

Research on modified silicone compound photocatalyst by doping N

DaWei Pan¹, GuangXu Shao¹ and QingWen Zhang²

¹Department of Environmental Engineering, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan, Liaoning, China

²Anshan Iron and Steel Group Engineering Technology Co., Ltd., Anshan, Liaoning, China

Abstract. In order to improve the visible light response and reaction efficiency of nitrogen-doped TiO₂ set urea as nitrogen source, and silica gel as the load reagent adopt sol-gel method to prepare powder of nitrogen-doped TiO₂ supported on SiO₂, use equal volume impregnation method to load MnO₂ on catalyst, and then obtain the composite photocatalyst after drying, and roasting. The prepared composite catalysts were characterized by XPS, TEM, SEM, XRD and other methods. Moreover, the photo-catalytic activity of the composite catalysts under visible-light region was tested, and the influences of nitrogen content and calcinations temperature on the photo-catalytic activity were investigated. The results show that: (1) the range of light response of modified composite catalyst was expanded from ultraviolet region to visible-light region, which results in high visible-light catalytic activity in the degradation of methyl orange. (2) Through the mechanism of photo-catalytic reaction and the treatment effect analysis, MnO₂ as catalytic resulting O₂ can be served as a good electronic capture agent and improve the reaction efficiency. (3) With the reduction of nitrogen content, and the increase of calcination temperature, the visible-light catalytic activity was weakened. (4) The activity of catalyst was reused six times, without significant reduction and had excellent efficiency and stability.

Introduction

With the increasingly serious energy shortage and environmental pollution, finding the suitable photocatalyst to realize the effective utilization of solar energy, has become a hot issue in the field. Therefore, TiO₂ with excellent catalytic performance attracts more attention in the environmental, [1] which has the advantages of low cost, good chemical stability, non-toxic, and no secondary pollution. But there are also shortcomings, e.g., the forbidden band of TiO₂ is wide (E_g=3.2eV) and can only absorb UV-light; In addition, the hole and electron stimulated by light are easily compounded so as to reduce the photo-quantum efficiency [2-3]. Many domestic and international experts and scholars have tried to use the nonmetal ion doping method to extend the visible light absorption of TiO₂, where nitrogen-doping can effectively hence the absorption of the catalyst in the visible-light region, as well as the efficiency of photo-catalytic oxidation [4]. SiO₂ as the load reagent can effectively control the growth of TiO₂ particles so as to get smaller size, and larger specific surface area, which can improve the separation performance, and make them inactivation to prolong the service life [5-6]. Researches show that quantum yield is the most important factor influencing treatment effect of photocatalyst, so improving the light quantum yield of photo-catalyst, promoting the separation of photon-generated carriers and reducing the recombination rate are key factors, in this paper, by preparing the nitrogen-

doped TiO₂/MnO₂ supported on SiO₂ composite photocatalyst the new ecological O₂ resolved from hydrogen peroxide which are produced in the process of catalytic hydrolysis can be used as electron capture agent to effectively promote the separation of photon-generated carriers and to reduce its compound probability [7]. This kind of photo-catalyst has advantages of visible light response, and smaller and equally distributed particle size, and can efficiently restrain the compound of electronic - hole pairs, which greatly improve the treatment effect of the pollutants.

Experiment

1.1 preparation of Nitrogen-Doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst

The preparation was made as follow: After adjusting the PH value of Solution B (10mL of deionized water and 20mL of anhydrous ethanol) to about 2, dropwise add Solution A (10mL of acetic acid, 10mL of dibutyl phthalate and 30mL anhydrous ethanol) into it with strong stirring, and then continue to strongly stir for 30 minutes after dropping, add different volumes of urea whose concentration is 1mol/L to the mixed Solution with N/Ti molar ratio of 10%, 15%, 20% and 25% respectively, and continue to stir for 30 minutes, add a certain amount of SiO₂ as load reagent and strongly stir for 60 minutes, stand and air dry the mixture at room temperature until it

^a Corresponding author: Tel: 86 13998091973; E-mail: wxq_as@163.com

become xerogel and then grind it in agate mortar, calcine it in muffle furnace for 3hours at different temperature of 350 °C, 400 °C, 450 °C and 500 °C respectively, grind it again and screen it by standard sieve with 300 meshes, adopt the equal volume impregnation method to load a certain concentration of manganese nitrate on the calcined sample of catalyst in ultrasonic instrument, after 1 hour's drying, and calcination a series of nitrogen-doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst with different calcination temperature is obtained.

