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Ordered mesoporous Fe/TiO₂ with light enhanced photo-Fenton activity

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ABSTRACT

Ordered mesoporous Fe/TiO₂ was prepared by an evaporation-induced self-assembly method. The iron ions were in situ embedded in the pore wall of the TiO₂ framework. The catalyst has excellent light-assisted Fenton catalytic performance under UV and visible light irradiation. X-ray diffraction and transmission electron microscopy results showed that the TiO₂ samples have an ordered two-dimensional hexagonal pore structure and an anatase phase structure with high crystallinity. The ordered pore structure of the TiO₂ photocatalyst with a large specific surface area is beneficial to mass transfer and light harvesting. Furthermore, iron ions can be controlled by embedding them into the TiO₂ framework to prevent iron ion loss and inactivation. After five cycles, the reaction rate of the ordered mesoporous Fe/TiO₂ remained unchanged, indicating that the material has stable performance and broad application prospects for the purification of environmental pollutants.

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1. Introduction

The traditional Fenton reaction is an advanced oxidation technology for wastewater treatment [1,2]. It involves the mixture of hydrogen peroxide (H₂O₂) and ferrous iron (Fe²⁺) in acidic solution to produce hydroxyl radicals (•OH) for the attack of organic pollutants [3,4]. However, the classical Fenton reaction has two obvious shortcomings: low activity under neutral or alkaline conditions and secondary pollution caused by iron sludge. To overcome these shortcomings, various Fenton-like reactions have been developed [5–7]. Heterogeneous Fenton-like reactions under neutral conditions have also been studied extensively [3,8–11]. The key of the heterogeneous

Fenton-like reaction is to develop an efficient heterogeneous Fenton-like catalyst to overcome the challenges of iron leaching and low catalytic activity [12]. Porous materials such as zeolite, clay, metal oxide, mesoporous silica, porous carbon, graphene, graphene oxide, and carbon nanotubes have a large surface area [13–19]. These can be used as a good supporter for iron species and are usually used to increase the surface area and the dispersion of active sites [20].

TiO₂ semiconductor materials are promising candidate materials because of their high photocatalytic activity, non-toxicity, good stability, and low cost [21–26]. Recently, Fe₂O₃ modified on the surface of TiO₂ showed enhanced visible light photocatalytic activity [27]. Some efforts have been fo-

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cused on the heterogeneous catalytic oxidation processes of Fe/Fe₂O₃-loaded TiO₂ nanoparticles or nanowires [28,29]. Deng et al. [30] prepared a TiO₂/Fe₂TiO₅/Fe₂O₃ triple-heterojunction structure with excellent visible-light responsive Fenton reaction. This work demonstrates that the porous structure of the TiO₂ is beneficial to the performance and stability of the catalyst.

Ordered mesoporous TiO₂ has a large specific surface area and a controllable pore structure, which is very beneficial to mass transfer and light harvesting. However, ordered mesoporous TiO₂ surface loaded with iron ions as a photo-Fenton catalyst has not been reported to date. Herein, we report the synthesis of highly active mesoporous titania photocatalyst by embedding iron ions in the ordered framework. Titanium precursors, surfactants, and iron ions were self-assembled by a one-step method. By homogeneously embedding iron ions into the TiO₂ framework, the pore structure and specific surface area of TiO₂ can be controlled, and the photocatalytic activity and light absorption of TiO₂ can be improved significantly.

2. Experimental

2.1. Preparation of ordered mesoporous Fe/TiO₂

Our synthesis method is based on the preparation reported by Li's group [31]. In a typical synthesis, transparent sols were prepared by mixing 1.0 g P123 (Sigma-Aldrich), 1.7 g TiCl₄ (Aladdin, AR), 3.0 g Ti(OBu)₄ (Aladdin, AR), and a certain amount of Fe(NO₃)₃·9H₂O with 20.0 mL absolute ethanol (Richjoint Chemical). The mixture was stirred vigorously at least for 30 min and transferred to a Petri dish. The ethanol was evaporated at 25 °C for 24 h with a relative humidity. After aging at 40 °C for 24 h and 100 °C for 24 h, the gels were finally calcined at 350 °C for 4 h in air using a heating rate of 0.5 °C/min with the Fe:Ti molar ratios 0.1%, 0.5%, 1.0%, and 1.5% and the as-synthesized mesoporous materials were denoted as FT-0.1, FT-0.5, FT-1.0, and FT-1.5, respectively. The ratio of Fe:Ti of the FT materials were tested by ICP, and the details are listed in Table S1 (in the Supporting Information).

