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ARTICLE

Preparation and Characterization of Nitrogen-Doped TiO_2/MnO_2 Supported on SiO_2 Composite Photo-Catalyst

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ABSTRACT

In order to improve the visible light response and reaction efficiency of nitrogen-doped TiO_2, urea is used as nitrogen source and silica gel as load agent. Sol-gel method is used to prepare powder of nitrogen-doped TiO_2 supported on SiO_2 and then by incipient-wetness impregnation method to load MnO_2 on catalyst, after drying, roasting to prepare the composite photo-catalyst. 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 were tested and the influences of nitrogen content and calcinations temperature on the photo-catalytic activity were investigated. The results showed that (1) the modified composite catalyst light response range from UV to visible-light region, which results in a high visible-light photo-catalytic activity in the degradation of methyl orange. (2) Through the mechanism of photo-catalytic reaction and the treatment effect analysis, MnO_2 as catalytic resulting O_2 can serve as a good electronic capture agent and improve the efficiency of reaction. (3) With the reduction of nitrogen content, and the increase in calcinations temperature, the visible-light photo-catalytic activity weakens. (4) The activity of catalyst was reused for six times, did not significantly reduced and has excellent efficiency and stability.

KEYWORDS

TiO_2, Nitrogen-doping, MnO_2, SiO_2, Urea, Visible light catalytic.

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INTRODUCTION

With the increasingly energy shortage and environmental pollution, suitable for light catalyst to realize the effective utilization of solar energy, has become a hot issue in the field of research. The TiO_2 with its excellent catalytic performance in the field of environmental concern [1] has the advantages of low cost, good chemical stability, non-toxic, no secondary pollution. But there are also shortcomings, the titanium forbidden band ($E_g = 3.2$ eV), a wide band gap can only absorb UV-light. In addition, the light stimulates the formation of electron hole and electron compound easily and reduce the photo-quantum efficiency [2,3]. Several scholars have tried to use the method of non-metal doped to extend TiO_2 on the absorption of visible light range, where nitrogen-doped can effectively increase the absorption in the visible-light region of the catalyst, while improving the efficiency of photo-catalytic oxidation [4]. SiO_2 as the load agent can effectively control the existence of TiO_2 particles grew up and help to get smaller particle size, larger specific surface area and can improve the separation performance, suppress their inactivation in order to improve its service life [5,6]. Research shows that the quantum yield is the most important affecting factor of the photo-catalytic treatment effect, which improving the light quantum yield of photo-catalyst, promoting the separation of photon-generated carriers and reducing the recombination rate is a key factor to improve the photo-catalyst treatment effect. In this paper, the preparation of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst, which produces in the process of catalytic hydrolysis of decomposition of hydrogen peroxide to produce new ecological O_2, can be used as electron capture agent to effectively promote photon-generated carriers separation and to reduce its chance to compound [7]. This kind of photo-catalyst with visible light response, smaller catalyst particle size with distribution of uniform, at the same time can restrain efficient electronic-hole for compound and other advantages and can greatly improve the treatment effect of the pollutants.

EXPERIMENTAL

Preparation of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst: It was prepared as follows: After solution B (10 mL of deionized water and 20 mL of anhydrous ethanol) adjusting the pH to about 3, under strong mixing dripped into solution A (10 mL of acetic acid, 10 mL of dibutyl phthalate and 30 mL anhydrous ethanol), then dropping to continue after the strong mixing 30 min, respectively according to 10, 15, 20 and 25 % of N/Ti molar ratio. The different volume of 1 mol/L urea added to the mixture, continue to stir for 30 min, then add a certain amount of SiO_2 as load agent and strong stirring after 60 min, after dry to be dry gel at room temperature grinding in agate mortar, respectively in different temperature 350, 400, 450 and 500 °C in muffle furnace under calcination for 3 h, grinding again and sieving by the 300 mesh points sample. Then using such as volume immersion method in ultrasonic instrument to load a certain concentration of manganese nitrate on the calcined sample of catalyst and drying, roasting for 1 h, getting a series with different calcination temperature of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst.

