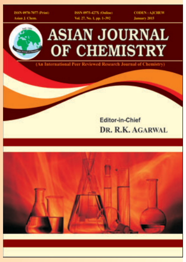
Asian Journal of Chemistry; Vol. 27, No. 3 (2015), 1066-1070

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18241



One Step Sol-Hydrothermal Synthesis of TiO_2 Doped with CdS and N for Visible Light Photocatalytic Degradation of Organic Pollutant

DAN LI*, HAIXIA TONG and LING ZHANG

Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha 410004, P.R. China

*Corresponding author: Tel/Fax: +86 731 85258733; E-mail: LD1004@126.com

Received: 3 June 2014; *Accepted*: 7 August 2014; *Published online*: 19 January 2015; AJC-16726

Titanium(IV) oxide photocatalytic oxidation process offers an efficient pollution control technology in environmental protection. However, the weak absorption of TiO_2 to visible light limits the application of this catalyst under natural solar illumination. To improve the visible light photocatalytic activity of TiO_2, this work developed a one-step sol-hydrothermal method to synthesize CdS and N co-doped TiO_2 (CdS/N-TiO_2). For comparison, N-TiO_2, CdS/TiO_2 and two CdS/N-TiO_2 namely CdS/N-TiO_2A (Cd:Ti:N=1:20:33) and CdS/N-TiO_2B (Cd:Ti:N=1:10:17) were synthesized and compared with pure TiO_2. The structure and morphology of all these synthesized materials were characterized by X-ray diffraction and scanning electron microscope. The photocatalytic performances of doped TiO_2 were investigated by the degradation of Rhodamine B under visible light irradiation. The results indicated CdS/N-TiO_2B calcined at 400 °C showed the highest visible light photocatalytic degradation efficiency for Rhodamine B. This catalyst provides a highly effective candidate for removal of bio-refractory organic pollutants using natural solar energy.

Keywords: Co-doped TiO_2, Sol-hydrothermal method, Rhodamine B, Visible light photocatalysis.

INTRODUCTION

Since the report of Fujishima and Honda on the photoinduced splitting of water on TiO_2 electrode[1], TiO_2 photocatalyst has attracted great attention in many research fields. Due to the advantages of high corrosion resistance, good stability, low cost, non-toxicity and strong degradation ability to organic pollutants, TiO_2-based photocatalysis has been extensively employed in wastewater treatment[2-5]. However, TiO_2 can mainly absorb UV light because of its wide bandgap ($E_g = 3.2$ eV), which limits the application of solar energy containing about only 4-6 % UV light[6,7]. To improve the photocatalytic performance of TiO_2 under visible light irradiation, different approaches such as modifying TiO_2 by precious metal deposition, element doping, surface sensitization and composite semiconductor have been developed[8-10].

As one of the most widely studied methods, doping TiO_2 with metal or non-metal elements has been revealed to effectively improve the visible light photocatalytic performance of TiO_2. The early researches have been focused on metal ion doping[2]. It is believed that metal ion doping could reduce the recombination probability of photoinduced charge carriers and promote the quantum efficiency[11]. Afterwards doping TiO_2 with non-metal elements such as B, C, N and F have attracted much interest[12], because non-metal element doping could change the valence band of TiO_2 and consequently reduce the band gap[13] of TiO_2.

As a narrow band-gap semiconductor ($E_g = 2.4$ eV) which can be excited by visible light, CdS has been intensively introduced as a promising photosensitizer for TiO_2. Kozlova *et al.*[14] have prepared multiphase CdS/TiO_2 photocatalysts for photocatalytic oxidation of ethanol vapors under visible light. Rawal *et al.*[15] have analyzed that in CdS/TiO_2 heterojunction, the conduction band of CdS sensitizer is positioned to a more negative side than that of TiO_2. Yang *et al.*[16] have synthesized hierarchically porous nanostructured CdS/TiO_2 heterojunction materials which exhibited enhanced visible-light-driven photocatalytic activity in decomposing organic dye pollutants such as methyl orange and Rhodamine B in water. Moreover, CdS sensitization can enhance the photocatalytic performance of TiO_2 for reduction of heavy metals under visible light irradiation[17].

