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Nature-Mimic Fabricated Polydopamine/MIL-53(Fe): Efficient Visible-light Responsive Photocatalysts for the Selective Oxidation of Alcohols

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Polydopamine/MIL-53(Fe) (PDA/MIL-53(Fe)) nanocomposite photocatalysts were synthesized with PDA (PDA = polydopamine) and MIL-53(Fe) by a naturemimicking method. The structures, morphologies, optical properties and thermal stabilities of all the synthesized materials were characterized by a series of methods. In particular, the separation efficiency of photogenerated charge significantly increased after the incorporation of PDA into MIL-53(Fe), which resulted in an elevated photocatalytic activity of PDA/MIL-53(Fe) compared with the control groups. PDA/MIL-53(Fe) nanocomposite could accelerate the converting of the primary or secondary alcohols into the corresponding aldehydes or ketones with a high specificity by direct hole-involving oxidation under visible-light irradiation and room temperature. The catalysts could be cycled at least three times without significant catalytic activity decrease and this result showed excellent recyclability and stability of the catalysts.

1. Introduction

Recently, the rapid increase of consumption of energy caused by growing population and industrialization worldwide and the shortage of clean and renewable energy is a major conflict of our world. Efficient use of solar energy is one of the promising ways to deal with the conflict^{1, 2}. Solar energy being directly converted into the form of heat or other energy forms is a problem that many researchers are trying to solve with different technologies³. Among many technologies, the use of photocatalysis is regarded as one of the most advantageous strategies.

Visible-light-responsive photocatalysts are pivotal in conversion of solar energy. Metalorganic frameworks (MOFs), a class of crystalline nanoporous materials, which are widely used in H₂ storage⁵, carbon dioxide capture⁶, catalysis⁷, gas storage⁸, gas separation⁹ and drug delivery¹⁰, are a new class of hybrid solids prepared by self-

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assembly strategy⁴ and regarded as potential photocatalysts¹¹. MOFs have unique micro structure, various adsorption properties, diverse catalyst sites¹², open metal sites^{13, 14}, high surface area¹⁵, easily functionalized structure¹⁶, well-defined pore structures^{15, 17} and tunable chemical properties¹⁸ compared inorganic with semiconductor. Varieties of photoactive MOFs, such as ZIFs, MILs and UiOs series, are developed by researchers as promising photocatalysts¹⁹ Among them, Fe-based MOFs attracted more and earth-abundant²⁰, the more attention for inexpensive, nontoxic properties and visible light responsible of Fe element²¹

MIL-53(Fe), a typical metal-organic frameworks, comprising 1,4-bezenedicarboxylate (H₂BDC) linker and FeO₄(OH)₂ octahedra, is a typical three-dimensional porous material²². MIL-53(Fe) has unique features, such as small size of Fe(III)-oxide cluster, better visible light absorption and limited recombination of the photogenerated charge. The application of MIL-53(Fe) in the decolorization of organic dyes²³, reduction of Cr(VI)²⁴, degradation of pollutant²⁵ and selective oxidation of alcohols is mediated by its excellent photogenerated.

Polydopamine (PDA) which is a catechol derivative and contains many catechol groups²⁷, a synthetic analogue of natural melanin

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59 60 (eumelanin)²⁸, is produced by oxidizing and selfpolymerizing under alkaline conditions (pH = 8.5) of dopamine²⁹, Excellent biocompatibility and low cytotoxicity³⁰ make it applied in chemistry, biology, medicine, materials sciences and photocatalytic degradation of methylene blue (MB)²⁷. Lee and coworkers described the current state of the art in polydopamine coating methods³¹. PDA which possesses good light responsiveness and promising photoconductivity under visible-light irradiation, separation efficiency showed high for photogenerated charge 32,33 . Due to its excellent photocatalytic properties, many researchers have applied polydopamine in the filed of photocatalysis, for example, Au-TiO₂ and Polydopamine for degradation of tetracycline under visible light³⁴, polydopamine-coated porous substrates as a platform for the wastewater treatment under sunlight³⁵ and Ag-Fe₃O₄ nanoparticles supported on polydopamine-functionalized porous cellulose acetate microspheres for catalytic and antibacterial applications³⁶.

In our previous study, we synthesized a series MOFs/conjugated polymer nanocomposite of photocatalysts and applied those materials to selective organic oxidation and reduction reactions ²⁹⁻³⁰. Following previous researches, we expected to synthesize materials with better light response properties, in addition, with higher conversion of selective oxidation products. Therefore, polydopamine/MIL-53(Fe) (PDA/MIL-53(Fe)) nanocomposites were generated in our lab concerned with the excellent light-involving properties of MIL-53(Fe) and polydopamine in this article. The properties and the application of the materials in the selective oxidation of alcohols were investigated.

