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REVIEW **Open Access**

Insights into functional polymer-based organic-inorganic nanocomposites as leather finishes

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Abstract

Nowadays, the increasing demands from consumer challenges the traditional leather products. Traditional polymer leather finishes gradually lose their dominant position in the market. To address this issue, recent research effort has been devoted to developing polymer-based organic-inorganic nanocomposite leather finishes due to their various functional properties including antibacterial, self-cleaning and water-resistant property. In this review, we provide a comprehensive overview of synthesis of polymer-based organic-inorganic nanocomposites and their application as functional leather finishes. With the perspective of their properties and current challenges, an outlook in the future development about crafting functional and high-quality leather finishes are further proposed.

Keywords: Organic-inorganic nanocomposites, Polymer, Functional leather finishes

1 Introduction

In leather industry, crafting coatings on leather surface is known as finishes. In this process, binders, pigments, auxiliaries, etc. are applied onto the surface of leather. Finishing has been recognized as one of the most essential processes in leather making industry, moreover, finishing agents could not only beautify leather appearance, but also render leather good mechanical properties in a simple way [1–5]. Nowadays, the increasing demands from consumer challenges the traditional leather products. Therefore, functional finishing agent has sparked strong interests in leather industry. In daily life, the long-term contact of clothes (for example, garment leather) with human body may result in a rapid growth of bacteria and fungi, thus greatly reducing the value of leather product [6]. To solve this problem, antibacterial coatings have been crafted on leather surface.

To date, a set of functional properties, such as self-cleaning, water-resistant, antibacterial properties, and so on, has been obtained via finishing technology on leather surfaces [7–13]. Generally, finishing agents are composed of polymers, which possess good film-forming properties. Among organic components, polyacrylates, polyurethane (PU) and casein have attracted much attention due to their special behavior as film-formers [4, 14–19]. However, pristine polymer binders only exhibit basic performance (e.g., adhesive property), which cannot meet the increasing demand of markets. As reported, inorganic units, especially several nanoparticles are responsible for outstanding thermal stability, mechanical properties, and other functions. Thus, combination of the polymer binder and inorganic nanoparticles together may be a good choice to acquire a set of intriguing functions. Therefore, exploration for functional organic-inorganic nanocomposite finishing agents is indeed necessary.

Organic-inorganic nanocomposites possess the advantages of organic and inorganic constituents to achieve excellent properties [20–24]. In leather processing, nanocomposite was firstly employed as tanning agents, while the report about its application in leather finishing was found started in the early twenty-first century [25]. They incorporated nano TiO_2 into polyacrlate emulsion, and then applied the composite emulsion on leather surface, which proved that mechanical and hygiene property of the finished leather are both enhanced. Since then, studies on organic-inorganic nanocomposite leather finishes have been gradually released. Nano SiO_2,

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TiO_2, graphene oxide, etc. have been introduced into various polymer matrixes via different methods, thus functionalizing leather surfaces.

In 2006, nano-SiO_2/acrylic resin nanocomposite was fabricated as leather finishes via in situ method in our group [26]. Compared with leather sample finished with acrylic resin, water-vapor permeability and air permeability of nanocomposite finished leather were increased by 7.42% and 7.33%, respectively. Furthermore, dry-wet rub fastness of the nanocomposite finished leather was raised by 1 grade, which resulted from the presence of inorganic phase to large extent, of course, superior distribution of inorganic nanoparticles in polymer matrix was of great importance. Up to now, in our group, fabrication and application of organic-inorganic nanocomposite leather finishes have been conducted for more than 10 years. For example, silica, TiO_2 and ZnO nanoparticles have been separately introduced into polyacrylate or casein matrix via various methods for leather finishing. Film-forming models and inter-facial interaction mechanism of the composite leather finishes were also established which may be of great significance for further study [27–29]. This review mainly gives an overview of synthesis of these polymer-based organic-inorganic nanocomposites and their application as functional leather finishes. Accordingly, research outlooks in this aspect are proposed.

2 Synthesis of polymer-based organic-inorganic nanocomposites

Since nanocomposites have attracted more and more interests, various routes are designed to engineer materials, for example, to integrate the superiority of nanoparticles and polymers. The integration of polymer matrix with inorganic nanoparticles can be carried out in many ways, which were summarized in the following.

2.1 Sol-gel processing

Sol-gel processing is recognized as the first method in fabrication of polymer-based organic-inorganic nanocomposites, which has been explored for more than two decades [30, 31]. Interpenetrating networks between inorganic and organic phases can be observed in the nanocomposite prepared by sol-gel processing, which endow nanocomposites with good compatibility. Epoxy resin/SiO_2 hybrid coatings were fabricated through photo-polymerization, where SiO_2 nanoparticles were generated via sol-gel process [32]. Good compatibility between the organic and inorganic units can be confirmed by atomic force microscope (AFM) measurement (Fig. 1). Functionalized graphene/PU nanocomposite coatings were prepared via sol-gel method [33]. Organosilanes were used for the functionalization of graphene. Addition of the functionalized graphene in PU coatings promises improved mechanical and thermal properties, which was mainly attributed to the well-dispersed graphene in polymer matrix.