In the present work, we prepared CdS and N co-doped TiO_2 (CdS/N-TiO_2) by a one-step sol-hydrothermal method. The obtained hybrid materials were characterized by various surface analytical techniques. The photocatalytic performance of CdS/N-TiO_2 was investigated by degradation of Rhodamine B under visible light irradiation. The result revealed that CdS and N co-doping could significantly enhance the visible light photocatalytic activity of TiO_2.

EXPERIMENTAL

Tetrabutyl orthotitante (TBOT), urea and $Na_2S·9H_2O$ were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Rhodamine B, hydrochloric acid, mercaptoacetic acid and $CdCl_2·2.5H_2O$ were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other chemicals were of analytical grade. Doubly distilled water was used throughout the investigation.

Scanning electron microscopic images were obtained with a Quanta 200 field emission scanning electron microscope (FEI, Netherlands). X-ray diffraction measurements were carried out on a Philips X'pert Pro X-ray diffractometer (PANalytical, Netherlands) equipped with a CuK_α radiation source (λ = 1.5406 Å). The accelerating voltage and applied current were 40 kV and 40 mA, respectively. UV-visible absorption spectra were measured with a TU-1900 UV-visible spectrophotometer (Beijing Purkinje General Instrument Company, China).

Synthesis of TiO_2 nanoparticles: Titanium(IV) oxide nanoparticles were synthesized using the sol-gel technique. Briefly, 10 mL tetrabutyl orthotitante were added dropwise to 30 mL ethanol, followed by 10 min stirring at room temperature to obtain solution a. Then, 1 mL H_2O and 0.1 mL hydrochloric acid were added drop-wise to 10 mL ethanol followed by 10 min stirring at room temperature to obtain solution b.

Solution b was added drop-wise to solution a under vigorous stirring. The stirring was continued for 1 h. Then, the mixture was transferred to a stainless steel hydrothermal synthesis reactor with Teflon to react at 110 °C for 12 h. After hydrothermal reaction, the product was separated by centrifugation and then calcined at 400 or 500 °C for 4 h.

Synthesis of N doped TiO_2 nanoparticles: The synthesis of N doped TiO_2 nanoparticles was similar to the synthesis of TiO_2, except that 1 g urea was dissolved in solution a.

Synthesis of CdS doped TiO_2 nanoparticles: The synthesis of CdS doped TiO_2 nanoparticles was similar to the synthesis of TiO_2, except that 0.1142 g $CdCl_2·2.5\ H_2O$ was dissolved in the mixed solution of a and b, followed by adding 0.25 mL mercaptoacetic acid and 0.1224 g $Na_2S·9H_2O$ and then the mixture was transferred to the stainless steel hydrothermal synthesis reactor.

Synthesis of N and CdS co-doped TiO_2 nanoparticles: In the synthesis process of N and CdS co-doped TiO_2 nanoparticles, three reaction solutions were prepared: (1) 10 mL tetrabutyl orthotitante were added dropwise to 30 mL ethanol, followed by 10 min stirring at room temperature; then 1 g urea was added and dissolved to obtain solution a. (2) 0.1 mL hydrochloric acid were added drop-wise to 5 mL ethanol followed by adding 0.1142g $CdCl_2·2.5\ H_2O$. After complete dissolution, 0.25 mL mercaptoacetic acid was added to obtain solution b. (3) 1 mL H_2O was added drop-wise to 5 mL ethanol, followed by dissolving 0.1224 g $Na_2S·9H_2O$ to obtain solution c.

Solution c was added drop-wise to solution b under gentle stirring. Then, the mixture of solutions b and c was added drop-wise to solution a under vigorous stirring. The stirring was continued for 1 h. Then, the mixture was transferred to a stainless steel hydrothermal synthesis reactor with Teflon to react at 110 °C for 12 h. After hydrothermal reaction, the product was separated by centrifugation, then calcined at 400 or 500 °C for 4 h. The molar ratio of Cd:Ti:N was 1:20:33 for the obtained CdS/N-TiO_2, which was marked as CdS/N-TiO_2A in this work.

For comparison, another type of CdS/N-TiO_2 particles (CdS/N-TiO_2B) with a molar ratio of Cd:Ti:N=1:10:17 were synthesized using the similar procedure except that the amount of urea was reduced to 0.5 g and the volume of tetrabutyl orthotitante was reduced to 5 mL during the preparation of solution a.

