nitrogen impurity atoms has a good characterization of low exciting beam intensity, resulting in the absorption peak red shifted and promoting the photon emission efficiency [36]. Both factors work synergistically to make the degradation efficiencies of titanium oxide impregnated with nitrogen and metal much higher than doping with N or single metal under visible light [37].

3.2. Modified N doped TiO₂ with noble metal

Using noble metal, including Ag, Au, Pt, Pd, Os, Ir, Ru or Rh to modify N doped TiO₂ is increasingly gaining interest in many reports. Different methods have been used to synthesize co-doped TiO₂ with N and noble metal, and it was found that these catalysts demonstrated an excellent photocatalytic performance compared to singly doped TiO₂.

Since the Fermi levels of these metals are close to the conduction band edge of TiO₂, these particles could serve as trapped sites for the electrons which transfer from the valence band to the conduction band and decrease the recombination rate, thus contributing to promoting charge separation and reaction rates [38].

Lu and co-workers [39] combined nitrogen-doped with Ag deposition by utilizing TiO₂ hollow sphere as a model to synthesize Ag-N-TiO₂ hollow spheres (HSs). It was observed that the co-modified TiO₂ hollow spheres exhibit a higher activity compared to other as-prepared samples, achieving 75% of degradation efficiency of methylene blue under visible light for 5 h, and the photocatalytic activity of these substances is in the following order: Ag-N/hollow spheres > Ag-hollow spheres > Ag-N/P25 > Ag-P25 > N/hollow spheres > N/P25. In addition, Ag-N/hollow spheres was found to show longer extending of photo-response towards larger visible spectra, which is partially due to reducing the band gap of the semiconductor by N doping. Ag nanoparticles could transfer the plasmonic energy from the Ag⁰ to the TiO₂ semiconductor due to its surface plasmonic resonance (SPR) effect [40], this also contributed to enlarging light absorption of the catalyst. On the other hand, the Schottky barrier which could serve as efficient electron traps was formed by Ag deposition, results in suppressing the recombination of electron-hole and enhancing photocatalytic activity [41].

Different from other groups, a simple wet-chemical method was proposed to prepare Au/N-TiO₂ by Tian and coworkers [42]. In this literature, it was evidently observed that the photocatalytic activities of as-prepared samples by measuring the degradation rates of 2, 4-dichlorophenol (2, 4-DCP) under visible light irradiation for 5h vary in the order: 2% Au/N-TiO₂ > N-TiO₂ > 2% Au/TiO₂ > pure TiO₂. Together with that, the co-doped TiO₂ showed a red-shift to the visible light region, which may be attributed to substitutional and interstitial nitrogen in the TiO₂ lattice, leading to the formation of the N impurity energy level, that is, the electron can directly excite from the impurity energy level to the conduction band, enhancing the light absorption of TiO₂. The presence of Au by forming Schottky barrier can favor the

transfer of photo-induced electrons and restrain the recombination of photo-induced electrons and holes, contributing to enhancement of photocatalytic activity [43].

They reported that the Pd-N-TiO₂ catalyst was synthesized by a modified sol-gel method showed an excellent photocatalytic performance for degradation of the three NOM fractions over a period of 120min under simulated solar irradiation, the degradation efficiency is 96%, 19 % and 14 % for the hydrophobic fraction, the hydrophilic fraction and the transphilic fraction, respectively, which is superior to many other catalysts mentioned in this paper [44]. The phenomenon of TiO₂ absorption edge shifted into the high-wavelength region was also observed, which may be attributed to the formation of impurity levels near or above the valence band, thus light with longer wavelength can also excite the electrons, leading to the increased absorption in the visible light region [45]. More electrons were trapped due to the introduction of Pd into the TiO₂ particles, reducing the chances of electron-hole recombination and enhancing the visible light activity [32].

3.3. Modified N doped TiO₂ with rare earth metal

In recent years, rare-earth metals were employed to modify N doped TiO₂ and the interest of their photocatalytic activities arose.

Lanthanide ions, owing to their special electronic structure of 4f^x 5d^y, can form complexes with various Lewis bases, which is beneficial to provide an effective adsorbability of organic pollutants on TiO₂ surface, therefore enhancing the photocatalytic activity [46].

Europium and nitrogen co-doped titanium dioxide (Eu/N-TiO₂) was prepared by using the precipitation-peptization method, and the co-modified catalyst has a good activity, Obviously, the best photocatalytic performance for degradation of salicylic acid under visible light irradiation for 5h is 88% for 5h, which was achieved by 1.0% Eu/N-TiO₂ [47]. The enhancement in the degradation of salicylic acid under visible light is attributed to several factors. For one reason, nitrogen atom which was doped into TiO₂ substituted the sites of oxygen atom, leading to a red shift toward the visible region. For another reason, the introduction of Eu and N could inhibit grain growth of TiO₂, resulting in smaller crystal size and larger specific surface area, and Eu ion can coordinate with salicylic acid due to its special structure [48], thus more salicylic acid would be absorbed on the surface.