In our previous study, acrylic resin/SiO_2 nanocomposite was prepared by integrating nano-SiO_2 sol gel with acrylic resin [34]. Results indicated that incorporation of nano-SiO_2 sol gel into acrylic resin matrix facilitates the compatibility between two phases, thus further improving the stability and water resistance of the as-prepared composite coating.

2.2 Blending

Combining nanoparticles with polymer matrix to form nanocomposites has been explored for decades, while

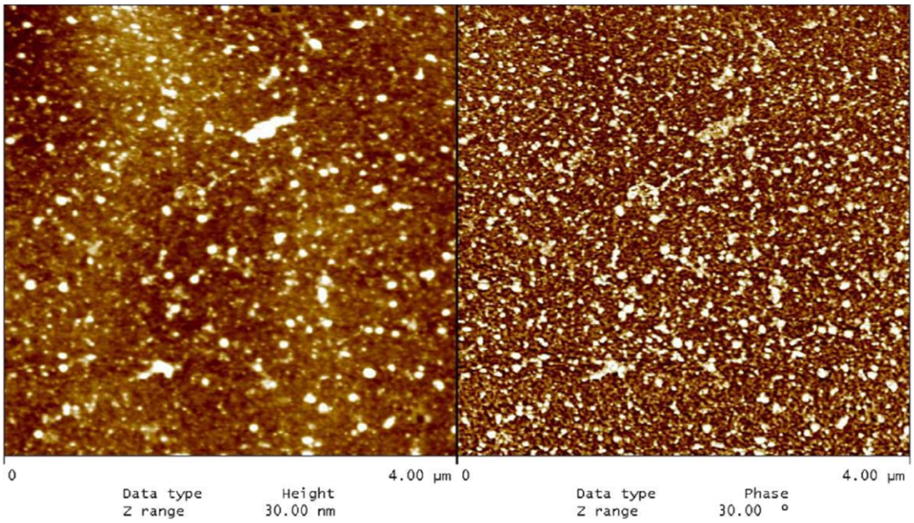

Fig. 1 AFM topography (left panel) and phase contrast image (right panel) for the functionalized graphene/PU hybrid coatings containing 50% TEOS[32]. Copyright 2005, Elsevier

blending is recognized as the most facile and direct approach [35]. Blending can be accomplished by several ways, including mechanical blending, melt blending, solution blending or emulsion blending, which mainly depends on the nature of polymer [36–38]. Nowadays, blending method has been extensively employed in the industry by relatively wider acceptance of inorganic particles with various shapes, sizes, or characters [35]. As for melt blending, although it can be done rapidly with facile polymer extrusion processes, it has been rarely used for water-based system. Regarding economic and environmental limitation, solvent-based processes were not accepted to produce composite materials. Of course, it is not suitable for leather finishing. Therefore, water-based emulsion blending holds much promise in fabricating polymer-based organic-inorganic nanocomposite for leather finishes.

Graphene has attracted extensive scientific interest due to its excellent physical properties. Waterborne polyurethane (WPU)/grapheme oxide (GO) complex leather finishes were prepared by mixing WPU and GO under ultrasonic treatment (Fig. 2) [39]. The results indicated that adding sodium dodecyl sulfate could improve the dispersion of GO nanosheets in WPU. To further improve the dispersion of GO in polymer emulsion, GO was modified by carboxylation with bromoacetic acid [40]. Results indicated that such hydrophilic modification of GO helped improve its dispersion in polymer emulsion. In addition, acrylic resin/nano TiO_2 nanocomposite was obtained by blending, where it was found that sodium hexametaphosphate can be used as a dispersing agent to reduce surface energy of nanoparticles, thus giving well-dispersion of nano TiO_2 in acrylic resin [41].

In our group, a series of functional nanocomposites has been developed via emulsion blending. Meanwhile, different shaped nanoparticles were fabricated and blended with polyacrylate, PU or casein emulsion. It's found that surface modification of nanoparticles can facilitate their well-dispersion in polymer matrix. For example, we prepared amino-functionalized graphene oxide (NGO) and blended it with polyacrylate emulsion. As is known, amino group is hydrophilic, so it can help the dispersion of NGO in aqueous solution or latex. Results showed that polyacrylate based NGO composite leather finishes exhibited enhanced thermal stability [42].

