to a Robust Catalytic Platform via a Novel Zirconium-Based MOF

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A Paradigm Shift in the Leather Lifecycle: Transforming Collagen into a

Robust Catalytic Platform via a Novel Zirconium-Based MOF

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Abstract

The leather industry has long faced the dual challenges of chromium pollution and solid waste management. This study proposes an innovative strategy that not only achieves chrome-free tanning by adopting a novel pH-responsive zirconium-based metal-organic framework (MOF) but also transforms waste leather into high-value functional catalysts. Firstly, by introducing a boronate ester pH-stimuli-responsive module into the ligand, a new pH-responsive MOF tanning agent is constructed. This agent maintains structural stability under neutral tanning conditions while undergoing controlled decomposition in acidic environments, thereby effectively addressing the long-standing issues of poor penetration and low utilization rate of zirconium ions in traditional zirconium tanning systems. Subsequently, by loading traditional zirconium tanning agents into the MOF framework, this study establishes a composite zirconium tanning agent with a controlled release mechanism, promoting the uniform distribution of zirconium ions within the collagen matrix. Test results show that the shrinkage temperature of the tanned leather exceeds 800C. Notably, the dispersed tanned leather can serve as an efficient heterogeneous catalyst

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for Knoevenagel condensation reactions. Thanks to the uniformly distributed zirconium active sites and the abundant amino groups derived from collagen, the catalyst demonstrates outstanding catalytic performance, maintaining a yield of over 87% through five consecutive Knoevenagel reaction cycles. This work not only provides an environmentally friendly alternative for tanning but also opens new pathways for the valorization of leather waste, achieving a complete paradigm shift from waste management to resource creation— turning waste into treasure.

1. Introduction

Collagen fibers, as a class of natural polymeric materials, are widely used in various fields such as biomedical engineering, tissue engineering, food packaging and leather manufacturing due to their excellent biocompatibility, biodegradability and ease of functional modification [1-7].

However, natural collagen fibers suffer from issues such as poor long-term stability, inferior mechanical properties, susceptibility to mold, and bacterial growth, which significantly limit their practical applications [8-12]. As a result, chemical cross-linking modification is often required to enhance their performance. In conventional

modification methods, chromium demonstrates remarkable stabilizing effects on collagen fibers, particularly in terms of high shrinkage temperature and superior mechanical strength [13-17]. Nevertheless, the chromium modification process generates wastewater containing chromium and can lead to the formation of hexavalent chromium compounds, which are highly carcinogenic, posing serious threats to both the ecological environment and human health [18-21].

Therefore, developing environmentally friendly alternatives to replace chromium-based modifying agents has become an urgent research priority. Zirconium (Zr) is widely regarded as one of the most promising alternatives to chromium, owing to its ability to form stable cross-linking bonds with collagen fibers [22-27]. However, the binding process between zirconium and collagen is excessively rapid and strong, which leads to the rapid deposition of a large amount of zirconium ions on the fiber surface, pore blockage, an uneven distribution of binding sites, and consequently, compromised modification effectiveness [2830]. Consequently, Chen et al. proposed a modification

Scheme 1. MOF based strategy for modification of collagen fibers and its catalytic application

in the Knoevenagel reaction.

strategy based on zirconium-based metal-organic frameworks (Zr-MOFs), which utilizes the masking effect of the organic ligands to moderate the binding kinetics between zirconium ions and collagen fibers, thereby improving the uniformity of cross-linking [31].

Nevertheless, conventional Zr-MOFs exhibit excessively stable structures, in which most zirconium ions remain tightly coordinated with the organic ligands. This strong bonding hinders the effective release and subsequent interaction of zirconium ions with collagen fibers, ultimately leading to low utilization efficiency of zirconium ions [32]. An alternative strategy involves utilizing the porous channels of MOFs to host conventional zirconium-based modifiers, such as zirconium tartrate complex (ZTA), leveraging the sustained-release effect of MOFs to regulate the binding behavior between zirconium ions and collagen fibers. However, the release kinetics of conventional MOFs are typically characterized by undesirably slow diffusion rates, which complicates the achievement of controllable release and significantly limits their production efficiency in modification of collagen fibers.

In recent years, researchers have attempted to incorporate stimulus-responsive switch into MOFs to achieve controlled release in response to external triggers. For instance, Wang et al. grafted a styrylpyrene photoswitch onto amino-functionalized MIL-53, constructing a light- controlled ammonia-release hydrogel system based on a [2+2] photocycloaddition reaction [33].

