Improvement in Recycling Times and Photodegradation Efficiency of Core-Shell Structured $\text{Fe}_3\text{O}_4@\text{C-TiO}_2$ Composites by pH Adjustment

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Recycling of photocatalysts is necessary for cost reduction. However, the photocatalytic properties of most reused photocatalysts deteriorate with recycled times. Thus, it is imperative to determine the dominant factor that affects the photocatalytic properties of recycled photocatalysts and find a way to improve the photocatalytic properties of recycled photocatalysts. In this work, microsized magnetic Fe_3O_4 powders were successfully encapsulated by carbon-doped anatase titanium (C-TiO_2) by the sol-gel method to form a core (Fe_3O_4)-shell (C-TiO_2) structure (DTF). The core-shell particles were characterized by X-ray diffraction, UV-vis diffuse reflectance spectral analysis, high-resolution transmission electron microscopy, specific surface area and magnetic properties. In addition, photocatalytic properties as well as the recovery rate were measured. It was evidenced that the as-prepared DTF powder has a larger specific surface area and a much higher dark adsorption than the nanosized C-TiO_2 and commercial Fe_3O_4 . Moreover, DTF has a high recovery rate and a first-order kinetic function k . Furthermore, it was evidenced that pH significantly affected the photodegradation efficiency of DTF. Thus, a strategy that the solution pH was modulated to a constant value of 3 was carried out, resulting in improved photodegradation efficiency of recycled DTF. The present work could provide a new route to improving the photocatalysis efficiency and the recycles of photocatalysts.

Keywords: Core-shell structured $\text{Fe}_3\text{O}_4@\text{C-TiO}_2$; Recycle; PH adjustment; Photocatalytic properties

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Introduction

Photocatalysis is a simple method to treat water containing hazardous pollutants. A good photocatalyst should be stable, eco-friendly, highly efficient, and inexpensive. Anatase TiO_2 has been regarded as good photocatalyst and is immensely studied, as it is stable, eco-friendly, economic, and has a strong intrinsic oxidizing power.¹ In previous studies, many efforts were made to increase its surface area to maximize the photocatalytic surface reactions by proposing various forms of TiO_2 nanomaterials such as nanoparticles,² nanowires,³ and nanotubes.⁴ However, three drawbacks remain for anatase TiO_2 : 1) limited absorption wavelength range ($< 380 \text{ nm}$; only 5% of sunlight) owing to its intrinsic energy bandgap ($E_g \sim 3.2 \text{ eV}$),⁵ 2) fast recombination rate of photo-induced electron-hole pairs,⁶ and 3) difficulty in its retrieval from media because of its very small size, resulting in secondary pollution of the medium.

In the last two decades, many efforts have been made by the scientific community to widen the photocatalysis spectral range of anatase TiO_2 to the visible range by doping nonmetal elements (e.g., carbon (C), nitrogen (N), sulfur (S), and fluorine (F)),⁷⁻¹⁰ or metal cations (e.g., Fe, Ag, Mo, W) into anatase TiO_2 ,¹¹⁻¹⁴ and its nanostructured

powder forms such as nanodots and heterojunctions.^{15,16} The dopants would generate donor or acceptor states in the band gap.^{17,18} On the other hand, heterojunctions have proved to be an effective route to prolonging the lifetime of photo-produced electrons and holes in recent years.^{19,20} Additionally, many efforts have been made to address the recyclability issue by immobilizing photocatalysts on supports such as glasses,²¹ wood,²² brick,²³ concrete,²⁴ activated carbon, and other bulk materials, which are large enough to be recycled,²⁵ or by combining the photocatalyst with microsized magnetic particles and retrieving the composites by applying a magnetic field.^{26,27} The above-said supports would shield the sunlight of the medium under supports,²⁸ while the microsized magnetic particles would not shield the sunlight. In addition, the latter recycling strategy could introduce a heterojunction, which can prolong the lifetime of the photo-generated electron-hole pairs.¹⁶ Therefore, the current recycling route focused on the latter approach.²⁹

Low-cost photocatalysis is welcome for the application. If a photocatalyst can be used for many times (denoted as N) with high photodegradation levels ($>90 \%$), the cost of photocatalysis would reduce to nearly one in N of that incurred by photocatalysis without recycling. Unfortunately, so far, the photocatalytic properties of recycled photocatalysts reduce significantly with increasing recycling time,^{30,31} especially for TiO_2 -based photocatalysts.³² Therefore, it is essential to determine the mechanism of the reduction in the photocatalytic properties of recycled photocatalysts and find an effective route to upgrade the photocatalytic properties of recycled photocatalysts.