2.3 In situ method

In situ method has been adopted as the most efficient way to produce nanocomposite with good stability, in which nanoparticles are well-dispersed in polymer matrix. There are three common ways to obtain nanocomposite via in situ method: 1) in situ growth of nanoparticles in polymer matrix; 2) in situ polymerization of polymer in the presence of pre-formed nanoparticles; 3) double in situ method, consisting of the simultaneous generation of polymer matrix and nanoparticles, as described in the following.

2.3.1 In situ growth of nanoparticles in polymer matrix

In this method, nanoparticles are generated from precursors, while polymer matrix is pre-formed. In situ preparation of nanoparticles can be conducted by various ways, including acid/alkali-induced hydrolysis, chemical reductions, and photo-reductions. Goyal, et al. demonstrated a one-step approach for crafting polydimethylsiloxane (PDMS)/noble metal nanoparticle composite films [43]. Metal salts (Ag, Au and Pt), silicone elastomer, and the hardener (curing agent) were mixed to form a homogenous mixture. Then coatings were crafted by curing. In curing process, the hardener plays double roles: crosslinking the elastomer and reducing metal salts to produce nanoparticles. In this study, reducing or stabilizing agent was avoided, meanwhile, an even distribution of nanoparticles in PDMS film was observed. In Lu's group, in-situ growth of Ag nanoparticles on polydopamine (PDA)-functionalized silk was achieved via a facile and green approach [44]. Ag nanoparticles were deposited evenly on the surface of fiber, where PDA was used as reduction agent.

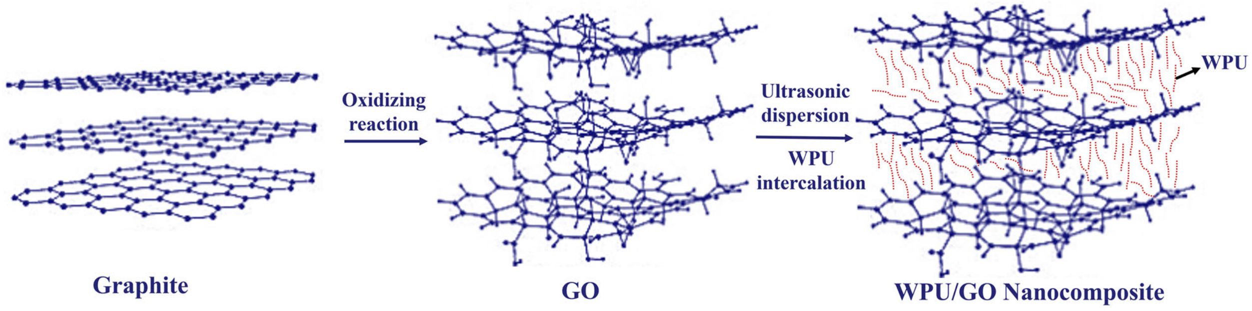

Fig. 2 Preparation of GO (**a**, graphite; **b**, GO) and WPU/GO composite (**c**) [39]. Copyright 2010, American Chemical Society

2.3.2 In situ polymerization of polymer in the presence of nanoparticles

Alternately, polymerization of monomers can be conducted around the pre-formed nanoparticles to obtain hybrid materials. In this method, inorganic nanoparticles are first dispersed in monomers, and then polymerization of monomers is processed. Homogeneous dispersion of nanoparticles can be acquired in this method due to low viscosity of monomers. Poly(methyl methacrylate)/$CaCO_3$ nanocomposites were obtained by in situ method [45]. Stearic acid capped $CaCO_3$ nanoparticles (~ 40 nm) were used as fillers. The presence of stearic acid renders $CaCO_3$ nanoparticles with hydrophobic properties, thus rendering it good compatibility with polymer matrix. Carbon nanotubes (CNT)/polymer composite films were prepared via in-situ bulk polymerization method [46]. CNT array was infiltrated with styrene monomer to prevent CNT aggregation, where polystyrene-polybutadiene copolymer was used as a plasticizer. In our group, inorganic/organic nanocomposites were fabricated utilizing synthetic or natural polymer matrix via in situ method. For example, caprolactam-casein/ZnO nanocomposite was prepared by in situ method, where commercially available ZnO nanoparticles were introduced during the condensation polymerization of caprolactam-casein [27]. Transmission electron microscopy measurements revealed that ZnO nanoperticles were incorporated in the casein micelles. Polyacrylate/ZnO nanocomposite was also crafted by this in situ method. In detail, a set of nanostructural ZnO particles have been separately introduced into polyacrylate emulsion [47]. It was noted that most of ZnO nanoparticles could be dispersed uniformly in polyacrylate emulsion, while flower-like ZnO nanoparticles exhibited their inhomogeneity in the composite emulsion.