2 Experimental

2.1 Materials

FeCl₃ 6H₂O, CCl₄ were supplied by Beijing Chemical Reagent Co., Ltd. Dopamine hydrochloride was obtained from Shanghai Yuheng Technology Center. Medical 1.4-Benzenedicarboxylic acid (H₂BDC), benzalcohol and its derivatives were obtained from Aladdin Reagent Co., Ltd. and Beijing J&K Scientific Co., Ltd. Absolute ethanol, anhydrous methanol, N,Ndimethylformamide (DMF) were obtained from Tianjin Chemical Reagent Co., Ltd. NaOH was obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2 Preparation of photocatalysts

2.2.1 Preparation of MIL-53(Fe)

MIL-53(Fe) was prepared by means_{Art}in the literature 32 . 1 mmol of FeCl₃ 6H₂O (0.5406 g)4and 1 mmol of H_2BDC (0.3323 g) were added to 0.56 mmol of DMF (43.14 mL) and stirred at room temperature for 60 min in a beaker, then the mixture was transferred into a 100 mL Teflon-lined autoclave and was sealed and heated to 170 °C keeping for 24 h. After the reaction, the autoclave was allowed to cool naturally to room temperature. The resultant suspension was washed with DMF and C_2H_5OH for three times, respectively. Sequentially, the raw product was soaked in methanol for three days to remove the guest molecules absorbed in the pores of the structure of MIL-53(Fe). The powder was then collected by centrifuging and dried under vacuum at 100 °C overnight.

2.2.2 Preparation of PDA

PDA was prepared according to the literature ²⁷. Dopamine hydrochloride was added in water and the solution was stirred at room temperature for 60 min. After the pH value of the mixture was adjusted to 8.5 with 1 M NaOH solution, the mixture was magnetically stirred vigorously at 60 °C for 24 h in an oil bath. The resulted black suspension was fully washed by water until the filtrate was neutral. The residual was then dried under vacuum at 60 °C overnight.

2.2.3 Preparation of PDA/MIL-53(Fe)

variety of polydopamine/MIL-53(Fe) A (PDA/MIL-53(Fe)) with different mass ratios of polydopamine (PDA) was prepared by a nature-mimicking method ²⁷. In detail, 500 mg of MIL-53(Fe) was added to 100 mL of water, the suspension was dispersed evenly after half an hour of sonication treatment. Then different mass of dopamine hydrochloride were added and stirred for 1 h. After the pH value of the mixture was adjusted to 8.5 with 1 M NaOH, the solution was stirred in an oil bath at 60 °C for 24 h and then cooled and centrifuged. In order to remove the unreacted dopamine, the collected solid samples were dispersed and rinsed with deionized water for several times. The final product was then dried under vacuum at 60 °C overnight.

2.3 Characterization

The Fourier transform infrared (FT-IR, Nicolet NEXUS 670 spectrometer) spectroscopy was used to characterize the structure of samples. X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe using an Al K radiation) measurements characterization was used for investigate the chemical states of the catalysts.

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The crystal morphology of the catalyst was characterized by powder X-ray diffraction (XRD, Rigaku D/ max-2400, k = 1.5418 Å). The UV-vis diffuse reflectance spectra (UV-vis DRS, Cary 500 spectrophotometer) UV-vis-NIR and the photoluminescence spectra (PL, FluoroSENS Luminescence Fluorescence spectrophotometer) were used to characterize the optical properties of the samples. The morphology and structure of catalysts were observed with a scanning electron microscope (SEM, Ultra Plus, Carl Zeiss, Germany, the test voltage was 6.0kV) and transmission electron microscope (TEM, JEOL model JEM 2010 EX microscope). The electrochemical analysis including the Mott-Schottky analysis (M-S), the electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation (CHI660E, Shanghaichenhua, Inc.). The thermo gravimetric analysis (TGA, TA Instruments Discovery Thermo gravimetric analyzer) was obtained from room temperature to 800 °C at the ramping of 10 °C min⁻¹ in N₂ atmosphere. The products of the selective oxidation of alcohols were recorded through gas chromatograph (GC, Shimadzu GC-2010) analyses. The BET specific surface areas (S_{BET}) were conducted on an Autosorb- iQ^2 -MP instrument (first, the samples were degassing at 250 °C to remove moistures and impurities, which were analyzed at -195 °C (liquid nitrogen) in the analysis room).

2. 4 Photocatalytic experimental details

The photooxidation ability of PDA/MIL-53(Fe) nanocomposites was texted by oxidation of aryl alcohol under visible light irradiation. In detail, 0.2 mmol of aryl alcohol and 5 mg of photocatalyst sample were added in a solution of 6 mL of CCl_4 in an open quartz tube. In order to ensure the adsorption-desorption equilibrium between catalysts and substrates before the photocatalytic reaction, so the suspension was stirred for 1 h in the dark. Then the mixture solution was performed for 9 h under a visible-light illumination. The visiblelight source was a 500 W metal halogen lamp (PLS-SXE 300, BiL on Co. Ltd. Shanghai China). After reaction, the reaction results were recorded on a gas chromatograph, the formulas (1) and (2) were used to calculate the conversion of alcohol and the selectivity of aldehyde or ketone in the reaction process, respectively.

Conversion of the product (%) = $[(C_0 - C_n) / C_0] \times 100\%$ (1)

Selectivity of the product (%) = $[C_a / (C_0 - C_n)] \times 100\%$ (2)

Where C_0 is the initial concentration of alcohol prior to reaction, C_n and C_a are the

concentrations of alcohol and aldehyde/ketone measured at the time *t*, respectively?!: 10.1039/C9NJ04929K

2. 5 Electrochemical measurements

The M-S curve and the EIS analysis were put into effect with AC impedance-potential model in a standard three-electrode system with an electrolyte solution of 0.2 M Na₂SO₄. That is to say, an saturated calomel electrode acted as the reference electrode, a Pt foil electrode acted as the counter electrode and a FTO glass electrodes acted as working electrodes, respectively. FTO glass is pretreated with isopropanol, acetone and water (V_1 : V_2 : $V_3=1$: 1: 1). Sequentially, the progress was operated at open circuit potential. The frequency range of open circuit potential with an AC voltage magnitude which increased 5 mV each time was between 10^5 and 10^{-2} Hz. For the sake of preparing photocatalyst-based composite electrodes, the prepared photocatalysts PDA/MIL-53(Fe) were dispersed in chitosan solution to form 3 $mg \cdot mL^{-1}$ solution and ultrasonicated for 30 min to form a colloidal solution, after then 60 uL of colloidal solution was dropped on the conductive side of the FTO glass and dry overnight at 100°C.