Performance of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst: The photo-catalyst adsorption ability and photo-catalytic properties of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst was evaluated by the degradation of methyl orange. The reaction was carried out in the self-made additional stirring temperature cycle optical instrument with 150 w iodine tungsten lamp as light source. The reaction device to keep the temperature of the reaction system of constant at 25 °C, magnetic stirring to keep system solution concentration and temperature uniformity. A certain quality of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst in reaction apparatus, add 100 mL of methyl orange solution with certain concentration, under the condition of no light, magnetic stirring for 30 min to adsorption-off balance, then turn on the iodine tungsten lamp for illumination. In the process of adsorption - off balance off light and the light, every 20 min taking a sample, using centrifugal separation to remove the photo-catalyst and using ultraviolet-visible spectrophotometer to measure supernatant fluid at the maximum absorption wavelength absorbance and according to the standard working curve to calculate the concentration. By the concentration of the supernatant fluid (c_t) at the degradation time (t) and the degradation of initial concentration (c_0) calculation rate of the degradation of methyl orange (D), to evaluate the activity of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst:

$$D\,(\%) = \frac{c_t - c_0}{c_0} \times 100$$

RESULTS AND DISCUSSION

X-ray diffraction analysis of the catalyst: XRD spectrum (Fig. 1) shows that the preparation of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst at 300, 350, 400 and 450 °C temperature of N/Ti molar ratio of 20 % of nitrogen-doping are anatase phase and does not appear Ti-N diffraction peak may be due to the high temperature makes the volatilization of N, resulting in low N levels or due to the complex catalyst did not form a larger Ti-N clusters. At the same time also does not appear, by N doping, the mobile phenomenon of the characteristic peak of anatase TiO_2, show nitrogen-doping unchanged its crystal phase structure. Using the Scherrer formula to calculate the average grain size were 13.8, 14.6, 12.3 and 17.2 nm. The increase of calcination temperature, anatase phase characteristic peak becomes more acute, crystal shape is more and more regular and grain size becomes larger and larger, this is because the calcination temperature cause grain together.

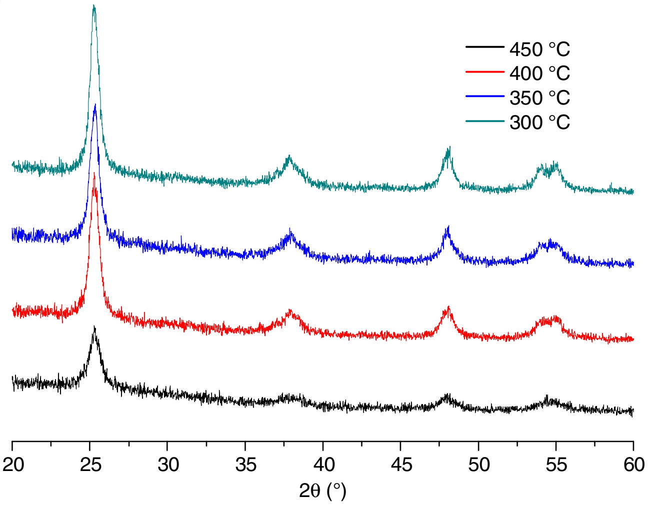


Fig. 1. XRD patterns of 20 % N of samples annealed at different temperature

XRD spectrum (Fig. 2) shows that the preparation of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst at 400 °C temperature with different molar ratio of nitrogen-doping. Using the Scherrer formula to calculate the average grain size were 9.1, 8.4, 14.7, 12.4, 13.2, 12.3 and 14.2 nm. Nitrogen-doped make the grain size of catalyst become large and with the molar ratio of N/Ti the particle size has a minimum

