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In Situ Growth of ZIF-8 Nanocrystals on the Pore Walls of 3D Ordered Macroporous TiO₂ for a One-Pot Cascade Reaction

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Abstract: It is wise to mimic a bioinspired system to design a nanoreactor as a catalyst containing multiple components for a cascade reaction. Here, we report the uniform growth of well-dispersed nano-scale ZIF-8 crystals on the pore walls of 3DOM TiO₂ via the TEA-assisted crystallization process. The UV-vis spectra indicate that the ZIF-8 photosensitizer can extend the visible-light absorption of 3DOM TiO₂. The obtained nanoreactor can efficiently catalyze the one-pot aromatic alcohol oxidization and Knoevenagel condensation cascade reaction for larger molecules. This work offers an important strategy for preparing semiconductor–MOF multifunctional composites with a spatially separated compartmentation for the cascade reaction.

Keywords: crystal growth; cascade reaction; nanoreactor; semiconductor–MOF composite

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1. Introduction

As a special class of crystalline microporous materials, the metal–organic framework (MOF) is a promising candidate for creating a composite heterogeneous catalyst system due to its thermal stability, ultrahigh surface area, tunable pore size, and versatile architectures [1–4]. The diverse chemical and structural properties of MOF make them attractive in the field of catalysis [5,6]. A type of MOF, known as zeolitic imidazolate frameworks (ZIFs), has attracted much attention since their initial discovery [7]. However, there have been some major hurdles to their implementation. First, the micropores of bulk ZIF-8 make it difficult for the macromolecules to contact its active sites, although the ZIF-8 nanocrystal (NC), which can expose more active sites, is a dominant catalyst to improve the catalytic efficiency [8]. However, ZIF-8 NCs are difficult to employ in practical systems [9]. Furthermore, pure ZIF-8 exhibits a single function that impedes the use of their full potential [10]. The above hurdles significantly limit the handling, operation, and processing of ZIF-8 materials for wider application. Therefore, it is important to develop a new method for the integration of ZIF-8 with a porous support matrix, in which ZIF-8 NCs are selectively and uniformly formed and protected in a continuous macroporous material. Specifically, the integration of ZIF-8 NCs and the macroporous material can remarkably promote the mass transfer for bulky-molecule-involved reactions and expose inside active sites [11]. Moreover, the ZIF-8 composites not only can combine the advantages but also mitigate the shortcomings of both components [12].

Furthermore, multifunctional heterogeneous catalysts for a one-pot cascade reaction have been recently widely researched in selective organic synthesis due to their eco-friendly, energy sustainable, and easily recycled characters [13]. The cascade reaction can complete the synthesis of multiple new bonds in one reactor without separating intermediates. In a short time, it can synthesize complex organic molecules in a highly atomic and economical manner [14,15]. Moreover, in some reaction systems, the protection–deprotection process

and purification process of the intermediate are omitted [16,17]. MOFs consist of compounds based on metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures that generate sites to anchor the catalysts [18–20]. Allowing metal nanoparticles to embed in MOF, achieving a catalytic cascade reaction, is a common strategy. Wang and co-workers recently reported a composite Au@Cu(II)-MOF catalyst that can gradually promote the benzyl alcohol oxidation and Knoevenagel condensation reactions [21]. Our group has designed a bifunctional catalyst integrated with a yolk-shell structure (IY-SO₃H/Rh@S-ZIF-8) to accomplish cascade reaction, which provides an innovative idea for preparing MOF composites with a hierarchical framework [11]. Therefore, driven by the need to continuously optimize the properties of composite materials, particular efforts are devoted to the design and formation of special structures rather than random mixtures [22]. Artificial nanodevices that are rationally designed will facilitate many cascade reactions that occur simultaneously with excellent specificity and efficiency.

Recently, research on semiconductor nanostructures/MOF composites are growing promptly; however, the research of hybrid photocatalysts is still in the preliminary stage [23]. TiO₂/ZIF-8 composites have been comprehensively reviewed as promising photocatalysts [24]. It has been proved that the properties of the ZIF-8 composite are better than that of the single component due to the synergistic effect of the semiconductor and ZIF-8 [23]. The charge transfer induced by the synergistic effect can appear between photoexcited inorganic TiO₂ and ZIF-8, which considerably overcome the electron-hole recombination in the TiO₂ and supplies long lifetime electrons for photocatalytic reaction [24].