3 Results and discussion

3.1 Studies on PDA/MIL-53(Fe)

Fig.1 showed the typical XRD patterns of the MIL-53(Fe) and a sequence of PDA/MIL-53(Fe) nanocomposites. Distinctly, the well-defined diffraction peaks disclosed the high crystallinity of experimental synthesis MIL-53(Fe), which was in good agreement with the simulated one ³². But PDA/MIL-53(Fe) had not similar crystal form with that of MIL-53(Fe). On the one hand, PDA might wrap closely on the surface of MIL-53(Fe), which blocking original MIL-53(Fe) diffraction peaks from appearance. On the other hand, with the increasing of the content of MIL-53(Fe), the diffractions of characteristic PDA were strengthened increasingly in the composites, and the diffraction peaks moved to the big 2θ degrees.



Fig. 1 XRD patterns of the samples

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For the sake of further studying the functional group of PDA/MIL-53(Fe) and analyzing its molecular structure, the general features of FT-IR spectroscopy for MIL-53(Fe) and different PDA/MIL-53(Fe) composites were carried out, and the results were shown in Fig.2. For the FT-IR spectra of MIL-53(Fe), the absorption peak at 1597 cm⁻¹ can be attributed to the stretching vibration of the benzene ring skeleton. The asymmetric and symmetric vibrations of the carboxyl group produced two strong peaks at 1504 and 1392 cm⁻¹, respectively. The absorption peaks of C-H in benzene in-plane bending vibrations could be observed at 1018 cm⁻¹. The peak at 749 cm⁻¹ corresponded to the C-H stretching mode of the benzene in the organic linkers. For PDA, the indoline and indole structures of the stretching vibration were observed at 1508 and 1620 $\text{cm}^{-1/2}$ Besides, the characteristic peaks of MIL-53(Fe) and PDA can be observed in the FT-IR of the PDA/MIL-53(Fe) composites.



Fig. 2 FT-IR spectra of the samples

The morphology and microstructures of MIL-53(Fe) and PDA/MIL-53(Fe) were observed using SEM and TEM as showed in Fig.3. PDA presents a microsphere structure as showed in Fig.3a. The original MIL-53(Fe) showed the shuttle-like structure with smooth surfaces in Fig.3b. From the SEM images of PDA/MIL-53(Fe) in Fig.3c, it could be seen that the nanocomposite approximately maintained the shuttle-like, and PDA was uniformly and tightly adhered on the surface of MIL-53(Fe), resulting in a rough surface of the nanocomposites, which might be due to the directing growth of PDA microspheres on the surface of MIL-53(Fe) during nature-mimicking preparation. With the small changes of the structure of the nanocomposites, the XRD analysis results changed accordingly (Fig. 1). In order to further confirm this conclusion, the TEM images of the PDA/MIL-53(1: 20) were showed in Fig.3d and Fig.3e. It can be seen that the surface of PDA/MIL-53(1: 20) composite was fuzzy, and PDA appeared at the edge of MIL-53(Fe). All results demonstrated that the MIL-53(Fe) was successfully modified by

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the PDA. The elemental mapping_viewforcle of the PDA/MIL-53(1:20) composites were presented 2n Fig.3f. It could be found that the surfaces of the composites were composed of carbon, oxygen, nitrogen, and iron element (Fig.3g-j.). The

composites were composed of carbon, oxygen, nitrogen, and iron element (**Fig.3g-j**.). The elements contents of the composites were also presented in **Fig.3k-I**, and the corresponding contents of carbon, oxygen, nitrogen, and iron elemental were 18.5, 25.01, 1.61, 54.88%, respectively.



Fig. 3 SEM images of pure PDA (a); MIL-53(Fe) (b); PDA/MIL-53(Fe) (1 : 20, c); TEM images (d, e), EDS mapping (f-j) and the elements content (k-l) of PDA/MIL-53(1 : 20)

Surface stoichiometry information of the chemical composition and valence state of PDA/MIL-53(1:20) composite was analyzed by XPS. Fig.4a showed a survey spectra demonstrating that Fe, N, O and C elements which could be observed in the PDA/MIL-53 (1 : 20) composites. The XPS spectra (Fig.4b) of C1s was deconvoluted into five component peaks corresponding to the binding energies at about 284.20, 285.45, 286.33 and 288.08 eV. The peak at 284.20 eV corresponded to the sp^2 carbon in PDA and benzoic rings. The peaks at 285.45 and 286.33 were in response to the C-C and the C-O bond in PDA, respectively. The carboxylate groups (C=O) in H₂BDC linkers was emerged at 288.08 eV 33 . In addition, the N1s spectra (Fig.4c) of PDA/MIL-53(Fe) was deconvoluted into two component peaks with the binding energies at about 400.58 and 399.58 eV, due to the sp²-bonded aromatic N of -NH₂ and the tertiary N of -NH^{37,38}, respectively. Fig.4d showed the XPS spectra of O 1s. The spectra could be deconvoluted into three peaks at the binding energies of 532.33, 531.33 and 530.08 eV, which were matched to the oxygen atoms in the carboxylate groups of the H₂BDC linkers (531.57