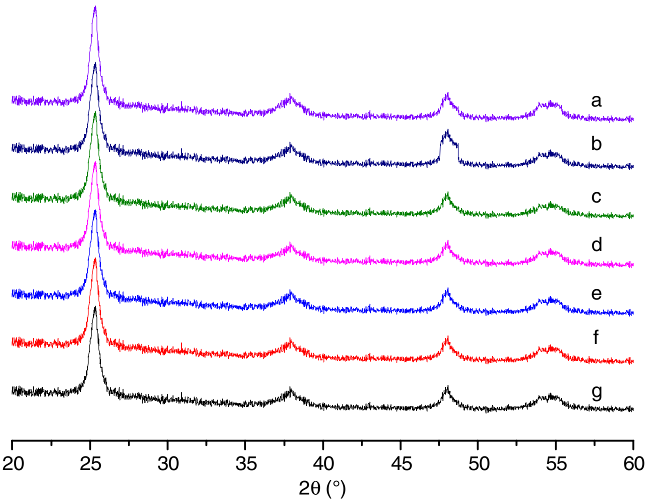


Fig. 2. XRD patterns of different molar ratio of nitrogen-doping samples annealed at 400 °C (a. 400 °C TiO_2, b. 400 °C TiO_2/SiO_2, c. 400 °C N/TiO_2, d. 400 °C 10 % $N/TiO_2/SiO_2/Mn^{2+}$, e. 4000 °C 15 % $N/TiO_2/SiO_2/Mn^{2+}$, f. 400 °C 20 % $N/TiO_2/SiO_2/Mn^{2+}$, g. 400 °C25 % $N/TiO_2/SiO_2/Mn^{2+}$)

value, corresponding to the 20 % molar ratio. It is consistent that the diffraction peak is sharp and half high width is small, so the grain is smaller, the better the crystallization.

Surface morphology analysis of catalyst

Scanning electron microscope (SEM): Fig. 3 is the SEM and energy spectrum for with Mn^{2+} and without adding Mn^{2+} of nitrogen-doped TiO_2 supported on SiO_2 composite photo-catalyst. Fig. 3 shows that TiO_2 particle size ranged from several to several tens of nanometer particles and success-fully load on SiO_2 particle surface, the distribution is relatively uniform. Comparison of the energy spectrum shows that Mn^{2+} has been successfully incorporated into and the load on the surface of SiO_2 and the incorporation of Mn^{2+} make TiO_2 particle size slightly increased. Thus SiO_2 as load agent can effectively improve the distribution of TiO_2 particles, improve the dispersion performance which clearly showed that Mn^{2+} has been successfully involved and the load on the surface of SiO_2.

Transmission electron microscope analysis: Fig. 4 shows the transmission electron microscope of the photo-catalysts with different composition. From the graph 4(a), (b) can be seen that the nitrogen-doped TiO_2 particle size is larger than the pure TiO_2 and the powder particle size distribution is more compact. From Fig. 4(c) shows that SiO_2 as load agent can improve TiO_2 separation properties and make it evenly distributed. From Fig. 4(d), (e) it is clear that the rise of temperature, particle size bigger, this is due to the calcination temperature cause grain together. In conclusion that TiO_2 particle size between several nanometers to dozens of nanometer corresponds with the XRD test results.

X-ray photoelectron spectroscopy of catalyst: The XPS spectra of catalysts with nitrogen-doped (Fig. 5A) and undoped nitrogen (Fig. 5B) under 400 °C of calcinations studied. Doped N catalyst samples showed a new N_{1s} peak in 396.1 eV and