In this work, a cascade catalyst that integrated ZIF-8 NCs on the pore walls of the three-dimensional ordered macroporous (3DOM) TiO₂ was constructed (ZIF-8@3DOM TiO₂), which is utilized for the one-pot aromatic alcohol oxidation–Knoevenagel condensation cascade reaction by illumination at room temperature. The metal and ligand salts of ZIF-8 were sequentially impregnated in the pore of 3DOM TiO₂, and then ZIF-8 NCs were in situ grown on the pore walls of 3DOM TiO₂ through the triethylamine (TEA)-assisted crystallization process (Scheme 1). The obtained structure has nano-sized ZIF-8 NCs, monolithically interconnected macropores, and an integrated micro-nano structure. The ZIF-8 NCs located on the pore walls of 3DOM TiO₂ can improve the visible-light absorbance of TiO₂ to efficiently promote the photocatalytic oxidation of aromatic alcohols to aromatic aldehydes by 3DOM TiO₂. Meanwhile, the ZIF-8 NCs can expose the active sites extremely well, which can then efficiently continue to exhibit high reactivity in the Knoevenagel condensation reaction of aromatic aldehydes at room temperature. Moreover, the monolithically ordered macropores can not only enhance the light absorption to improve their photoreaction efficiency and the integrated micro-nano structure, but also have excellent cycle stabilization.

Scheme 1. Schematic illustration showing the fabrication of the ZIF-8@3DOM TiO₂.

2. Results and Discussion

2.1. Characterization of the Microscopic Morphology of Catalyst

The overall synthesis process of ZIF-8@3DOM TiO₂ is shown in Scheme 1. First, the monodisperse CLPS microspheres with a diameter of around 210 nm were synthesized by emulsion polymerization. Subsequently, the highly ordered opal was formed through a self-assembled process of the CLPS microspheres by centrifuge at 2500 rpm (Figure 1a), which was used as a hard template for making a 3D interconnected network. The average macropore size of 3DOM TiO₂ is approximately 150 ± 5 nm (Figure 1b). Compared with the diameter of the CLPS microspheres, the macropores of 3DOM TiO₂ are smaller due to calcination. The periodic macroporous structure of 3DOM TiO₂ restricts the propagation of light at certain energies, causing stopband reflection due to coherent Bragg diffraction and increasing the path length of light through the slow proton effect, thus improving photocatalytic activity [25]. Besides, the interconnected macroporous structure of 3DOM TiO₂ facilitates the immobilization and dispersion of ZIF-8 NCs and reduces mass transfer limitations. Then, the Zn(NO₃)₂·6H₂O and 2-MeIM of the ZIF-8 precursor were successively filled into the macropores of the 3DOM TiO₂ and further crystallized with the assistance of TEA vapor. The ZIF-8 NCs were gestated on the pore walls of the macropores without any need for surface modification of the pore walls. In Figure 1c, it can be observed that a lot of ZIF-8 NCs (about 20 nm, inset of Figure 1c) are scattered on the pore walls of 3DOM TiO₂, which are not full of the macropores nor blocking the connected windows. The void space between the nested NCs and the TiO₂ skeleton can accommodate guest macromolecules participating in the cascade catalytic reaction. Furthermore, the multifunctional composite not only combines the merits but also mitigates the shortcomings of the components. On one hand, the ZIF-8 NCs scattered on the pore walls of 3DOM TiO₂ can improve the visible-light absorbance of 3DOM TiO₂, which is typically a UV-active photocatalyst. On the other hand, the size of the ZIF-8 NCs anchored onto the 3DOM TiO₂ walls is much smaller compared to the bulk ZIF-8 (Figure 1d, larger crystals and heavily aggregated), which is more conducive to exposing more active sites and increasing the contact area between ZIF-8 and the reaction substrate. In addition, the in situ growth of ZIF-8 NCs on the 3DOM TiO₂ walls can avoid the problem of an uneven ZIF-8 distribution.

Figure 1. SEM images of (a) CLPS-CCCT (inset is particle size distributions), (b) 3DOM TiO₂, (c) ZIF-8@3DOM TiO₂ (inset is corresponding magnified image), and (d) bulk ZIF-8.