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eV), the Fe-O bonds in MIL-53(Fe) (532.45 eV), and the O-C in H₂BDC (530.20 eV), respectively. Fig.4e showed the Fe2p spectra of PDA/MIL-53(Fe), which displayed two peaks with the binding energies at about 711.20 and 725.08 eV. The peak at 711.20 eV was owing to the $Fe2p_{3/2}$, and the binding energy peak at 725.08 eV was assigned to the Fe2p_{1/2} ³⁹. The peak separation of the two peaks of Fe2p, as follows, $\Delta = 2p_{1/2} - 2p_{3/2} = 13.88$ eV, was on the verge of previously reported for α - $Fe_2O_3^{25}$. Besides, at the peak of the binding energy of 713.33 eV, a shake up line of the lower Fe2p $_{3/2}$ to $Fe2p_{1/2}$ transition in the satellite peak was also observed ⁴⁰. These results were consistent with FTwhich further IR spectra, confirmed the conformation of PDA/MIL-53(Fe) composites.



Fig.4 XPS spectra of PDA/MIL-53(1 : 20): survey (a); C 1s (b); N 1s (c); O 1s (d); Fe 2p (e)

UV-vis diffuse reflectance spectra (UV-vis DRS) revealed the optical absorption properties of the samples. As showed in **Fig.5a**, all of the asprepared samples showed the strong absorption bands in the wavelength range of 200-420 nm. The spectra of MIL-53(Fe) characteristic absorption signal was observed at about 250 nm, it was assigned to the ligand-to-metal charge transfer (LMCT), implying the bonding of carboxylate

oxygen to metal ⁴¹. Moreover, the assmall characteristic peak at 445 nm may be directed the state transition (${}^{6}A_{1g} = {}^{4}A_{1g} + {}^{4}E_{g}$ (G)) in Fe (III) ⁴². Obviously, the onset of the main characteristic absorption edge in the visible-light region with a wavelength of MIL-53(Fe) was estimated to be 456 nm. Based on the relation of $E_{g} = 1240/\lambda$ ⁴³, as a result, the calculated optical band gap of MIL-53(Fe) was 2.72 eV. With more and more PDA being wrapped on the surface of MIL-53(Fe), the absorption spectra exhibited a slight red shift to 710 nm and an enhanced absorption intensity of light in the visible-light region, which suggested that the PDA/MIL-53(Fe) composites had a better ability to harvest more visible light than the pure MIL-53(Fe).



Fig.5 The UV-vis DRS (a), PL spectra (b, c), EIS Nyquist plot (d) and Mott-Schottky plot (e) of the samples

As for photocatalysis, the lifetime of the generated charge carriers: the hole (h^+) as well as the electron (e^-) , was a vital factor. Longer lifetime would give higher photocatalytic activity. The lifetime of the charge carriers can be revealed by PL spectra of the catalyst ⁴⁴. **Fig.5b** showed the PL spectra of the as-prepared samples. Generally, a lower PL intensity means a higher lifetime of electron-hole pairs. Obviously, MIL-53(Fe) had

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higher photoluminescence intensity in comparison with that of the PDA/MIL-53(Fe) composites. As shown in **Fig.5c**, it could also be observed that the PL intensity of the as-prepared samples followed as the order: PDA/MIL-53(1 : 5) > PDA/MIL-53(1 : 5)10) > PDA/MIL-53(1 : 100) > PDA/MIL-53 (1 : 100)50) > PDA/MIL-53(1:1) > PDA/MIL-53(1:2) >PDA/MIL-53(1 : 20), the results showed that the PDA/MIL-53(1 : 20) composites had the high separation efficiency of electron-hole pairs. With structure reference to the morphology of PDA/MIL-53(1 : 20) composites (Fig. 3c-3e), it could be concluded that the good interfacial contact between MIL-53(Fe) and PDA could prolong the lifetime of the photon-generated carrier. Namely, PDA could be regarded as a good acceptor for the photogenerated electrons, as a result, the separation of the photoelectron-hole was promoted, thus the long-lived hole (h^{+}) produced, which would make the PDA/MIL-53 (1 : 20) composites more widely used in photocatalytic applications.

EIS Nyquist plot could more closely explain the separation efficiency of photogenerated electrons and holes. **Fig.5d** showed the EIS Nyquist plots of the MIL-53(Fe) and PDA/MIL-53(1 : 20) composites. It could be found that PDA/MIL-53(1 : 20) had a much smaller arc than that of MIL-53(Fe), indicating that the transfer efficiency of charge carriers was higher on the surface of PDA/MIL-53(1 : 20) nanoparticles.

Thermal stability and composition of materials were studied by TGA. As showed in Fig.6, the as-prepared MIL-53(Fe) presents four stages in weight loss profiles. The weight loss below 120°C was attributed to the evaporation of moisture on the surface of the material, and between 150-420°C was the decomposition of DMF, the structure collapse of MIL-53(Fe) (450- 550° C) and the completely decomposition (> 700° C) of the material, respectively. As for PDA, an initial weight loss was at about 100°C owing to the evaporation of moisture absorbed on the surface of materials. The weight loss in the second stage was 100-800°C, mainly because the dopant molecules was removed from the polymer structure and the polymer chain fractured. The PDA/MIL-53(1 : 20) composites also had the similar weight loss trend as that of PDA, but the weight loss was more slow than PDA, especially when the temperature was higher than 430°C. It meant that PDA/MIL-53(1 : 20) composites presented better thermal stability.