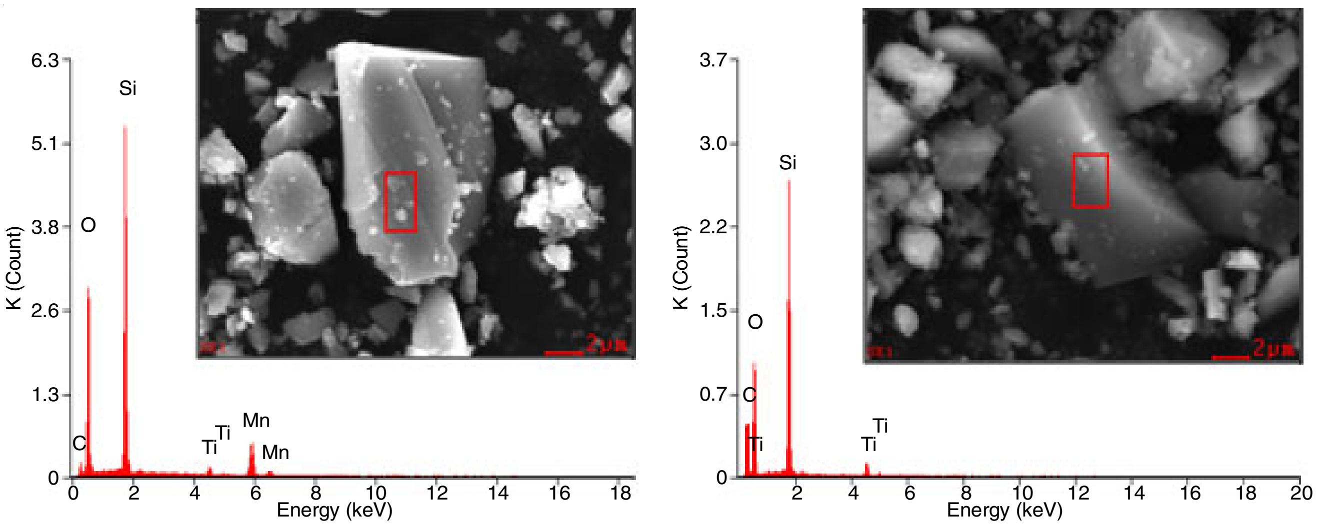
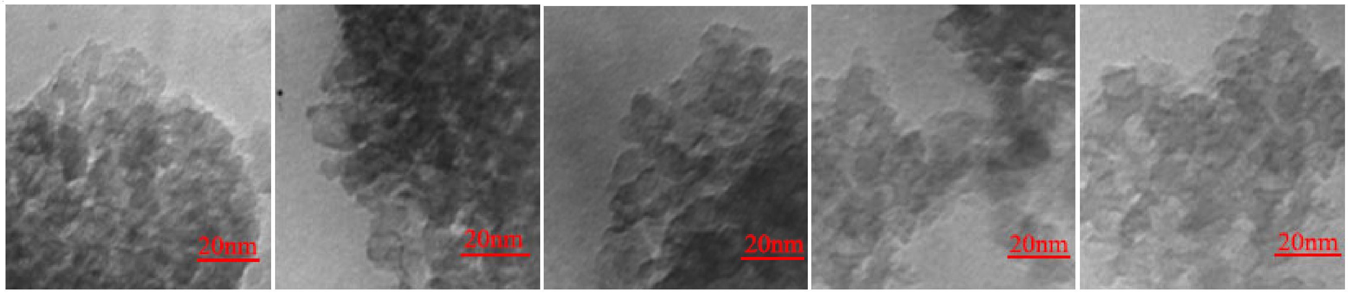


Fig. 3. SEM microgragh of TiO_2 photo-catalysts



(a) 400 °C TiO_2 (b) 400 °C N/TiO_2 (c) 400 °C TiO_2/SiO_2 (d) 450 °C $N/SiO_2/TiO_2/Mn^{2+}$ (e) 400 °C $N/SiO_2/TiO_2/Mn^{2+}$