2.2. Preparation of Fe/TiO₂-Im

The ordered mesoporous TiO₂ was dispersed in Fe(NO₃)₃ solution, and the suspension was held for 24 h until the suspension had dried. The sample was then calcined at 350 °C for 4 h in conditioned air. These samples were denoted as FT-X-Im.

2.3. Preparation of Fe/TiO₂-SG

Solution A was formed by dripping 10 mL Ti(OBu)₄ into 35 mL ethanol. Solution B was obtained by adding 4 mL glacial acetic acid, 10 mL distilled water, a certain amount of Fe(NO₃)₃·9H₂O, and 35 mL ethanol. Then, solution A was slowly dripped into solution B and heated for 18 h at 40 °C to obtain the gel. The gel was transferred to an oven at 80 °C and aged for 24 h. The as-synthesized samples were calcined at 350 °C for 4 h. These samples were denoted as FT-X-SG.

2.4. Characterization

The crystal structure was recorded by X-ray diffraction (XRD, Rigaku Dmax-3C, Cu-K α), and the morphology was observed by transmission electron microscopy (TEM, JEOL-2010F, 200 kV). The UV-Vis diffuse reflectance spectra (DRS) were obtained on a UV-Vis spectrophotometer (UV-Vis DRS, Shimadzu UV-2450). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S_{BET}), and the Barrett-Joyner-Halenda (BJH) model was used to calculate pore volume (V_{p}) and pore diameter (D_{p}). Surface electronic states were determined by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe II). The shift of the binding energy due to relative surface charging was corrected using the C 1s level at 284.8 eV as an internal standard. The Fe-loadings were determined on an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VISTAMPX).

2.5. Photo-Fenton activity test

The photocatalyst (100 mg) was added into 50 mL of RhB (10 ppm), and 100 μ L of H₂O₂ was added to the mixture and ultrasonically dispersed for 30 min. The photo-Fenton reaction under UV or visible light irradiation was initiated by a xenon lamp with a filter ($\lambda < 400$ nm or > 420 nm). After dark adsorption for 30 min, the lamp was turned on upon adsorption equilibrium. A volume of 2 mL of reaction solution was taken each time, and the liquid membrane was filtered. The absorbance of the solution was measured by a UV spectrophotometer (UV 7502/PC) at the characteristic wavelength, and the reaction rate was calculated by $(1 - C/C_0)$, where C is the test concentration and C_0 is the initial concentration [32].

3. Results and discussion

To determine the structure of the materials, the XRD patterns, TEM images, XPS results, and N₂ adsorption-desorption isotherms of the samples were analyzed. The wide-angle XRD and low-angle XRD patterns of representative samples are shown in Fig. 1, respectively. As shown in Fig. 1(a), seven high-intensity peaks could be observed at $2\theta = 25.2^\circ$ – 76.1° , corresponding to (101), (004), (200), (105), (204), (220), and (215) of anatase (JCPDS No. 21-1272), respectively [33]. No characteristic diffraction peaks of iron compounds were observed in the TiO₂ samples with different iron ion loadings because of the good dispersion of the iron ions. The XRD diffraction peak did not change with increase of iron ion content, indicating that the crystallinity of the samples did not change.

The typical small-angle XRD patterns of the mesoporous TiO₂ with different iron ion loadings are shown in Fig. 1(b). The small-angle XRD patterns demonstrated that the samples displayed a representative diffraction peak, suggesting a highly ordered mesoporous structure [34]. With increase of iron ion content, the small angle diffraction intensity decreases and the diffraction peak shifts to a large angle, indicating that the ordered mesoporous structure of the samples remains and that the pore size of the samples decreases gradually. The results

Fig. 1. (a) Wide-angle XRD patterns and (b) small-angle XRD patterns of TiO_2 with different iron ions doping.

show that the self-assembly process of TiO_2 is affected by the increase of iron ion content, which results in local collapse of the mesoporous structure. The effect of temperature on FT-1.5 was tested by low-angle XRD (Fig. S1, see the Supporting Information). It is important to note that the highly ordered mesoporous structure can be maintained at 350°C . The peak intensity of the prepared samples decreased gradually with increase of calcination temperature.