Fig. 6 TGA profiles of the samples

The BET specific surface area test method (S_{BET}) was widely used in the adsorption performance of catalyst surface. **Fig.7** displayed the N₂ adsorption-desorption curve and the pores of the photocatalyst. The pore volume was calculated using BJH method. The S_{BET} of MIL-53 was 67.534 m² g⁻¹ accompanied with an average pore diameter of 4.2 nm. The S_{BET} of PDA was found to be 23.54 m² g⁻¹, and the average pore diameter of PDA was 10.8 nm. However, the PDA/MIL-53(1 : 20) nanocomposite had a S_{BET} value of 146.4 m² g⁻¹ higher than that of MIL-53(Fe) and PDA, it also had an average pore diameter of 4.5 nm. Therefore, larger S_{BET} of PDA/MIL-53 (1 : 20) were favorable for improving the photocatalytic activity.



Fig. 7 Nitrogen adsorption-desorption isotherms (a) and pore size distribution curves (b) of the samples

3.2 Photocatalytic oxidation of alcohols

In order to evaluate the photocatalytic activity of PDA/MIL-53 (Fe) (1 : 20), we chose photooxidation of aromatic alcohols under visiblelight irradiation. All experimental data were listed in **Table 1**. Obviously, compared with MIL-53(Fe) and PDA, PDA/MIL-53(1 : 20) composites effectively enhanced the photocatalytic activity. The conversion of benzalcohol was only 30% when used MIL-53(Fe) as the catalyst under the same conditions, but no oxidation reaction occurred when PDA was used. When the PDA/MIL-53(1 : 20) composites was employed as photocatalyst, the conversion of benzalcohol was enhanced from 30% to 85% superior to that of MIL-53(Fe) at the same conditions. Visible light without catalysts or catalysts without visible light was used as two controlled experiment. It showed that benzalcohol

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The results convinced that the oxidation of benzalcohol to benzaldehyde was a photodriving reaction. For different proportions PDA/MIL-53(Fe) composites, they had different catalytic activities in the oxidation reaction process, due to their different sizes and different adsorption ability in visible light. the as-prepared PDA/MIL-53(Fe) series, PDA/MIL-53 (1:20)achieved the optimal conversion (85%) under the same conditions, which was exactly the same as the previous optical performance. Table 1 Blank control experiments of the photocatalytic oxidation of benzalcohol Entry Catalyst Con./% Sel./% **1**^a None None None 2 ^b MIL-53(Fe) 30 >99 3 ° **PDA** 0 0 4 d PDA/MIL-53 85 >99

under

experimental conditions of PDA/MIL-53(1 : 20).

the

^a Benzalcohol 0.2 mmol, CCl₄ 6 mL, 9 h, visible light, illumination under ambient conditions.

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- ^bBenzalcohol 0.2 mmol, MIL-53(Fe) 5 mg, CCl₄ 6 mL, 9 h, visible light, illumination under ambient conditions.
- ^c Benzalcohol 0.2 mmol, PDA 5 mg, CCl₄ 6 mL, 9 h, visible light, illumination under ambient conditions.
- ^d Benzalcohol 0.2 mmol, PDA/MIL-53(1 : 20) 5 mg, CCl₄ 6 mL, 9 h, visible light, illumination under ambient conditions.

^e All the conditions was the same as d except for the visible light illumination.

In order to investigate the influence of solvent on photocatalytic oxidation, the corresponding results were summarized in Table 2. Various solvents such as trichloromethane, methanol, tetrachloromethane 1,2-dichloroethane, $(CCl_4),$ THF, dichloromethane, isopropanol, toluene. acetonitrile, brominated *n*-butane, ethanol, DMF, and ethyl acetate made a different results on the oxidation reactions. From the results we could found that CCl₄ was the suitable solvent for the selective oxidation of benzalcohol in this photocatalytic system.

Table 2 Photooxidation of benzalcohol in different solvents

^a Entry	Solvent	^b Con./%	° Sel./%
1^{a}	CCl_4	84	99
2	trichloromet hane	53	94

3	ethyl acetate	37 DOI: :	View 99 View 9 View 9 View 9 View 9 View 9
4	acetonitrile	26	99
5	dichloromet hane	25	99
6	1,2- dichloroeth ane	16	99
7	THF	12	99
8	brominated <i>n</i> -butane	6	99
9	methanol	5	99
10	toluene	4	99
11	ethanol	2	99
12	isopropanol	1	99
13	DMF	1	99

^a Conditions: benzalcohol 0.2 mmol; PDA/MIL-53(1 : 20) 5 mg; visible light illumination; 9 h.

^b and ^c: Calculated by GC analysis.

PDA/MIL-53(1:20) was applied to benzalcohol derivatives with different substituents to investigate the catalytic range of the catalytic system and to evaluated its photocatalytic activity. Benzalcohol derivatives were oxidized into corresponding aryl aldehydes or ketones exposure to visible light for 9 h, and the results were summarized in table 3. Due to the steric hindrance near the hydroxyl group in 2-methylbenzalcohol, the oxidation gave the lowest conversion in this series. As for the secondary benzylic substrates, all of the oxidation had relative lower conversions compared with primary benzylic because of their steric hindrance from themselves. It also could be found that the electronic effect of the substituent group on the benzene ring did not play an important role in the oxidations.