Similarly, Hecht et al. constructed a core-shell photogated molecular system through solvent- assisted ligand exchange, engineering a shell functionalized with tetrafluoroazobenzene motifs on UiO-68 crystals to enable visible light mediated controllable guest release [34]. Despite these advances, such MOF carriers often fail to further engage effectively with collagen fibers after releasing the zirconium-based modifiers, resulting in suboptimal utilization efficiency of zirconium ions. Therefore, the development of Zr-MOFs featuring precisely tunable structural stability represents a critical research objective. A fundamental requirement for such MOFs is the ability to achieve uniform dispersion within the collagen fibers while intact, followed by controlled disintegration under specific stimuli to liberate the zirconium active sites inherent in their structure, thereby maximizing the utilization efficiency of zirconium ions. Herein, a boronic ester module was incorporated into the organic ligand, leading to the design and synthesis of a Zr-MOF designated as Zr-TB, which exhibits pH-responsive structural controllability (Scheme 1). The controlled dissociation of the framework and the subsequent release of zirconium ions can be achieved by modulating the environmental pH, thereby addressing the issue of low zirconium ion utilization efficiency in conventional zirconium-based MOFs. Subsequently, ZTA@Zr-TB was constructed by loading ZTA into the channels of Zr-TB, thereby addressing the issue of poor binding uniformity between conventional zirconium-based modifiers and collagen fibers. Furthermore, the surface of the modified collagen fibers is rich in uniformly distributed zirconium active sites, endowing them with catalytic activity that was demonstrated for the first time in the important Knoevenagel condensation reaction. Following ball milling of the modified collagen fibers, the resulting catalyst

demonstrated superior catalytic efficiency and more stable recyclability compared to traditional MOF-based catalysts, while operating without the need for alkaline additives. Collectively, this work offers a novel strategy for utilizing collagen fibers as efficient and sustainable supports, paving the way for their application as a platform for heterogeneous catalysis.

2. Materials and methods

2.1 Materials

L-(+)-tartaric acid, DL-tartaric acid, anhydrous zirconium chloride ($ZrCl_4$), 4-boronobenzoic acid, calcium hydride was purchased from Macklin Biochemical Co., Ltd. Formic acid (HCOOH), sodium bicarbonate ($NaHCO_3$), sodium hydroxide (NaOH), acetonitrile (CH_3CN), anhydrous ethanol (C_2H_5OH) and anhydrous tetrahydrofuran (THF) were obtained from Energy Chemical Co., Ltd. The collagen fibers were derived from pickled goatskins (about 0.8 mm thick)were commercially available.

2.2 Synthesis of Modifier for Collagen Fibers

In a flame-dried flask equipped with a reflux condenser and pressure equalizing addition funnel under argon atmosphere, 4-carboxyphenylboronic acid (1 mmol, 1.0 equiv.), L-(+)- tartaric acid (1 mmol, 1.0 equiv.), and anhydrous THF (15 mL) were charged sequentially. The reaction vessel was purged with argon via three vacuum argon cycles. Subsequently, The mixture was heated to 50°C with vigorous stirring for 30 minutes. Meanwhile, calcium hydride (2.5 mmol, 2.5 equiv.) and anhydrous CH3CN (3 mL) was added. Then, the reaction was maintained at 50°C for 12 hours. Afterwards, the reaction mixture was cooled to room temperature and filtered through a sintered glass funnel (pore size 10-16 μm) to remove insoluble precipitates. The filtrate was concentrated under reduced pressure and purified by flash column chromatography on silica gel using ethyl acetate/ petroleum ether (1:4 v/v) as eluent to afford product TB.

