available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Fe-TiO₂ and Fe₂O₃ quantum dots co-loaded on MCM-41 for removing aqueous rose bengal by combined adsorption/photocatalysis

Guoqiang Shen ^{a,b,†}, Lun Pan ^{a,b,†}, Zhe Lü ^{a,b}, Chongqing Wang ^{a,b}, Fazal-e-Aleem ^c,
Xiangwen Zhang ^{a,b,#}, Ji-Jun Zou ^{a,b,*}

^a Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

^c Department of Physics, The University of Lahore, Lahore 54600, Pakistan

ARTICLE INFO

Article history:

Received 20 December 2017

Accepted 19 January 2018

Published 5 May 2018

Keywords:

Quantum dot

Titania

Ferric oxide

Photocatalysis

Adsorption

ABSTRACT

Adsorption and photodegradation are promising approaches for removing organic pollutions. In this study, we combined these two processes by co-loading Fe-TiO₂ and Fe₂O₃ quantum dots (QDs) on porous MCM-41, using a simple hydrolysis method. X-ray diffraction, high-resolution transmission electron microscopy, and X-ray photoelectron spectroscopy results indicated that Fe-TiO₂ QDs are formed at low Fe precursor concentrations, while additional Fe₂O₃ QDs are formed at higher Fe precursor concentrations. The Fe₂O₃ and Fe-TiO₂ QDs impart high adsorption capacity and high photoactivity to the porous MCM-41, respectively. Thus, their combination results in a synergic effect of the adsorption and photodegradation. The highest-performing sample exhibits excellent performance in removing rose bengal from aqueous solution.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Environment protection is a continuing challenge for all engineering disciplines [1–3]. Wastewater discharged by industry frequently contains high concentrations of organic contaminants in large volumes. Such wastewater is usually poorly biodegradable and difficult to treat using chemical oxidants [4,5]. Among the many reported water treatment technologies, photodegradation and adsorption are two promising technologies with high efficiencies and low energy requirements for removing pollutants like organic dyes [4–9]. TiO₂ has been extensively

studied for this purpose, along with methods for improving its photocatalytic performance [10,11]. These have included doping TiO₂ with other metal ions [12–15], and controlling the TiO₂ nanostructure by forming structures such as quantum dots (QDs) [16–19]. Loading QDs into porous materials with large surface areas is an effective method for avoiding QD agglomeration [20,21]. Fe₂O₃ is also an efficient adsorbent for organic dyes [22–25] and has been widely investigated for water treatment because of its good chemical stability, low toxicity, and ease of preparation. However, the large dimensions of Fe₂O₃ limits its adsorption capacity and adsorption rate. De-

* Corresponding author. Tel/Fax: +86-22-85356969; E-mail: jj_zou@tju.edu.cn

Corresponding author. Tel/Fax: +86-22-27892340; E-mail: zhangxiangwen@tju.edu.cn

† The authors contributed equally to this work.

This work was supported by the National Natural Science Foundation of China (21506156, 51661145026, 21676193), the Tianjin Municipal Natural Science Foundation (15JCZDJC37300, 16JCQNJC05200), and the Pakistan Science Foundation (PSF/257NSFC-Eng/P-UoL (02)).

DOI: 10.1016/S1872-2067(17)62976-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 5, May 2018

creasing the Fe_2O_3 particle size from micrometers to nanometers can reportedly increase the adsorptive area by 100 to 1000 times [26].

The synergy of adsorption and photodegradation can enhance the removal of pollutants from water, in comparison to a single technology [27]. Herein, to realize this synergetic effect, we loaded both Fe-doped TiO_2 QDs and Fe_2O_3 QDs into MCM-41, using a direct hydrolysis method. The Fe-doped TiO_2 QDs exhibit high photoactivity due to their quantum-size effect and dopant-mediated band levels. The Fe_2O_3 QDs exhibit significant adsorption toward organic dye. Thus, the fabricated materials possess enhanced efficiency for degrading organic dye.

2. Experimental

2.1. Materials

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, rose bengal (RB), tetrabutyl titanate (TBT), commercial Fe_2O_3 (average diameter of 100 nm, abbreviated as C- Fe_2O_3) and ethanol were of reagent grade and purchased from Shanghai Aladdin Reagent Co. Ltd, P. R. China. MCM-41 was purchased from Tianjin Chemist Ltd, P. R. China. Milli-Q ultrapure water ($>18 \text{ m}\Omega \cdot \text{cm}$) was used in all experiments. All reagents were used as received.