 Table 3 Photooxidation of various substituted aromatic
 alcohols over PDA/MIL-53(1:20)

^a Entry	Substrate	Product	^b Con./%	° Sel./%
1	—СН ₂ ОН	С—сно	85	>99
2	O ₂ N-CH ₂ OH	о2N-СНО	69	>99
3	H ₃ CO-CH ₂ OH	н ₃ со-Сно	72	>99
4	СН ₃	СН3	35	>99

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^a Conditions: Substrate (0.2 mmol); PDA/MIL-53(1 : 20)
5 mg; CCl₄ 6 mL; visible light illumination; 9 h;
^b and ^c: Calculated by GC analysis.

3.3 Reusability of the photocatalyst

The stability of materials has a critical position in photocatalysis. The stability and reusability of PDA/MIL-53(1 : 20) nanocomposites was appraised by carrying out the recycle experiments under identical conditions. After the first photocatalysis, **PDA/MIL-53(1** 20) nanocomposite, which was simply washed, filtered and dried at 60 °C under vacuum for 10 h, was applied to another batch of oxidation in the same conditions. After three times of photocatalytic oxidation, the conversion efficiency of benzalcohol into benzaldehyde decreased by 10% when PDA/MIL-53(Fe) was as catalyst (Fig.8). It was clear that this catalyst performed outstanding circulation in the oxidation and excellent photo stability.

To further evaluate the structural stability of the catalyst, FT-IR, XRD and SEM were used to crystalline characterize the structures and morphology of fresh and the three-time reused PDA/MIL-53(1:20) nanocomposites. The position and intensity of the diffraction peaks in the XRD pattern were basically the same (Fig. 8b), and no new characteristic peaks appeared after the catalyst being recycled, which fully proved that the crystal structure had no obvious change in the photocatalytic reaction process. Fig. 8c was the infrared spectra of the samples, indicating that there was no significant change before and after the reaction. But the SEM image (Fig.8d) showed that the crystal particle was somewhat destroyed after the reaction. In short, it clearly indicated that the PDA/MIL-53(1:20) nanocomposite had promising stability in this reaction system.



Fig. 8 The cycling result of PDA/MIL-53(1 : 20) composites in the oxidation of the benzalcohol. The conversion as well as selectivity (a); The XRD patterns (b); FT-IR spectra (c) and the SEM image(d) of PDA/MIL-53(1 : 20) before and after the catalytic reactions.

3.4 Mechanism for the photooxidation of benzalcohol over PDA/MIL-53(1:20)

We used a blank control experiment, the active species trapping experiments and the M-S curve to further investigate the possible photooxidation mechanism of benzalcohol over PDA/MIL-53(1:20).

The M-S curve was drawn by the Mott-Schottky equation, while the Mott-Schottky equation described the relationship between the space charge layer differential capacitance $C_{\rm sc}$ of a semiconductor and the potential Δ_{ϕ} of the semiconductor surface to the body, as shown in **Fig. 5e**. It could be observed that the slope of the M-S curve was positive, indicating that the PDA/MIL-53 (1 : 20) composites was an *n*-type semiconductor 45 . By calculation, the flat band potential of PDA/MIL-53 (1 : 20) was 0.18 V vs SCE at pH 7.0, and consistent with the -0.02 V vs NHE. In general, for an *n*-type semiconductor, the flat band potential is more positive than the conduction band potential for about 0.2 eV^{46} . Therefore, it was possible to obtain a conduction band potential (E_{CB}) of PDA/MIL-53 (1 : 20) composites of 0.18 eV vs NHE. Then, with the band gap energy (E_g) of the previous UV-vis DRS spectral data, the optical E_g of PDA/MIL-53 (1 : 20) could be calculated to be 1.75 eV. Accordingly to the empirical formula of $E_g = E_{VB} - E_{CB}$, it could be concluded that the final valence band position (E_{VB}) of the PDA/MIL-53 (1 : 20) nanocomposites was determined to be 1.93 eV vs NHE, which was between the potential of benzalcohol (1.88 eV vs

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NHE) and the potential of benzaldehyde (2.27 eV *vs* NHE). 26 . As a result, in thermodynamically, the conversion of benzalcohol to benzaldehyde was satisfied and benzaldehyde could not be further oxidized at the identical conditions. In addition, by comparing E_{CB} potential (0.18 eV vs NHE) and the oxidation potential of O_2/O_2 (-0.33 eV vs NHE), it was believed that PDA/MIL-53(1 : 20) was incapable to generate $\cdot O_2^-$ by the reduction of O_2 with the photo-induced electron. Therefore, the oxidation of benzalcohol to benzaldehyde by $\cdot O_2$ radicals could not occur. PDA had a more negative potential of -0.08 eV (vs NHE) than that of \tilde{E}_{CB} of MIL-53(Fe) ⁴⁷, but the outstanding ability of PDA to accept electron made it beneficial for the transfer of electrons from MIL-53(Fe) to PDA. Therefore, the high photocatalytic activity of PDA/MIL-53(1: 20) in this system could be ascribed to the excellent light-harvesting ability as well as the fast separation efficiency of photogenerated electrons of PDA on the interface of PDA/MIL-53(Fe) nanoparticles. In addition, CCl₄ was a typical electron canceller in the photocatalysis researches $\frac{26}{10}$ the model of the m , the most of the photogenerated electrons could be captured by CCl_4 , so CCl_4 was selected as the ideal solvent for this oxidation (**Table 2**).