1.2 performance of Nitrogen-Doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst

The adsorption ability and photo-catalytic performance of nitrogen-doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst was evaluated by the degradation of methyl orange, and the reaction was carried out in the self-made additional stirring temperature cycle optical instrument with 150w iodine tungsten lamp as light source. The reaction device keeps the temperature of the reaction system at 25 °C, and the magnetic stir keeps uniform concentration and temperature of solution in the system. Take a certain quality of nitrogen-doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst in reaction device, add 100mL of methyl orange solution with certain concentration, and make it adsorption-desorption balance through 30 minutes' magnetic stirring under the condition of no light, and then turn on the iodine tungsten lamp for illumination. In the process of aphotc adsorption - desorption balance and illumination, take a sample every 20 minutes, use the principle of centrifugal separation to remove the photo-catalyst, adopt ultraviolet-visible spectrophotometer to measure the absorbance of supernatant fluid at the longest absorption wave, and then calculate the concentration according to the standard working curve based on the concentration(C_t) of the supernatant fluid at the degradation time(t) and the initial concentration(C₀) of degradation, calculat the degradation rate (D) of methyl orange to evaluate the photocatalytic activity of nitrogen-doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst:

$$D = (c_t - c_0) / c_0 \times 100\%$$

Results and Discussion

2.1 Characterization of Catalysts

2.1.1 X-ray diffraction (XRD) analysis of the catalyst

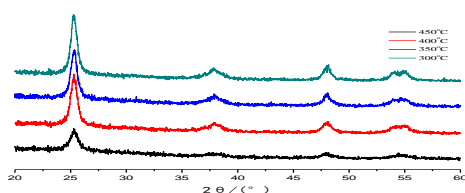
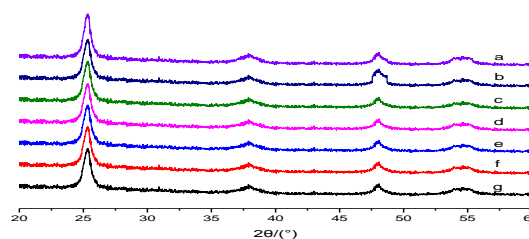


Figure1. The XRD spectrum of 20%N at different calcination temperatures

The X-ray diffraction (XRD) spectrum in Figure 1 shows that: all nitrogen doped TiO₂/MnO₂ supported on SiO₂ composite photocatalysts with N/Ti molar ratio of 20% prepared at 300 °C, 350 °C, 400 °C and 450 °C respectively, are anatase phases, and the Ti-N diffraction peak does not appear, because high temperature made N volatilize, resulting in low N content, or larger Ti - N clusters fail to form in the complex catalyst; Meanwhile the movement of characteristic peak of anatase type TiO₂ does not appear, because of nitrogen-doping, it shows that nitrogen doping does not change its crystal structure. Using Scherrer formula to calculate the average particle size, the results are 13.8nm, 14.6nm, 12.3nm, and 17.2nm. With the increase of calcination temperature, the characteristic peak of anatase crystal phase becomes more keen-edged, which means the crystal shape is more and more regular and the size becomes larger and larger, because the increase of calcination temperature causes agglomeration of particles.