2.2. Sample preparation

In a typical synthesis, 0.681 g of TBT was first adsorbed on the surface and pore channels of MCM-41 (0.800 g) in ethanol (50 mL), under stirring for 40 min. Then, 6.0 mL of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution was added dropwise to the mixture, which was stirred for another 24 h at room temperature. The resulting gel was collected by filtration, dried at 60°C for 12 h, and then calcined at 550°C for 2 h at a heating rate of $5^\circ\text{C}/\text{min}$. Ti/Fe molar ratios (x) of 30, 10, 3.0, and 1.0 were used in this study, and the resulting samples are referred to as FT/M- x . As shown in Scheme 1, pure TiO_2 QDs loaded on MCM-41 synthesized without $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is referred to as T/M. A series of samples loaded with Fe- TiO_2 QDs and Fe_2O_3 QDs were synthesized by adjusting the concentration of FeSO_4 solution. Pure

$\text{Fe}_2\text{O}_3/\text{MCM-41}$ synthesized without TBT is referred to as F/M. As a reference sample, pure Fe_2O_3 was synthesized by the direct calcination of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 550°C for 2 h at a heating rate of $5^\circ\text{C}/\text{min}$, and is referred to as S- Fe_2O_3 .

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a D8-Focus X-ray diffractometer (BRUKER AXS GMBH) equipped with $\text{Cu K}\alpha$ radiation, at 40 kV and 40 mA, at a scan rate of $5^\circ/\text{min}$. Fourier-transform infrared (FT-IR) spectra were obtained using a Bruker Vertex-70 FT-IR spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) observations were carried out using a Tecnai G2 F-20 microscope with a field-emission gun, operated at 200 kV. Zeta potentials (ζ -potentials) were measured in suspensions (0.5 mg/min, 25°C) using a Zeta Nanosizer (Nano ZS, Malvern Ltd.). Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were recorded using a Shimadzu UV-2600 spectrometer equipped with a 60-mm-diameter integrating sphere, using BaSO_4 as the reference sample. X-ray photoelectron spectroscopy (XPS) was conducted with a PHI-1600 X-ray photoelectron spectrometer equipped with $\text{Al K}\alpha$ radiation. Binding energies were calibrated to the C 1s peak (284.6 eV) of adventitious carbon.

2.4. Adsorption and photodegradation evaluation

The adsorption of the model organic dye RB was conducted in an opening jacketed glass beaker (150 mL) in the dark. Typically, 20 mg of catalyst and 0.2 mL of RB (20 mmol/L) were dispersed in 100 mL of pure water. The suspension was stirred until the adsorption of RB reached equilibrium. During this evaluation, 1.5 mL aliquots of suspension were withdrawn after given intervals, centrifuged, and the concentration of RB in the supernatant determined from the absorbance at 548 nm, using a Hitachi U-3010 UV-Vis spectrometer. 0.2 mL of RB (20 mmol/L) solution was added again, which was repeated several times until the adsorption reached saturation. In addition, appropriate volumes of pure water were added to compensate for the loss during sampling.

The photodegradation of RB was conducted in the same jacketed glass beaker (150 mL), which was irradiated from the vertical direction by a 300 W high-pressure xenon lamp (PLS-SXE300UV, Beijing Trusttech. Co., Ltd.). The irradiation area was *ca.* 20 cm^2 . The reaction conditions were: temperature $25 \pm 0.2^\circ\text{C}$, initial concentration of RB ($C_0(\text{RB})$) $40 \mu\text{mol/L}$, and synthetic photocatalyst concentration 0.2 g/L ; no acidic or alkaline reagents were added. The reaction was magnetically stirred under atmospheric conditions, after stirring for 30 min in the dark to achieve adsorption equilibrium. Samples were then withdrawn, separated by centrifugation, and analyzed. Once UV-vis spectrometry indicated that the RB had been completely photodegraded, 0.200 mL of RB (20 mmol/L) was added again, and the overall process was repeated several times. To evaluate the efficiency of the decontamination process, we measured the chemical oxygen demand (dichromate method,

Scheme 1. Synthesis of MCM-41 loaded with TiO_2 QDs and Fe_2O_3 QDs.

COD_{Cr}) using a DR3900 apparatus (HACH), the final total organic carbon (TOC) contents of aqueous samples treated by synthesized catalysts in the first and tenth cycles using a Multi c/n2100s apparatus (Analytik Jena AG), and the concentrations of remanent Na⁺ and Cl[−] using a PXS-270 apparatus (INESA Scientific Instrument Co., Ltd.).

