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# Progress in Polymer-Ceramic Hybrid Antifouling Coatings

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**Abstract** Simultaneous realization of superior mechanical and antifouling properties is critical for a coating. The use of stereoscopic polysiloxanes in place of linear polysiloxanes to fabricate antifouling coatings can combine properties of organic and inorganic materials, *i.e.*, they can exhibit both high hardness and wear resistance from inorganic components as well as the flexibility and tunability from organic components. This strategy is used to prepare hard yet flexible antifouling coatings or polymer-ceramic hybrid antifouling coatings. In this mini-review, we report the recent advances in this field. Particularly, the effects of stereoscopic polysiloxane structures on their mechanical and antifouling properties are discussed in detail.

**Keywords** Antifouling coating; Organic-inorganic hybrid; Sol-gel; Hard yet flexible

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## INTRODUCTION

Marine biofouling refers to the adhesion and reproduction of marine organisms, including marine microorganisms, plants, and animals on submerged surfaces, which has numerous detrimental consequences for maritime industries.[1–3] For example, marine biofouling on ship hull surfaces promotes surface deterioration, resulting in slower speed and higher fuel consumption for the ships.[4] Moreover, higher fuel consumption causes carbon dioxide emissions.[5] Biofouling can also induce biocorrosion of cross-sea bridge piers and marine oil platforms.[6] Additionally, the unwanted accumulation of marine microorganisms on the surface will clog pipelines of tidal power plants and nuclear power plants.[7]

Accordingly, fouling-release coatings,[8] degradable polymers,[9] amphiphilic polymers,[10] protein-resistant polymers,[11] and biomimetic polymers[12] have been prepared to inhibit biofouling. Among these, fouling-release coatings have received considerable attention in both academia and industry due to their biocide-free and drag-reducing effects on the ship hull surface.[13] Silicone-based elastomers are mostly used in fouling-release coatings. Because of silicone-based coatings' low surface energy and low modulus characteristics, fouling organisms cannot firmly adhere to the surface and are readily detached by an external shear force.[14] Moreover, silicone-based coatings have been widely used in medical devices due to their biocompatibility and elasticity. However, traditional silicone-based coatings generally suffer from weak mechanical properties, poor substrate adhesion, and limited fouling resistance. Therefore, various micro- or nanometer-sized fillers[15–18] ($SiO_2$, $TiO_2$, nanodiamond, multi-walled carbon nanotubes, *etc.*) or groups[19–23] (epoxy, catechol, urethane, urea, 2-ureido-4[1*H*]-pyrimidinone, *etc.*) have been introduced into silicone-based coatings to improve their mechanical properties and substrate adhesion. Meanwhile, amphiphiles,[24] zwitterions,[25] quaternary ammonium salts,[26] and antifoulants[27] have been introduced to offer fouling resistance. It should be noted that the above modification approaches to materials are based on the linear polydimethylsiloxane (PDMS) elastomer, which does not simultaneously have superior mechanical and antifouling properties.

Compared to linear polysiloxanes with high chain flexibility, stereoscopic polysiloxanes (nanoclusters, hyperbranched structures, cage-like, or ladder-like)[28,29] with a rigid inorganic core and organic periphery are promising to develop into hard yet flexible antifouling coatings. Recently, to realize the combination of ceramic-like hardness and polymer-like flexibility (two mutually exclusive characteristics) in an antifouling coating, methods about developing linear polysiloxanes into stereoscopic polysiloxanes *via* chemical hybridization have been extensively employed for the creation of polymer-ceramic hybrid antifouling coatings. Compared with a PDMS elastomer, a polymer-ceramic hybrid coating usually exhibits much higher hardness and wear resistance owing to its inorganic silicon core. Moreover, the flexibility and antifouling properties of the coatings can be achieved by introducing functional polymers *via* chemical hybridization. Such a coating is expected to be used on the surface of marine facilities, electronic displays, and biomedical devices.

Herein, we focus on recent progress in the conceptual design of polymer-ceramic hybrid antifouling coatings, and

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how stereoscopic polysiloxanes affect the mechanical and antifouling properties of the final coatings. Some of their emerging applications are also discussed. Finally, conclusions and future outlooks for the design of polymer-ceramic hybrid antifouling coatings are presented.

## METHODOLOGY FOR THE SYNTHESIS OF POLYMER-CERAMIC HYBRID ANTIFOULING COATINGS

The complementary properties of inorganic ceramic materials and organic polymers can be combined into a monolithic entity through chemical hybridization.[30,31] Unlike the relatively weak interactions (van der Waals, hydrogen bonding, or weak electrostatic interactions) between the two components *via* physical blending, chemical hybridization connects components with covalent bonds at the nanometer level, namely, the chemical interactions are strong. Furthermore, the maximum level of chemical bonding in the intra-/interphases can improve the mechanical performance of the hybrid coatings.[32] Based on the concept, the polymer-ceramic hybrid antifouling coatings can be classified into two major categories according to the procedure of chemical hybridization: (i) one-step sol-gel hybrid strategy and (ii) step-by-step hybrid strategy (Fig. 1).