Photocatalytic evaluation: 0.05 g TiO_2, N-TiO_2, CdS/TiO_2, CdS/TiO_2A or CdS/TiO_2B was added to 1.5 μmol/L aqueous solution of Rhodamine B. After 5 min ultrasonication to uniformly disperse the catalyst, Rhodamine B solution was irradiated with a visible light for degradation. A PLS-SXE300 xenon lamp (Beijing Perfect Co., China) with an optical filter ($\lambda > 420$ nm) was used as the irradiation source and the distance between the light source and solution was 10 cm. During the degradation, the Rhodamine B solution was stirred with a magnetic stirrer. Every 20 min, the absorbance of solution was monitored with the UV-visible spectrophotometer to evaluate the degradation efficiency of Rhodamine B by photocatalysis.

RESULTS AND DISCUSSION

X-ray diffraction: Fig. 1 shows the XRD patterns of synthesized products namely TiO_2, N-TiO_2, CdS/TiO_2, CdS/N-TiO_2A and CdS/N-TiO_2B. The XRD pattern of TiO_2 shows the diffraction peaks at 25.36, 37.93, 48.07, 54.03 and 55.13° corresponding, respectively to (101), (004), (200), (105), (211) crystal planes of anatase. For the XRD pattern of N-TiO_2, no new diffraction peak is observed, indicating that N doping does not change the main crystal species. For CdS/TiO_2 and CdS/N-TiO_2A, although there is no new diffraction peak, the diffraction intensity of anatase is decreased due to the reduced absorption of anatase to X-ray by CdS. We speculated that the molar ratio of Cd in CdS/TiO_2 or CdS/N-TiO_2A (Cd:Ti:N=1:20:33) was too low to exhibit the obvious diffraction peaks of CdS in doped TiO_2. So, we prepared CdS/N-TiO_2B with a higher molar ratio of Cd (Cd:Ti:N=1:10:17) and clearly observed the diffraction peak of CdS(101) crystal plane at 26.6°, confirming our speculation. On the other hand, as compared with Fig. 1a, Fig. 1b shows higher diffraction intensity, confirming that the crystallization of TiO_2 is increased with increasing calcination temperature.

SEM: The surface morphology of TiO_2, N-TiO_2, CdS/TiO_2, CdS/N-TiO_2A and CdS/N-TiO_2B were observed by SEM. Fig. 2a shows that the size of TiO_2 is in the range of 2-6 μm and few particles are aggregated. While the size of N-TiO_2 is obviously decreased to 0.2-2 μm and many particles are aggregated (Fig. 2b), which might be attributed to the fact that N doping increases the electrostatic attraction between TiO_2 particles or van der Waals force between molecules. Fig. 2c shows that the size of CdS/TiO_2 is in the range of 1-5 μm and many particles are aggregated,indicating the formation of CdS/TiO_2 composites. The SEM observation on CdS/N-TiO_2A shows an aggregated structure with the particle size of 0.4-3 μm. For CdS/N-TiO_2B, the particle size is not uniform, which varied in the range of 0.1-5 μm. The aggregation of particles