3. Results and discussion

3.1. Crystal structure and morphology

As shown in Fig. 1(a), the XRD pattern of pure MCM-41 shows a wide diffraction peak at *ca.* 22°, while a new peak at 25.3° appears after loading with TiO₂ (T/M), which is characteristic of anatase TiO₂ (JCPDS No. 21-1272). The XRD pattern of T/M shows broadened diffraction peaks at about 25.3°, which indicates that the synthesized TiO₂ nanoparticles have a very small crystal size [28]. The XRD patterns of FT/M-*x* (with *x* ≥ 3.0) show characteristic peaks similar to the pattern of T/M, but a gradual main-peak shift from 25.3° to 23.7° is observed from *x* = 30 to *x* = 3.0. This is caused by distortion from crystal expansion resulting from the substitution of Ti⁴⁺ (0.075 nm) with Fe³⁺ (0.079 nm) [29,30]. In the XRD pattern of FT/M-1.0, the diffraction peaks of α -Fe₂O₃ appear at 27.7°, 30.1° and 32.9° (JCPDS No. 52-1449). To understand the formation mechanism, we synthesized pure TiO₂ and Fe-doped TiO₂ without MCM-41 by the same method. The crystal sizes of undoped and Fe-doped (Ti/Fe = 10) TiO₂ are 65.2 and 79.5 nm, respectively. This demonstrates that loading TiO₂ into MCM-41 is an important factor accounting for the formation of quantum-sized TiO₂ [12]. As shown in Scheme 1, the surface hydroxyl groups of MCM-41 provide adsorption sites for TBT. The interaction between the host MCM-41 and TiO₂ is evidenced by peaks of Ti-O-Si vibrations at 960 cm^{−1} in the FT-IR spectra of FT/M-10 (Fig. 1(b)).

The morphologies of samples were determined by TEM. TEM images of MCM-41 show porous channels with no obvious surface particles (Fig. 2(a)). For T/M (Fig. 2(b)), TiO₂ nanoparticles with an average diameter of 4.78 nm give rise of lattice fringes at intervals of 0.351 nm ((101) plane of anatase TiO₂),

indicating that they are pure TiO₂ QDs. For FT/M (Fig. 2(b)–(f)), the anatase (101) lattice spacing increases from 0.351 nm to 0.380 nm with increasing Fe content, which is consistent with the XRD results. Meanwhile, the average diameter of the TiO₂ QDs increases from 4.78 to 6.65 nm. Fe₂O₃ QDs are formed when the Ti/Fe molar ratio is lower than 3.0. Fig. 2(e) and (f) show obvious Fe₂O₃ nanoparticles with lattice spacings of 0.271 and 0.321 nm, which are consistent with the (122) and (112) planes of α -Fe₂O₃, respectively. The average diameters of FT/M-3.0 and FT/M-1.0 are 3.94 and 4.51 nm, respectively, which are typical α -Fe₂O₃ QDs. The formation of Fe₂O₃ QDs is attributed to the solubility difference of FeSO₄·7H₂O in water and ethanol. FeSO₄·7H₂O is water-soluble but alcohol-insoluble, so precipitates and deposits on MCM-41 when adding high concentration FeSO₄·7H₂O aqueous solution to ethanol. Calcining at 550 °C causes the FeSO₄·7H₂O nanocrystals to decompose to Fe₂O₃ QDs. The energy dispersive X-ray (EDX) spectroscopy image in Fig. 2(i) shows uniform distributions of Fe₂O₃ and TiO₂ on MCM-41. In addition, F/M, *i.e.* Fe₂O₃ loaded on MCM-41 (Fig. 2(g)), has an average diameter of 40 nm, while Fe₂O₃ synthesized in the absence of MCM-41 has an average diameter of *ca.* 200 nm (Fig. 2(h)).

The Ti and Fe contents of the samples were measured by EDX. Table 1 shows that T/M contains 4.02 wt.% of TiO₂ loaded on MCM-41, and that the loading amount increases with the addition of FeSO₄. FT/M-3.0 and FT/M-1.0 contain about the same amount of TiO₂ (8.54–8.62) wt.%. The presence of the acidic FeSO₄ solution improves the hydrolysis of TBT to TiO₂.

3.2. Chemical states

XPS was used to characterize the chemical states of the sample surfaces, and XPS spectra are shown in Fig. 3. The Si 2*p* peaks in the spectra of T/M and FT/M show high-binding-energy-shifts of 0.12 eV, compared with the spectrum of pure MCM-41 (Fig. 3(a)). The Ti 2*p* peaks show low-binding-energy-shifts of 0.26 eV compared with the spectrum of pure anatase TiO₂ (Fig. 3(b)), which confirms the formation of Ti-O-Si bonds between TiO₂ and MCM-41 [12,30,31]. No Si 2*p* peak shift is observed in the spectrum of F/M, suggesting no chemical in-

Fig. 1. (a) XRD patterns and (b) FT-IR spectra of the samples.

Fig. 2. TEM images, HR-TEM images (scale bar: 5 nm), and particle size distribution of (a) MCM-41, (b) T/M, (c) FT/M-30, (d) FT/M-10, (e) FT/M-3.0, (f) FT/M-1.0, (g) F/M, and (h) Fe₂O₃. (i) Scanning TEM and EDX mapping images of FT/M-3.0.

Table 1

Elemental contents (as measured by EDX spectroscopy) and ζ -potentials of the samples.