2.2. Characterization of the Catalyst Composition

The compositions of the materials were analyzed via FT-IR, XPS, the Raman spectrum, elemental analysis, and zeta potential, seen in Table 1, Figure 2 and Figure S3. The FT-IR spectra of CLPS CCT, 3DOM TiO₂, and ZIF-8@3DOM TiO₂ are demonstrated in Figure 2a. In the spectrum of the CLPS CCT, the peaks in 1470, 765, and 700 cm^{−1} are characteristic absorption peaks of CLPS. In the spectrum of 3DOM TiO₂, the characteristic Ti–O–Ti peak in the range of 400–800 cm^{−1} can be observed. In comparison, the peaks in the spectrum of ZIF-8@3DOM TiO₂ at 1578, 1145, 750, and 1387 cm^{−1} are assigned to the imidazole group [26]. In addition, the peak at 423 cm^{−1} is related to the Zn–N stretch mode. The peak at around 675 cm^{−1} is associated with the Ti–O–Ti bond in TiO₂. In Figure 2b, the XPS wide-scan spectrum shows that ZIF-8@3DOM TiO₂ contains Ti, Zn, N, C, and O elements. The spectrum of Ti 2p depicts two bands with the binding energies of 457.9 and 463.6 eV assigned to Ti 2p_{3/2} and 2p_{1/2}, respectively (Figure 2c), which correspond to Ti⁴⁺ in a tetragonal structure such as anatase titania [27]. In Figure 2d, the peaks located at 1021.8 and 1044.9 eV are assigned to the Zn 2p_{3/2} and 2p_{1/2} orbitals, respectively. The N 1s region consists of three peaks, as shown in Figure 2e. The three peaks at 399.9, 399.4, and 398.8 eV are attributed to the N–Ti–O, C–N, and C=N chemical bonds, respectively, indicating the formation of typical N–Ti–O bonds between ZIF-8 NCs and 3DOM TiO₂ [28]. The C 1s spectrum can be deconvoluted into two peaks at 284.4 and 285.9 eV (Figure S2a), which correspond to the C–C bond and C–N bond, respectively [29]. In Figure S2b, the fitting peaks at 529.1 and 531.8 eV are attributed to Ti–O and Zn–OH chemical bonds [30]. Moreover, the structure of the TiO₂/ZIF-8 composite was also analyzed via the Raman spectrum (Figure 2f). The Raman active fundamental modes correspond to 142.65 (Eg), 398.34 (B1g), 512.64 (A1g), and 637.57 cm^{−1} (Eg) for the 3DOM TiO₂ [31]. It is worth noting that the peak (143.72 cm^{−1}) ascribed to the Eg mode of the ZIF-8@3DOM TiO₂ composite has a redshift compared with the 3DOM TiO₂ (142.65 cm^{−1}). The redshift of the Eg band can be attributed to the strain on the TiO₂/ZIF-8 surface, which has arisen from the introduction of N–Ti–O bonds on the 3DOM TiO₂ [24]. In order to determine the content of ZIF-8 in ZIF-8@3DOM TiO₂, according to the proportions of the C, H, and N elements in ZIF-8 and ZIF-8@3DOM TiO₂, the prepared ZIF-8@3DOM TiO₂ is calculated containing around 60.93 wt% ZIF-8 and 39.07 wt% TiO₂, respectively. As shown in Figure S3, the zeta potential values of the 3DOM TiO₂, bulk ZIF-8, and ZIF-8@3DOM TiO₂ measured by a Malvern Zetasizer Nano-ZS90 are −22.7 mV, +23.2 mV, and +7.67 mV, respectively. Under these initial conditions, the surface of TiO₂ is negatively charged. After loading positively charged ZIF-8 on the pore walls, the potential value increased significantly, indicating that ZIF-8 NC has been successfully loaded on the 3DOM TiO₂.

Table 1. Element content of ZIF-8@3DOM TiO₂ and 3DOM TiO₂.

Sample	Element * (%)		
	N	C	H
ZIF-8@3DOM TiO ₂	17.14	27.57	3.82
ZIF-8	28.33	45.52	6.19

* The weight ratios of ZIF-8 in ZIF-8@3DOM TiO₂ were calculated according to the mass fractions of N, C, and H in ZIF-8@3DOM TiO₂ and ZIF-8, i.e., 60.50, 60.57, and 61.71 wt%, respectively. Therefore, the average of the ZIF-8 mass fraction in ZIF-8@3DOM TiO₂ is 60.93 wt%. The random mixture catalyst contains the same amount of ZIF-8 and 3DOM TiO₂ as ZIF-8@3DOM TiO₂.

2.3. Characterization of Catalyst Crystal Phase, Nanoporous Structure, Optical Properties, and Thermal Stability

To further examine the crystal phase, nanoporous structure, and optical properties of the obtained catalyst, the XRD analysis, nitrogen adsorption–desorption isotherms, and optical absorption spectra of the catalysts were investigated, respectively. The XRD patterns of the 3DOM TiO₂, ZIF-8, and ZIF-8@3DOM TiO₂ are shown in Figure 3a. The XRD pattern of 3DOM TiO₂ shows three peaks at 2θ = 25.3°, 37.9°, and 48.0°, corresponding to the

crystal planes of (101), (004), and (200), respectively, which indicates that the TiO_2 sample adopts an anatase phase after calcination at 570°C . In the XRD pattern of ZIF-8, the obvious peaks, including 011, 002, 112, 022, 013, and 222, are observed [11]. The diffraction pattern of ZIF-8@3DOM TiO_2 exhibits that the patterns include those of ZIF-8 and 3DOM TiO_2 , indicating that ZIF-8 NCs are dispersed in the 3DOM TiO_2 and this is consistent with the SEM results. Furthermore, Figure 3b shows the nitrogen adsorption-desorption isotherms of the ZIF-8@3DOM TiO_2 composite. The ZIF-8@3DOM TiO_2 showed a significant high uptake at very low relative pressure, suggesting the presence of a microporous structure, which can be attributed to the frameworks of ZIF-8 NCs. Compared with 3DOM TiO_2 , the specific surface area of the ZIF-8@3DOM TiO_2 increased from 52 to $235\text{ m}^2\cdot\text{g}^{-1}$, ascribed to the high specific surface area of ZIF-8 ($427\text{ m}^2\cdot\text{g}^{-1}$, Figure S4).