Another approach, so called double in situ method, has been developed, in which the generation of polymer and nanoparticles was carried out at the same time. It has been accepted as the most efficient method for synthesis of polymer-based organic-inorganic nanocomposites with good stability. MgAl layered double hydroxide (LDH) was added in poly(methyl methacrylate) matrix by Chen, et al. via double in situ method [48]. The width of as-prepared MgAl LDHs is 60–120 nm and thickness is 25–40 nm, which could be dispersed evenly in PMMA matrix. In our previous work, casein-based silica nanocomposite emulsion was fabricated via double in situ method [29]. Compared with the control system (single in situ polymerization), silica nanoparticles were dispersed uniformly in the outer layer of the resultant nanocomposite films. Furthermore, polyacrylate/TiO_2 nanocomposite was prepared via double in situ polymerization [49]. Results revealed that TiO_2 particles were mainly dispersed on the outer layer of latex particles.

As described above, polymer-based organic-inorganic nanocomposites have been developed by sol-gel processing, blending, and in situ method. However, stability of the as-synthesized nanocomposites still needs to be improved, and distribution of inorganic nanoparticles in polymer matrix is difficult to be tunable, when precipitates are easily found during transportation or storage before use. Nevertheless, only uniform dispersion of inorganic nanoparticles in polymer matrix can promise the desired functional composite leather finishes. Notably, nanocomposites obtained by double in situ method showed improved stability. In this approach, in situ formation of nanoparticles during the polymerization of monomers facilitates the H-bond formation between inorganic and organic phases, thus giving good stability of resultant nanocomposite. Therefore, double in situ method holds much promise in preparing functional composite leather finishes both in the fundamental and industrial view.

3 Application of polymer-based organic-inorganic nanocomposites as functional leather finishes

3.1 Antibacterial leather finishes

As mentioned above, the long-term contact of clothes (for example, garment leather) with human body may result in a rapid growth of bacteria and fungi, thus affecting the wear feeling. In Gaidau's research, Ag-TiO_2 and Ag-N-TiO_2 nanoparticles were embedded in binders and applied in leather finishing [50]. The finished leather exhibited excellent antibacterial and self-cleaning behaviors under visible light irradiation. Additionally, in our group, polyacrylate-based ZnO nanocomposite was prepared, where PA30, an anionic polymer, was employed to modify ZnO [51]. Capping PA30 on ZnO surface endowed the finished leather with improved antimicrobial behaviors. In addition, ZnO nanoparticles with different structures were incorporated into polyacrylate binder [52]. The composite emulsion containing hollow columnar-like ZnO was applied on leather surface, and the results revealed that finished leather showed improved hygienic and antibacterial behaviors. To investigate the effect of ZnO nanoparticle structure on the performance of composite, different structural ZnO nanoparticles have been incorporated into polyacrylate emulsion [47]. Results indicated that addition of sphere-like ZnO and flower-like ZnO nanoparticles could endowed the composite films with enhanced antibacterial properties. By incorporating flower-like ZnO nanoparticles, water vapor permeability of the resultant film was boosted by 122.17%. Conversely, the addition of sphere-like ZnO nanoparticles in polyacrylate film is beneficial for enhancing it mechanical properties. Polyacrylate-based TiO_2 composite emulsion was also synthesized via double in situ method. Antibacterial properties and thermal stability of the polyacrylate film was improved by incorporating nano TiO_2 [48]. As is known, casein, a natural protein, is sensitive to bacteria. In our recent work, casein-based ZnO nanocomposite was prepared by in situ method to solve this problem [27]. ZnO nanoparticles could be found on the surface and cross-section of casein-based composite film through scanning electron microscope images. Moreover, the as-prepared films exhibited outstanding antibacterial ability against *Escherichia coli* and *S. aureus*, as shown in Fig. 3.

3.2 Water resistant leather finishes

It is well known that there are abundant hydrophilic groups in collagen-based materials, such as $-NH_2$, –COOH and -OH, so leather can be called a naturally hydrophilic material. Leather products can be easily attacked by water or bacteria. If the leather product is water resistant, the above issues can be avoided. Cu nanoparticles have been added into commonly used leather finishing agent, and then applied in leather finishing [3]. Leather finishing agent containing Cu nanoparticles was sprayed on the base and top layer. Notably, addition of Cu nanoparticles could endow leather with good wet and rub fastness, and color fastness to water due to the relative hydrophobicity of Cu nanoparticles (compared to other finishing ingredients).