Sample	F/M	T/M	FT/M-30	FT/M-10	FT/M-3.0	FT/M-1.0
Ti/Fe molar ratio	—	—	30.35	11.08	3.14	2.36
TiO ₂ content (wt%)	0	4.02	6.76	7.38	8.62	8.54
ζ -potential	12.4	−1.22	−0.19	2.45	4.85	5.99

teraction between Fe₂O₃ and MCM-41.

Fig. 3(c) shows doublet Fe 2p_{3/2} and Fe 2p_{1/2} peaks of Fe(III) at binding energies of 711 and 725 eV, respectively [32]. For FT/M-30 and FT/M-10, the satellite peak of α -Fe₂O₃ should be located at *ca.* 8 eV higher than the main peak of Fe 2p_{3/2}, but this is not observed. This suggests that Fe(III) is doped into the inner lattice of TiO₂. The spectra of FT/M-3.0 and FT/M-1.0 show weak satellite peaks at 719 eV, because of the presence of α -Fe₂O₃. The valence band (VB) XPS spectra in Fig. 3(d) show obvious shifts, because of the newly formed Fe(III) dopant-mediated band levels in TiO₂.

3.3. Optical properties

Fig. 4(a) shows UV-Vis DRS spectra of the samples. MCM-41 shows no absorption of the full-spectrum light. T/M strongly absorbs wavelengths below 380 nm, but not above 380 nm. FT/M-30 and FT/M-10 show red-shifted absorption, which is attributed to the newly formed Fe(III) dopant-mediated band levels. For FT/M-3.0, FT/M-1.0, and M-Fe₂O₃, absorption peaks at about 540 nm and 690 nm are observed due to the presence

of the Fe₂O₃ QDs. The band gaps of the samples were calculated from the corresponding plots of the transformed Kubelka-Munk functions (Fig. 4(b)). Pure TiO₂ QDs (3.40 eV) exhibit a typical quantum-size effect, and their bandgap is 0.20 eV wider than that of bulk TiO₂, because the VB shifts towards higher energy [33,34]. For FT/M, the bandgap decreases from 3.40 to 2.65 eV with increasing Fe content. This is because Fe doping results in a new peak due to transition between Fe³⁺ and the VB. The energy of this transition changes with the Fe(III) dopant content [33,34], as confirmed by the VB density of states in Fig. 4(b).

3.4. Adsorption and photodegradation properties of the samples

The samples were applied to remove RB, by adsorption in the dark and then subsequent photodegradation under irradiation [35–37]. Fig. 5(a) shows the adsorption capacities of the samples in the dark. Pure MCM-41 and T/M show small adsorptions of RB, of less than 10 mg/g. FT/M-30 and FT/M-10 which contain Fe-doped TiO₂ QDs show slightly higher RB adsorptions. FT/M-3.0 and FT/M-1.0 which contain Fe₂O₃ QDs, show *ca.* 6.4 and 9.3 times higher RB adsorption than that of T/M, respectively. The RB adsorption capacity of F/M is the highest among the tested samples at *ca.* 75 mg/g. The adsorption rate constants (*k*₁) derived from these adsorption capacities were fitted by the Lagergren rate equation, as shown in Fig. 5c [38]. The adsorption capacities of the Fe-based materials should be related to their surface charge. The ζ -potentials of the

Fig. 3. (a) Si 2p, (b) Ti 2p, (c) Fe 2p, and (d) VB XPS spectra of the samples.

samples follow the order $F/M > FT/M-1.0 > FT/M-3.0 > FT/M-10 > 0 > FT/M-30 > T/M$ (Table 1), which correlates with their Fe contents and adsorption capacities. In addition, a sample prepared by thermally calcining $FeSO_4$ (S- Fe_2O_3), and another sample of commercial nano- Fe_2O_3 (C- Fe_2O_3), show saturation adsorption capacities of 46 mg/g and 5.68 mg/g, respectively. These are much lower than that of F/M, because F/M

contains well-dispersed Fe_2O_3 QDs with a high surface area accessible for adsorption.

Fe_2O_3 is inactive in photodegradation due to its short hole diffusion length (*ca.* 2–4 nm) and significant recombination of photogenerated electron-hole pairs [39–43]. Fig. 5(a) shows that MCM-41, S- Fe_2O_3 , and C- Fe_2O_3 exhibit no photoactivity, while weak photodegradation is observed for F/M (*ca.* 5.32

Fig. 4. (a) UV-Vis DRS spectra of the samples and (b) corresponding plots of the transformed Kubelka-Munk function versus photo energy.