Huang and coworkers [49] had prepared Sm and nitrogen co-doped TiO₂ catalysts via the modified sol-gel hydrothermal method and the results showed that the removal rate could be up to 40.4% for the degradation of 4-chlorophenol under visible-light irradiation for 10 h by co-doped TiO₂, however, only 16.7% and 1.5% was achieved by N-TiO₂ and Sm-TiO₂, respectively, and the extending of light-absorbing was also realized. When N atoms were incorporated into the TiO₂ crystal lattice, the N2p and O2p states mixed, leading to a narrowing of the band gap by forming isolated levels that consisted of N2p orbital above the O2p valence band, consequently, light absorption edge shifted toward longer wavelengths. Sm³⁺ doping in TiO₂ can acts as electron traps, thus improving charge separation, and then electrons would be transferred to electron acceptors adsorbed on the surface of TiO₂, further forming reactive oxidizing species. Therefore, both of these contributed to the increase in photocatalytic activity of Sm-N-TiO₂ catalyst.

Ma and coworkers [50] reported that Yb, N co-doped ordered mesoporous TiO₂ was successfully synthesized via an evaporation-induced self-assembly process and it was found that for 3.0Yb/N-TiO₂, the degradation rate of 20 mg/L phenol was 75% after 10 h under visible light irradiation, moreover, given the same circumstance, 10 mg/L rhodamine B was completely degraded in 4 h. By the doping of nitrogen, an obvious red shift toward the visible region was observed, which was attributed to the generation of oxygen vacancy, or inducing the TiO₂ lattice distortion, leading to a narrowing band. The existence of Yb dopant was able to significantly restrain the growth of the nanoparticles, larger surface area and pore volume was obtained, furthermore, it was very easy for Yb³⁺ to capture the excited electrons, thus suppressing the recombination of electron and hole efficiently, which are beneficial for the catalytic reaction.

3.4. Modified N doped TiO₂ with transition metal

Doping with transition metals such as V, Cr, Fe, W, Zn, Mn and Mo into TiO₂ also have been greatly investigated in recent years, since many reports demonstrated that doping would extend the optical

absorption spectra of TiO₂ red shifted into the visible light region and act as the trapping sites to suppress the recombination of charge carriers efficiently, and which was a more cost effective choice compared with noble metals.

Ahmed and coworkers [51] prepared W, N co-doped TiO₂ photocatalysts by simple sol-gel method and the 4.5% W, N co-doped TiO₂ showed far superior activity as compared to other samples for the degradation of RhB and 2,4-DCP, and the removal rate were 100% and 70.0% in 150 min under visible light irradiations, respectively. This phenomenon might be attributed to new linkages of N-Ti-O, N-W-O, Ti-O-N and W-O-N, which lead to the formation new energy states, for N doping, new states were formed above the valence band of TiO₂, impurity states just lower the conduction band of TiO₂ emerged by W doping, consequently, narrowing the band gap of TiO₂, extending the sensitivity of photo catalyst to longer wavelength in visible light region, furthermore, the doped W ions can act as trapping sites and favor to separate photo excited electron/hole pairs and decrease recombination rate. In brief, both these two processes are responsible to enhance the W, N-TiO₂ photo catalytic activity under visible light.

It was also reported by Song and coworkers [52] that TiO₂ photocatalysts codoped with nitrogen and cobalt(II) were prepared via a modified sol-gel method, and 3mol% N-Co/TiO₂ had the highest activity for photodegradation of papermaking wastewater, and the CODCr values of papermaking wastewater reduced approximately 31.6% after and visible light irradiation for 12 h. This result confirmed N, Co co-doping was an effective way of improving the photoactivity of TiO₂, which was probably attributed to the synergistic effect of the co-modification. Superior visible light absorption abilities of the co-doping catalysts was considered by the formation of a dopant level that lies just above the valence band of the substitutional nitrogen and a another dopant energy level within the TiO₂ band gap caused by the charge transfer and the d-d transitions of metal doping, thus narrowing the band gap and leading to the red-shift of the absorption edge. Meanwhile, the efficient separation of charge carriers due to cobalt doping, porous structures of the mesoporous TiO₂, decrease in the particle size and increase in the surface area were also beneficial to enhancement of reaction activity.

Cheng and coworkers [53] fabricated the nanoparticles of TiO₂ co-doped with Mo and N through hydrolysis-precipitation method, combined with sonication posttreatment and the photocatalytic activity of as-synthesized samples, which was evaluate by using phenol as a degradation model can be ranged in the following order: Mo-N-TiO₂ > N-TiO₂ > TiO₂, the removal rate was 89.2% after 2 h of visible light irradiation by Mo-N-TiO₂. It was considered that titanium and oxygen elements could be substituted by molybdenum and nitrogen, respectively, leading to the formation of the impurity levels within the band of TiO₂, the band gap of Mo-N-codoped TiO₂ catalyst has been further narrowed compared with doping sing element, resulting in extending the photo-response of TiO₂ into the visible region and effectively separation of charge carriers in the photocatalytic process and enhancing photocatalytic activity of co-modified samples.

4. Conclusions

Based on research findings, it could be concluded that nitrogen and metal co-doped TiO₂ exhibited higher photocatalytic activity compared to singly doped TiO₂, the enhanced photocatalytic activity of co-modified TiO₂ was mainly attributed to the synergistic effects caused by the combination of the two dopants. This high photocatalytic activity of the co-doped samples is probably due to narrowing the band gap, or the formation of localized mid-gap states or generating oxygen vacancies by N doping resulting in the red shift of the absorption onset of TiO₂ to the visible region and reducing the recombination rate of charge carriers by metal doping, as well as the synergistic effect caused by co-doped these two elements. All of which confirmed that doping TiO₂ with N and metal was a promising way to promote the photocatalytic efficiency.

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