In our group, acrylic resin-based SiO_2 leather finishing agent crafted by emulsifier-free emulsion polymerization was used in leather finishing [53]. Water uptake rate of leather finished by nanocomposite was increased by 17.89%. In another work, acrylic resin-based SiO_2 composite obtained by blending acrylic resin with nano SiO_2 sol-gel was applied in leather finishing [42]. Water resistance and solvent resistance of as-prepared composite finished leather were improved by 55.94% and 54.79%, respectively, compared with those of acrylic resin finished leather. Similar results can be found in polyacrylate-based nano SiO_2 composites [54]. In the study of polyacrylate-based nano SiO_2 composite leather finishes [55], it was observed that water resistance and mechanical properties of the composite film were improved in the presence of lauryl methacrylate. Additionally, in 2015, a facile layer-by layer (LBL) spraying method was employed in our group to craft superhydrophobic coatings on leather surfaces [56]. The coating was crafted by simply spraying polyacrylate emulsion and hydrophobic silica nanoparticles on leather surface, as depicted in Fig. 4. The hydrophobicity of coated leather surface could be tuned by controlling spraying layers of SiO_2 nanoparticles. This spraying method can also be used for fabricating superhydrophobic coatings on other substrates. Notably, re-spraying of hydrophobic SiO_2 dispersion can restore cracks or scratches on the coated leather surface. This method was simple to operate and cost-effective, thus holding much promise for practical applications.

3.3 Self-cleaning leather finishes

In daily life, garment surface is easily attacked by dirt. Unlike clothes made of other materials, leather garments cannot be washed directly. To address this issue, intelligent surface has been developed to modify leather surfaces. Recently, crafting self-cleaning coatings on leather surface has been explored. In this field, the commonly used method is to produce superhydrophilic coatings that prevent stains touch. As is known, intrinsic hydrophilicity and singular photocatalytic ability of TiO_2 make it a good candidate for fabricating superhydrophilic self-cleaning coatings. In Petica's work, TiO_2 nanoparticles (TiO_2 NPs) doped with N and Fe were prepared. The obtained NPs exhibited improved photocatalytic activity under visible light [57]. Doped TiO_2 NPs were embedded in acrylic binder, and then used in leather finishing. Leather finished with Fe-N co-doped TiO_2 NPs showed obvious degradation behavior for methylene blue (MB) under visible light irradiation. After 30 h of exposure to visible light, MB spots and ball pen ink lines on the leather surface were almost invisible. Water contact

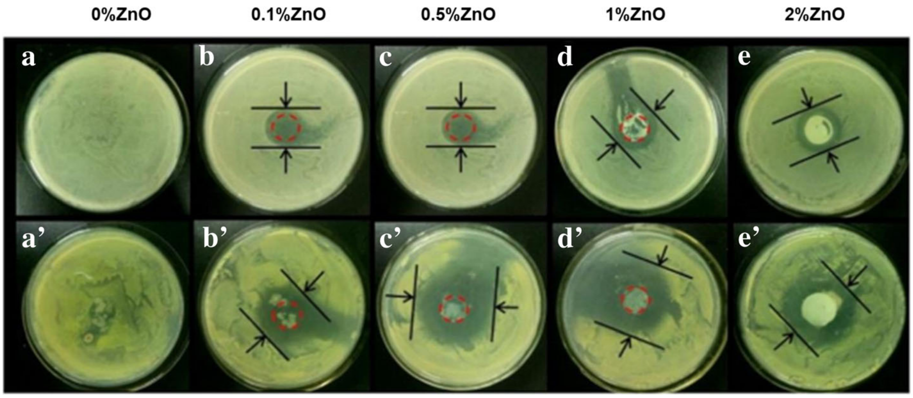

Fig. 3 Antibacterial property of caprolactam-casein (a, a') and caprolactam-casein/ZnO (b-e, b'-e') nanocomposites against (a-e) *E.coli* and (a'–e') *S. aureus* [27]. Copyright 2017, Elsevier