Fig. 5. Saturation adsorption and photocatalytic degradation of RB by the synthesized catalysts in the (a) first and (b) tenth cycles; (c) Adsorption rate constants (k_1) fitted by the Lagergren rate equation (1st-order) and (d) real reaction rate constants (k_2) fitted by the Langmuir-Hinshelwood equation.

mg/g), which is attributed to the well dispersed Fe₂O₃ on MCM-41. T/M shows obvious photodegradation when using 30.2 mg/g of photocatalyst. The doping of Fe species in TiO₂ significantly increases the photoactivity. The highest photodegradation is observed for FT/M-3.0 (124 mg/g). FT/M-1.0 which contains a large amount of Fe₂O₃ shows lower photoactivity. In Fig. 5(d), the real reaction rate constant (k_2) of the photodegradation is fitted by the Langmuir-Hinshelwood equation [44]. The photoactivity follows the order: FT/M-3.0 > FT/M-10 > FT/M-30 > FT/M-1.0 > T/M > F/M. The highest photoactivity of FT/M-3.0 is attributed to the effective doping of Fe(III) into the TiO₂ lattice. This leads to a new impurity band above the VB, which benefits charge separation and optical absorption.

Fig. 5(c) and (d) show that the adsorption rate (k_1) is com-

parable to the photocatalytic rate (k_2) for T/M, FT/M-30, FT/M-10, and FT/M-3.0. This enables RB to be adsorbed on the Fe₂O₃ QDs and then photodegraded by the Fe-TiO₂ QDs. For FT/M-1.0, k_1 is 12.2 times higher than k_2 , and the catalyst is covered by adsorbed RB after adsorption equilibrium, which will block light absorption and degradation. Therefore, during the ten cycle test (Fig. 5(b)) there are no obvious decreases in the adsorption capabilities of T/M, FT/M-30, FT/M-10, and FT/M-3.0, while the adsorption capability of FT/M-1.0 decreases significantly.

The initial COD_{Cr}, TOC, and C_{Na} of the RB solution are 32.93, 12.59, and 1.89 ppm, respectively, and there is nearly no Cl⁻. The TOC and COD_{Cr} of samples treated by F/M and T/M decrease by about 23.9% and 21.5% in the first cycle, respectively, and decrease by about 79.6% when treated by FT/M-3.0

Table 2

COD_{Cr}, TOC, and Na⁺ and Cl⁻ concentrations of treated solution samples.

Catalyst	Initial RB solution	F/M		T/M		FT/M-3.0	
		1st	10th	1st	10th	1st	10th
COD _{Cr} (ppm)	32.93	25.05	322.7	25.85	288.9	6.73	10.67
TOC (ppm)	12.59	8.17	121.3	9.57	97.32	2.53	4.01
C _{Na} (ppm)	1.89	1.92	18.10	1.89	18.55	1.88	18.51
C _{Cl} (ppm)	0.31	0.43	0.64	1.27	5.01	5.42	58.01

Scheme 2. Synergetic effect of adsorption and photocatalysis over FT/M.

(Table 2). The increased Na^+ concentration results from ionization of the RB dye. For the solution treated by F/M, the Cl^- concentration shows no significant increase (from 0.31 ppm to 0.43 ppm), while those treated by T/M and FT/M-3.0 show increases after one cycle of ca. 0.96 ppm and 5.11 ppm, respectively. This confirms that the Cl atoms of RB molecules are degraded to Cl^- , and dissolve into the water during the degradation process. F/M and T/M remove only about 2% and 12% of COD_{Cr} and TOC during the tenth cycle, respectively, while 96.6% of TOC and 96.9% of COD_{Cr} are removed by FT/M-3.0, respectively. The concentrations of Cl^- and Na^+ increase from near-zero to 58.01 ppm and 18.51 ppm, respectively, which indicates the high efficiency and stability of FT/M-3.0 for degrading RB. The high efficiency is attributed to the synergic effects of adsorption and photodegradation. To confirm the active species during photodegradation, 0.1 mol/L methanol was introduced as a hole sacrificial reagent, and 0.1 mol/L isopropanol was introduced as a radical sacrificial reagent. The photodegradation rate does not significantly change in the presence of 0.1 mol/L methanol, but significantly decreases in the presence of 0.1 mol/L isopropanol. Thus, the photodegradation is considered to occur via a free radical pathway [45–47]. Scheme 2 shows that RB molecules are first concentrated on the surface by the strong adsorption capacity of the Fe_2O_3 QDs, then migrate to the Fe-TiO₂ QDs, and are finally degraded to CO_2 , H_2O , Cl^- , etc. To achieve the synergetic advantage of adsorption and photoreaction, the structures of the Fe_2O_3 QDs and Fe-TiO₂ QDs should be suitably controlled. With its suitable structure, FT/M-3.0 provides a high RB elimination of ca. 160 mg/g in the first cycle, and retains this high efficiency during the ten cycle test. Even after ten cycles, FT/M-3.0 removes more than 96% of COD_{Cr} and TOC.