TB (1 mmol, 1 equiv.) and anhydrous ZrCl4 (1 mmol, 1 equiv.) were dissolved separately in DCE (150 mL) by using ultrasonic. Afterwards, the two liquids were mixed and transferred to a hydrothermal reactor, which was heated at 1400C for 48 hours. After the reaction was completed, the reaction mixture was separated by a centrifuge, the supernatant was discarded, and the solid component was washed three times with DCE. Finally, the solid component was heated at 800C for 24 hours to obtain a off-white powder of Zr-TB. Anhydrous ZrCl4 (1 mmol, 1 equiv.), DL-tartaric acid (2 mmol, 2 equiv.), and anhydrous ethanol (20 mL) were successively added to a dried flask equipped with a condenser reflux setup. The mixture was stirred at 60°C for 5 minutes. Subsequently, NaOH solution in ethanol was slowly added dropwise over 2 hours to adjust the pH to 7.5, and the reaction was continued for 4 hours. Upon completion, the solvent was removed from the mixture under reduced pressure by rotary evaporation, yielding a white powder. This powder was further dried at 80°C for 6 hours to obtain the final product, zirconium tartrate complex (ZTA). Zr-TB (1 mmol 1 equiv.) and ZTA (6 mmol, 6 equiv.) were added to a mixture of THF/ H2O (30 mL, v/v=3:1), and the suspension was dynamically loaded on a water bath shaker for 6 hours. After completion, the mixed solution was distilled under reduced pressure to remove the solvent and dried at 1000C for 12 hours to obtain ZTA@Zr-TB.

2.3 Characterization of Modifier for Collagen Fibers

The FT-IR spectrum of Zr-TB was obtained by infrared spectrometer Invenio (Bruker,Germany). The precise chemical structure of TB was analyzed by using 400MHz nuclear magnetic resonance spectrometer (QOne China). The XRD spectrum of Zr-TB was obtained by X-ray diffractometer D8 Advance (Bruker, Germany). The specific surface area and pore size of Zr-TB were investigated by using surface area analyzer (Micromeritics, USA). The elemental and chemical bond types of Zr-TB were analyzed by using X-ray Photoelectron Spectroscopy AXIS SUPRA (Kratos, UK). The microstructure of Zr-TB was captured by emission

scanning electron microscopy (SEM, ZEISS SIGMA 300, Germany). The XRD spectrum of ZTA@Zr-TB was obtained by XRD. The TG curve of ZTA@Zr-TB was obtained by thermogravimetric analyzer TGA-55 (Discovery, USA), and its release behavior in different pH value was investigated by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Bovei China).

2.4 Study on the acid-base stability of Zr-TB

The standard solutions of HCOOH, NaHCO3, Na2HPO4, and NaH2PO4 were prepared by using ultrapure water, and pH adjusters were used to prepare standard solutions (10 mL) with pH=2, 3, 4, 5, 6, 7, 8, and 9, respectively. Subsequently, Zr-TB (100 mg) was placed in standard solutions and allowed to stand for 12 hours. After completion, the standard solutions of Zr-TB suspension was centrifuged to collect the solid, and residual moisture was removed by freeze drying. Finally, the structure of the dried solid was characterized by SEM and XRD.

2.5 The process of modifying collagen fibers

The pickled skin was cut to the appropriate size and placed in a drum containing NaCl aqueous solution (8 Baume degrees, 250% pickled skin weight). After rotating the drum at room temperature for 15 minutes, the pH value of the bath was around 5.5. Then, NaHCO3 was continuously added to the bath until the pH value reached 7. Subsequently, the modifier was added to the drum and allowed to rotate continuously for 4 hours. Then, the pH was gradually adjusted to 4 by using formic acid over a period of 2 hours. Finally, the heater was turned off and the drum was left to stand overnight to facilitate sufficient binding between the modifying agent and the collagen fibers. Finally, the heater was turned off and the drum was left to stand overnight to promote sufficient binding between the modifier and the collagen fiber. On the following day, remove the modified collagen fibers from the drum and wash it with pure water.

2.6 Evaluation of the performance of modified collagen fibers

The shrinkage temperature (Ts) of collagen fibers is an important indicator to reflect their hydrothermal stability. The Ts of modified collagen fibers were tested by using the shrinkage temperature tester MSW-YD4. In order to further investigate the modification effect of collagen fibers, the surface and sectional morphology were captured by using super depth of field microscope (Keyence, Japan) and SEM, and the distribution of zirconium ions was investigated by using energy dispersive spectroscopy (EDS). Moreover, the softness of collagen fibers were tested by using softness tester NBC-7124 (TST, China), and their thickness changes were measured by using thickness gauge GB8949 (MZHU China). On the other hand, in order to evaluate the physical and chemical properties of collagen fibers, their tensile strength, tear strength, and breaking elongation were tested by using digital rupture strength tester TX031 (TST, China), and their chemical stability was investigated through trypsin degradation experiments.