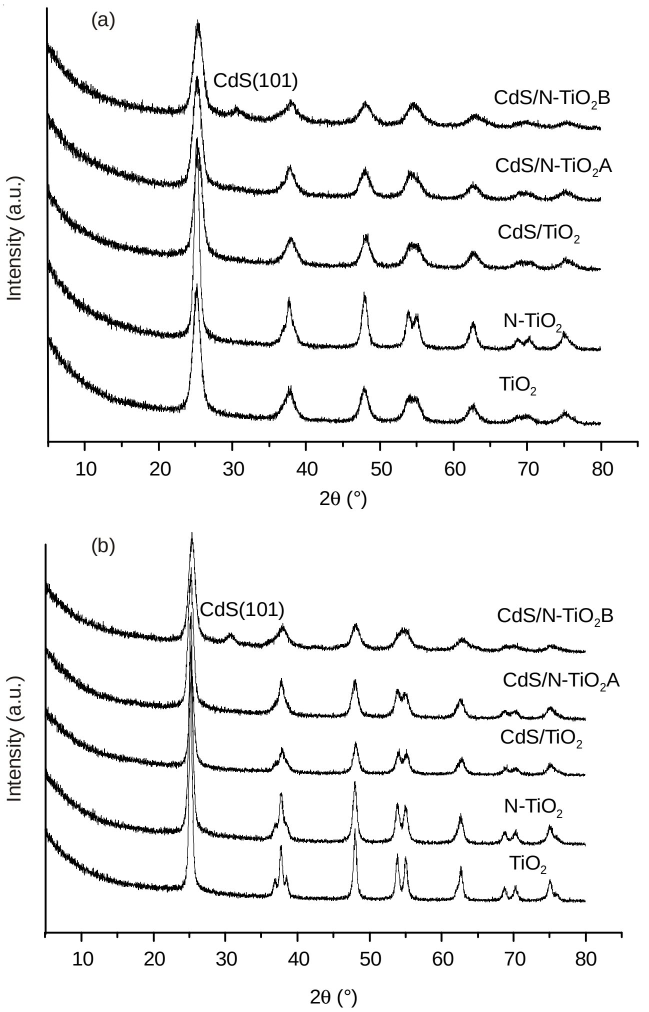


Fig. 1. XRD patterns of obtained materials calcined at (a) 400 °C and (b) 500 °C

could be due to the effect of N doping while the increased particle size might be due to the influences of Cl^- and some excessive amount of Cd^{2+} during CdS doping[18,19].

Photocatalytic degradation of Rhodamine B: The visible light photocatalytic performances of TiO_2, N-TiO_2, CdS/TiO_2, CdS/N-TiO_2A and CdS/N-TiO_2B were evaluated using Rhodamine B a pollutant. Fig. 3 shows the UV-visible absorption curves of Rhodamine B solution recorded during the visible light photocatalytic degradation on various catalysts calcined at 400 °C. It was observed that TiO_2 exhibited a low visible light photocatalytic activity and only 42.80 % Rhodamine B is degraded on TiO_2. When N-TiO_2 was used instead of pure TiO_2, the 2 h degradation efficiency was improved to 77.57 %, demonstrating that N doping could promote the visible light photocatalytic activity of TiO_2. The 2 h degradation efficiency was 65.10 % on CdS/TiO_2, showing the effective photosensitization of TiO_2 by CdS. While on CdS/N-TiO_2A, the 2 h degradation efficiency was further improved to 82.81 %. In comparison, CdS/N-TiO_2B showed the highest photocatalytic activity and the 2 h degradation efficiency reached 97.77 %, indicating that increasing the doping amount of CdS by controlling the molar ratio of Cd could significantly promote the photocatalytic activity of doped TiO_2. In addition, we observed that the maximum absorption peak of Rhodamine B showed blueshift during the degradation process on most catalysts except pure TiO_2. This phenomenon should be due to the formation of intermediated degradation products during the quick degradation process of Rhodamine B on all doped catalysts.

At the same time, the photocatalytic performances of catalysts calcined at 500 °C were also investigated. Although the results were similar to those obtained on catalysts calcined at 400 °C, the photocatalytic activity of catalysts calcined at 500 °C was relatively lower (Fig. 4). This result might be due