Figure 2. (a) FT-IR spectra of CLPS CCT, 3DOM TiO_2 , and ZIF-8@3DOM TiO_2 . XPS analysis of ZIF-8@3DOM TiO_2 : (b) survey scan, (c) Ti 2p, (d) Zn 2p, and (e) N 1s. (f) Raman spectra of 3DOM TiO_2 and ZIF-8@3DOM TiO_2 (inset is the magnified image).

It is known that TiO_2 has attracted attention because of its abundance, low price, and nontoxicity among many other photocatalysts [32]. However, the anatase TiO_2 , which has a large bandgap, responds extremely only to UV-light irradiation, leading to the lower utility of light; this means that more strategic methods are needed to be proposed to improve the visible-light absorbance of TiO_2 [33]. The optical properties of the bulk ZIF-8, 3DOM TiO_2 , the random mixture (3DOM TiO_2 and bulk ZIF-8), and ZIF-8@3DOM TiO_2 were investigated and the results are presented in Figure 3c. The absorption spectrum of ZIF-8 shows a weak absorption peak in the range from 260 to 350 nm (green curve). 3DOM TiO_2 shows a strong absorption peak in the UV domain (200–405 nm) with a bandgap of 3.06 eV (black curve). The UV-vis spectrum of the random mixture shows slightly higher visible light absorption compared with 3DOM TiO_2 (blue curve). Interestingly, the ZIF-8@3DOM TiO_2 composite shows obvious absorption in the visible domain surrounded 400–600 nm (red curve). It is reasonable to explain that the N–Ti–O chemical bonding in the composite interface can easily improve the visible-light absorbance of TiO_2 [34,35]. In order to investigate the thermal stability of the obtained 3DOM TiO_2 , bulk ZIF-8, and ZIF-8@3DOM TiO_2 , the thermogravimetric curves are shown in Figure 3d. From 40°C to

1000 °C, the 3DOM TiO₂ mass remains stable, indicating that it does not degrade in the temperature range. The TGA curves of ZIF-8 and ZIF-8@3DOM TiO₂ are also similar to the ZIF-8 crystals prepared in TEA [36]. The first step of weight loss of bulk ZIF-8 (40 °C to 230 °C) is due to the release of solvent methanol and other absorbed unreacted molecules. The sharp weight loss from 230 °C to 1000 °C is due to the structural degradation and decomposition of the organic ligand. From the thermogravimetric curves, it can be obtained that there is a total weight loss of about 67% for bulk ZIF-8 and about 42% for ZIF-8@3DOM TiO₂ in the heating range from 40 °C to 1000 °C. Thus, the approximate weight ratio of ZIF-8 in ZIF-8@3DOM TiO₂ can be calculated as 63%, which is consistent with the results obtained from the elemental analysis (Table 1).

Figure 3. (a) XRD patterns of 3DOM TiO₂, ZIF-8, and ZIF-8@3DOM TiO₂. (b) N₂ adsorption–desorption isotherms and pore diameter distribution (inset) of ZIF-8@3DOM TiO₂. (c) UV-visible spectra of ZIF-8@3DOM TiO₂, random mixture, 3DOM TiO₂, and ZIF-8. (d) The TG analysis of 3DOM TiO₂, ZIF-8, and ZIF-8@3DOM TiO₂.

2.4. Analysis of Catalytic Performance

The benzylidenemalonitrile (BMN) and its derivatives (usually as the product of the aryl aldehydes Knoevenagel condensation reaction) can be used for synthetic reaction transformation and molecules of biological value [37]. Herein, the prepared ZIF-8@3DOM TiO₂ was utilized as a micro-nano reactor to synthesize the BMN derivatives from aromatic alcohol via a cascade reaction at 25 °C (Table 2). First, the aromatic alcohol was oxidized to arylaldehyde by the catalysis of the 3DOM TiO₂ skeleton under continuous illumination in O₂, and then the arylaldehyde was further transformed into BMN derivative by the catalysis of ZIF-8 NCs located on the pore walls of ZIF-8@3DOM TiO₂. Generally, it is difficult to oxidize aromatic alcohol to arylaldehydes with molecular oxygen under ambient condition. This particular conversion usually requires inorganic oxidants, such as stoichiometric chromium, manganese oxides, or organic oxidants, resulting in a large amount of carcinogenic or toxic wastes being generated subsequently [38]. However, the ZIF-8 NCs located on the 3DOM TiO₂ skeleton can extend the absorbance of the 3DOM TiO₂ to the visible light domain for the photocatalytic oxidation reactions (Figure 3c). The ZIF-8@3DOM TiO₂ catalyst constructed with ZIF-8 NCs and 3DOM TiO₂ is beneficial to the cascade reaction, especially bulky-molecule catalysis. To certify the benefits of the unique

structure of the ZIF-8@3DOM TiO₂ involved in bulky-molecule catalysis, the catalytic performances of ZIF-8@3DOM TiO₂, the mixture of 3DOM TiO₂ and the bulk ZIF-8, and 3DOM TiO₂ were tested in the aromatic oxidation and Knoevenagel condensation cascade reaction, as illustrated in Table 2.