2.7 Study on the interaction mechanism between modifiers and collagen fibers

In order to investigate the interaction mechanism between the modifier and collagen fibers, the integrity of the triple helix structure of collagen fibers were analyzed by using XRD and FT-IR. Meanwhile, in order to investigate the changes in the charge properties of collagen fibers, the zeta potential of collagen fibers were tested by using laser particle size analyzer (Mastersizer, UK). In addition, the elemental content and chemical bond types of collagen fibers were analyzed by using XPS.

Furthermore, the binding mechanism between zirconium cluster complex generated by Zr-TB decomposition and collagen fibers was further analyzed through density functional theory (DFT) calculation technology. All calculation results are implemented through CP2K code [35-36]. The electronic structure was described and optimized by using a hybrid basis set approach combining

Gaussian-type orbitals with plane waves. Core electron interactions were approximated by GTH pseudopotentials under the norm-conserving formalism [37]. The valence electrons wavefunction was expanded through a polarized double-zeta basis set (DZVP) and a complementary plane-wave basis with 450 Ry energy cutoff [38]. The generalized gradient approximation exchange-correlation effects were treated with the Perdew, Burke, and Enzerhof (PBE) [39].

All configuration was optimized by using Broyden Fletcher Goldfarb Shanno (BGFS) algorithm with SCF convergence criteria of 1.0×10-5 au. The adopted Grimme DFT-D3 model was corrected by van der Waals [40].

2.8 The process of Knoevenagel reaction

A dry round-bottom flask was charged with benzaldehyde (0.2 mmol, 1.0 equiv.), malononitrile (0.2 mmol, 1.0 equiv.), and the heterogeneous catalyst (20 wt% relative to the substrate). Methanol (5 mL) was added, and the mixture was stirred at room temperature for 4 hours. Upon completion, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 30:1) to afford the Knoevenagel product.

A dry round-bottom flask was charged with acetophenone (0.2 mmol, 1.0 equiv.), malononitrile (0.2 mmol, 1.0 equiv.), and the heterogeneous catalyst (20 wt% relative to substrate). Ethanol (5 mL) was added, and the mixture was stirred at 75°C for 4 hours. Upon completion, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 50:1) to afford the Knoevenagel product.

3. Results and discussion

3.1 Characterization of Zr-TB

The boronic ester functionalized ligand TB was synthesized via dehydration condensation between 4carboxyphenylboronic acid and DL-tartaric acid, and

its structure was characterized by 1H NMR. As shown in Figure 1a, the double peaks at 7.75 ppm and 7.78 ppm are attributed to the unsubstituted hydrogen signal in benzene, while the single peak at 4.32 ppm is attributed to the alkyl hydrogen signal in boronic acid esters. In addition, due to proton exchange with DMSO-d6, no carboxyl hydrogen signal was detected.

Subsequently, Zr-TB was synthesized by solvothermal method and its functional group structure was analyzed by fourier transform infrared spectroscopy (FT-IR). As shown in Figure 1b, the absorption peaks at 1114 cm-1 and 1409 cm-1 are attributed to the stretching vibrations of CB and O-B bonds, respectively, confirming the successful

Fig. 1. (a) 1H NMR of TB, (b) FT-IR of Zr-TB, (c) N2 adsorption/desorption isotherms of Zr-TB, (d) XPS

spectra of Zr-TB, (e) XRD pattern of Zr-TB at different pH values, (f-i) high-resolution XPS spectra, and (j)

SEM micrographs of Zr-TB at different pH values.

incorporation of boron element [41].

Concurrently, no significant -OH absorption peak was observed in the region above 3000 cm-1, while the C-H stretching vibration peak of alkanes was detected at 2823 cm-1 [42]. These results demonstrate the structural integrity of the boronated ester in the ligand, and without decomposition under high temperature and high pressure reaction conditions. Moreover, the peaks at 1356 cm-1 and 1613 cm-1 are attributed to the symmetric and asymmetric stretching vibrations of the carboxyl C-O in the TB ligand, respectively. The absorption peak at 777 cm-1 is attributed to the vibrational signal of the Zr-(μ3)- O coordination bond in Zr-TB, proving the formation of zirconium-oxo cluster.