In this work, magnetic particles (Fe_3O_4) was encapsulated by carbon doped anatase TiO_2 (C-TiO_2) and formed core-shell composites ($\text{Fe}_3\text{O}_4@(\text{C-TiO}_2)$, denoted as DTF). The Fe_3O_4 powder used in this work

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was micro-sized and possessed sufficient magnetic field to retrieve the DTF powder from the solution. In this study, pH was found to be the dominant factor affecting the photocatalytic properties of reused DTF. Accordingly, a method to improve the photocatalytic properties of reused DTF was devised.

2. Experimental

2.1 Starting materials

Tetra-n-butyl titanate (TBT, AR), acetic acid alcohol (AcOH, AR), and ethanol (C_2H_5OH , AR) were purchased from Tianjin Zhiyuan Chemical Reagent, China. Guanidine hydrochloride (AR) and iron (II, III) oxide (AR) were purchased from Aladdin Chemistry Co. Ltd., China. Deionized water was laboratory-made.

2.2 Sample preparation

DTF was synthesized in three steps. In the first step, *liquor A* and *liquor B* were prepared. *Liquor A* was obtained by mixing TBT (36 mL), AcOH (18 mL), and C_2H_5OH (34 mL), while *liquor B* was acquired by mixing C_2H_5OH (18 mL) and deionized water (11 mL). In the second step, *liquor A* was mixed with 1 g of Fe_3O_4 in a beaker and sonicated for 5 min, during which *liquor B* was slowly added dropwise with stirring to form a gel. The mixture was then dried in an oven at 80 °C followed by grinding to obtain a powder sample. In the third step, the mixture of the as-fabricated powder and guanidine hydrochloride was calcined in vacuum at 450 °C for 2 h in a mass ratio of 1.5:0.2 (denoted as DTF). For comparison, nanosized doped TiO_2 powder was prepared by calcinating a mixture of TiO_2 gel powder and guanidine hydrochloride in the same mass ratio (denoted as C- TiO_2) under the same conditions.

2.3 Characterization

X-ray diffraction (XRD) analysis was performed using an X'Celerator detector (XRD, X'Pert Pro, PANalytical) at a slow scanning speed of 1°/min using Cu K_α radiation ($k = 1.5406 \text{ \AA}$) in the 2θ range of 5–80°. The detailed microstructures were observed by high-resolution transmission electron microscopy (HRTEM, JEM-2100HR, JEOL). The binding energies of Ti, Fe, C and O atoms were investigated using an ESCALAB 250 X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific, USA). All of the binding energies were calibrated to the C 1s peak of adventitious surface carbon at 284.8 eV. UV-vis diffuse reflectance spectral (UV-Vis-DRS) measurements were performed with a Shimadzu 2550PC spectrophotometer (Japan) using $BaSO_4$ as a reference sample. Zeta potential measurements were performed using a Zeta Potential Analyzer (NanoPlus, Micromeritics Ltd., USA). The specific surface area was measured using a microelectrophoresis apparatus (JS94K2, Shanghai Zhongcheng Data Technology Equipment Co. Ltd., China). The magnetic properties were assessed using a vibrating sample magnetometer (VSM, Quantum Design Inc. USA) at room temperature. An electronic balance (FA2004B, $d=0.1\text{mg}$, Shanghai Tianmei Company) was employed to measure the weight of the samples.