4. Conclusions

We fabricated Fe-doped TiO₂ and Fe_2O_3 QD co-loaded MCM-41 via simple hydrolysis, to combine the effects of adsorption and photodegradation. With increasing Ti/Fe molar ratio during synthesis, Fe-doped TiO₂ QDs form at low Fe precursor concentrations, while additional Fe_2O_3 QDs form at higher Fe concentrations. The material with a Ti/Fe molar ratio

of 3.0 shows the best performance in the removal of RB (160 mg/g), which is two and four times higher than those of Fe_2O_3 QDs and TiO₂ QDs separately loaded on MCM-41. The best performing catalyst retains its high efficiency over ten consecutive cycles.

References

- [1] J. T. Liu, X. Ge, X. X. Ye, G. Z. Wang, H. M. Zhang, H. Zhou, Y. X. Zhang, H. Zhao, *J. Mater. Chem. A*, **2016**, 4, 1970–1979.
- [2] Z. F. Huang, J. J. Song, L. Pan, F. L. Lv, Q. Wang, J. J. Zou, X. W. Zhang, L. Wang, *Chem. Commun.*, **2014**, 50, 10959–10962.
- [3] L. Pan, G. Q. Shen, J. W. Zhang, X. C. Wei, L. Wang, J. J. Zou, X. W. Zhang, *Ind. Eng. Chem. Res.*, **2015**, 54, 7226–7232.
- [4] C. S. Cheng, J. Deng, B. Lei, A. He, X. Zhang, L. Ma, S. Li, C. S. Zhao, *J. Hazard. Mater.*, **2013**, 263, 467–478.
- [5] B. Wang, H. B. Wu, L. Yu, R. Xu, T. T. Lim, X. W. Lou, *Adv. Mater.*, **2012**, 24, 1111–1116.
- [6] J. Li, Q. H. Fan, Y. J. Wu, X. X. Wang, C. L. Chen, Z. Y. Tang, X. K. Wang, *J. Mater. Chem. A*, **2016**, 4, 1737–1746.
- [7] S. B. Wang, X. W. Zhang, L. Pan, F. M. Zhao, J. J. Zou, T. R. Zhang, L. Wang, *Appl. Catal. B*, **2015**, 164, 234–240.
- [8] L. Pan, S. B. Wang, W. B. Mi, J. J. Song, J. J. Zou, L. Wang, X. W. Zhang, *Nano Energy*, **2014**, 9, 71–79.
- [9] X. Jia, M. Tahir, L. Pan, Z. F. Huang, X. W. Zhang, L. Wang, J. J. Zou, *Appl. Catal. B*, **2016**, 198, 154–161.
- [10] L. Pan, S. B. Wang, J. Xie, L. Wang, X. Zhang, J. J. Zou, *Nano Energy*, **2016**, 28, 296–303.
- [11] L. Pan, J. Zhang, X. Jia, Y. H. Ma, X. W. Zhang, L. Wang, J. J. Zou, *Chinese J. Catal.*, **2017**, 38, 253–259.
- [12] L. Pan, S. B. Wang, J. J. Zou, Z. F. Huang, L. Wang, X. W. Zhang, *Chem. Commun.*, **2014**, 50, 988–990.
- [13] R. Daghrir, P. Drogui, D. Robert, *Ind. Eng. Chem. Res.*, **2013**, 52, 3581–3599.
- [14] B. Liu, H. M. Chen, C. Liu, S. C. Andrews, C. Hahn, P. D. Yang, *J. Am. Chem. Soc.*, **2013**, 135, 9995–9998.
- [15] S. George, S. Pokhrel, Z. X. Ji, B. L. Henderson, T. Xia, L. J. Li, J. I. Zink, A. E. Nel, L. Madler, *J. Am. Chem. Soc.*, **2011**, 133, 11270–11278.
- [16] W. L. Wang, Z. F. Wang, J. J. Liu, Z. G. Zhang, L. Y. Sun, *Sci. Rep.*, **2017**, 7, 43755.
- [17] P. S. Niphadkar, S. K. Chitale, S. K. Sonar, S. S. Deshpande, P. N. Joshi, S. V. Awate, *J. Mater. Sci.*, **2014**, 49, 6383–6391.
- [18] V. Etacheri, G. Michlits, M. K. Seery, S. J. Hinder, S. C. Pillai, *ACS Appl. Mater. Interfaces*, **2013**, 5, 1663–1672.
- [19] J. G. Yu, J. X. Low, W. Xiao, P. Zhou, M. Jaroniec, *J. Am. Chem. Soc.*, **2014**, 136, 8839–8842.
- [20] H. J. Jouybari, S. Saedodin, A. Zamzamin, M. E. Nimvari, S. Wongwises, *Renew. Energy*, **2017**, 114, 1407–1418.
- [21] A. Fabre, S. Salameh, L. C. Ciacchi, M. T. Kreutzer, J. R. van Ommen, *J. Nanopart. Res.*, **2016**, 18, 200.
- [22] H. Y. Zhu, R. Jiang, L. Xiao, W. Li, *J. Hazard. Mater.*, **2010**, 179, 251–257.
- [23] J. Y. Liu, L. M. Wong, G. Gurudayal, L. H. Wong, S. Y. Chiam, S. F. Yau, Y. Ren, *J. Mater. Chem. A*, **2016**, 4, 13280–13288.
- [24] L. Lu, J. Li, J. Yu, P. Song, D. H. L. Ng, *Chem. Eng. J.*, **2016**, 283, 524–534.
- [25] T. Wen, J. Wang, S. J. Yu, Z. S. Chen, T. Hayat, X. K. Wang, *ACS Sustain. Chem. Eng.*, **2017**, 5, 4371–4380.
- [26] J. F. Berry, E. Bill, E. Bothe, S. DeBeer, George, B. Mienert, F. Neese, K. Wieghardt, *Science*, **2006**, 312, 1937–1941.
- [27] C. T. Yavuz, J. T. Mayo, W. W. Yu, A. Prakash, J. C. Falkner, S. Yean, L.