The structures of the samples were further confirmed by TEM. Fig. 2(a)–(b) shows the TEM images of FT-1.0 and FT-1.5, respectively. Both of these exhibit a 2D hexagonal mesoporous structure with average diameter of 5.0–7.0 nm and average thickness of pore walls of 3.0–4.0 nm. Fig. 2a exhibits well-arranged pores, which confirms the ordered mesoporous structure [31]. The ordered pore structure of FT-1.5 has damage at some edges, which is in agreement with the small-angle XRD result. No iron compounds or aggregations were observed inside the pore channels. This result might indicate that iron ions are embedded in pore wall. The EDX analysis (Fig. 2f) revealed the presence of Fe, which was homogeneously dispersed in the whole TiO_2 framework.

The XPS spectra of different elements in FT-1.5 are shown in Fig. 3. The full-scanned XPS spectrum indicates that the FT-1.5 is composed mainly of the three elements of Ti, O, and Fe (Fig. 3a) [30,31]. The Fe 2p XPS spectra are shown in Fig. 3b. The

peaks at 711.8 and 725.6 eV are assigned to $\text{Fe}^{3+} 2p_{3/2}$ and $\text{Fe}^{3+} 2p_{1/2}$, respectively. The peaks at 708.9 and 722.7 eV are assigned to $\text{Fe}^{2+} 2p_{3/2}$ and $\text{Fe}^{2+} 2p_{1/2}$, respectively. This result suggested that the Fe cations in the FT-1.5 have mixed valence (Fe^{2+} , Fe^{3+}).

Fig. 4(a) shows the N_2 adsorption-desorption isotherms of the mesoporous TiO_2 with different iron ion loadings. At relatively high pressure (0.4–0.8), the curves exhibit small hysteresis loops and type IV isotherms, which are typical of mesoporous solids with uniform pore size (Fig. 4(b)). The pore size distribution curves calculated by the BJH method for the mesoporous composite exhibit narrow peaks centered at about 5 nm, which confirms the ordered mesoporous structure [35,36].

Fig. 2. HRTEM images of (a) FT-1.0 and (b) FT-1.5; (c–e) The corresponding EDX elemental mapping of (b).

Fig. 3. (a) Full scanned XPS spectrum and (b) Fe 2p XPS spectra of FT-1.5.

Fig. 4. (a) N₂ sorption isotherms and (b) pore-size distribution curves of the TiO₂ with different iron ions doping.

Table 1

BET properties of TiO₂ with different iron ions doping.

Sample	D _p (nm)	P _v (m ³ /g)	S _{BET} (m ² /g)
FT-0.1	6.1	0.23	191.1
FT-0.5	5.1	0.21	165.2
FT-1.0	5.0	0.16	136.9
FT-1.5	3.7	0.11	113.4

This result is consistent with the XRD and TEM results. The catalysts possessed high surface areas (>120 m²/g) and large pore volumes (> 0.2 cm³/g). With increase of iron ion loading, the pore size of the samples becomes larger. The specific BET surface area also decreases, which indicates that some pore structures have been destroyed (Table 1).

The UV-Vis diffuse reflectance spectra (DRS) of the samples are shown in Fig. 5. The initial absorption wavelength of TiO₂ is 385 nm, which is consistent with the intrinsic band gap absorption of anatase-type TiO₂. When doped with iron ions, the light harvesting ability of TiO₂ is improved and the adsorption range is extended to the visible light region.

The band gap energy of the FT-X can be confirmed by the plot in Fig. 5(b) [37]. The bandgap values of TiO₂ and the FT-0.1, FT-0.5, FT-1.0, and FT-1.5 nanocomposites are 3.20,

2.92, 2.90, 2.82, and 2.80 eV, respectively. Therefore, it can be concluded that the light response of FT-X can be changed from ultraviolet to visible light by controlling the content of iron ions. Briefly, the optical properties of FT-X can be tuned by adjusting the molar ratio of iron ion to titanium source.