2.4 Investigation of photocatalytic properties, pH values, and recyclability

The photocatalytic activities of the as-prepared samples were evaluated by the degradation of an organic dye methyl orange (MO, AR, Aladdin Industrial Corporation, China) using a 350 W Xe lamp as the simulated solar light source and a quartz reactor with a water-cooling outer pack (Shanghai Lansheng Company, China). In these experiments, 0.1 g of photocatalyst was added to the photoreactor containing 100 mL of MO solution (10 ppm). Before irradiation, the suspension was stirred in the dark for 30 min to ensure an adsorption–desorption equilibrium. During

irradiation, at certain time intervals, ~3.0 mL of the MO solution was removed from the reactor to monitor the MO concentration of the solution by UV-vis spectrometry according to the maximum absorption intensity of the peak at the wavelength of 464 nm.³³ During photodegradation, the pH value was investigated using a pH meter (PHB-3, Shanghai San-Xin Instrumentation Inc., China).

After photodegradation, the used photocatalyst was retrieved from the medium for recycling by applying a magnetic field produced by a magnet. In each cycle, the photodegradation was investigated using the above-described method. The retrieved power was dried in an oven at 80 °C. The recyclability was evaluated by the recovery rate (%), defined as the ratio (in percentage) of the mass of the retrieved photocatalyst from the medium after photodegradation to the mass of the photocatalyst before photodegradation.

3. Results and discussion

3.1 Phase identification and microstructural analyses

Fig. 1 shows the XRD profiles of as-prepared DTF, C- TiO_2 , and commercial Fe_3O_4 . It can be seen from Fig. 1 that there are two phases in as-prepared DTF, i.e., anatase TiO_2 phase (JCPDS No. 21-1272, labeled by the symbol “●”) and Fe_3O_4 phase (JCPDS No. 19-0629, labeled by the symbol “▽”).^{34,35} In addition, only a weak peak corresponding to the (311) plane of Fe_3O_4 appeared in the XRD profile of DTF, suggesting that most of the Fe_3O_4 was covered by the as-grown anatase TiO_2 .

SEM and TEM investigation (Fig. 2) can supply evidences of core-shell structure C- TiO_2 @ Fe_3O_4 . Fig. 2(a) shows the typical SEM image of DTF, indicating that the micro-sized particles are covered by nanosized particles. The micro-sized particles (around 2 μm) could be the commercial Fe_3O_4 particles, while the nanosized particles should be the grown nanosized C- TiO_2 .³⁶ In addition, the TEM image of the DTF in Fig. 2(b) suggests a obvious core-shell structure in DTF and the thickness of the C- TiO_2 layer is around 30 nm, while those of Fe_3O_4 particles is around 330 nm, much less than 2 μm found in Fig. 2(a). The agglomeration of Fe_3O_4 particles in Fig. 2(a) might account for the big difference in Fe_3O_4 particle size between Fig. 2(a) and Fig. 2(b). Meanwhile, the high-resolution TEM image (Fig. 2(c)) indicates that the interplanar spacings of the shell layer (0.357 nm) and the core (0.259 nm) are close to that of the (101) plane of anatase TiO_2 and the (311) plane of Fe_3O_4 , respectively. Therefore, it can be concluded that the composites possess a core-shell structure, i.e., C- TiO_2 @ Fe_3O_4 , which

Fig. 1 XRD of as-prepared DTF, C- TiO_2 and commercial Fe_3O_4

can explain the low-intensity XRD peak of Fe_3O_4 in the as-prepared DTF.^{37,38}

The specific BET surface areas are listed in **Table 1**. The calculated BET surface area of DTF was $44.46 \text{ m}^2/\text{g}$, which was notably higher than that of commercial Fe_3O_4 ($11.22 \text{ m}^2/\text{g}$) and that of as-prepared C-TiO_2 ($35.50 \text{ m}^2/\text{g}$).

Table 1 Specific BET surface areas of Fe_3O_4 , C-TiO_2 , and DTF.

