Research on Micro-Analysis System of Dye in Water Sample Based on Magnetic Nano-TiO$_2$

Zhu Xiaoting, Cheng Heyong, Ye Meiyin*

School of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou, Zhejiang 311021
Email: yemy@hznu.edu.cn

Abstract

Magnetic Nano-Photocatalytic Material (NMPC) helps separate and recover nano photocatalyst in water treatment. However, it is rarely reported that a photocatalyst can be separated online in photocatalytic microreactors. In this paper, a typical dye methylene blue was photocatalytically degraded in glass microfluidic chip by using Fe$_3$O$_4$@SiO$_2$@TiO$_2$ (FST) as the magnetic nanocatalyst, the UV-LED as the ultraviolet light source, and ultraviolet-visible spectrophotometer as the detector. The FST was easily separated by an external magnetic field, thereby realizing rapid online detection of methylene blue. During the preparation of FST, the hydrothermal method was used to treat the obtained FST nanoparticles in 100°C boiling water bath, and the titanium-iron ratio was optimized, so as to obtain FST nano-photocatalyst with high photocatalytic performance and good dispersibility. With 1.0 g/L FST/8%H$_2$O$_2$ being the catalytic oxidation system, the sample flow rate being 300 μL/h, the reaction temperature being 45 ℃, the degradation rate of methylene blue has reached 100%. It only took 25 min to complete one measurement. The FST consumed per measurement was only 125 μg. The RSD of the photodegradation rate was 2.5% (n=9).

1. Introduction

TiO$_2$ is the most common photocatalytic semiconductor catalyst. It is non-toxic, stable, and easy to obtain (constituting 0.44% of the earth’s crust) [1]. It serves as a strong oxidant under ultraviolet light and is widely used in the degradation treatment of sewage with dyes [2], pesticides [3] and phenolic compounds [4]. Nano-sized TiO$_2$ is an excellent catalyst. However, in a liquid phase system, its extremely small size may cause difficulty in separation and recovery. Loading TiO$_2$ on an inert substrate (such as the inner wall of a microreactor) can realize the reuse of TiO$_2$ [5] and avoid separation and recovery. However, loading of the photocatalyst will reduce the number of active sites in contact with the pollutants. Compared with the unloaded nanocatalyst, the catalytic activity after it is loaded will be reduced [6].

Magnetic Nano-Photocatalytic (MNPC) is a novel method to separate and recover nanocatalyst [7,8]. The separation can be easily performed by applying an external magnetic field, thereby allowing multiple cycles of the nano-photocatalyst and obtaining a more efficient, economical and environmentally-friendly water purification process. Generally, with a core-shell structure, MNPC are composed of magnetic composites and photocatalytic nanomaterials. The core is usually composed of magnetic elements such as magnetite (Fe$_3$O$_4$) [9]. The shell is generally used as a photocatalyst, such as TiO$_2$, ZnO, AgBr, BiOCl, etc., among which TiO$_2$ is a widely studied coating material [10]. In order to prevent the photolysis of the magnetic core due to direct contact with TiO$_2$, a layer of SiO$_2$ is generally coated between the two [11]. The simplest and most common MNPC is Fe$_3$O$_4$@SiO$_2$@TiO$_2$ (FST).
Photocatalytic microreactors have high photocatalytic efficiency since it has advantages such as homogenous illumination \[12\]. However, it is still rarely reported on the use of magnetic nanoparticles as catalysts for photocatalytic reactions in microreactors. The main objectives of this study were to synthesize FSTs and to apply the FSTs to the photocatalytic microanalysis system of methylene blue (MB) in water by UV A irradiation. Specifically, FSTs with high catalytic activity and good dispersivity were prepared by mild heat treating of FST nanoparticles and varying the molar ratio of Ti/Fe in FST. Furthermore, the degradation rate for the oxidation of MB by UV A using the FSTs as catalyst and H$_2$O$_2$ as oxidant were determined in self-made photocatalytic microreactor on the basis of the amount of FST utilized and temperature, flow rate of the samples. Meanwhile, an external magnetic field was used to separate FST quickly before online detection.