Zr-TB 622.69 384.46 0.16 2.78

a SBET is the Brunauer Emmett Teller (BET) specific surface area. b SMirco is the specific surface area of micropores calculated by the t-plot method. c VMirco is the volume of micropores calculated by the t-plot method. d Average pore diameter is the adsorption average pore size determined by BET method.

Furthermore, the specific surface area and pore structure of Zr-TB were analyzed through N2 adsorption/desorption tests at 77 K (Table 1). As shown

Table 1 : Pore features of Zr-TB

b VMirco(cm

2/g)

a SMirco(m

2/g)

Sample SBET(m

As shown in Figure 1d, the elemental composition of ZrTB was qualitatively analyzed by X- ray photoelectron spectrometer (XPS), and the chemical bonding states of constituent elements were investigated by using high resolution XPS spectra. As shown in Figure 1f, the high resolution XPS spectrum of Zr 3d displays two characteristic peaks at 182.6 eV and 180.2 eV, corresponding to Zr 3d 3/2 and Zr 3d 5/2 of Zr-TB, respectively [44]. Deconvolution analysis reveals peaks at 180.1 eV and 182.5 eV attributed to Zr-OH, and peaks at 180.9 eV and 183.5 eV attributed to COO-Zr coordination. These results confirm the existence of zirconium secondary Building units (SBUs). Figure 1g shows the high resolution XPS spectrum of C 1s, which was deconvoluted into multiple peaks corresponding to C=O (288.6 eV), C-O (286.0 eV), C-C/C-H (284.8 eV), and C-B (286.3 eV). The high-resolution B 1s XPS spectrum (Figure 1h) was deconvoluted into two peaks at 197.9 eV and 196.8 eV, corresponding to BO and C-B bonds, respectively [45]. Additionally, the high-resolution O 1s XPS spectrum was deconvoluted into multiple peaks corresponding to C=O (530.7 eV), C-O (529.8 eV), B-O (529.3 eV), and Zr-O (528.7 eV), providing further evidence for the presence of boronate ester structures in Zr-TB (Figure 1i).

The microstructure of Zr-TB was characterized by SEM,

revealing that Zr-TB is an octahedral crystal with sizes

in Figure 1c, Zr-TB exhibits a characteristic Type I adsorption isotherm, which is typical of microporous materials [43].

c Average pore diameter (nm)

3/g

-1)

d

ranging from 80 to 300 nm (Figure S1). The X-ray diffraction (XRD) results showed that the diffraction peaks of Zr-TB were mainly at 13.1° and 13.9° (Figure S2). Based on this, the acid-base stability of Zr-TB was further investigated by XRD. As shown in Figure 1e, Zr-TB maintains sharp diffraction peaks after aqueous treatment at pH 7, demonstrating remarkable retention of both MOF structural integrity and crystallinity.

As the pH value of the aqueous solution gradually decreases, the characteristic diffraction peaks of Zr-TB exhibit continuous attenuation. These peaks essentially disappeared below pH 4, indicating complete structural decomposition of the MOF framework, confirming an inverse correlation between aqueous phase stability and proton concentration for Zr-TB. This result was further confirmed through SEM. As shown in Figure 1j, Zr-TB maintains its octahedral crystal structure in aqueous environments at pH 7.

As the pH decreases, Zr-TB progressively transformed into irregular polyhedra with pronounced particle agglomeration, demonstrating both increased defect density and diminished structural stability in the MOF. The morphology of Zr-TB transformed into irregular spherical structures upon decreasing the aqueous pH below 4, confirming the essential collapse of the MOF architecture. In addtiton, exposure to alkaline conditions (pH 8) triggered instantaneous dissolution of Zr-TB, and no precipitate observe

≥

after centrifugation, demonstrating its poor alkaline stability.

3.2 Characterization of ZTA@Zr-TB

The XRD results are shown in Figure 2a. The diffraction peaks of ZTA are mainly at 32.1° and 45.8°, while the ZTA@Zr-TB exhibits distinct diffraction peaks at 32.2° and 45.7°, confirming the successful loading of ZTA [46].

The thermal stability of Zr-TB before and after loading was investigated by thermogravimetric analysis (TG). As shown in Figure 2b, the thermal weight loss in the first stage is mainly caused by the evaporation of solvents such as DCE, HCOOH, and water [33].