Samples	$S_{\text{BET}} (\text{m}^2/\text{g})$
Fe_3O_4	11.22
C-TiO_2	35.50
DTF	44.46

3.2 Compositional analysis

To further determine the composition and elemental valence states of the prepared samples, XPS was performed. Fig. 3(a) shows the typical full survey XPS spectrum of DTF, which clearly indicates that DTF is mainly composed of C, Ti, Fe, and O elements. It should be noted that the XPS peak of Fe 2p is much lower than that of Ti 2p. This result indicates, on the other side, that the Fe_3O_4 particles are covered by C-TiO_2 particles. Fig. 3(b) shows the XPS of Ti 2p. The peaks located at 458.7 eV and 464.3 eV can be attributed to $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$.³⁹ Fig. 3(c) shows the XPS of Fe 2p, in which there are two peaks at 712.3 and 723.5 eV, corresponding to typical $\text{Fe}^{3+} 2p_{3/2}$ and $\text{Fe}^{3+} 2p_{1/2}$ in Fe_3O_4 , respectively.⁴⁰⁻⁴³ As shown in Fig. 3(d), the C 1s peaks could be fitted into three peaks at 284.7, 283.9, and 282.1 eV, which were assigned to the C–C bond in residual carbon⁴⁴, Fe–C bond⁴⁵, and Ti–C bond⁴⁶, respectively, suggesting that carbon possibly substituted for oxygen in TiO_2 , as well as in Fe_3O_4 in the boundary of $\text{TiO}_2/\text{Fe}_3\text{O}_4$. As shown in Fig. 3(e), the O 1s XPS spectrum was resolved into three peaks at 530.5, 529.8, and 528.0 eV, which can be attributed to Ti–O

Fig. 2 (a) SEM image, TEM images (b) with low resolution and (c) with high resolution of DTF.

Fig. 3 XPS spectra of DTF: (a) survey (b) Ti 2p (c) Fe 2p (d) C 1s (e) O 1s (f) N 1s.

bond,⁴⁷ Fe–O bond,⁴⁸ and Ti–O–Fe bond,⁴⁹ respectively. It should be noted that the intensity of the peak at 529.8 eV is much lower than that of the peak at 530.5 eV, possibly because most of the Fe_3O_4 was encapsulated by C–TiO₂ or TiO₂.

3.3 Absorption of UV-vis light and the band gap

The UV–vis absorption spectra of C–TiO₂, Fe_3O_4 , and DTF are shown in Fig. 4. We can clearly see that DTF has a higher light absorption in the range of 250–500 nm than the nanosized C–TiO₂ and commercial Fe_3O_4 . One possible reason is that the heterojunction of C–TiO₂/g Fe_3O_4 could improve the absorption of visible light in a certain range.^{50,52} Another possible reason is that pores formed on the surface of the DTF particles during the growth of C–TiO₂.

3.4 Magnetic property

The plot of magnetization versus magnetic field (M–H loop) at room temperature for DTF is illustrated in Fig. 5. A saturation magnetization (M_s) of 3.75 emu/g was obtained. This value is significantly less than that of pure Fe_3O_4 particles (55.1 emu/g) reported in a previous work.⁵³ The magnetic hysteresis loop indicates a small coercivity of about 80 Oe. The magnetic separability of DTF from the medium was examined in water by placing a magnet near the glass beaker, as shown in the inset picture in Fig. 5. The DTF powders were absorbed by the magnet

Fig. 4 UV-Vis light absorption spectra of C–TiO₂, Fe_3O_4 and DTF.

Fig. 5 Room-temperature Magnetic hysteresis curves of Fe_3O_4 and DTF nanocomposite. (The inset shows the separation of particles dispersed in water by a magnet in 60 s).

in a few seconds, confirming that the products possessed enough magnetic properties for retrieving DTF from the medium after photodegradation. This assured a convenient separation of the magnetic nanohybrid photocatalyst from the aqueous medium under an external magnetic field.

3.5 Recovery performance

Owing to its better magnetic properties, the recovery rate of DTF is relatively high (Fig. 6). After 5 recycles, the recovery rate was 90 %, indicating that DTF has good recovery yield.

3.6 Dark adsorption and photodegradation

Fig. 7(a) and Fig. 7(b) show the dark adsorption, photodegradation, and

Fig. 6 Recovery rate in different cycles.