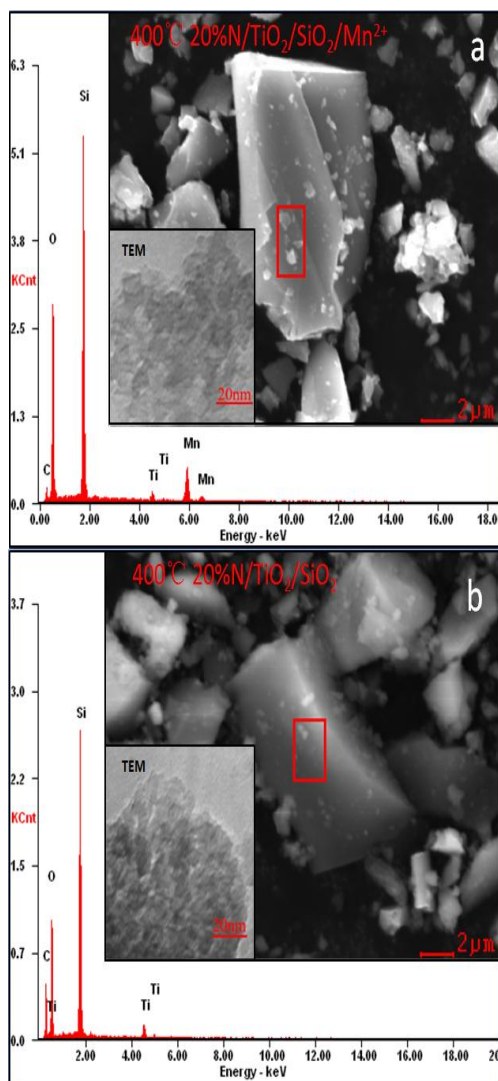
(a. 400 °C TiO₂ b. 400 °C TiO₂/SiO₂ c. 400 °C N/TiO₂ d. 400 °C 10% N/TiO₂/SiO₂/Mn²⁺ e. 400 °C 15% N/TiO₂/SiO₂/Mn²⁺ f. 400 °C 20% N/TiO₂/SiO₂/Mn²⁺ g. 400 °C 25% N/TiO₂/SiO₂/Mn²⁺)

Figure 2. XRD spectrum of nitrogen doped samples with different molar ratios at calcination temperature of 400 °C

Figure 2 shows that: all nitrogen-doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalysts with different N/Ti molar ratio prepared at temperature of 400 °C are anatase phases. Using the Scherrer formula to calculate the average grain size, the results are 9.1nm, 8.4nm, 14.7nm, 12.4nm, 13.2 nm, 12.3nm, and 14.2nm. Nitrogen-doping enlarges the catalyst particles, and the size has a minimum value with the change of N/Ti molar ratio, which is corresponding to the catalyst with molar ratio of 20%. It is consistent with the verification results according to theoretical basis that more keen-edged diffraction peak and smaller full width at half maximum means smaller particle and better crystal.

2.1.2 Surface morphology analysis of Catalyst

Scanning electron microscope (SEM)