2. Experiment

2.1 Materials

Materials and chemicals were specified as follows: Tetrabutyl titanate; Ethyl Orthosilicate; Anhydrous Ethanol; Fe$_2$(SO$_4$)$_3$·$x$H$_2$O; FeSO$_4$·7H$_2$O; Ammonia Water; Methylene Blue; Hydrogen Peroxide. All the chemicals were of analytical grade (> 99.7%).

2.2 Synthesis methods

2.2.1 Preparation of Fe$_3$O$_4$ @SiO$_2$

In the first step, the Fe$_3$O$_4$ MNPs were prepared through a chemical method called co-precipitation. 0.2288g dehydrated Fe$_2$(SO$_4$)$_3$ and 0.2739g ferrous sulfate (FeSO$_4$·7H$_2$O) were dissolved in 52 mL of deoxygenated water under a nitrogen atmosphere, and being mechanically stirred for about 10 minutes to be a clear orange-yellow solution. Afterward, the mixed solution was dropped into a three-necked flask mixed with 150 mL ammonia water (0.18%) at a speed of 4-5 s/d. The chemical reaction was carried out for 90 min under continuous ultrasonically stirring in an N$_2$ atmosphere. When the reaction was over and the solution was cooled to room temperature, it was poured into a 100 mL beaker. The magnetite precipitates were separated by a strong magnetic field, and washed with distilled water to pH = 7, washed 3 times with ethanol, and stored in ethanol to obtain a magnetic Fe$_3$O$_4$ particle/ethanol system. The next step involved a synthetic strategy based on the hydrolysis and condensation of TEOS on the surface of Fe$_3$O$_4$ nanoparticles. 4mL Ammonia (1.8%) was added to the Fe$_3$O$_4$ / ethanol (0.50 g /14 mL) system, ultrasonically dispersed for 1 hour. Then, ethyl orthosilicate /ethanol (0.12 g/14 mL) mixture was slowly (5 s/d) dropped into the mixture with continuous stirring for 3 hours. After the reaction was over, the particles were separated with a strong magnetic field, washed with distilled water to neutrality. Then it was washed 3 times with ethanol and dried with N$_2$.

2.2.2 Preparation of Fe$_3$O$_4$−SiO$_2$ coated with TiO$_2$

0.32 g tetrabutyl titanate was dissolved in 10 mL ethanol, then 0.05 g Fe$_3$O$_4$@SiO$_2$ was added. After an ultrasonicication for 5 min, 10 mL ethanol: water (5:1) (5 S/d) was slowly dropped into the tetrabutyl titanate solution under stirring at 450 rpm until the drop was over. A reflux of the tetrabutyl titanate solution in a water bath was conducted at 80°C for 3 hours. When the mixture was cooled to room temperature, the nanoparticles produced in the process was separated by a strong magnetic field, washed several times with ethanol and distilled water in turn. Then the nanoparticles were heated in a water bath at a constant temperature of 100°C for 1 hour. Finally, Fe$_3$O$_4$@SiO$_2$@TiO$_2$ (FST) nanoparticles were obtained after the particles were separated by a strong magnetic field, washed and dried.

2.3 Characterization

The crystallinity and structure of FST NPs were determined by using XRD analysis on D8 Advance X-ray Powder Diffractometer (German Bruker). A Scan electron microscopy (SEM) was used to verify particle size and morphology of the FST NPs using an S4800 scanning electron microscope.
Glass chip microreactors were prepared according to reference [13]. As shown in Figure 1, a syringe pump (Baoding Longer Pump Co., Ltd.) was used to inject catalyst solution (8%H2O2 and 1.0g/L FST suspension) and 0.2 mM methylene blue solution into channels A and B, respectively, at a flow rate of 500μL/min to perform the photocatalytic reaction. Two radiators of UV lamps NSHU590B UV-LED (365nm) (Japan NICHIA Ltd.) were set above the chip, and the entire chip channel could be irradiated (light intensity was 80 mW/cm²); below the chip was a heating block that could control the reaction temperature of the chip. The reaction solution flowed out of the chip from outlet C, through a polytetrafluoroethylene (PTFE) tube, before underwent separation by a strong magnetic field, and then flowed into the cuvette (volume was 60 μL) of the TU-1900 UV-Vis spectrophotometer (Beijing Persee General Instrument Co., Ltd.) for online detection. The absorbance of degraded MB was detected at 664 nm and recorded as Ax; The apparent degradation rate η of methylene blue could be calculated according to the formula η (%) = 100% × (A0 -Ax) /A0, in which A0 is the absorbance of the effluent from the microreactor when catalyst solution was changed with distilled water.