Fig. 7 (a) dark adsorption and photodegradation, (b) PH value of C–TiO₂, DTF and commercial Fe_3O_4 during the first-circle photodegradation.

pH values of the as-prepared DTF, C-TiO₂, and commercial Fe₃O₄, respectively. In Fig. 7(a), C₀ is the initial concentration of MO (10 mg/L) and C is the concentration corresponding to the irradiation time t. It can be seen from Fig. 7(a) that after 30 min of dark adsorption, Fe₃O₄ shows nearly no adsorption and C-TiO₂ adsorbs less than 10 %. In contrast, DTF adsorbs nearly 80 %, possibly owing to its high specific surface area. Fig. 7(b) shows that after dark adsorption, DTF is acidic (pH≤4), while the nanosized C-TiO₂ and Fe₃O₄ are alkaline (pH≥8). Because DTF is composed of a nanosized C-TiO₂ shell and a Fe₃O₄ core, the acidic property should not result from the original nanosized C-TiO₂ and Fe₃O₄, but from the heterojunction of Fe₃O₄/C-TiO₂. The zeta potential measurements in Fig. 8 show that the sample particles have positive charges at pH≤5, while the functional groups of MO are negatively charged, which indicates good adsorption properties. In ref 54, Thu et al have found that the initial solution pH had affected the adsorption capacity and the photocatalytic behaviour of the Cu-doped TiO₂ in the decolourisation of these dyes. But they haven't the effect of PH on the recyclability of Cu-doped TiO₂.

From Fig. 7(a), it can be seen that the MO degradation by DTF occurred dominantly from dark adsorption, while that by C-TiO₂ occurred dominantly from photodegradation. This is possibly owing to the high adsorption because the excess of MO on the DTF particle

surface blocked the active photodegradation site.⁵⁵

We can evaluate the photocatalytic property according to Langmuir-Hinshelwood first-order kinetic parameter, *k*, which is defined by the following formula:⁵⁶

$$\ln(C_0/C) = kt + \ln(C_0/C_1)$$

where C₁ is the concentration of the solution after dark adsorption, and C₀ and C are the initial concentration of MO before dark adsorption and the concentration at photodegradation time t, respectively. The photocatalytic degradation rates of the MO solution under visible light (λ≥420 nm) by Fe₃O₄, C-TiO₂, and DTF are shown in Fig 9. The degradation efficiency of the C-TiO₂ and DTF samples were respectively 0.0220 min⁻¹ and 0.0156 min⁻¹. This is possibly because DTF contains Fe₃O₄; thus, for the same quantity of C-TiO₂ and DTF, the photocatalysis efficiency of C-TiO₂ is higher than that of DTF.

We have also measured the photocatalytic performance of DTF during stable PH values at 1, 3, 5, 7, and 9 (Fig. 10). It was found that photocatalytic performances of DTF increase with increasing the stabilized environmental PH values, conforming to the results in ref.54. But when the the stabilized environmental PH value is 1, the DTF particle was partly dissolved in the solution. Therefore, the stabilized environmental PH value of 1 is not suitable, while the stabilized

Fig. 8 Zeta potential of DTF, C-TiO₂ and Fe₃O₄

Fig. 9 First-order kinetic function of Fe₃O₄, DTF and C-TiO₂

Fig. 10 the photocatalytic performance of DTF during stable PH values at 1, 3, 5, 7, and 9.

Fig. 11 Cyclic photocatalytic performance of DTF (a)without PH adjustment and (b)with PH adjustment to a constant 3.

environmental PH value of 3 is suitable.

3.7. Cyclic photocatalytic performance

To evaluate the recyclability of DTF, we performed 5 cycles of photodegradation (0.5g DTF degrades 100ml MO), during which the pH value was monitored. The degradation rates for the 5 cycles are shown in Fig. 11(a) and the corresponding pH values are shown in Fig. 12. From Fig. 11(a), it can be seen that the maximum degradation rates of the first three cycles are above 80 %, while that of the fourth cycle is slightly less. In the fifth cycle, the maximum photodegradation efficiency of DTF decreased to about 30 %. As can be seen from Fig. 12, the solution pH gradually increases with reuse numbers of DTF. Therefore, we speculated that pH is a crucial factor that affects the maximum photodegradation rate of DTF.