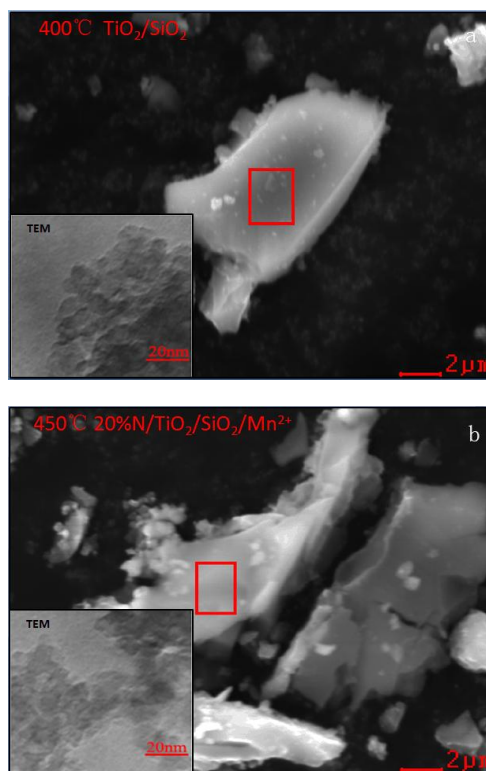


(a) 20%N/TiO₂/SiO₂/Mn²⁺ (b) 20%N/TiO₂/SiO₂

Figure 3. The SEM images of TiO₂ photo-catalysts

Figure 3 is the SEM images and energy spectrum diagrams of nitrogen-doped TiO₂ supported on SiO₂ composite photocatalyst, to which Mn²⁺ is added. It can be seen from the figure: TiO₂ particle size ranges from few nanometers to dozens of nanometers which is successfully loaded on the surface of SiO₂ particle which relatively uniform distribution; the comparison of energy spectrum diagram shows that Mn²⁺ has been successfully incorporated into and loaded on the surface of SiO₂, which slightly increases TiO₂ particle size. Thus it shows SiO₂ as loaded reagent can effectively improve the distribution of TiO₂ particles, and enhance the dispersing performance; and the Mn²⁺ has been successfully incorporated and loaded on the surface of SiO₂.

Transmission electron microscope (TEM)



(a) 400°C TiO₂/SiO₂ (d) 450°C 20% N/SiO₂/TiO₂/Mn²⁺

Figure 4. TEM micrographs of complex photo-catalyst

Figure 4 is the transmission electron microscope (TEM) images of different composition photo-catalysts. We can see from Figure 4 (a) that the TiO₂ particles are uniformly distributed on the surface of SiO₂, indicating that SiO₂ loading can effectively improve the dispersibility of TiO₂ particles; through the comparison of Figure 3 (a) and Figure 4 (b) it can be seen that the particle size increases with the increase of calcination temperature, which is due to the agglomeration of the grain caused by the increase of calcination temperature, verifying the analysis conclusion in XRD.

2.1.3 UV-vis diffuse reflectance.

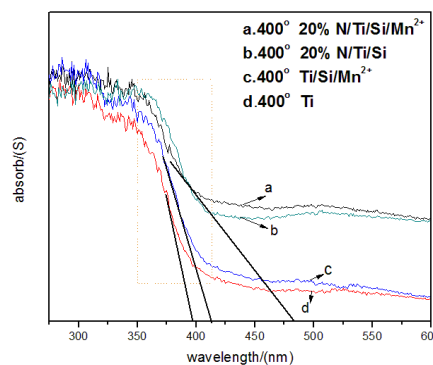


Figure 5 . UV-Vis Diffuse reflectance spectra of complex photo-catalyst

The UV-Vis diffuse reflectance spectra of Fig. 5 show that the absorption range of the modified catalyst is extended to visible light region from 390 nm to 480 nm, and the absorption wavelength range is increased by 90 nm, which indicates that nitrogen doping can effectively improve the visible light response activity of the catalyst. According to the tangent comparison of the curves (c) and (d), the addition of Mn only enlarges the absorption range of the catalyst by about 20 nm (from 390 nm to 410 nm). This shows that Mn is helpful to increase the number of photons involved in the photocatalytic reaction and enhance the absorption intensity of the composite photocatalyst, but does not produce obvious visible light response. According to the tangent comparison of curves a and (c), it is shown that doping N can effectively improve the visible light response activity of the catalyst, but Mn can not produce this effect. From the slope of the light absorption threshold region of the curves (a) and (d), the visible light response range of the composite photocatalyst is obviously enlarged, which indicates that the N_{2p} orbital replaces part of the O_{2p} orbital and forms a new hybrid orbital. The formation of Ti-O-N bonds on the surface of titanium dioxide forms a new energy level structure, which reduces the band gap of titanium dioxide and thus obtains visible light activity.