Fig. 4. TEM microgragh of TiO_2 photo-catalysts

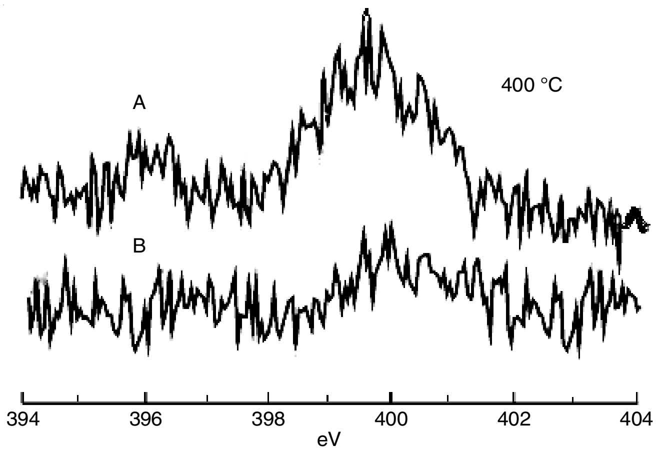


Fig. 5. XPS spectra of N_{1s} for TiO_2 at 400 °C

the peak which is N_2 adsorption on the surface of the catalyst at 401.7 eV called N_{1s} peak, thus between the N atoms and TiO_2 molecules are combined by chemical bonds. Asahi *et al.* [8] indicated the peak appearing at 396 eV belonging to N atoms which were mixed into the crystal lattice and peaks appearing in the 400 and 402 eV as the molecular adsorption of N_2 on the catalyst surface. They pointed out that the catalyst has the visible light activity is associated with the atomic N, this is because the N_{2p} orbital and O_{2p} orbital happened hybridization, can make the TiO_2 forbidden band width decreases and thus can be visible light excitation.

Photo-catalytic activity of nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst: Fig. 6(A) shows the under visible-light photo-catalytic activity test results of catalyst. It is observed from Fig. 6A that the comparison between d and a (or b) shows the doping significantly improvement of photo-catalytic activity in the visible light. This is because doped N atoms parts replaced O atoms into titanium dioxide lattice, above the valence band formed an independent N_{2p} narrow band, causing composite catalyst response to visible light [8]. From the figure of f, g, i and j, we can see that with the increment of N doping the catalytic activity of the composite photo-catalyst also increases. The best catalytic activity appearing when the nitrogen doping amount is 20 %, the composite catalyst can be used for 120 min for complete removal of methyl orange and the same conditions of different doping amounts of catalyst did not meet completely for the removing methyl organe. The reason may be due to the N doping newly creating a valence band level and TiO_2 in the bulk phase form a compound semiconductor structure, the valence band electric potential difference can make the hole of TiO_2's valence band migrate to the new form energy levels, so as to effectively reduce the light electronic-hole recombination time, thus improve the activity of catalyst [6]. From i, h of Fig. 6, we can see that with the increase of temperature the removal rate decreases. The reason may be that under high temperature, N element was oxidized and happened volatilization in the process of heating, leading to the N content in TiO_2 lattice was reduced and the grain size, specific surface area decreases, also can cause the activity of visible-light response. Fig. 6(b) shows the catalyst activity test results of UV-light. It can be observed from Fig. 6(b) that the composite catalyst in UV-light region also has a good effect. Fig. 7 shows that Mn^{2+} has obviously improved the processing efficiency of the catalyst, this is because Mn^{2+} oxidized into MnO_2 during the process of calcining and loads on the catalyst surface, which acts as a catalyst for catalyzing H_2O_2 producing O_2 as electron capture agent effectively promotes photo-generated carrier separation and reduces its compound probability.

Fig. 8 shows the catalyst repeated use and compared to the same cycle times. It is found that nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst is much higher than catalytic activity of catalyst. After six repeated uses, composite catalyst degradation rate was 75 % and the same condition without doping SiO_2 composite catalyst degradation rate is only 27 %. In conclusion, SiO_2 as load agent can effectively inhibit the deactivation of catalyst, so as to improve its life.