To verify this speculation, we performed 5 cycles of photocatalytic degradation, keeping the other conditions unchanged, and adjusting the solution pH to 3 before each cycle of light irradiation. The pH of 3 was chosen because the zeta potential of DTF was the highest at pH=3, at which the dark adsorption would be the highest, and because the pH value of the first cycle of photodegradation was around 3.

As can be seen from Fig. 11(b), after adjusting the pH to 3, the degradation rates in the 5 cycles changed slightly. In the first three cycles, the degradation rates reached more than 90% at 120 min, while the degradation rates in the fourth and fifth cycles after pH adjustment were about 80 %. For unadjusted pH, the degradation rates in the fourth and fifth cycles were 60 % and 30 %, respectively. Therefore, it can be concluded that the recovery property can be improved by adjusting the pH to the value at which the zeta potential corresponds to the largest dark adsorption.

Conclusion

In this work, microsized magnetic Fe_3O_4 powders were successfully encapsulated by carbon-doped anatase TiO_2 (C- TiO_2) by the sol-gel method. The XPS results proved that carbon was doped into TiO_2 and slightly into Fe_3O_4 . The specific surface area of the as-prepared DTF powder was larger than that of the nanosized C- TiO_2 and commercial Fe_3O_4 , which resulted in a much higher dark adsorption. It also showed that DTF has a high recovery rate, and a first-order kinetic function, k . Importantly, it was evidenced that the pH significantly affected the photodegradation efficiency of DTF. The photodegradation efficiency of DTF was improved by adjusting the solution pH to a constant value

of 3. The present work could provide new perspectives for improving the photocatalytic efficiency and the reuse number of recycled photocatalyst by adjusting the pH to the value at which the zeta potential corresponds to the largest dark adsorption.