As the temperature further increases, Zr-TB enters the second stage of thermal degradation, which is mainly caused by the decomposition of MOF structure. After the end of the second stage, the residual components are mainly ZrO2 and carbides [47]. By the way, ZTA@Zr-TB demonstrates a higher carbon residue content (47.3% and

Fig. 2. (a) XRD patterns of ZTA@Zr-TB and ZTA, (b) TG curves of samples, (c) Controlled release performance of Zr-TB, (d-f) Ts of collagen fibers, (g) the softness and the thickening rate, (h) trypsin degradation,

and (i) the physical properties.

42.4% at 600°C) compared to the Zr-TB, which can be rationally attributed to the thermal decomposition of highdensity ZTA clusters yielding additional ZrO2.

Furthermore, the release behavior of Zr-TB was investigated by inductively coupled plasma- atomic emission spectrometry (ICP-AES).

As shown in Figure 2c, in an aqueous solution at pH 7, the concentration of zirconium ions was 16.7 mg/L, primarily attributed to the slight dissolution of ZTA adsorbed on the surface of Zr-TB and the trace release of ZTA caused by structural defects in Zr-TB.

As the pH decreases, the concentration of zirconium ions in the solution gradually increased. With the pH drops to 4, the concentration of zirconium ions in the aqueous solution surged dramatically, demonstrating rapid decomposition of Zr-TB with the pH of 4. However, further reduction in pH did not lead to significant changes in concentration of zirconium ions, indicating that the basically decomposition of Zr-TB.

3.3 Performance of modified collagen fibers

The hydrothermal stability of modified collagen fibers was evaluated by using the shrinkage temperature (Ts) as an indicator. As shown in Figure 2d, the collagen fibers modified by Zr-TB (Zr-TB MC) reached their maximum Ts (71.5°C) in a pH 7 bath solution, indicating that Zr-TB maintains structural stability in the neutral pH environment, making it more conducive to penetrating into the interior of collagen fibers, which consistent with the above research results.

On the contrary, ZTA has the best modification effect in a pH 2 bath solution (Ts =75.70C), because the high proton concentration in the acidic bath inhibits the ionization of - COOH in collagen fibers, thereby avoiding excessive binding with ZTA. However, at a pH of 7 in the bath, The Ts of the collagen fibers modified by ZTA@Zr-TB (ZTA@Zr-TB MC) reached 80.40C (Figure 2f), which is better than the effect of modifying them separately, proving the defect of excessive binding between ZTA and collagen fibers has been improved.

To investigate the sensory properties of modified collagen fibers through thickening rate and softness testing. As shown in Figure 2g, the ZTA@Zr-TB MC exhibits comparable softness to ZTA MC, and the thickening rate is significantly higher, indicating the bundles of ZTA@Zr-

Fig. 3. (a-c) The ultra-depth optical microscopy graphs of the of collagen fibers, (d-f) the SEM micrographs of

collagen fibers.

TB MC possess a more loosely organized structure with enhanced crosslinking efficiency. The chemical stability of modified collagen fibers was analyzed through enzyme degradation experiments. As shown in Figure 2h, the residual mass of pickled skin treated with trypsin was 62.5%, while the residual mass of collagen fibers modified by ZTA (ZTA MC) was significantly improved (84.5%). This is because the ZTA forms a stable cross-linked

network in collagen fibers, inhibiting the enzymatic hydrolysis of collagen fibers. In addition, the residual mass of ZTA@Zr-TB MC reached 88.5%, indicating stronger stability of the cross-linked network. The physical and mechanical properties of modified collagen fibers were investigated by testing tensile strength, elongation at break, and tensile strength. The results indicate that the physical and mechanical properties of ZTA@Zr-TB MC have been improved compared to ZTA. The surface morphology of modified collagen fibers was observed by using super depth of field microscope. As shown in Figure 3a, the pickled skin surface is relatively smooth. On the contrary, the surface of ZTA MC exhibits convergence, indicating that ZTA formed crosslinking bonds between collagen fibers (Figure 3b) [48]. However, the pores on the surface of ZTA MC are indistinct, attributable to rapid binding leads to excessive ZTA accumulation and pore blockage. In contrast, ZTA@Zr-TB MC exhibits superior convergence, and with clearly observable pores, demonstrating more homogeneous fiber crosslinking.