This work showed that the nitrogen-doped TiO_2/MnO_2 supported on SiO_2 composite photo-catalyst, nitrogen-doped can expand the light response range of TiO_2 and improve the activity of visible-light and UV-light area. SiO_2 as load agent to obtain the smaller particle size, large specific surface area

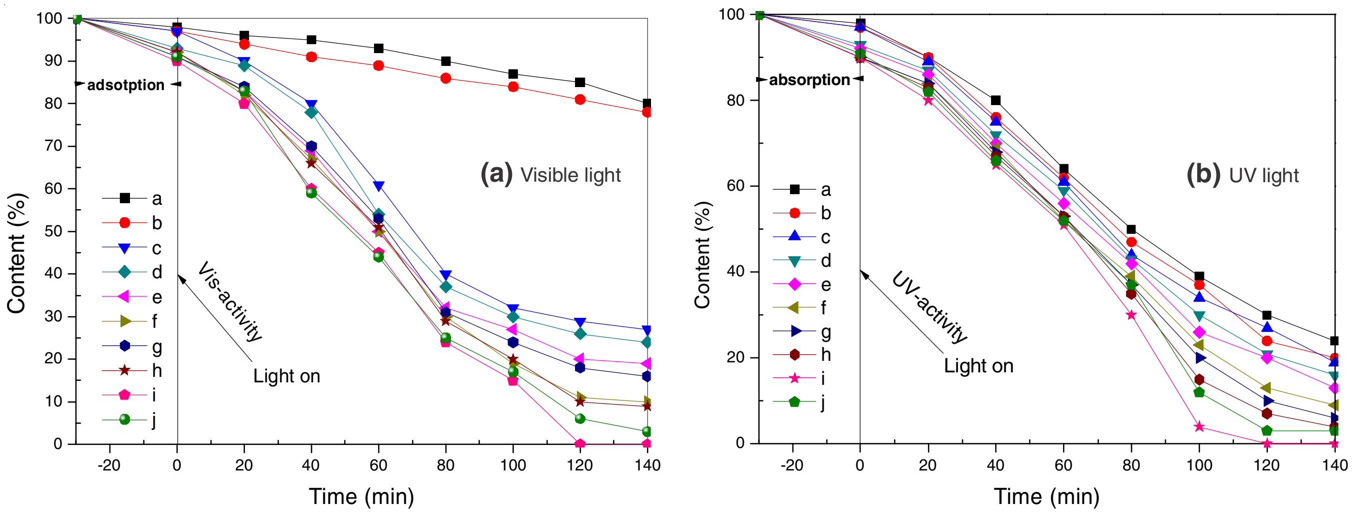


Fig. 6. Photo-catalytic activity of TiO_2 with different condition [a. 400 °C TiO_2, b. 400 °C TiO_2/SiO_2, c. 300 °C 20 % $N/TiO_2/SiO_2/Mn^{2+}$, d. 400 °C 20 % $N/TiO_2/SiO_2$, e. 350 °C 20 % $N/TiO_2/SiO_2/Mn^{2+}$, f. 400 °C 10 % $N/TiO_2/SiO_2/Mn^{2+}$, g. 400 °C 15 % $N/TiO_2/SiO_2/Mn^{2+}$, h. 450 °C 20 % $N/TiO_2/SiO_2/Mn^{2+}$, i. 400 °C 20 % $N/TiO_2/SiO_2/Mn^{2+}$, j. 400 °C 25 %$N/TiO_2/SiO_2/Mn^{2+}$]