2.1.3 X-ray photoelectron spectroscopy of Catalyst

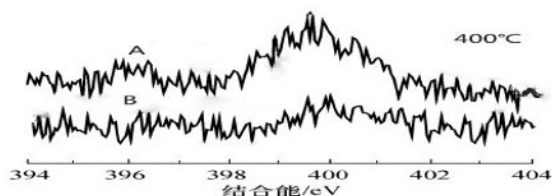
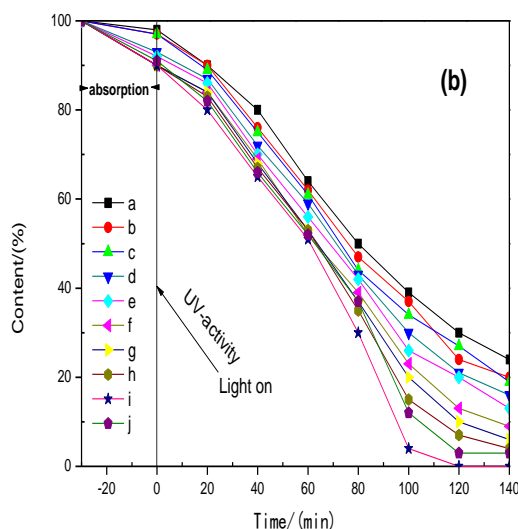
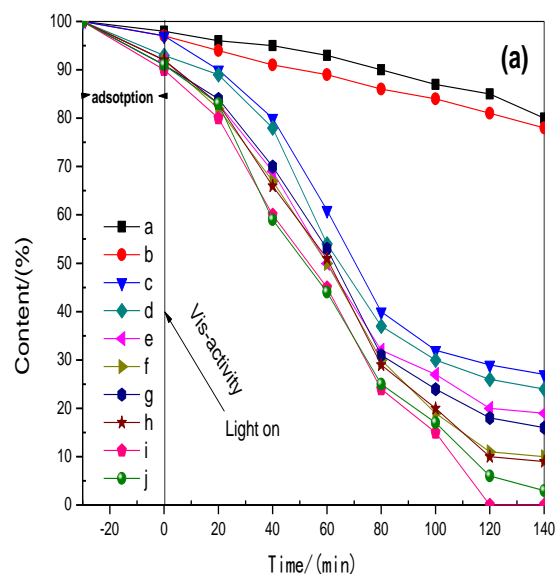


Figure 6. XPS energy spectrum diagram of N_{1s} of TiO_2 photocatalyst at calcination temperature of $400\text{ }^\circ\text{C}$

Figure 6 is the XPS energy spectrum diagram of composite catalysts at calcination temperature of $400\text{ }^\circ\text{C}$, where A and B respectively represent the catalysts with and without nitrogen-doping. It can be seen from the figure that, for the nitrogen-doped catalyst samples, there is a new N_{1s} peak at 396.1 eV , and a N_{1s} peak of the catalyst surface adsorbed N_2 at 401.7 eV , thus the N atoms and TiO_2 molecules are combined by chemical bonds. Asahi^[8] et al, attributed the peak appearing in the 396 eV to N atoms mixed with the crystal lattice, and attributed peaks appearing in the 400 eV and 402 eV to the molecular adsorption of N_2 on the catalyst surface. They pointed out that the catalyst with visible light activity is associated with the N atoms, and this is because the hybridization of N_{2p} orbital and O_{2p} orbital happened, which can decrease the forbidden band width of TiO_2 , so as to be motivated by the visible light.

2.2 Photo-catalytic activity of Nitrogen-Doped TiO_2/MnO_2 supported on SiO_2 composite photocatalyst



(1)Visible light (2)Uv light)(a. $400\text{ }^\circ\text{C TiO}_2$ b. $400\text{ }^\circ\text{C TiO}_2/SiO_2$ c. $300\text{ }^\circ\text{C } 20\%N/TiO_2/SiO_2/Mn^{2+}$ d. $400\text{ }^\circ\text{C } 20\%N/TiO_2/SiO_2$ e. $350\text{ }^\circ\text{C } 20\%N/TiO_2/SiO_2/Mn^{2+}$ f. $400\text{ }^\circ\text{C } 10\%N/TiO_2/SiO_2/Mn^{2+}$ g. $400\text{ }^\circ\text{C } 15\%N/TiO_2/SiO_2/Mn^{2+}$ h. $450\text{ }^\circ\text{C } 20\%N/TiO_2/SiO_2/Mn^{2+}$ i. $400\text{ }^\circ\text{C } 20\%N/TiO_2/SiO_2/Mn^{2+}$ j. $400\text{ }^\circ\text{C } 25\%N/TiO_2/SiO_2/Mn^{2+}$)