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References

1. S. Singh, H. Mahalingam and P. K. Singh, *Appl. Catal. A-Gen.*, 2013, **462**, 178.
2. N. Li, G. Liu, C. Zhen, F. Li, L. L. Zhang and H. M. Cheng, *Adv. Funct. Mater.*, 2011, **21**, 1717.
3. Y. B. Mao and S. S. Wong, *J. Am. Chem. Soc.*, 2006, **128**, 8217.
4. I. Paramasivam, H. Jha, N. Liu and P. Schmuki, *Small*, 2012, **8**, 3073.
5. X. B. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746.
6. Y. H. Zhang, Z. R. Tang, X. Z. Fu and Y. J. Xu, *ACS Nano*, 2010, **4**, 7303.
7. Y. Huang, W. K. Ho, S. C. Lee, L. Z. Zhang, G. S. Li and J. C. Yu, *Langmuir*, 2008, **24**, 3510.
8. S. Livraghi, M. C. Paganini, E. Giamello, A. Selloni, C. Di Valentin and G. Pacchioni, *J. Am. Chem. Soc.*, 2006, **128**, 15666.
9. X. Q. Yan, K. Yuan, N. Lu, H. J. Xu, S. Y. Zhang, N. Takeuchi, H. Kobayashi and R. H. Li, *Appl. Catal. B-Environ.*, 2017, **218**, 20.
10. J. C. Yu, J. G. Yu, W. K. Ho, Z. T. Jiang and L. Z. Zhang, *Chem. Mat.*, 2002, **14**, 3808.
11. J. G. Yu, Q. J. Xiang, M. H. Zhou and Preparation, *Appl. Catal. B-Environ.*, 2009, **90**, 595.
12. J. G. Yu, J. F. Xiong, B. Cheng and S. W. Liu, *Appl. Catal. B-Environ.*, 2005, **60**, 211.
13. Y. Yang, X. J. Li, J. T. Chen and L.Y. Wang, *J. Photochem. Photobiol. A-Chem.*, 2004, **163**, 517.
14. A. Fuerte, M. D. Hernandez-Alonso, A. J. Maira, A. Martinez-Arias, M. Fernandez-Garcia and J. C. Conesa, *J. Soria, G. Munuera, J. Catal.*, 2002, **212**, 1.
15. W. F. Yao, B. Zhang, C. P. Huang, C. Ma, X. L. Song and Q. J. Xu, *J. Mater. Chem.*, 2012, **22**, 4050.
16. W. J. Zhou, H. Liu, J. Y. Wang, D. Liu, G. J. Du and J. J. Cui, *ACS Appl. Mater. Interfaces.*, 2010, **2**, 2385.
17. J.G. Yu, G. P. Dai and B. B. Huang, *J. Phys. Chem. C.*, 2009, **113**, 16394.
18. T. Hirakawa and P. V. Kamat, *J. Am. Chem. Soc.*, 2005, **127**, 3928.
19. J. M. Du, H. J. Chen, H. Yang, R. R. Sang, Y. T. Qian, Y. X. Li, G. G. Zhu, Y. J. Mao, W. He and D. J. Kang, *Microporous Mesoporous Mat.*, 2013, **182**, 87.
20. K. C. Christoforidis and M. Fernandez-Garcia, *Catal. Sci. Technol.*, 2016, **6**, 1094.
21. A. Fernandez, G. Lassaletta, V. M. Jimenez, A. Justo, A. R. GonzalezElipse, J. M. Herrmann, H. Tahiri and Y. Aitlchou, *Appl. Catal. B-Environ.*, 1995, **7**, 49.
22. L. J. Luo, Y. Yang, M. Xiao, L. C. Bian, B. Yuan, Y. J. Liu, F. Z. Jiang and X. J. Pan, *Chem. Eng. J.*, 2015, **262**, 1275.
23. F. Z. Li, J. S. Zhou, C. Du, W. Li, Y. Z. Wang, G. N. He and Q.Y. He, *J. Environ. Sci.*, 2017, **60**, 24-32.
24. A. Folli, C. Pade, T. B. Hansen, T. De Marco and D. E. Macphee, *Cem. Concr. Res.*, 2012, **42**, 539.
25. J. S. Zhou, F. Z. Li, C. Du, J. M. Liu, Y. Z. Wang, W. Li, G. N. He and Q.Y. He, *RSC Adv.*, 2016, **6**, 84457.
26. S. H. Xuan, W. Q. Jiang, X. L. Gong, Y. Hu and Z. Y. Chen, *J. Phys. Chem. C.*, 2009, **113**, 553.
27. C. X. Wang, L.W. Yin, L.Y. Zhang, L. Kang, X. F. Wang and R. Gao, *J. Phys. Chem. C.*, 2009, **113**, 4008.
28. M.W. Zhang, B. Tang, L. Sun and X. G. Wang, *Text. Res. J.*, 2014, **84**, 1840.
29. P. Wang, J. Wang, X. F. Wang, H.G. Yu, J.G. Yu, M. Lei and Y. G. Wang, *Appl. Catal. B-Environ.*, 2013, **132**, 452.
30. A. Arimi, M. Farhadian, A. R. S. Nazar and M. Homayoonfal, *Res. Chem. Intermed.*, 2016, **42**, 4021.

Fig. 12 PH value variation of DTF vs cycles.