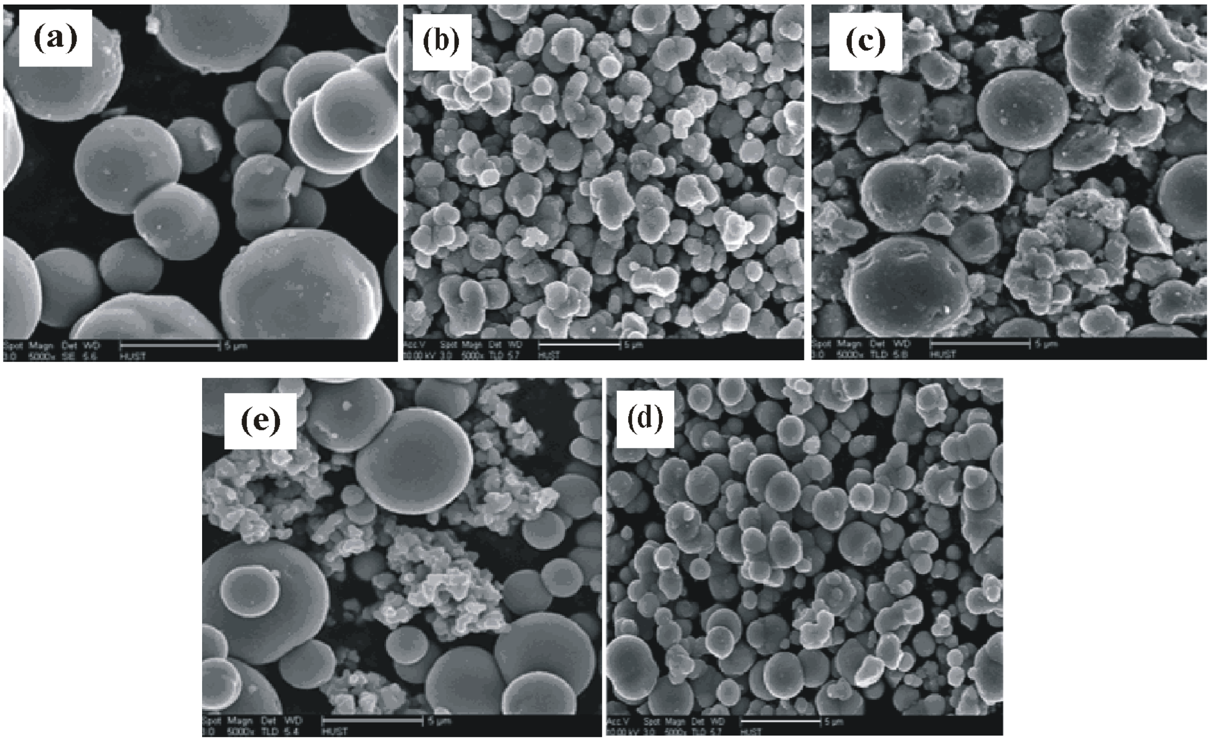


Fig. 2. SEM images of (a) TiO_2, (b) N-TiO_2, (c) CdS/TiO_2, (d) CdS/N-TiO_2A and (e) CdS/N-TiO_2B