Fig. 1 Schematic illustration of microanalysis system for degradation of methylene blue and online detection photocatalysis. The reaction solution flowed out of the chip from outlet C, through a polytetrafluoroethylene (PTFE) tube, before underwent separation by a strong magnetic field, and then flowed into the cuvette (volume was 60 μL) of the TU-1900 UV-Vis spectrophotometer (Beijing Persee General Instrument Co., Ltd.) for online detection. The absorbance of degraded MB was detected at 664 nm and recorded as Ax; The apparent degradation rate η of methylene blue could be calculated according to the formula η (%) = 100% × (A0 -Ax) /A0, in which A0 is the absorbance of the effluent from the microreactor when catalyst solution was changed with distilled water.

3. Results and Discussion

3.1 Evaluation of photocatalytic and dispersion performance of Fe3O4@SiO2@TiO2
When passing FST into the chip as catalyst, we have to ensure that the particles of FST have high catalytic efficiency, also have a good dispersibility to be suspended in the syringe for a long time and will not settle in the chip. The dispersibility of FST was evaluated by observing the clear time of FST suspension. It was found that in the process of preparing FST, heat treatment of the obtained FST nanoparticles could increase the particle size and crystallinity of nano-TiO2, thereby affecting its catalyst performance.

| Temperature of reflux (℃) | heat treatment | Degradation rate |
|--------------------------|----------------|------------------|
| 80                       | 100℃           | 73%              |
| 80                       | 250℃           | 66%              |
| 80                       | 350℃           | 92%              |

a. Heat treatment with boiling water. Ti/Fe ratio: 6:1

As can be seen from Table 1, the nano-TiO2 obtained by the hydrothermal method at 100℃ has a
smaller particle size, narrow particle size distribution, and light agglomeration. As can be seen in Figure 3, The surface of the FST catalyst was rougher, so it has good catalytic efficiency (Degradation rate of MB>70%).

The catalyst particles calcined at 350°C have the best catalytic efficiency (92%). However, the particle size was more than 200nm (see Figure 3) and the sedimentation speed was too fast, so they were easy to settle in the chip channel and block the chip. Therefore, 100°C boiling water bath treatment was selected for heat treatment of FST.

The greater the molar ratio of tetrabutyl titanate to ferroferric oxide (Ti/Fe), the more TiO₂ was coated on the magnetic particles, resulting in a better catalytic performance. However, the dispersion performance of FST declined when more TiO₂ was coated. A complete separation occurred in less than 1h when the Ti/Fe ratio was higher than 8. While the complete separation time for FST particles with Ti/Fe 6:1 was more than 24h. And no significant sedimentation was observed in the syringe and the microchannel during the period of measurement when FST particles with Ti/Fe 6:1 were used as the catalyst.

3.2 Fe₃O₄@SiO₂@TiO₂ Characterization

Figure 2 is the XRD diffraction pattern of FST. According to the standard card JCPDS 75-0449, the diffraction peaks of 30.21°, 35.55°, 43.12°, 53.40°, 57.19° and 62.60° corresponded to magnetite (220), (311), (400), (422), (511) and (440) crystal planes, which are characteristic peaks of Fe₃O₄. According to the standard card JCPDS 21-1276 of anatase TiO₂, the 27.45° and 36.08° characteristic peaks corresponding to the (110) and (101) crystal planes of anatase TiO₂.

In the synthesized catalyst, SiO₂ existed in an amorphous form, so its characteristic peak could not be observed in the XRD pattern. The coated TiO₂ showed a higher crystallinity and the broadening of diffraction peaks, indicating that the particle size was relatively small, so it had a good catalytic efficient. Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@TiO₂ were scanned with a scanning electron microscope to observe their appearance, morphology and particle size, as shown in Figure 3. Fe₃O₄(A) was spherical in uniform size, with a particle size of about 20 nm, but there was obvious agglomeration, which was due to the magnetic attraction and nano-effect of Fe₃O₄ nanoparticles.