Table 2. Aromatic alcohol oxidation and Knoevenagel condensation cascade reaction catalyzed by different catalysts.

Reaction scheme: R-CH2OH (A) $\xrightarrow[\text{TiO}_2]{\text{O}_2, h\nu}$ R-CHO (B) $\xrightarrow[\text{ZIF-8}]{\text{CN-CH}_2\text{-CN}}$ R-CH=C(CN)2 (C)

Entry	Substrates A	Products C	ZIF-8@3DOM TiO ₂ ^[a]			Random Mixtures ^[b]			3DOM TiO ₂		
			Conv. of A (%)	Yield of B (%)	Yield of C (%)	Conv. of A (%)	Yield of B (%)	Yield of C (%)	Conv. of A (%)	Yield of B (%)	Yield of C (%)
1			98.0	trace	98.0	90.0	2.0	88.0	58.0	58.0	0
2			80.1	9.0	71.1	74.0	23.0	51.0	50.1	50.1	0
3			73.0	13.0	60.0	64.8	30.0	34.8	40.0	40.0	0

^[a] Reaction conditions: ZIF-8@3DOM TiO₂ (55 mg), acetonitrile (10 mL), benzyl alcohol (0.5 mmol), malononitrile (1 mmol), 25 °C, 8 h, 300 W Xenon-arc lamp, and 0.1 MPa O₂. ^[b] The random mixture catalyst containing the same amount of ZIF-8 and 3DOM TiO₂ as ZIF-8@3DOM TiO₂. All the conversion and yield were determined by GC.

In the conversion reaction of aromatic alcohols to aromatic aldehydes, ZIF-8@3DOM TiO₂ has the highest conversions (73.0–98.0%), followed by the random mixture catalyst (64.8–90.0%), and the 3DOM TiO₂ is the weakest among them (40–58.0%). For ZIF-8@3DOM TiO₂, the composite can effectively combine ZIF-8 and TiO₂ so that the ZIF-8 NCs are uniformly loaded on the pore walls of the 3DOM TiO₂ (Figure 1c). It also can be seen from the XPS spectra of Figure 2e that 3DOM TiO₂ and ZIF-8 NCs are tightly combined through the N–Ti–O bonds. Such a unique structure is extremely beneficial to the conversion of aromatic alcohols: first, the ZIF-8 NCs supported on 3DOM TiO₂ can promote the absorption of visible light by 3DOM TiO₂ due to the existence of the N–Ti–O bond (Figures 2e and 3c), which is beneficial to the photocatalytic conversion of aromatic alcohols; second, the uniform dispersion of ZIF-8 NCs in the 3DOM TiO₂ allows the conversion products of aromatic alcohols (aromatic aldehydes) to easily contact the surface of ZIF-8 NCs. Accordingly, the ZIF-8 NCs can continue to convert aromatic aldehydes into BMN, so the presence of the ZIF-8 NCs is conducive to the forward conversion of aromatic alcohols to aromatic aldehydes. For a random mixture catalyst, the catalytic effect is weaker than that of ZIF-8@3DOM TiO₂, but it is higher than that of 3DOM TiO₂ in the conversion reaction of aromatic alcohols to aromatic aldehydes. On the one hand, the lower visible light absorption of the random mixture compared with ZIF-8@3DOM TiO₂ leads to a lower light utilization efficiency, so that the yield is lower in the photocatalytic reaction. On the other hand, the bulk ZIF-8 cannot disperse evenly with 3DOM TiO₂, causing the aromatic aldehydes to take a long reaction path to touch the bulk ZIF-8 in the random mixture. Moreover, a few active sites exposed in the ZIF-8 are not conducive to the further conversion of aromatic aldehydes. Therefore, the random mixture catalyst is less favorable to the forward conversion of aromatic alcohols to aromatic aldehydes than the ZIF-8@3DOM TiO₂. As for 3DOM TiO₂,

the photocatalytic efficiency is the lowest because of the large intrinsic bandgap (3.06 eV), severely restricting its utilization of the visible light (Figure 3c).