3.4 Modification mechanism of collagen fibers

The sectional morphology of modified collagen fibers was characterized by SEM. As shown in Figure 3d, the fibers in the sectional of the pickled skin exhibits densely packed, which is due to the fiber bonding phenomenon caused by the lack of crosslinking. In contrast, the modified collagen fibers displays significantly larger gaps, resulting from

Fig. 4. (a) Distribution of zirconium elements, (b) XRD patterns of collagen fibers, (c) FT-IR spectra of

collagen fibers, (d-h) high-resolution XPS spectra of samples, and (i) zeta potentials of collagen fibers.

The integrity of triple helical structure of ZTA@Zr-TB MC was investigated by using XRD. As shown in Figure 4b, no characteristic peaks of Zr-TB were detected in ZTA@Zr-TB MC, indicating complete decomposition of Zr-TB. Meanwhile, the diffraction peak at 7° corresponds to the lateral intermolecular distance between the constituent fibrils of collagen, while the diffraction peak

the cross-linked network effectively reduces fiber packing density. It is obvious that the ZTA@Zr-TB MC demonstrates looser fiber organization compared to ZTA MC (Figure 3e-3f), indicating a more uniform distribution of crosslinking bonds between zirconium ions and collagen fibers [34]. This observation is further confirmed by the Line Scan of Energy-Dispersive X-ray Spectroscopy (EDS) analysis (Figure 4a).

at 20° represents the diffuse scattering peak caused by the multi-level structural hierarchy within the collagen fibers. On the other hand, FT-IR analysis detected two broad peaks at 3367 cm-1 and 2921 cm-1, which are attributed to the amide A and amide B bands, respectively.

Additionally, multiple peaks at 1631 cm-1, 1541 cm-1,

and 1226 cm-1 were observed, corresponding to the amide I, II, and III bands (Figure 4c). These results collectively confirm the intact triple helical structure of the ZTA@ZrTB MC [49].

Further investigate the binding mechanism between ZTA@Zr-TB and collagen fibers was conducted through XPS. As shown in Figure 4d, the binding energy of the -COO-Zr bond in ZTA@Zr-TB MC increased by 0.4 eV compared to Zr-TB, while the binding energy of the C-O bond decreased by 0.3 eV relative to pickled skin (Figure 4e) [50]. These results confirm the presence of coordination crosslinking between zirconium ions and the -COOH of collagen fibers. Nevertheless, the binding energy of the C-N bond decreased by 0.1 eV, proving crosslinking interactions between zirconium ions and the -

Fig. 5. DFT calculation of the binding mechanism between decomposed Zr-TB and collagen fibers.

Density functional theory (DFT) calculations were employed to investigate the binding mechanism between the zirconium cluster complex generated by Zr-TB decomposition and collagen fibers. The DFT calculations results (Figure 5) demonstrate that the ligand exchange reaction between zirconium cluster complex and the -NH2 of peptide requires an activation energy of +289.43kJ/mol, corresponding to

NH2 of collagen fibers simultaneously (Figure 4g).

Moreover, as shown in Figure 4h, the binding energy of the B-O bond in ZTA@Zr-TB MC exhibits a significant decrease compared to Zr-TB, indicating an increased electron density in its chemical environment. It is speculated that the dehydration condensation between multiple aromatic boronic acids generated by the decomposition of Zr-TB formed boroxane. The zeta potential of ZTA@Zr-TB MC was investigated through laser particle size analyzer. As shown in Figure 4i, the isoelectric point of ZTA@Zr-TB MC exhibits a significant increase (pI=6.16) compared to pickled skin (pI=5.67), confirming the coordination between zirconium ions and the -COOH of collagen fibers, which consequently reduced the negative charge density of the collagen fibers

anendothermic process, which is thermodynamically unfavorable. Conversely, the ligand exchange with the -COOH of peptide exhibits a negative binding energy of -42.96 kJ/mol, indicating a thermodynamically favorable

exothermic process. These results establish that the zirconium cluster complex generated by Zr-TB decomposition preferentially coordinates with the -COOH of collagen fibers.