As shown in **Fig.9**, investigating the mechanism of the oxidation, a sequence of control experiments with different kinds radical scavengers were added to the reaction system. In all of these reagents, p-benzoquinone (BQ) was applied to the capture of superoxide radicals ($\bullet O_2$), AgNO₃ for the capture of electron (e-), isopropyl alcohol (IPA) for the quenching of $\bullet OH$, N_2 flow for the excluding of O_2 and ethylenediamine tetraacetic acid dis-odium (EDTA-2Na) for the holes (h^+) capturing ⁴⁸. The experimental results showed that h^+ was one of the core active substances for the oxidation of benzalcohol, because only by adding EDTA-2Na into the oxidation reaction system, the conversion of benzalcohol would decrease rapidly. When the other scavengers were added, the conversion of benzalcohol was not decreased. Although the electron capture agent of AgNO₃ was added, the conversion was largely unaffected, which was ascribe to the electron transfer of PDA as well as the canceller of electrons by CCl₄. In a word, it was clear that the selective oxidation of benzalcohol to benzaldehyde was mainly triggered by the positive photogerated holes (h^+) .





4 Conclusions

In conclusion, a range of PDA/MIL-53(Fe) nanocomposites was prepared via nature-mimic method. It was certified that the as-prepared PDA/MIL-53(Fe) nanocomposites showed more outstanding photocatalytic activity than the MIL-53(Fe) or PDA, the cause was that the existence of the PDA would prolong the lifetime and maximize the separation of photogenerated carrier. With the catalysis of PDA/MIL-53(Fe) composites, a series of aromatic alcohols were converted to the corresponding aldehydes or ketones through an h^+ dominated oxidation process. Meanwhile, the photocatalyst was reused at least three times, and the catalytic performance did not change obviously. It could be used as a potential and promising visible-light-involving system for the selective oxidation of alcohols.

Conflicts of interest

There are no conflicts to declar.

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Notes and references

- V.S. Vyas, W.-H. Lau and B.-V. Lotsch, *Chem. Mater.* 2016, 28, 5191-5204.
- 2 N.-S. Lewis, *Science*. 2016, **351**, 1920-1929.
- 3 S. Zhu and D. Wang, *Adv. Energy Mater.* 2017, **7**, 1700841 (1-24).
- 4 H. Furukawa, K.-E. Cordova, M. O'Keeffe and O.-M. Yaghi, *Science*. 2013, **341**, 12304440(1-12).

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- 5 S. Proch, J. Herrmannsd örfer, R. Kempe, C. Kern, A. Jess, L. Seyfarth and J. Senker, *Chem. Eur. J.* 2008, 14, 8204-8212.
- 6 E. López-Maya, C. Montoro, V. Colombo, E. Barea and J.-A.-R. Navarro, *Adv. Funct. Mater.* 2014, **24**, 6130-6135.
- 7 M. Zhao, S. Ou, and C.-D. Wu, Acc. Chem. Res. 2014, **45**, 1199-1207.
- L. Murray, M. Dincă, and J. Long, *Chem. Soc. Rev.* 2009, 38, 1294-1314.
- 9 J. Li, J. Sculley, and H. Zhou, *Chem. Rev.* 2012, **112**, 869-932.
- 10 P. Horcajada, R. Gref, T. Baati, P. Allan, G. Maurin, P. Couvreur, G. Ferey, R. Morris, and C. Serre, *Chem. Rev.* 2012, **112**, 1232-1268.
- 11 T. Zhang, and W. Lin, Chem. Soc. Rev. 2014, 43, 5982-5993.
- 12 X. Li, Q. Deng, L.-K. Zhang, J. Wang, R. Wang, Z.-L. Zeng, S.-G. Deng, *Appl. Catal. A Gen.* 2019, **575**, 152-158.
- 13 J.-Y. Lee, O.-K. Farha, J Roberts, K.-A. Scheidt, S.-T. Nguyen and J.-T. Hupp, *Chem. Soc. Rev.* 2009, **38**, 1450-1459.
- 14 H.-Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S.-H. Yu and H.-J. Jiang, J. Am. Chem. Soc. 2015, 137, 13440-13443.
- 15 Y. Chen, D. Wang, X. Deng and Z. Li, *Catal. Sci. Technol.* 2017, **7**, 01-13.
- 16 T. Uemura, Y. Ono, Y. Hijikata and S. Kitagawa, J. Am. Chem. Soc. 2010, **132**, 4917-4924.
- 17 D.-J. Xiao, J. Oktawiec, P.-J. Milner and J.-R. Long. J. Am. Chem. Soc. 2016, **138**, 14371-14379.
- 18 C.-A. Trickett, A. Helal, B.-A. Almaythalony, Z.-H. Yamani, K.-E. Cordora and O.-M. Yoghi, *Nat. Rev. Mater.* 2017, 17045, 1-16.
- 19 Q. Liu, C. Zeng, L. Ai, Z. Hao and J. Jiang, *Appl. Catal. B Environ.* 2017, **224**, 38-45.
- 20 J. Qiu, X. Zhang, Y. Feng, X. Zhang, H. Wang and J. Yao, *Appl. Catal. B Environ.* 2018, **231**, 317-342.
- 21 T. Araya, M. Jia, J. Yang, P. Zhan, K. Cai, W. Ma and Y. Huang, *Appl. Catal. B Environ.* 2016, **203**, 768-777.
- 22 R. Liang, L. Shen, F. Jing, N. Qin and L. Wu, *ACS Appl. Mater. Interfaces.* 2015, **7**, 9507-9515.
- 23 L. Ai, C. Zhang, L. Li and J. Jiang, Appl. Catal. B Environ. 2014, 148-149, 191-200.
- 24 R. Liang, F. Jing, L. Shen, N. Qin and L. Wu, J. Hazard. Mater. 2015, 287, 364-372.
- 25 Y. Gao, S. Li, Y. Li, L. Yao and H Zhang, *Appl. Catal. B* Environ. 2017, **202**, 165-174.
- 26 Z.-W. Yang, X.-Q. Xu, X.-X. Liang, C. Lei, Y.-L Wei, P. He, B.-L. Lv, H.-C. Ma and Z.-Q. Lei, *Appl. Catal. B Environ.* 2016, **198**, 112-123.
- 27 Z. Yu, F. Li, Q. Yang, H. Shi, Q. Chen and M. Xu, ACS Sustainable Chem. Eng. 2017, **5**, 7840-7850.
- 28 Z.-W. Deng, B. Shang and B. Peng, *Chem. Rec.* 2018, **18**, 410-432.
- 29 Y. Liu, K. Ai and L. Lu, Chem. Rev. 2014, 114, 5057-5115.
- 30 S.-H. Ku, J.-K. Ryu, S.-K. Hong, H.-S Lee and C.-B. Park, *Biomaterials*, 2010, **31**, 2535-2541.
- 31 J.-H. Ryu, P.-B. Messersmith and H. Lee, *ACS Appl. Mater. Interfaces* 2018, **10**, 7523-7540.
- 32 D. Wang, R. Huang, W. Liu, D. Sun and Z. Li, *ACS Catal.* 2014, **4**, 4254-4260.
- P. Llewellyn, P. Horcajada, G. Maurin, T. Devic, N. Rosenbach, S. Bourrelly, C. Serre, D. Vincent, S. Loeras-Serna, Y. Filinchuk and G. Ferey, *J. Am Chem. Soc.* 2010, 131, 13002-13008.
- 34 C. Wang, Y.-L. Wu, J. Lu, J. Zhao, J.-Y. Cui, X.-L. Wu, Y.-S. Yan and P.-W. Huo, ACS Appl. Mater. Interfaces 2017, 9, 23687-23697.