In the Knoevenagel condensation reaction, among the three catalysts, the ZIF-8@3DOM TiO₂ still has the highest yields (60.0–98.0%), especially in the reactions of aromatic alcohols with multiple benzene rings (Table 2). The random mixture catalyst takes second place (34.8–89.0%), and the 3DOM TiO₂ is inactive. This phenomenon is mainly due to the fact that only the ZIF-8 has reactivity in Knoevenagel condensation reactions. However, the 11.6 Å large pores connected by pores of 3.4 Å in diameter is the main characterization of the ZIF-8 structure [39]. Such a microporous structure makes them relatively inert to macromolecular reactions, which can only be catalyzed by the surface of the catalyst. Therefore, the bulk ZIF-8 can only provide fewer active centers and has a poor catalytic effect on reactions involving large molecules. Besides, the bulk ZIF-8 cannot be uniformly mixed with 3DOM TiO₂ because of the large agglomerate size of bulk ZIF-8, which extends the reaction route of the substance. On the contrary, the ZIF-8@3DOM TiO₂ composite catalyst is loaded with ZIF-8 CNs on the pore walls. Such a unique structure is beneficial to the reaction: (1) the nano-scale ZIF-8 can greatly increase the contacting area between the reaction substrate and the ZIF-8 NCs, thus improving the catalytic performance; (2) the diffusion path of the first step product (the intermediate product aromatic aldehyde) is shortened, which is more conducive to contact with the ZIF-8, thereby increasing the catalytic yield.

2.5. Catalyst Stability Test and Explanation of Catalytic Mechanism

The stability and the reusability of the ZIF-8@3DOM TiO₂ were also investigated in this study. After the cascade reaction was performed for 2 h, the solid catalyst ZIF-8@3DOM TiO₂ was filtered out and we continued stirring the mother liquor under the same experimental conditions. The findings show that the amount of 2-benzylidenemalononitrile was the same as the previous time, which reflects that the leaching was absent (Figure 4a). The effects of the reaction time from 1 to 10 h on the yield of benzylidenemalononitrile were also investigated, as shown in Figure 4a. Whether the catalyst is ZIF-8@3DOM TiO₂ or the random mixtures, the yield rapidly increases with the reaction time from 1 to 8 h until the reaction equilibrium appears for the rest of the time. Hence, the time of 8 h was selected as the optimal condition of the reaction time. The ZIF-8@3DOM TiO₂ was recovered by filtration and reused for the next run of the benzyl alcohol oxidation–Knoevenagel condensation cascade reaction. The results confirm that the ZIF-8@3DOM TiO₂ can be stably reused for at least 5 circulations with no significant decrease in activity (Figure 4b). From the SEM as well as the XPS analysis (Figure 5 and Figure S5), the morphology and the chemical bonds between ZIF-8 and 3DOM TiO₂ were well maintained after 5 times of reuse. Figure S6a shows that the ZIF-8 characteristic absorption peaks (423 cm^{−1}) and TiO₂ characteristic absorption peaks (400–800 cm^{−1}) did not change significantly after the catalytic cascade reaction of ZIF-8@3DOM TiO₂, and no other spurious peaks appeared. The XRD pattern of ZIF-8@3DOM TiO₂ after recycling in Figure S6b shows that the peak positions and relative intensities of its diffraction peaks did not change significantly before and after use. Figure S6c shows the structural parameters obtained after N₂ adsorption–desorption characterization of the recycled ZIF-8@3DOM TiO₂ catalyst. The results show that the specific surface area of the ZIF-8@3DOM TiO₂ catalyst decreased to some extent after 5 times of use. This may be caused by the residual reactants in the recycled catalyst, but the ZIF-8@3DOM TiO₂ still has a high specific surface area value after five cycles, and thus still has some catalytic activity. All the above analysis results indicated that the catalyst ZIF-8@3DOM TiO₂ was structurally stable and could be recycled. This can be attributed to the monolithically interconnected TiO₂ skeleton and the immobilized ZIF-8 NCs. The high performance of the ZIF-8@3DOM TiO₂ was explained through the reaction path in Figure 4c. The cascade reaction in micro-nano structures can shorten the reaction paths, and the aromatic alcohol first passes through the interconnected macropores and is catalyzed by TiO₂ to transform into intermediate arylaldehyde. Then, the intermediate arylaldehyde

reaches the ZIF-8 NCs immobilized on the wall of 3DOM TiO_2 and is transformed into the final products. Specifically, multiple reactions are carried out in this nanoreactor because of the integration of the multiple micro-nano reactor units. The integration of the ZIF-8 NCs and the macroporous TiO_2 in one micro-nano reactor can lessen the diffusion distance of the substances and can be beneficial to the exposure of the active sites.

Figure 4. (a) Time-yield plots of benzyl alcohol oxidation and Knoevenagel condensation reactions for the first run of the ZIF-8@3DOM TiO_2 , the random mixtures, and filtration experiments of the ZIF-8@3DOM TiO_2 . (b) Catalytic recyclability of the ZIF-8@3DOM TiO_2 for the benzyl alcohol oxidation–Knoevenagel condensation cascade reaction. (c) Schematic diagram of the one-pot cascade reaction in the ZIF-8@3DOM TiO_2 . (d) Possible photocatalytic mechanism of the ZIF-8@ TiO_2 nanocomposite.

Figure 5. The SEM of ZIF-8@3DOM TiO_2 after being used 5 times.