3.5 Catalytic properties of modified collagen fibers

It is widely recognized that the Knoevenagel reaction is frequently utilized to construct C=C bonds, representing a fundamental organic transformation for the production of -unsaturated compounds used in fine chemicals, functional materials, and natural products [51-54]. As shown in Figure 6a, the catalytic performance of ZTA@Zr-TB MC was evaluated through the Knoevenagel reaction between aromatic aldehydes and ketones. Considering the abundant -NH2 present in the collagen fibers, which facilitate the deprotonation of active methylene compounds to form nucleophiles, no additional base was added to the reaction system. Simultaneously, the zirconium ions uniformly distributed on the collagen fiber were able to coordinate with the carbonyl groups of the substrates, thereby activating the carbonyl groups and making them more susceptible to nucleophilic attack (Figure 6b). The reaction results demonstrated that when ZTA@Zr-TB MC

α, β

was employed as the catalyst, the highly reactive aldehyde substrate was efficiently converted at room temperature with a yield of 96.3%, while the less reactive ketone substrate was converted at 75°C with a yield of 74.4%. After five catalytic cycles, the reaction yields were maintained at 87.2% and 57.5%, respectively, confirming its excellent cycling stability (Figure 6c). As shown in Figure 6d, the amino-modified UiO-66 (UiO-66-NH2) demonstrated catalytic performance comparable to ZTA@Zr-TB MC. This comparable activity can be attributed to the amino groups in UiO-66-NH2, which facilitate deprotonation of active methylene compounds similarly to the amino groups in collagen fibers [55]. In contrast, pure collagen fibers alone showed negligible catalytic activity. Furthermore, when ZTA@Zr-TB was used without the integrated active sites, the reaction yields for aldehyde and ketone substrates were only 53.4% and 13.1%, respectively. These results confirm that the synergistic catalytic effect between components significantly enhances the Knoevenagel conversion efficiency.

Fig. 6. (a) Knoevenagel reactions catalyzed by ZTA@Zr-TB MC, (b) schematic diagram of the synergistic catalytic mechanism of ZTA@Zr-TB MC, (c) recyclability test of catalysts, (d) comparative catalytic efficiency among various catalysts, (e-f) scale-dependent catalytic efficiency experiments, (g-h) NMR spectrum of the aldehyde substrate, (i) monitoring the time course of the catalytic reaction for aldehyde substrates, (j-k) NMR spectrum of the ketone substrate, (l) monitoring the time course of the catalytic reaction for ketone substrates.

Scale-up experiments comparing ZTA@Zr-TB MC with UiO-66-NH2 demonstrated the superior scalability of the former. When the reaction scale was increased from 2.5 mmol to 10 mmol, the yield reduction for aldehyde and ketone substrates catalyzed by ZTA@Zr-TB MC was only 8.1% and 11.2%, respectively, significantly lower than the 13.5% and 20.9% observed with UiO-66-NH2 (Figures 6e and 6f). This result highlights the greater potential of ZTA@Zr-TB MC for industrial application.

The structures of both products were verified by NMR spectroscopy (Figures 6j, 6h, 6j, and 6k) [56-57]. Furthermore, kinetic studies revealed that ZTA@Zr-TB MC achieved maximum yields in 90 minutes for aldehyde substrates and 210 minutes for ketone substrates, while UiO-66-NH2 required 180 minutes and 240 minutes respectively (Figures 6i and 6l). These results demonstrate the faster reaction rate and higher catalytic activity of ZTA@Zr-TB MC in the Knoevenagel condensation.

4. Conclusion

In summary, Zr-TB exhibits both definitive MOF structural characteristics and remarkable capacity of controllable structural stability by pH responsive. The ICP-AES results demonstrate that Zr-TB loaded with ZTA exhibits favorable controlled release properties based on its pH responsive characteristics, enabling ZTA to be successfully delivered into the interior of collagen fibers and efficiently released by disassembling the Zr-TB carrier through simple pH regulation.

Meanwhile, the ZTA@Zr-TB MC exhibit excellent hydrothermal stability, enzyme degradation resistance, and mechanical properties, effectively improving the problem of pore blockage caused by poor uniformity of binding between ZTA and collagen fibers. Notably, the DFT

calculation results indicate that the zirconium cluster complex generated by Zr-TB decomposition can also bind with the -COOH of collagen fibers, thereby further improving the utilization rate of zirconium ions. Zr-TB has shown great potential in the green modification of collagen fibers and is expected to create application value in more controlled release demand fields.

Furthermore, the ZTA@Zr-TB MC was ball-milled into a powder and employed as an effective catalyst for the Knoevenagel reaction. It exhibited high conversion rates for both aldehyde and ketone substrates, along with a

simple catalytic system, excellent recyclability, and robust catalytic stability. These results demonstrate the potential of collagen fibers as a support for heterogeneous catalysts.

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