Graphical Abstract

Chin. J. Catal., 2018, 39: 920–928 doi: 10.1016/S1872-2067(17)62976-0

Fe-TiO₂ and Fe₂O₃ quantum dots co-loaded on MCM-41 for removing aqueous rose bengal by combined adsorption/photocatalysis

Guoqiang Shen, Lun Pan, Zhe Lü, Chongqing Wang, Fazal-e-Aleem, Xiangwen Zhang*, Ji-Jun Zou*

Tianjin University, China;

Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), China;

The University of Lahore, Pakistan

Fe-TiO₂ quantum dots and Fe₂O₃ quantum dots are co-loaded on MCM-41 by direct hydrolysis, which provides synergy between adsorption and photocatalysis and allows the efficient removal of aqueous rose bengal.

- L. Cong, H. J. Shipley, A. Kan, M. Tomson, D. Natelson, V. L. Colvin, *Science*, **2006**, 314, 964–967.
- [28] J. Engel, S. R. Bishop, L. Vayssieres, H. L. Tuller, *Adv. Funct. Mater.*, **2014**, 24, 4952–4958.
- [29] M. S. Nahar, K. Hasegawa, S. Kagaya, *Chemosphere*, **2006**, 65, 1976–1982.
- [30] W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.*, **1994**, 98, 13669–13679.
- [31] L. Pan, G. Q. Shen, J. W. Zhang, X. C. Wei, L. Wang, J. J. Zou, X. W. Zhang, *Ind. Eng. Chem. Res.*, **2015**, 54, 7226–7232.
- [32] Z. Zhang, M. F. Hossain, T. Takahashi, *Appl. Catal. B*, **2010**, 95, 423–429.
- [33] G. Salvinelli, G. Drera, C. Baratto, A. Braga, L. Sangaletti, *ACS Appl. Mater. Interfaces*, **2015**, 7, 765–773.
- [34] T. G. Kim, H. Choi, S. Jeong, J. W. Kim, *J. Phys. Chem. C*, **2014**, 118, 27884–27889.
- [35] A. K. Dutta, S. K. Maji, B. Adhikary, *Mater. Res. Bull.*, **2014**, 49, 28–34.
- [36] M. A. Salam, R. M. El-Shishtawy, A. Y. Obaid, *J. Ind. Eng. Chem.*, **2014**, 20, 3559–3567.
- [37] J. J. Shen, R. Steinbach, J. M. Tobin, M. Mouro Nakata, M. Bower, M. R. S. McCoustra, H. Bridle, V. Arrighi, F. Vilela, *Appl. Catal. B*, **2016**, 193, 226–233.
- [38] R. J. Li, L. F. Liu, F. L. Yang, *J. Hazard. Mater.*, **2014**, 280, 20–30.
- [39] J. Z. Zhang, *J. Phys. Chem. B*, **2000**, 104, 7239–7253.
- [40] C. J. Sartoretti, B. D. Alexander, R. Solarska, I. A. Rutkowska, J. Augustynski, R. Cerny, *J. Phys. Chem. B*, **2005**, 109, 13685–13692.
- [41] M. Zhang, Y. J. Lin, T. J. Mullen, W. F. Lin, L. D. Sun, C. H. Yan, T. E. Patten, D. Wang, G. Y. Liu, *J. Phys. Chem. Lett.*, **2012**, 3, 3188–3192.
- [42] C. H. Miao, T. F. Shi, G. P. Xu, S. L. Ji, C. H. Ye, *ACS Appl. Mater. Interfaces*, **2013**, 5, 1310–1316.
- [43] D. K. Zhong, J. W. Sun, H. Inumaru, D. R. Gamelin, *J. Am. Chem. Soc.*, **2009**, 131, 6086–6087.
- [44] A. T. Nguyen, R. S. Juang, *J. Environ. Manage.*, **2015**, 147, 271–277.
- [45] T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.*, **2010**, 2, 527–532.
- [46] S. Ghosh, N. A. Kouame, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P. H. Aubert, H. Remita, *Nat. Mater.*, **2015**, 14, 505–511.
- [47] A. Zada, Y. Qu, S. Ali, N. Sun, H. W. Lu, R. Yan, X. L. Zhang, L. Q. Jing, *J. Hazard. Mater.*, **2018**, 342, 715–723.