Furthermore, the ZIF-8 NCs located on 3DOM TiO_2 not only improve the photore-sponse of 3DOM TiO_2 to the visible light domain but also improve the conversion of

aromatic alcohol by 3DOM TiO₂ under the light. Because of the above phenomenon, a provisional mechanism for the photocatalytic performance of TiO₂/ZIF-8 nanocomposite was proposed. The main reason is that the Ti–O–N bond between 3DOM TiO₂ and ZIF-8 NCs can enhance the visible-light activation of 3DOM TiO₂. The illustration in Figure 4d shows the generation and conversion process of electron-hole pairs between the 3DOM TiO₂ and the ZIF-8 NCs interface. First, the electrons and holes are generated on the 3DOM TiO₂ under excitation by light. The ZIF-8 is conducive to charge separation and reduces the bandgap of 3DOM TiO₂ (Eg1 to Eg2) [20]. Under the circumstances, the photoelectrons transfer to the surface of 3DOM TiO₂ is easily achieved. The photogenerated electron can combine with oxygen molecules in the solution to form OH[•]. Simultaneously, the holes (h⁺) first oxidize HOCH₂–Ph to (HOCH–Ph)⁺, and then (HOCH–Ph)⁺ is oxidized to Ph–CHO [40].

3. Materials and Methods

3.1. Materials

Divinylbenzene (DVB, 80% isomer) and styrene (St) were purchased from Aladdin Industrial Corporation (Shanghai, China) and distilled under reduced pressure before use. Tetrabutyl titanate (AR) and acetic acid (AR) were received from Guangfujingxi Chemical Corporation (Tianjin, China). Sodium laurylsulfonate (CP), acetonitrile (AR), benzyl alcohol (99.0%), potassium persulfate (AR), TEA (AR), and methyl alcohol (AR) were purchased from Fuchen Chemical Reagent Company (Tianjin, China). NaHCO₃ (99.8%), 2-methylimidazole (2-MeIM, 99%), 1-naphthalenemethanol (99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), and 9-anthracenemethanol (99%) were received from Aladdin Industrial Corporation (Shanghai, China). Potassium persulfate (KPS) was obtained from Fengchuan Chemical Reagent Company (Tianjin, China) and refined by methanol. All other chemicals were used as obtained.

3.2. Preparation of 3DOM TiO₂

First, the cross-linked polystyrene (CLPS) microspheres were prepared according to the previous report [41]. Then, the product was collected by centrifugation and finally dried in a dryer to obtain CLPS colloidal crystal template (CCT).

The 3DOM TiO₂ was prepared by a sol-gel method using the CLPS CCT as the template. The precursor was prepared by mixing 1 mL of tetrabutyl titanate with 1 mL of ethyl alcohol and 1 mL acetic acid under magnetic stirring, then a mixture of 3 mL deionized water and 1 mL hydrochloric acid was added into the above-mentioned solution under continuous stirring until the solution became clear. Afterward, the precursor was injected into a tube loaded with CLPS CCT under vacuum and immersed for 5 min. After the excess liquid was taken out, the samples were aged in an air-dry oven at 60 °C for 2 h. The whole process was repeated 3 times. Finally, the TiO₂/CLPS hybrid materials were calcined at 300 °C for 4 h and then 570 °C for 5 h in the air using a ramp rate of 4 °C/min to remove the CLPS CCT and form anatase TiO₂, and the product 3DOM TiO₂ was obtained.

3.3. Preparation of ZIF-8@3DOM TiO₂

The ZIF-8 precursor solutions included Zn(NO₃)₂·6H₂O and 2-MeIM methanol solution. Their concentrations were all 120 mg/mL, and the volume ratio V(Zn(NO₃)₂·6H₂O)/V(2-MeIM) was 4/3. Initially, a Zn(NO₃)₂·6H₂O methanol solution (2 mL) was added into a glass vial containing 200 mg of 3DOM TiO₂, and the mixture was rotary evaporated under vacuum at 50 °C to remove the methanol solvent. Subsequently, the dried Zn(NO₃)₂·6H₂O/3DOM TiO₂ was immersed into the 2-MeIM solution, and then rotary evaporated at 50 °C to obtain the Zn(NO₃)₂·6H₂O/2-MeIM/3DOM TiO₂ composite. The whole filling process was repeated 2 times. Afterward, a small container containing TEA was placed in the glass flask and sealed at room temperature for 24 h (diagram as shown in Figure S1). Finally, the resulting composite was washed with methanol three times and dried at 60 °C overnight to obtain ZIF-8@3DOM TiO₂. In comparison, the bulk ZIF-8 was synthesized by the same

method as ZIF-8@3DOM TiO₂ as follows: Zn(NO₃)₂·6H₂O (0.480 g) and 2-MeIM (0.360 g) were dissolved in 10 mL of methanol. Then, the mixture was rotary evaporated in a glass flask under vacuum at 50 °C to remove the methanol solvent. Subsequently, a small container containing TEA was placed in the glass flask and sealed at room temperature for 24 h. Finally, the product was washed with methanol three times and dried at 60 °C overnight.