The visible light-Fenton-like catalytic activities of TiO₂ and Fe/TiO₂ samples were evaluated via RhB degradation (Fig. 6). The degradation efficiency of FT-X was higher than that of bare TiO₂ under visible light irradiation. The conversion of RhB continuously increases to nearly 90% after 80 min when the Fe₂O₃ content is 1.5%.

To understand the reaction mechanism further, we investigated the performance of the light-assisted Fenton catalytic activity under different conditions. As shown in Fig. 7(a), FT-1.5 showed no activity when there is no light and H₂O₂ in the reaction. In the absence of H₂O₂, the activity of FT-1.5 for RhB removal under visible light is very low, which is attributable to the visible light photocatalytic activity of iron-doped TiO₂. The FT-1.5 sample also showed weak activity in the absence of light, mainly due to the Fenton process. However, under the conditions of visible light and H₂O₂, the catalytic reaction rate of the sample increased by nearly 7 times. To evaluate the photocatalytic activity of FT-1.5 under different conditions further, the

Fig. 5. (a) The UV-Vis diffuse reflectance spectra (DRS) of TiO₂ with different iron ions doping; (b) The plot of transformed Kubelka-Munk function versus the energy of light.

Fig. 6. Photo-Fenton activity of the TiO_2 with different iron ions doping.

photo-Fenton catalytic degradation of RhB under UV light irradiation was also studied (Fig. 7(b)). The degradation rate under the UV light-Fenton process was 9.5 times that under the UV light photocatalytic condition, but about 130 times that the under the Fenton condition.

The photo-Fenton ability of FT-1.5 to RhB at different concentrations was also studied. As shown in Fig. S2, RhB can be completely degraded within 45 min when the concentration is 5 ppm. When the concentration was increased to 10 ppm, 80% of RhB was eliminated. Even at a concentration of 20 ppm, about 50% of RhB was degraded. This indicates that FT-1.5 has

Fig. 7. Photo-Fenton activity of the FT-1.5 in degradation of RhB under (a) visible light and (b) UV irradiation.

Fig. 8. Photo-Fenton activity of the FT-1.5 in degradation of RhB under different pH.

a very good degradation efficiency.

The photo-Fenton reaction is significantly influenced by the pH of the solution. Therefore, the effect of pH value was explored further in the range from 3 to 9 (Fig. 8). We found that the FT-1.5 still has excellent activity for the degradation of RhB, even under alkaline conditions. When the pH value is 9.0, more than 80% of RhB can be removed within 80 min. The performance is slightly lower than that at pH 6.0 and 3.0. This means that FT-1.5 has excellent performance in a wide range of pH value.

To investigate the effects of different structures of TiO_2 on photo-Fenton activity, the performances of FT-1.5-SG (preparation by sol-gel) and FT-1.5-Im (preparation by impregnation) were also investigated. As seen in Fig. S3, about 75% and 85% removal efficiencies were achieved within 80 min in the presence of FT-1.5-SG and FT-1.5-Im, respectively. This result demonstrated that the ordered mesoporous structure is more advantageous than the disordered mesoporous structure for photo-Fenton reaction.

The stability and reusability of FT-1.5 were evaluated by recycling tests (Fig. 9). As is apparent from the figure, almost no loss of catalytic activity was observed after five consecutive cycles of catalytic reactions. Under visible light irradiation, the performance of each cycle exceeded 90%. Furthermore, the

Fig. 9. Recycling test of photo-Fenton activity of FT-1.5.

Fig. 10. Photo-Fenton mechanism of FT-1.5.

structure of FT-1.5 was also unchanged after 5 cycles, as shown in the TEM image of Fig. S4. The results show that FT-1.5 has good stability in the process of photo-Fenton reaction.

The above experimental results proved that the photocatalysis of TiO_2 and Fenton of iron ions are synergistic in the photo-Fenton process. A schematic of the detailed mechanism is shown in Fig. 10. Under visible light irradiation, the energy band of TiO_2 is narrowed due to doping of iron ions, which can be irradiated by visible light to generate electrons, thus promoting the transformation of Fe^{3+} to Fe^{2+} in the Fenton process [38]. Under ultraviolet light, this process is more rapid. Thus, the reaction rate is accelerated greatly.