- 35 C. Zhang, H.-C. Yang, L.-S. Wan, H.-Q. Liang, H.-Y. Li and Z.-K. Xu, ACS Appl. Mater. Interfaces 12015, 54, 11574.
- 36 S. Peng, F. Gao, D. Zeng, C. Peng and Y. -M. Chen, *Cellulose* 2018 25, 4771-4782.
- 37 Q.-R. Zhang, Y.-X. Li, Q.-G. Yang, H. Chen, X.-Q. Chen, T.-F. Jiao, Q.-M. Peng, J. Hazard. Mater. 2018, 342, 732-740.
- 38 J.-W. Fu, Q.-Q. Xin, X.-C. Wu, Z.-H. Chen, Y. Yan, S.-J. Liu, M.-H. Wang, J. Colloid Interf. Sci. 2016, 461, 292-304
- 39 Z. Zhang, Y. Jiang, M. Chi, Z. Yang, G. Nie, X. Lu and C. Wang, *Appl. Surface Sci.* 2016, **363**, 578-585.
- 40 S. Sepúlveda-Guzmán, L. Lara, O. Pérez-Camacho, O. Rodriguez-Fernandez, A. Olivas and R. Escudero, *Polymer*. 2007, 48, 720-727.
- M. Alvaro, E. Carbonell, B. Ferrer, F.-X. Llabres i Xamena, H. Garcia, *Chem. Eur. J.* 2007, 13, 5106-5112.
- 42 G.-T. Vuong, M.-H. Pham and T.-O. Do, *Dalton Trans.* 2013, **42**, 550-557.
- 43 W. Yue, S. Suraru, D. Bialas, M. Mvller and F. Wvrthner, *Angew. Chem. Int. Ed.* 2014, **53**, 6159-6162.
- 44 S. Wang, J. Lin and X. Wang, *Phys. Chem. Chem. Phys.* 2014, **16**, 14656-14660.
- 45 L.-P. Sun, S.-Y. Niu, J. Jin, G. Yang and L. Ye, *Inorg. Chem. Commun.* 2006, **9**, 679-682.
- 46 Y.-P. Yuan, L.-S. Yin, S.-W. Cao, G.-S. Xu, C.-H. Li and C. Xue, *Appl. Catal. B Environ.* 2015, **168**, 572-576.
- 47 J.-H. Kim, M. Lee and C.-B. Park, *Angew. Chem. Int. Ed.* 2014, **53**, 6364-6368.
- 48 X.-Q. Xu, R.-X. Liu, Y. Cui, X. Liang, C. Lei, S.-Y Meng, Y.-L. Ma, Z.-Q. Lei and Z.-W. Yang. *Appl. Catal. B Environ.* 2017, **210**, 484-494.

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Graphical Abstract

Nature-Mimic Fabricated Polydopamine/MIL-53(Fe): Efficient Visible-light Responsive Photocatalysts for the Selective Oxidation of Alcohols

PDA/MIL-53(Fe) nanocomposites was prepared via nature-mimic method. It showed that PDA/MIL-53(Fe) nanocomposites were efficient catalysts toward the photocatalytic selectively oxidation of alcohols to aldehydes or ketones by a direct hole-oxidation process under visible-light illuminated conditions. A possible photocatalytic mechanism concerned to the direct photogenerated hole-oxidation process was also proposed.