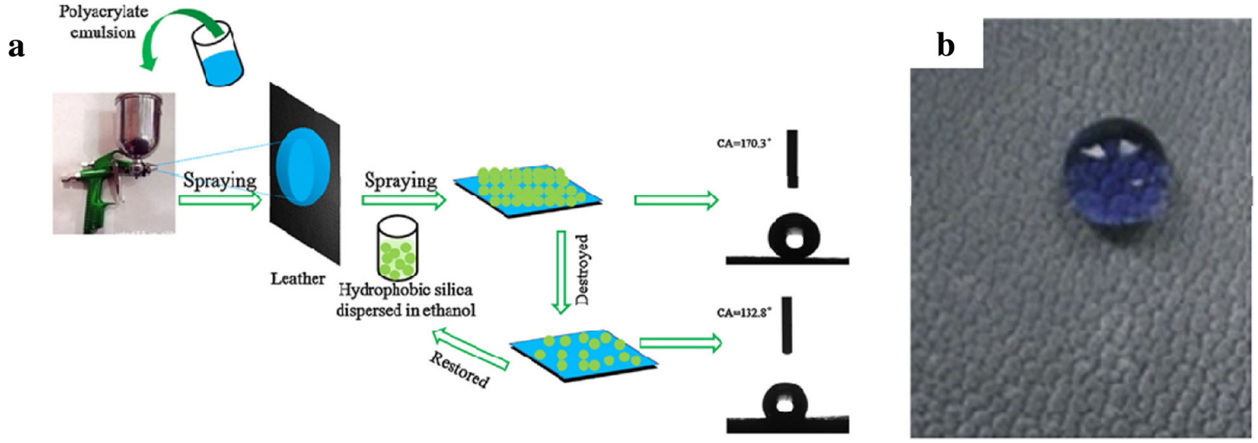

Fig. 4 Fabrication of superhydrophobic leather coating via spraying method (**a**); Optical image of water droplet on the superhydrophobic leather coating surface (**b**) [56]. Copyright 2015, Elsevier

angle tests confirmed that photo-induced hydrophilicity process was mainly responsible for the degradation phenomena on leather surface. In addition, silica doped TiO_2 NPs were also used for leather finishing [58]. Leather finished with the composites demonstrated obvious photocatalytic properties against MB under UV and visible light exposure due to the hydrophilicity of leather surface.

In our study, casein, polyacrylate and commercially available TiO_2 NPs was integrated to obtain casein-based TiO_2 nanocomposite via single in-situ method [29]. Significantly, the composite film exhibited efficient self-cleaning ability to stains including coffee, red wine, dye, and oil, which shows its potential application as functional coatings on various substrates. Figure 5 shows the results of discoloration of coffee stains on nanocomposite treated fabric under UV irradiation. It is noted that composite treated fabrics exhibited obvious color degradation under UV irritation. Degradation of coffee stains is attributed to the oxidative degradation induced by generated active radicals from TiO_2. Accordingly, schematic illustration of the self-cleaning behavior has been demonstrated in Fig. 6. Under UV irradiation, electron-hole pairs can be generated from TiO_2 and transfer to the fabric surface. Subsequently, the generated hole reacts with adsorbed water or hydroxyl ion, thus producing hydroxyl radicals. These hydroxyl radicals have been recognized as the strongest oxidant, which is responsible for the photocatalytic decomposition of organic stains. Coffee stains on the casein-based TiO_2 nanocomposite treated fabric were decomposed under the photocatalytic action of hydroxyl radicals. Thus, obvious stain discoloration could be observed on the fabric surface.

3.4 Other functional leather finishes

Besides the functional leather finishes described above, other functional finishes are on exploring to endow leather products with continuous performance, such as, high water vapor permeability, yellowing resistance, fragrance/mildew preventive sustained releasing property, etc., which will better meet the requirement of consumers and market.

To enhance water vapor permeability of finished leather, hollow silica spheres were blended with polymer binder, and then applied on leather surface [59, 60]. The results showed that hollow size and shell thickness of hollow silica spheres were much important for the improvement of water vapor permeability of finished leather. The presence of hollow silica spheres could

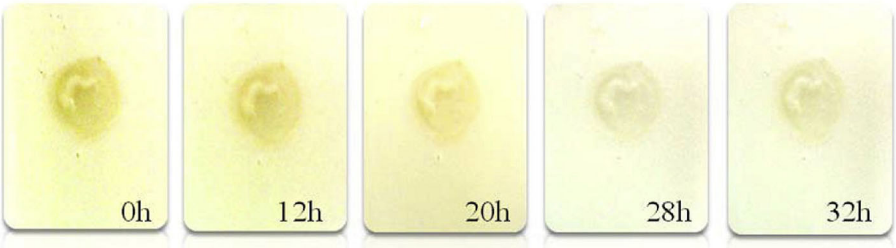

Fig. 5 Discoloration of coffee stain on casein-based TiO_2 nanocomposite treated fabric under UV irradiation [29]. Copyright 2016, Elsevier