4. Conclusions

In summary, ordered mesoporous Fe/TiO_2 was prepared by a solvent evaporation self-assembly method. TEM, XRD, and BET measurements showed that the samples doped by iron ions had an ordered pore structure with high crystallinity of anatase and a large specific surface area. There are several reasons for the stable and high photo-Fenton performance of the samples. One is that the photocatalysis accelerates the conversion process between Fe^{3+} and Fe^{2+} under both UV and visible light irradiation. The other is that porous TiO_2 has a large specific surface area, which is conducive to the exposure of active sites. The third is that the ordered pore structure is conducive to the retention of iron ions during the photo-Fenton process. This work provides a new pathway for designing and

fabricating high-performance catalysts for environmental purification.

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Graphical Abstract

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Ordered mesoporous Fe/TiO_2 was prepared by an evaporation-induced self-assembly method. It is a new highly efficient photo-Fenton catalyst that provides a new pathway for designing and fabricating high-performance catalysts for environmental purification.

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具有光增强芬顿活性的有序介孔Fe/TiO₂的制备

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摘要: Fenton反应能够无选择性地降解有机物, 甚至能够处理一些不能被生物降解的污染物, 其原理为过氧化氢(H₂O₂)和亚铁离子(Fe²⁺)在酸性溶液中生成具有强氧化性的羟基自由基(•OH), 后者将有机物氧化分解. 因此, Fenton反应在处理环境问题中占有重要地位. 将光催化与Fenton反应结合, 相比单独的Fenton反应可提高氧化矿化性能, 大大加快反应速率, 减少H₂O₂使用量, 降低成本, 拓宽反应pH范围, 其协同作用主要体现在两方面: (1)光催化产生的电子加速Fe³⁺转变成Fe²⁺, 促进Fenton反应进行; (2)Fenton反应中的H₂O₂与光生电子反应降低了电子-空穴的复合率, 从而提高光催化降解效率. 由于协同作用的存在, 污染物的降解效率大大增加.

到目前为止, Fenton反应中催化剂的载体多为惰性多孔材料, 如沸石、粘土、金属氧化物、介孔二氧化硅、多孔碳和sp²型石墨(石墨烯、氧化石墨烯、碳纳米管等)等具有较大比表面积的材料. 通常, 增加载体的表面积有利于活性位点的分散, 但是大比表面积的载体材料会削弱铁催化剂组分之间的相互作用, 导致催化剂稳定性差, 循环利用几次后会增加铁浸出量. 因此, 寻求大比表面积和高稳定性的光催化材料依然是巨大的挑战.

本文首次通过蒸发诱导自组装法成功制备了Fe离子修饰的有序介孔TiO₂(FT-X), 并通过XRD、BET、TEM、XPS和UV-Vis等分析手段对催化剂的结构进行了表征, 同时以光芬顿降解罗丹明B反应考察了pH、污染物浓度及载体(TiO₂)结构对催化性能的影响. 结果表明, 由于Fe离子修饰减小了TiO₂的禁带宽度, FT复合材料具有更宽的可见光响应距离和更强的可见光吸收, 在光芬顿反应过程中可以迅速转移电子, 避免电子-空穴对的重组, 同时加速了Fe³⁺和Fe²⁺的转化, 显著提高了催化剂的催化性能. 另外, 将Fe离子原位锚定在有序介孔TiO₂的孔壁上, 使FT具有规整的孔道结构和高的比表面积. 与不规则多孔材料相比, 一方面, 该结构有利于活性位点的暴露, 另一方面, 有序的孔道更有利于光吸收和溶质传输. 同时, Fe离子与载体之间具有较强的相互作用, 可以有效地抑制反应过程中Fe离子的流失, FT-1.5样品(Fe:Ti摩尔比为1.5%)在经过5次循环测试后依然保持较高的催化活性.

关键词: 有序介孔TiO₂; 铁离子掺杂; 光芬顿; 光催化

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