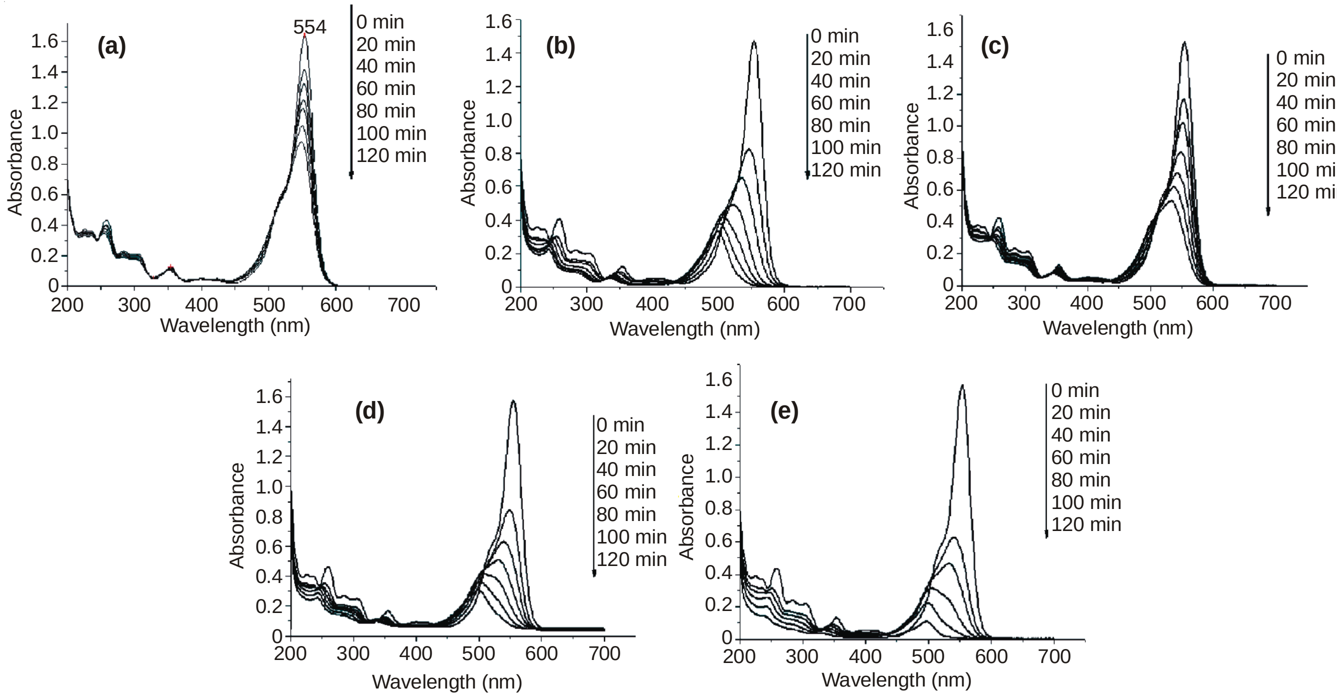


Fig. 3. UV-visible absorption curves of Rhodamine B solution during the visible light photocatalytic degradation on various catalysts calcined at 400 °C: (a) TiO_2, (b) N-TiO_2, (c) CdS/TiO_2, (d) CdS/N-TiO_2A and (e) CdS/N-TiO_2B and corresponding degradation curves

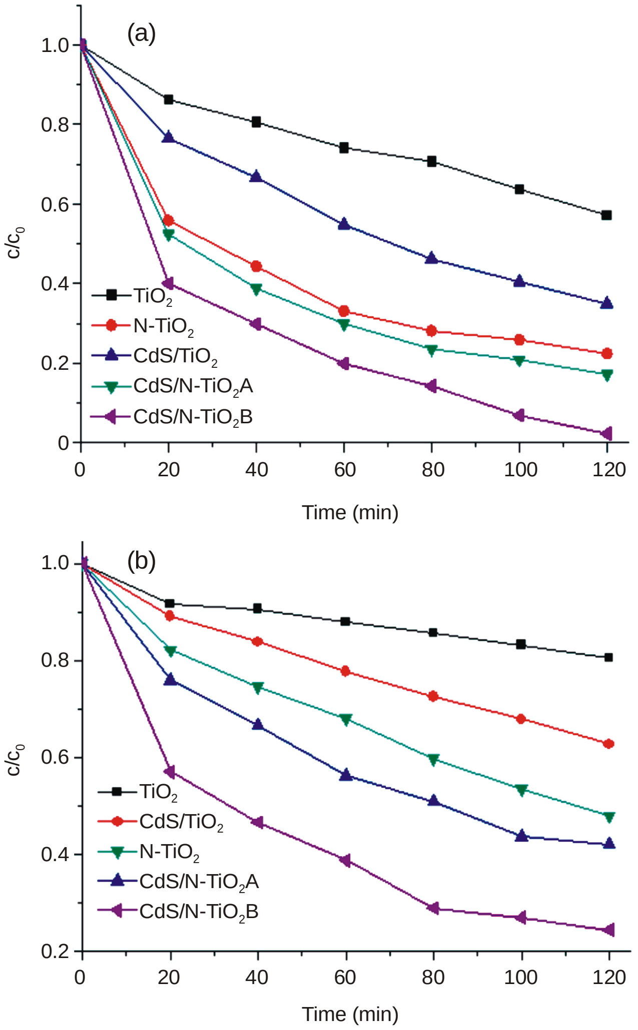


Fig. 4. Degradation curves of Rhodamine B on various catalysts calcined at (a) 400 °C and (b) 500 °C

to the increased particle size under higher cacination temperature which reduces the effective adsorption of pollutant molecules on the catalyst particles. Moreover, the excessive high-temperature treatment might destroy the stability of some CdS which reduces the activity of doped catalyst. Therefore, CdS/N-TiO_2B calcined at 400 °C showing the highest photocatalytic activity is the optimum catalyst for pollutant degradation.

Stability test: The stability of the best catalyst namely CdS/N-TiO_2B calcined at 400 °C was tested by three repeated use in photocatalytic degradation of Rhodamine B solution. As can be seen from Fig. 5, the activity of the catalyst does not show obvious decrease during the first two recycles. Although the activity of the catalyst shows a slight decrease in the third recycle, the 2 h degradation efficiency still reaches 95.10 %, which is highly applicable for removal of pollutant.