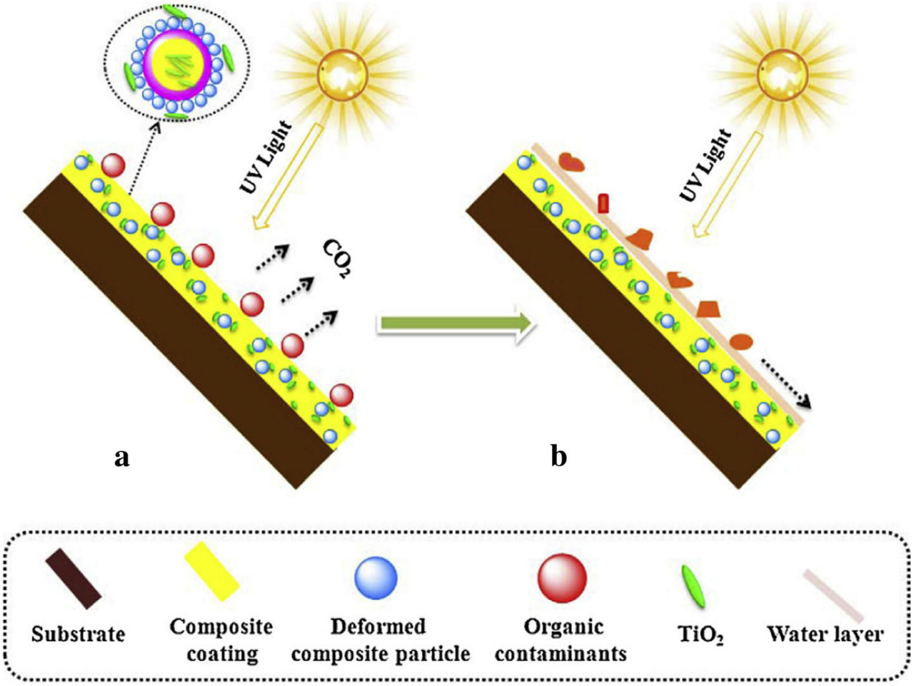

Fig. 6 Schematic illustration of the self-cleaning behavior of casein-based TiO_2 composite coatings in the initial (**a**) and intermediate (**b**) stage [29]. Copyright 2016, Elsevier

provide more free volume for the composite film, so water vapor permeability was improved. Furthermore, to restraint yellowing of leather products, especially for the one with light color, polyacrylate/ZnO nanocomposite was employed as leather finishes since ZnO nanoparticles can absorbed ultraviolet light, thus reducing the effect of ultraviolet light on polymeric coating and leather itself [61]. In our recent research, chitosan-coated silica nanocapsules with a double-shelled structure were added into casein binder as leather finishes (Fig. 7) [62, 63]. The finished leather showed sustained fragrance release behaviors. Meanwhile, casein-based silica hollow spheres were used as carrier for mildew preventive, and then applied on leather surface to endow leather with long-term

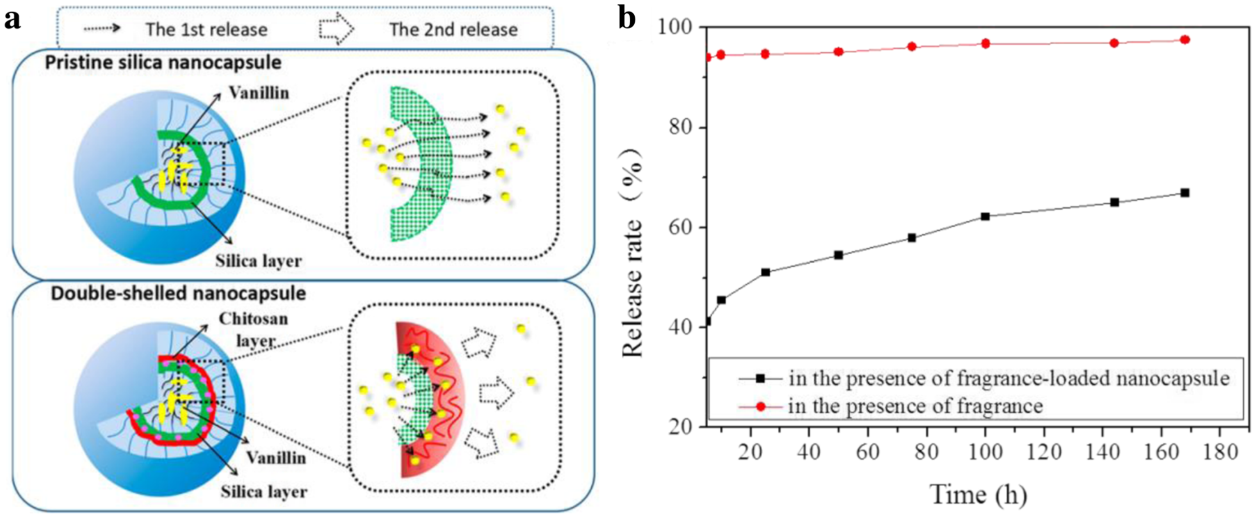

Fig. 7 Scheme of vanillin release from pristine silica capsule and double-shelled nanocapsule (**a**); Vanillin release rate of the leather samples finished by vanillin-loaded chitosan-based silica nanocapsules (red line) and vanillin (black line) (**b**)[62, 63]. Copyright 2018, American Chemical Society

mildew resistance [64]. However, encapsulation approaches often results in high cost and complicated operations. Accordingly, a facile LBL spraying method was employed to crafting sustained aromatic coatings separately in our recent work [65]. In the coating process (Fig. 8), polyacrylate emulsion was firstly sprayed on the substrate as base layer. Next, vanillin, and commercially available SiO_2 NPs were sprayed separately, then covered by chitosan. In this study, fragrance was covered by SiO_2 and chitosan layer that hinder its rapid diffusion. This LBL spraying method holds much promise in fabrication of functional leather finishes due to its simple operation.