Fig. 2 The XRD spectra of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@TiO₂
Fig. 3 The SEM spectra of Fe₃O₄(A), Fe₃O₄@SiO₂(B), Fe₃O₄@SiO₂@TiO₂ treated with 100 ℃ boiling water bath (C), Fe₃O₄@SiO₂@TiO₂ calcined under 350 ℃ (D)

After coated with SiO₂(B), the particle size was about 25 nm. Independent particles increased and agglomeration weakened, indicating that the magnetic Fe₃O₄ particles coated with a layer of SiO₂ could effectively shield the magnetic attraction. After coating with TiO₂, the particle size increased significantly. The particle size of FST(C) treated in a boiling water bath at 100 ℃ was about 80 nm, and the surface was rough and porous with a large specific surface area and light degree of agglomeration. The particle size of FST(D) calcined at 350 ℃ was larger than 200 nm, and it agglomerated closely, resulting in poor dispersion performance.

3.3 Catalytic system

Methylene blue was photocatalytically degraded with different catalyst solution and online detected in the microanalysis system shown in Figure 1. As can be seen in Figure 4, when the catalyst solution contained only H₂O₂ or only FST, the degradation rate of MB stood at around 10% and 20%, respectively. Fe₃O₄ / H₂O₂ were also used in the catalyst system under the same condition to test its photocatalytic efficiency. The degradation rate of methylene blue with Fe₃O₄ / H₂O₂ was only 12% (Fig. 4), basically the same as that with H₂O₂ alone, indicating that Fe₃O₄ in FST made very little contributions to degradating MB in water samples. However, the degradation rate of MB reached nearly 90% when 1.0 g/L FST and 8% H₂O₂ were both in the catalyst solution. This can be attributed to the synergistic catalytic effect between FST and H₂O₂. Hence, the catalytic efficiency was significantly improved.

Fig. 4 Absorbance spectra of four chip effluents in different catalysis system: a. H₂O; b. 8% H₂O₂; c. 1.0g/L Fe₃O₄, 8% H₂O₂; d. 1.0 g/L FST; e. 1.0 g/L FST, 8% H₂O₂ (UV, 25℃, 0.2 mM MB, 500 μL/h)
3.4 Temperature and catalyst concentration
As shown in Figure 5, the micro-analysis system showed a higher photodegradation efficiency under higher temperature (45°C), which can be put down to the desorption of MB on the surface of FST and the photocatalytic reaction become easier to occur at a higher temperature. The effect of FST dosage on the degradation rate of MB is shown in Figure 5. The degradation rate of MB increased as the catalyst dosage gradually increased in the range of 0.25-1.0 g/L; The maximum degradation rate of MB reached 98% at 1.0 g/L FST. Too much catalyst would reduce the permeability of UV light in the solution and accelerate the precipitation of the catalyst in the chip. As only 125 μg FST was consumed in each measurement, which was not suitable for the recovery and reuse of the catalyst.

3.5 Sample flow rate
The flow rate determines the time consumed in online detection and the duration of UV radiation for the reaction. It can be seen from Fig. 6 that when the flow rate was higher than 600 μL/h, the absorbance of the product could hardly be stable, indicating that a small amount of catalyst had been flushed into the cuvette of the UV-Vis spectrophotometer by the high pressure in the channel; at the flow rates of 500 μL/h and 300 μL/h, The degradation rate reached 98% and 100%, respectively, and remained stable after 900s and 1200s respectively. When the flow rate was 300 μL/h, it took about 25 minutes to complete a measurement. Under this condition, the experiment was repeated 9 times, and the RSD of the photodegradation rate was 2.5%.