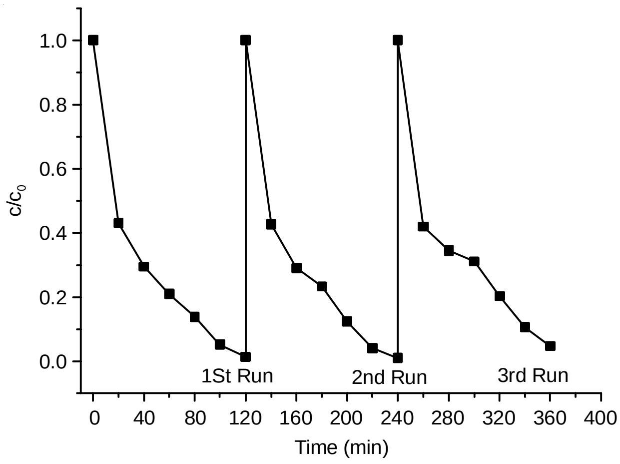


Fig. 5. Comparison of degradation of Rhodamine B on CdS/N-TiO_2B for three recycles

Conclusion

A CdS and N element have ben employed to modify TiO_2 *via* a one step sol-hydrothermal method and studied the photocatalytic performance of doped TiO_2 for degradation of Rhodamine B. The results indicated that although either CdS or N doping could improve the visible light photocatalytic performance of TiO_2, CdS and N co-doped TiO_2 showed the highest photocatalytic activity. The synthesized CdS/N-TiO_2B with a higher molar ratio of Cd (Cd:Ti:N=1:10:17) which was calcined at 400 °C possessed the best visible light photocatalytic activity and 2 h degradation efficiency for Rhodamine B reached 97.77 %.

ACKNOWLEDGEMENTS

This work was supported by the Hunan Provincial Natural Science Foundation of China (Grant No. 12JJ3013), Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, China (Grant No. 2013CL04) and Planned Science and Technology Program of Hunan Province, China (Grant Nos. 2013NK3002, 2011RS4069).

REFERENCES

1. A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
2. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
3. J. Jing, M. Liu, V.L. Colvin, W. Li and W.W. Yu, *J. Mol. Catal. A*, **351**, 17 (2011).
4. L. Prieto-Rodriguez, S. Miralles-Cuevas, I. Oller, A. Agüera, G.L. Puma and S. Malato, *J. Hazard. Mater.*, **211-212**, 131 (2012).
5. M.S. Vohra, *Fresenius Environ. Bull.*, **20**, 1308 (2011).
6. G.X. Shen, Y.C. Chen and C.J. Lin, *Thin Solid Films*, **489**, 130 (2005).
7. J.H. Carey, J. Lawrence and H.M. Tosine, *Bull. Environ. Contam. Toxicol.*, **16**, 697 (1976).
8. S.Y. Lee and S.J. Park, *J. Ind. Eng. Chem.*, **19**, 1761 (2013).
9. H. Park, Y. Park, W. Kim and W. Choi, *J. Photochem. Photobiol. Chem.*, **15**, 1 (2013).
10. R. Daghrir, P. Drogui and D. Robert, *Ind. Eng. Chem. Res.*, **52**, 3581 (2013).
11. W. Choi, A. Termin and M.R. Hoffmann, *J. Phys. Chem.*, **98**, 13669 (1994).
12. L.G. Devi and R. Kavitha, *Appl. Catal. B*, **140-141**, 559 (2013).
13. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, **293**, 269 (2001).
14. E.A. Kozlova, N.S. Kozhevnikova, S.V. Cherepanova, T.P. Lyubina, E.Y. Gerasimov, V.V. Kaichev, A.V. Vorontsov, S.V. Tsybulya, A.A. Rempel and V.N. Parmon, *J. Photochem. Photobiol. Chem.*, **250**, 103 (2012).
15. S.B. Rawal, S. Bera, D. Lee, D.J. Jang and W.I. Lee, *Catal. Sci. Technol.*, **3**, 1822 (2013).
16. G. Yang, B. Yang, T. Xiao and Z. Yan, *Appl. Surf. Sci.*, **283**, 402 (2013).
17. X. Liu, L. Pan, T. Lv and Z. Sun, *J. Alloys Comp.*, **583**, 390 (2014).
18. S.H. Yu, L. Shu, J. Yang, K.B. Tang, Y. Xie, Y.T. Qian and Y.H. Zhang, *Nanostruct. Mater.*, **10**, 1307 (1998).
19. W. Cao, K. Zhang and J. Zhang, *Wuji Huaxue Xuebao*, **18**, 997 (2002).