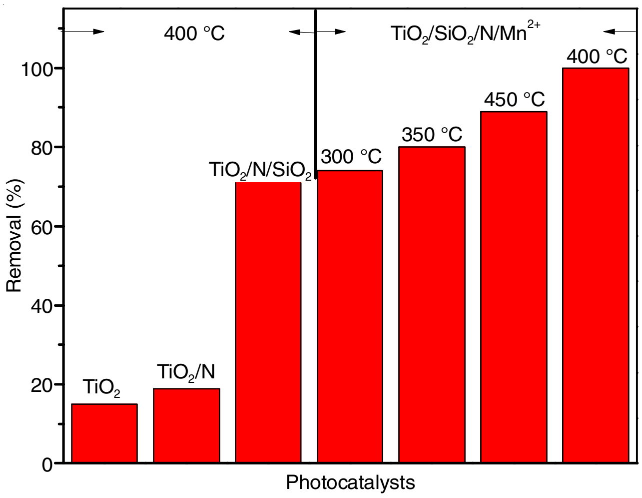


Fig. 7. Photo-catalytic activity of TiO_2 with different condition of Mn^{2+} under visible light

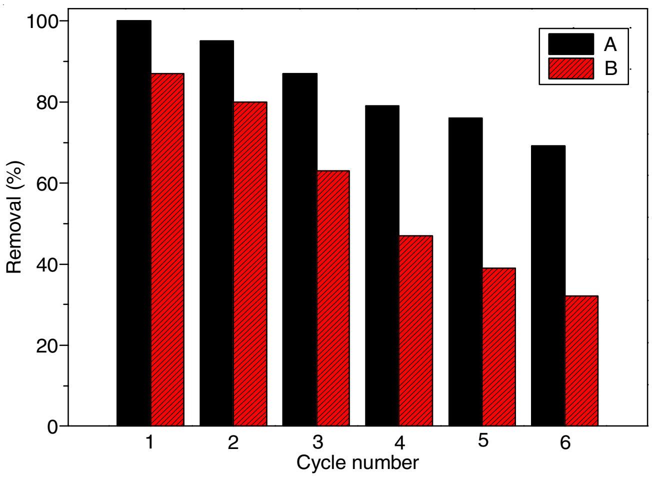


Fig. 8. Effect of run times on the photo-catalytic activity of TiO_2 (A. 400 °C 20 % $N/TiO_2/SiO_2/Mn^{2+}$, B. 400 °C 20 %$N/TiO_2/Mn^{2+}$)

and can improve the catalyst separation performance, in order to improve the service life of catalyst. The mechanism shows that holes migrate to the surface of the semiconductor TiO_2 and H_2O or OH^- absorbing on the surface react to generate $^\bullet OH$, a strong oxidizing free radicals, which can oxidize a variety of organic pollutants and plays a main role in photo-catalytic system as an oxidizing agent. Mn^{2+} by oxidation converted into MnO_2 loading on catalyst surface catalyzed $^\bullet OH$ producing O_2 which migrated to the surface of semiconductor TiO_2 and worked with electron to generate O^{2-}, *etc.* As reactive oxygen species free radicals, the reactive group will also be able to participate in oxidation-reduction reactions and the catalytic O_2 as electron capture agent to promote the separation of photo-generated carrier and reduce the recombination probability, which signifi-cantly improve the photo-catalytic activity of the catalyst. At the same time, according to the reaction dynamics equation of this process can promote to generate $^\bullet OH$ as a hole capture agent.

Conclusion

The good performance of visible-light response of nitrogen-doping TiO_2 and excellent 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 showed that the urea in the form of N atom replaced O atoms into titanium dioxide lattice and formed the new energy level structure by Ti-O-N bond on the surface of TiO_2, made the absorption of catalyst appear red-shift and induced its visible light response and composite catalyst in both the UV-light and visible-light can show higher catalytic activity. SiO_2 as load agent can not only control the titanium dioxide particles grew up, get the smaller particle size and large specific surface area and can improve the catalyst separation performance, in order to improve the service life of catalyst. The Mn^{2+} by oxidation converted into MnO_2 loading on catalyst surface catalyzed producing O_2 which migrated to the surface of semiconductor TiO_2 as electron capture agent to promote the separation of photo-generated carrier and reduce the recombination probability and generated active oxygen free radicals in oxidation-reduction reactions to degrade the dye pollutants, thus improve the photo-catalytic activity of catalyst.

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