4 Conclusion and outlook

Up to now, great efforts have been made to organic-inorganic nanocomposite, which show unique performance for functional leather finishes. However, there are relatively less researches on functional organic-inorganic nanocomposite-based leather finishes, especially in leather industry. Meanwhile, several issues listed in the following still need to be further addressed.

Firstly, stability of organic-inorganic nanocomposite is much important for giving expected performance. However, aggregation of inorganic nanoparticles in water-based polymer binder is still found during storage or transportation before use in industry. Solutions to this problem can not only be focused on hydrophilic treatment on the surface of nanoparticles, but also on searching novel synthesis method to obtain nanocomposite with better compatibility between inorganic and organic phases. Furthermore, deep and systematical study on the interface interactions between different phases should also be paid much attention.

Secondly, selections of polymer or nanoparticles are limited based on recent research advance, which are not conducive to obtain leather finishes with diverse functions. As is known, different nanoparticles show different properties. Therefore, other inorganic particles or polymer binder should be explored. For example, in the case of polymer binder, chitosan, zein or other natural polymers should be tried to develop green leather finishes. For inorganic particles, quantum dot material can be chosen to fabricate novel finishing agent, thus giving leather products with singular property.

Finally, effects of the microstructure of nanocomposite on performance of finished leather are not in-depth, further studies should be carried out on this part. As leather is derived from natural product, the effects on the performance of finished leather may be complicated. Advanced characterization technologies should be tried a lot to investigate the microstructure changes of leather surfaces before and after finishing. Meanwhile, computer modeling technique can also be used to explore the interface interactions between nanocomposite and leather surface, which may facilitate to reveal relationship between the microstructure of nanocomposite and performance of finished leather.

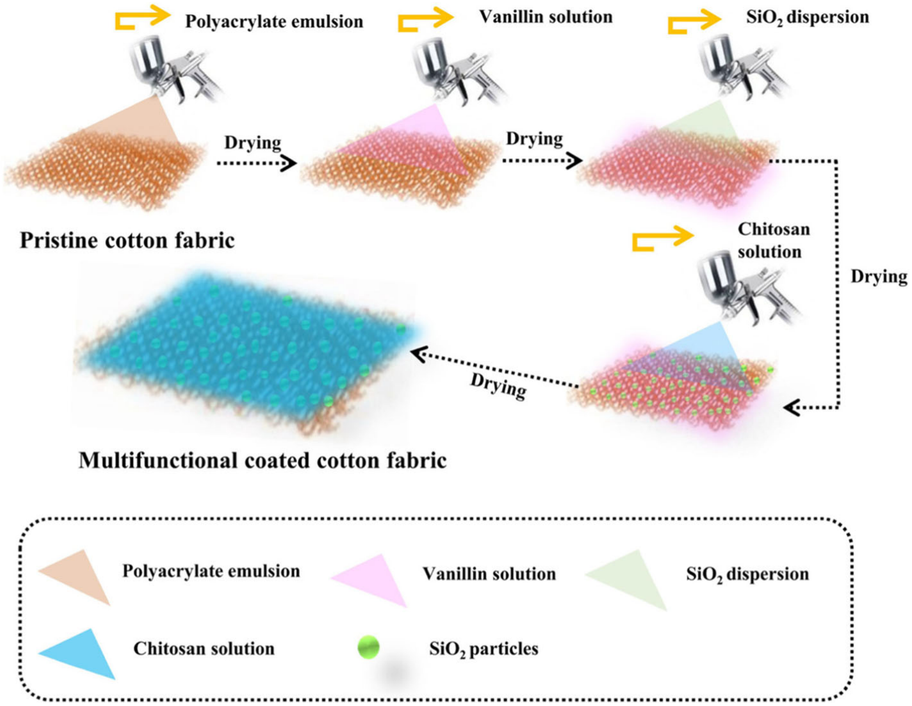

Fig. 8 Illustration for fabrication of the sustained aromatic coatings on cotton fabrics [65]. Copyright 2018, Elsevier

In our further researches, high-quality and robust leather finishes will be investigated with an emphasis on multifunctional inorganic/organic nanocomposites. More facile and versatile approaches, as well as future applications of nanocomposites materials will be developed from both fundamental and practical viewpoints.

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Availability of data and materials
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Authors' contributions
QF---Writing this review article, summarizing the literatures; JM---Designing the outline of this article, revising the draft; QX---Revising the draft, mainly focus on the language and logicality. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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