31. W. J. Liu, J.Y. Cai and Z. H. Li, *ACS Sustain. Chem. Eng.*, 2015, **3**, 277.
32. S. E. Kim, J. Y. Woo, S.Y. Kang, B. K. Min, J. K. Lee and S.W. Lee, *J. Ind. Eng. Chem.*, 2016, **43**, 142.
33. C. Du, J. S. Zhou, F. Z. Li, W. Li, Y. Z. Wang and Q.Y. He, *Appl. Phys. A-Mater. Sci. Process.* 2016, **122**, 714.
34. Y. P. Wang, D. P. Sun, G. Z. Liu and W. Jiang, *Adv. Powder Technol.*, 2015, **26**, 1537.
35. J. H. Pan, X. Z. Wang, Q. Z. Huang, C. Shen, Z.Y. Koh, Q. Wang, A. Engel and D. W. Bahnemann, *Adv. Funct. Mater.*, 2014, **24**, 95.
36. Q. L. Kang, Y. Bao, M. Li and J. Z. Ma, *Prog. Org. Coat.*, 2017, **112**, 153.
37. H. U. Lee, S. C. Lee, S. H. Choi, B. Son, S. J. Lee, H. J. Kim and J. Lee, *Appl. Catal. B-Environ.*, 2013, **129**, 106.
38. S. M. Yuan, Z. Zhou and G. Li, *Crystengcomm.*, 2011, **13**, 4709.
39. M. Sathish, B. Viswanathan, R. P. Viswanath and C. S. Gopinath, *Chem. Mat.*, 2005, **17**, 6349.
40. K. Liu, Y. L. Qin, Y. Muhammad, Y. Zhu, R. Tang, N. H. Chen, H. Z. Shi, H. B. Zhang, Z. F. Tong and B. B. Yu, *J. Alloy. Compd.*, 2019, **781**, 790.
41. P. L. Tan, *J. Catal.*, 2016, **338**, 21.
42. J. Liu, J. N. Cui, T. Y. Zhou, S. Y. Fan, C. L. Zhang, Q. Hu and X. H. Hou, *Colloid Surf. A-Physicochem. Eng. Asp.*, 2019, **565**, 59.
43. Y. Y. Xie, X. Z. Yuan, Z. B. Wu, G. M. Zeng, L. B. Jiang, X. Peng and H. Li, *J. Colloid Interface Sci.*, 2019, **536**, 440.
44. C. Xie, S. H. Yang, B. B. Li, H. K. Wang, J. W. Shi, G. D. Li and C. M. Niu, *J. Colloid Interface Sci.*, 2016, **476**, 1.
45. I. N. Shabanova and V. A. Trapeznikov, *J. Electron Spectrosc. Relat. Phenom. (Netherlands)*, 1975, **6**, 297.
46. K. R. Wu and C.H. Hung, *Appl. Surf. Sci.*, 2009, **256**, 1595.
47. G. M. Ingo, S. Dire and F. Babonneau, *Appl. Surf. Sci.*, 1993, **70**, 230.
48. S. Hamzezadeh-Nakhjavani, O. Tavakoli, S. P. Akhlaghi, Z. Salehi, P. Esmailnejad-Ahranjani and A. Arpanaci, *Environ. Sci. Pollut. Res.*, 2015, **22**, 18859.
49. X. Q. Chen, H. X. Zhang and W. H. Shen, *Mater. Chem. Phys.*, 2018, **216**, 496.
50. J. A. Navio, G. Colon, M. Trillas, J. Peral, X. Domenech, J. J. Testa, J. Padron, D. Rodriguez and M. I. Litter, *Appl. Catal. B-Environ.*, 1998, **16**, 187.
51. Y. X. Li, M. Zhang, M. Guo and X. D. Wang, *Rare Metals.*, 2009, **28**, 423.
52. Y. Q. Sun, J. B. Tan, H. H. Lin, X. J. Wang, J. Liu, Y. X. Li and C. X. Wang, *J. Colloid Interface Sci.*, 2018, **516**, 138.
53. M. Ahmadzadeh, C. Romero and J. McCloy, *AIP Adv.*, 2018, **8**, 6.
54. T. N.T. Thu, N. N. Thi, V. T. Quang, K. N. Hong, T. N. Minh and N. L.T. Hoai, *J EXP NANOSCI.*, 2016, **11**, 226.
55. C.T. Brigden, S. Poulston, M.V. Twigg, A. P. Walker and A. J. J. Wilkins, *Appl. Catal. B-Environ.*, 2001, **32**, 63.
56. F. T. Li, Y. Zhao, Y. Liu, Y. J. Hao, R. H. Liu and D. S. Zhao, *Chem. Eng. J.*, 2011, **173**, 750.

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