Figure 7. The photo-catalytic activity of TiO_2 under different conditions

Figure 7 (1) shows test results of visible-light activity of catalyst. The comparison between d and a/b shows that the catalytic activity of visible light of nitrogen-doped TiO_2/SiO_2 has been significantly improved. This is because the doped N atoms partly replaced O atoms enter into crystal lattice of TiO_2 , and formed an independent N_{2p} narrowband above the valence band, causing the response of composite catalysts to the visible light^[8]. It can be seen from f, g, i and j in the figure, the catalytic activity of the composite photo-catalysts gradually

increases with the increment of nitrogen-doping content, It will be optimal when the percentage of nitrogen doping content is 20%, at this moment the composite catalyst can completely get rid of methyl orange within 120 minutes, and that with different doping amount will not have the same effect under the same conditions. The reason may be that the newly created energy level after nitrogen-doping and the bulk phase of TiO₂ form a compound semiconductor structure, hence the electric potential difference of both valence bands can make the hole of TiO₂'s valence band migrate to the newly formed energy levels, so as to effectively reduce the recombination probability of photo-generated electron hole, and improve the activity of catalyst^[6]. can be seen from I and h in the figure that the removal rate decreases with the increase of temperature, and the reason may be that under high temperature, N element was oxidized and volatilized in the heating process, leading to the decrease of N content in TiO₂ lattice, and the enlargement of size, and decrease of specific surface area, can also lower the activity of visible-light response. Figure 6(1) shows the catalyst activity test results of UV-light. It can be seen from the figure that the composite catalyst in ultraviolet region also has a good degradation effect. simultaneously, Figure 7 shows, Mn²⁺ has obviously improved the processing efficiency of catalyst. This is because the Mn²⁺ is oxidized into MnO₂ through calcination and loads on the surface of catalyst. It is used as catalyst to catalyze H₂O₂ to produce O₂ which is served as electron capture agent to effectively promote the separation of photo-generated carrier and reduces its compound probability.

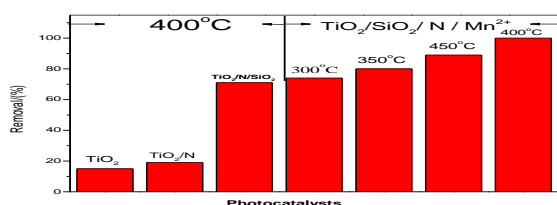
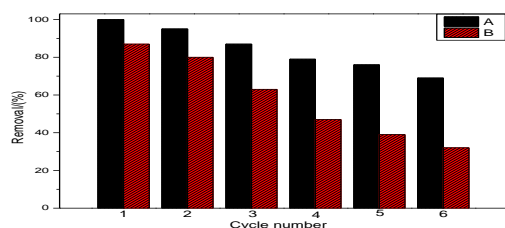


Figure 8. Photo-catalytic activity of TiO₂ with different condition of Mn²⁺ under Visible light



(A.400°C 20%N/TiO₂/SiO₂/Mn²⁺ B. 400°C 20%N/TiO₂/Mn²⁺)

Figure 9 Effect of run times on the photo-catalytic activity of TiO₂

Figure 9 shows the experimental results of repeated use of catalyst. Under the same cycle times, the catalytic activity of the composite catalyst adding SiO₂ as lode reagent is obviously higher. After reused six times, the degradation rate of composite catalyst is 75%, while that

without SiO₂ is only 27% under the same condition. In conclusion, SiO₂ as load reagent can effectively inhibit the deactivation of catalyst, so as to improve its service life.