Fe掺杂TiO₂和Fe₂O₃量子点共负载催化剂：吸附与光催化协同作用 高效降解有机染料

沈国强^{a,b,†}, 潘伦^{a,b,†}, 吕哲^{a,b}, 王重庆^{a,b}, Fazal-e-Aleem^c, 张香文^{a,b,#}, 邹吉军^{a,b,*}

^a天津大学化工学院, 绿色合成与转化教育部重点实验室, 天津300072, 中国

^b天津化学化工协同创新中心, 天津300072, 中国

^c拉哈尔大学物理系, 巴基斯坦

摘要: 光催化作为节能、清洁的环境处理技术, 被广泛应用于污染物处理领域, 如室内气体净化、尾气VOCs处理和水体有机污染降解等。在众多光催化剂中, TiO₂以其良好的化学稳定性、无二次污染、无刺激性和安全无毒等优势得到广泛研究。

然而TiO₂是宽禁带材料, 仅能吸收太阳光谱的紫外光部分, 通常需要用紫外光源来激发, 光生电子-空穴易复合, 这限制了其应用. 过渡金属离子掺杂能在TiO₂价带之上形成新的掺杂能级, 从而提高其光谱响应范围, 提高全光谱反应活性; 与体相TiO₂相比, 纳米尺寸的TiO₂具有更高的光催化活性, 尤其小于10 nm的量子点尺寸TiO₂有着高活性面积、较短的光生电子-空穴迁移路径和独特的量子尺寸效应; Fe₂O₃作为吸附材料与TiO₂构建复合材料能够发挥吸附与光催化协同作用, 从而提高污染物处理效率.

我们以构建Fe掺杂TiO₂和Fe₂O₃量子点共负载催化剂为目标, 以钛酸四丁酯(TBT)和硫酸亚铁为前驱体, 采用常温水解方法将Fe掺杂的TiO₂量子点生长在MCM-41分子筛表面, 并通过调节硫酸亚铁加入量合成了MCM-41负载的Fe掺杂TiO₂和Fe₂O₃量子点催化剂. 采用透射电子显微镜和X射线衍射研究了复合晶体结构, 采用X射线光电子能谱、紫外-可见光谱和傅里叶变换红外光谱等表征手段研究了复合量子点材料生长机理和能带结构. 结合吸附过程和光降解过程建立了吸附与光催化协同作用与污染物处理效率之间的关联关系.

表征结果表明, 硫酸亚铁水溶液加速TBT水解成功地在MCM-41表面生长了Fe掺杂TiO₂量子点, 并且量子点粒径随Fe前驱体量的增加而变大; 前驱体比例Ti/Fe ≤ 3.0时, 过量的硫酸亚铁会析出并在焙烧过程中在MCM-41上分解为Fe₂O₃量子点, Fe₂O₃量随着硫酸亚铁加入量提高而增多. 通过调节Fe前驱体的量, 一方面Fe掺杂在二氧化钛价带之上形成了掺杂能级, 减小了带隙, 拓宽了光响应范围, 另一方面引入适量Fe₂O₃量子点, 实现了Fe掺杂TiO₂和Fe₂O₃量子点共负载催化剂的构建. 复合材料实现了吸附过程与光催化降解过程的协同作用, Fe₂O₃将污染物富集于催化剂表面, Fe掺杂TiO₂将其有效降解, 大大提高了污染物处理能力, 其中FT/M-3.0处理效率最高, 并在10次循环处理后依然维持较高的吸附能力和光催化降解能力. 该工作为高效光催化水处理催化剂的设计和构建提供了新思路 and 策略.

关键词: 量子点; 二氧化钛; 氧化铁; 光催化; 吸附

收稿日期: 2017-12-20. 接受日期: 2018-01-19. 出版日期: 2018-05-05.

*通讯联系人. 电话/传真: (022)85356969; 电子信箱: jj_zou@tju.edu.cn

#通讯联系人. 电话/传真: (022)27892340; 电子信箱: zhangxiangwen@tju.edu.cn

†共同第一作者.

基金来源: 国家自然科学基金(21506156, 51661145026, 21676193); 天津市自然科学基金(15JCZDJC37300, 16JCQNJC05200); 巴基斯坦自然科学基金(PSF/257NSFC-Eng/P-UoL (02)).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).