Fig. 5 Effect of concentration of FST on photodegradation of MB (UV, 500μL/h, MB: 0.2mM, H2O2: 8%)

4. Summary
In this paper, a micro-analysis system for photocatalytic degradation of dye methylene blue was established on the basis of Fe3O4@SiO2@TiO2 (FST) as the catalyst. H2O2 was selected as the oxidant, and online detection of the photodegradation product was realized after the FST particles being attracted by the magnet infront of the cuvette of the UV-Vis spectrophotometer. The FST nanoparticles were prepared under optimized conditions to have good photocatalytic and dispersion performance.
Conditions for online detection of MB were also investigated and optimized. It only took 25 minutes to complete degradation and determination. And the method has a good reproducibility.

Compared with the photocatalytic reactor prepared by directly coating TiO₂ on the chip channel, this method is simple to operate, and the nanocatalyst can be directly separated by an external magnetic field; at the same time, it avoids the problem of TiO₂ falling off, and make the degradation and measurement under the same conditions more stable.

**Acknowledgments**

This paper is funded by the National Natural Science Foundation of China (No.21407039).

**References**

[1] Chen X. B., Liu L., Yu P. Y., Mao S. S.. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science*. 2011. 331(6018): 746-750.

[2] Hu H., Lin Y., Hu Y. H.. Core-shell structured TiO₂ as highly efficient visible light photocatalyst for dye degradation. *Catalysis Today*. 2020. 341: 90-95.

[3] Vicente R., Soler J., Arques A., Amat A. M., Frontistis Z., Xekoukoulotakis N., Mantzavinos D.. Comparison of different TiO₂ samples as photocatalyst for the degradation of a mixture of four commercial pesticides. *Journal of Chemical Technology & Biotechnology*. 2014. 89(8): 1259-1264.

[4] Grabowska E., Reszczynańska J., Zaleska A.. Mechanism of phenol photodegradation in the presence of pure and modified-TiO₂: A review. *Water Research*. 2012. 46(17): 5453-5471.

[5] Zhu Z. X., Ye M. Y.. Low Temperature Preparation of Titanium Dioxide Thin Films in Microfluidic Chip. *Bulletin of the Chinese Ceramic Society*. 2017. 36(7): 2397-2403.

[6] Gehrke I., Geiser A., Somborn-Schulz A. Innovations in nanotechnology for water treatment. *Nanotechnol Sci Appl*. 2015. 8: 1-17.

[7] Zhang L., Wang W., Sun S., Sun Y., Gao E., Zhang Z.. Elimination of BPA endocrine disruptor by magnetic BiOBr@SiO₂@Fe₃O₄ photocatalyst. *Applied Catalysis B: Environmental*. 2014. 148-149: 164-169.

[8] Rasheed H. U., Lv X., Zhang S., Wei W., Ullah N., Xie J.. Ternary MIL-100(Fe)@Fe₃O₄/CA magnetic nanophotocatalysts (MNPCs): Magnetically separable and Fenton-like degradation of tetracycline hydrochloride. *Advanced Powder Technology*. 2018. 29(12): 3305-3314.

[9] Chi Y., Yuan Q., Li Y., Zhao L., Li N., Li X., Yan W.. Magnetically separable Fe₃O₄@SiO₂@TiO₂-Ag microspheres with well-designed nanostructure and enhanced photocatalytic activity. *Journal of Hazardous Materials*. 2013. 262: 404-411.

[10] Gómez-Pastora J., Dominguez S., Bringas E., Rivero M. J., Ortiz I., Dionysiou D. D.. Review and perspectives on the use of magnetic nanophotocatalysts (MNPCs) in water treatment. *Chemical Engineering Journal*. 2017, 310(P2): 407-427.

[11] Costa A. L., Ballarin B., Spenzi A., Casoli F., Gardini D.. Synthesis of nanostructured magnetic photocatalyst by colloidal approach and spray–drying technique. *Journal of Colloid and Interface Science*. 2012. 388(1): 31-39.

[12] Takei G., Kitamori T., Kim H-B.. Photocatalytic redox-combined synthesis of l-pipecolinic acid with a titania-modified microchannel chip. *Catalysis Communications*. 2005. 6(5): 357-360.

[13] Yin X. F., Shen H., Fang Z. L.. A Simplified Microfabrication Technology for Production of Glass Microfluidic Chips. *Chinese Journal of Analytical Chemistry*. 2003. 31(1): 116-1119.