3.4. Catalytic Applications in a Cascade Reaction

The one-pot cascade aromatic alcohol oxidization–Knoevenagel condensation reaction was carried out on Labsolar-6A system (Perfect Light Co., Beijing, China). The Labsolar-6A system mainly includes a 300 W Xenon-arc lamp and a reactor system. The Xenon-arc lamp is used as the photo source for the photocatalytic oxidation of aromatic alcohol. To remove the radiant heat, the circulating water flowing through the reactor is used to keep the temperature at 25 °C. During the reaction, 55 mg catalyst was added to 10 mL of acetonitrile in the reactor under continuous stirring. Subsequently, 0.5 mmol benzyl alcohol and 1 mmol malononitrile were introduced into the quartz glass reactor. Before illumination, the reaction reactor was vacuum treated and purged with 0.1 MPa high purity O₂. The mixture was then illuminated using the Xenon lamp for 8 h and sampled once every hour. Then, the ZIF-8@3DOM TiO₂ was filtered out, washed with methanol, and reutilized in the next cycle. Finally, the product was quantified by gas chromatography (GC). For comparison, the catalytic conditions of the random mixture and 3DOM TiO₂ were the same as above.

3.5. Characterization

Fourier transform infrared (FT-IR) spectra between 4000 and 400 cm^{−1} were recorded on a Bruker VECTOR-22 (Bruker, Karlsruhe, Germany) spectrometer using KBr pellets. Particle diameters, size distribution, and zeta potentials were measured on a Malvern Nano ZS90 Zetasizer (Malvern, UK) at room temperature. X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (D8-Davinci, Bruker, Karlsruhe, Germany). Scanning electron microscopy (SEM) images were recorded by an FEI Nova NanoSEM450 (FEI, Portland, OR, USA). X-ray photoelectron spectroscopy patterns were collected on an X-ray photoelectron spectrometer (XPS, Thermo ESCALAB-250Xi, Thermo Scientific, Waltham, MA, USA). Thermogravimetric analysis (TGA) was investigated by the TGA system (SDT-Q600, TA Instruments, Newcastle, PA, USA) from 40 °C to about 1000 °C and a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) pattern was measured on a Bruker D8-Davinci (Bruker, Germany) diffractometer with Cu Kα radiation (40 kV, 150 mA). Raman spectra were recorded on an InVia Raman microprobe with 785 nm laser excitation. UV-vis diffuse reflectance spectra were obtained on a UV-vis spectrophotometer (Agilent Technologies Ltd., Beijing, China) at room temperature. Nitrogen adsorption-desorption dates were obtained by Micromeritics ASAP 2020 (Micromeritics, Norcross, GA, USA). The content of ZIF-8 in ZIF-8@3DOM TiO₂ was calculated according to the content of nitrogen, carbon, and hydrogen measured by the elemental analyzer (Flash EA 1112, Thermo Electron Corporation, Waltham, MA, USA). The identification of the liquid solution obtained by centrifugation after the one-pot cascade reaction was carried out by GC (Agilent 7890, Agilent, Palo Alto, CA, USA) using a KB-Wax column (30 m × 0.32 mm). The temperature was increased from 80 to 250 °C at a rate of 10 °C/min and kept at 250 °C for 5 min. The flame ionization detector (FID) temperature was set to 250 °C, and the flow rate of the carrier gas was 30 mL/min. The GC was calibrated with standard samples in advance.

4. Conclusions

In summary, a cascade catalyst, from the in situ growth of ZIF-8 NCs on the pore walls of 3DOM TiO₂, was constructed. The constructed hybrid materials were fully characterized and appraised using different approaches, including SEM, FTIR, Raman, XPS, XRD, BET, and UV-vis spectra. The novel structural composite material with integrated functionalities

is more conducive to improving the recovery of the catalyst. Particularly, the obtained ZIF-8@3DOM TiO₂ can catalyze the cascade reaction of aromatic alcohol oxidization by illumination and the Knoevenagel condensation reaction at room temperature. In the oxidation reaction of alcohol, the semiconductor–ZIF composite structure can make the TiO₂ more beneficial to the absorption of visible light. In the Knoevenagel condensation reactions, the interconnected porous structure and nano-scale ZIF-8 crystals are more conducive to the contact of macromolecular substances. This work provides a novel method for fabricating a multifunctional MOF/semiconductor composite.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11050533/s1>, Figure S1: diagram of experimental device for composite crystallization, Figure S2: XPS spectra of ZIF-8@3DOM TiO₂: (a) N 1s and (b) O 1s, Figure S3: Zeta potentials of (a) 3DOM TiO₂, (b) bulk ZIF-8, (c) ZIF-8@3DOM TiO₂, Figure S4: N₂ adsorption-desorption isotherms and pore diameter distribution (inset) of (a) 3DOM TiO₂ and (b) bulk ZIF-8, Figure S5: XPS spectra of ZIF-8@3DOM TiO₂ after 5 successive cycles: (a) survey scan, (b) Ti 2p, (c) Zn 1p, (d) C 1s, (e) N 1s, and (f) O 1s.

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