In conclusion, for nitrogen-doped TiO₂/MnO₂ supported on SiO₂ composite photo-catalyst, nitrogen-doping can expand the range of light response of TiO₂ and improve the activity in visible and ultraviolet region. SiO₂ as load reagent has smaller particle size, and larger specific surface area, which can improve the separation performance of catalyst, so as to prolong the service life of catalyst. The mechanism shows that holes migrating to the surface of the semiconductor TiO₂ react with H₂O or OH⁻ absorbing on the surface and the generated ·OH, is free radical with strong oxidability, which can oxidize a variety of organic pollutants, and plays a main role in photo-catalytic system as oxidizing agent. The Mn²⁺ is oxidized into MnO₂ by calcination, which loads on catalyst surface, and catalyzes ·OH. The generated O₂ can react with electrons which migrate to the surface of the semiconductor TiO₂ to generate O₂, and other active-oxygen free radicals. The reactive group will also be able to participate in oxidation-reduction reactions, and the generated O₂ is served as electron capture agent to promote the separation of photo-generated carrier and reduce the recombination probability, which significantly improve the photo-catalytic activity of the catalyst. At the same time, according to the reaction dynamics, this process can promote the generation of ·OH which is served as the capture agent of hole.

2.3 Photocatalytic reaction mechanism diagram

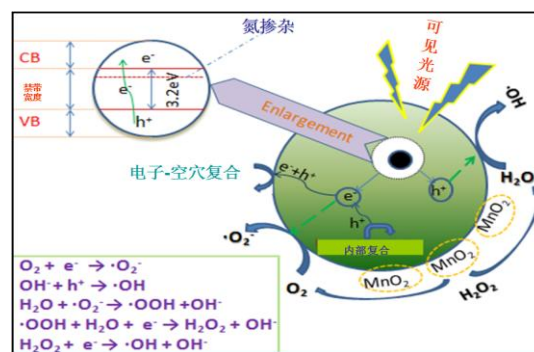


Figure 10. Catalytic reaction mechanism of N-doping TiO₂/MnO₂ load on SiO₂ composite photo-catalyst

According to the simulated catalytic reaction mechanism of Fig.10, the N_{2p} orbital and O_{2p} orbital in the bulk phase of TiO₂ were hybridized by nitrogen doping, thus the width of the forbidden band of TiO₂ was reduced and therefore could be excited by visible light. Electrons and holes migrate to the surface of catalyst particles under the action of electric field or through diffusion to react with the adsorbed substances on the surface. Holes are usually trapped by OH⁻ and surface-adsorbed H₂O molecules to form ·OH, and hydroxyl radicals are the main active substances in photocatalysis. Electrons are usually trapped by O₂ molecules adsorbed on the surface of

particles, resulting in free radicals such as O_2^- , $\cdot OOH$, which can participate in many redox processes. Electron-hole recombination is the most important reason for the serious decrease of reaction efficiency. Electron-hole recombination is very fast, but the rate of trapping carriers is relatively slow. Electrons are more active than holes. Therefore, O_2 produced by high temperature oxidation of Mn^{2+} to MnO_2 is used as electron trapping agent in advance. Adsorption on the catalyst surface is very important, it can improve the surface electron migration rate to inhibit carrier recombination, thereby increasing the quantum efficiency of photocatalytic reaction, but also promote the formation of hydrogen peroxide molecules adsorbed on the catalyst surface. Therefore, the prepared composite catalyst can achieve visible light response and obtain high treatment effect.

Conclusions

Make full use of the good performance of visible-light response of nitrogen doped TiO_2 , great adsorption of SiO_2 and excellent catalytic activity of MnO_2 , through the effective combination of sol-gel method [9] and incipient-wetness impregnation method to prepare nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst. The results show that the urea in the form of N atom replaces O atoms in the TiO_2 lattice, form Ti - O - N bond on the surface of TiO_2 , and constitute the new energy level structure, which made the absorption of catalyst cause red-shift and induce the visible light response, while the composite catalysts in both the ultraviolet and visible region show higher catalytic activity. SiO_2 as load reagent can not only control the growth of TiO_2 particles, to get smaller size and larger specific surface area, but

also improve the separation performance of catalyst, so as to extend its service life. The Mn^{2+} is oxidized to MnO_2 and loads on catalyst surface to make O_2 which migrated to the surface of the semiconductor TiO_2 as electron capture agent to promote the separation of photo-generated carrier and reduce the recombination probability. Then the generated active oxygen free radicals participate in oxidation-reduction reaction of dye pollutants to make them degrade, which significantly improves the photo-catalytic activity of the catalyst.

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