### One-Step Sol-Gel Hybrid Strategy toward Polymer-Ceramic Hybrid Antifouling Coatings

The chemical hybridization of organic and inorganic components at the nanometer level generates a material with synergetic characteristics of organic polymers and inorganic materials. In particular, the sol-gel reaction has emerged as an attractive candidate for preparing organic-inorganic hybrid materials. It has been widely used to prepare various structuralized forms, such as monoliths, films, and powder materials, owing to its controllable stoichiometry, easy functionalization, low-temperature process, and ease of application.[33] In general, sol-gel reactions are classified as hydrolytic or nonhydrolytic. The former is silane or metal-containing alkoxy groups ($-OC_nH_{2n+1}$) hydrolyzed under acidic or basic aqueous conditions; then, the hydroxyl groups ($-OH$) condense with other hydroxyl and alkoxy groups in processes referred to as water and alcohol condensations, respectively.[34] The latter is a condensation of metal alkoxides, hydroxyl silane, or halide. In the last few decades, siloxane-based organic-inorganic hybrid materials derived from sol-gel have received considerable attention.[35] The desired properties of the hybrid materials can be readily tuned by controlling the sol-gel procedure and organic groups of the silane precursor.

In recent years, a series of sol-gel hybrid coatings *via* one-step hydrolytic polycondensation of silane-bearing aliphatic chains and amino/fluoro functional groups were reported.[36–39] The hard hybrid coating prepared by *n*-octyltriethoxysilane (C8) and tetraethoxysilane (TEOS) in a 1:1 molar ratio exhibited better fouling resistance to algae and juvenile barnacles compared with glass or PDMS elastomers. Particularly, the low surface roughness (0.1–1 nm) can significantly decrease the settlement and the ease of removal of fouling organisms from these surfaces. However, this coating becomes brittle and susceptible to damage when it forms a thick film. Meanwhile, such a coating has limited fouling resistance due to the lack of antifouling moieties, particularly under static conditions.

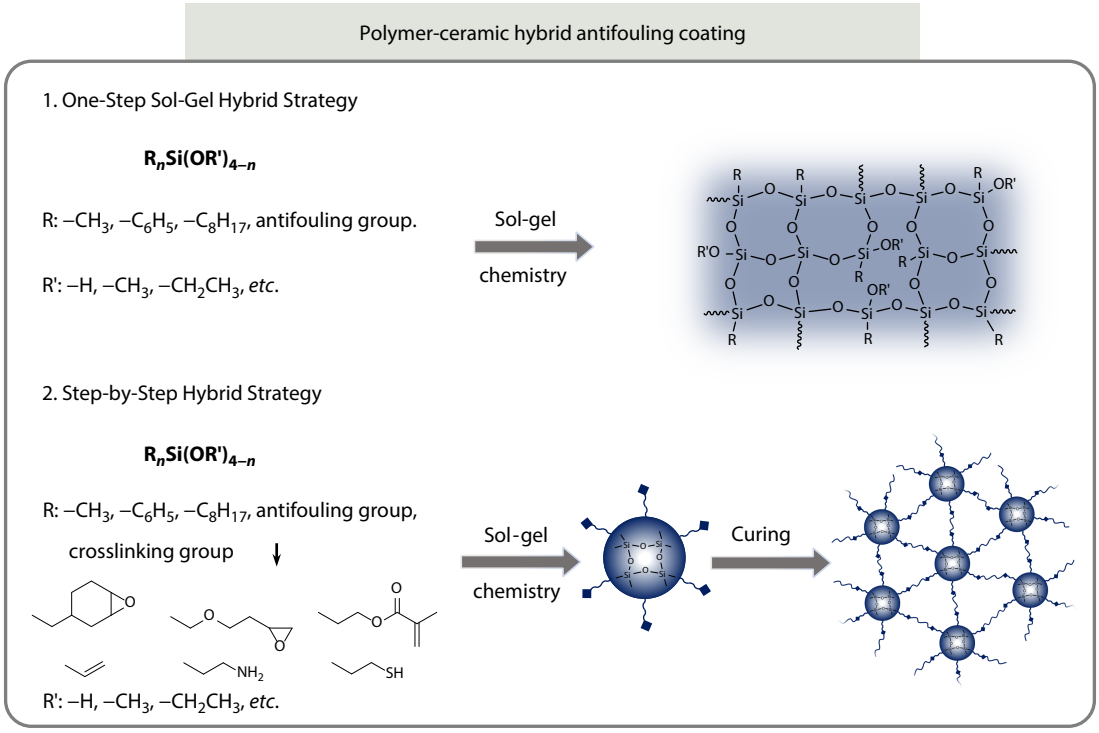


**Fig. 1** Two main strategies for constructing polymer-ceramic hybrid antifouling coatings: one-step sol-gel hybrid strategy and step-by-step hybrid strategy.

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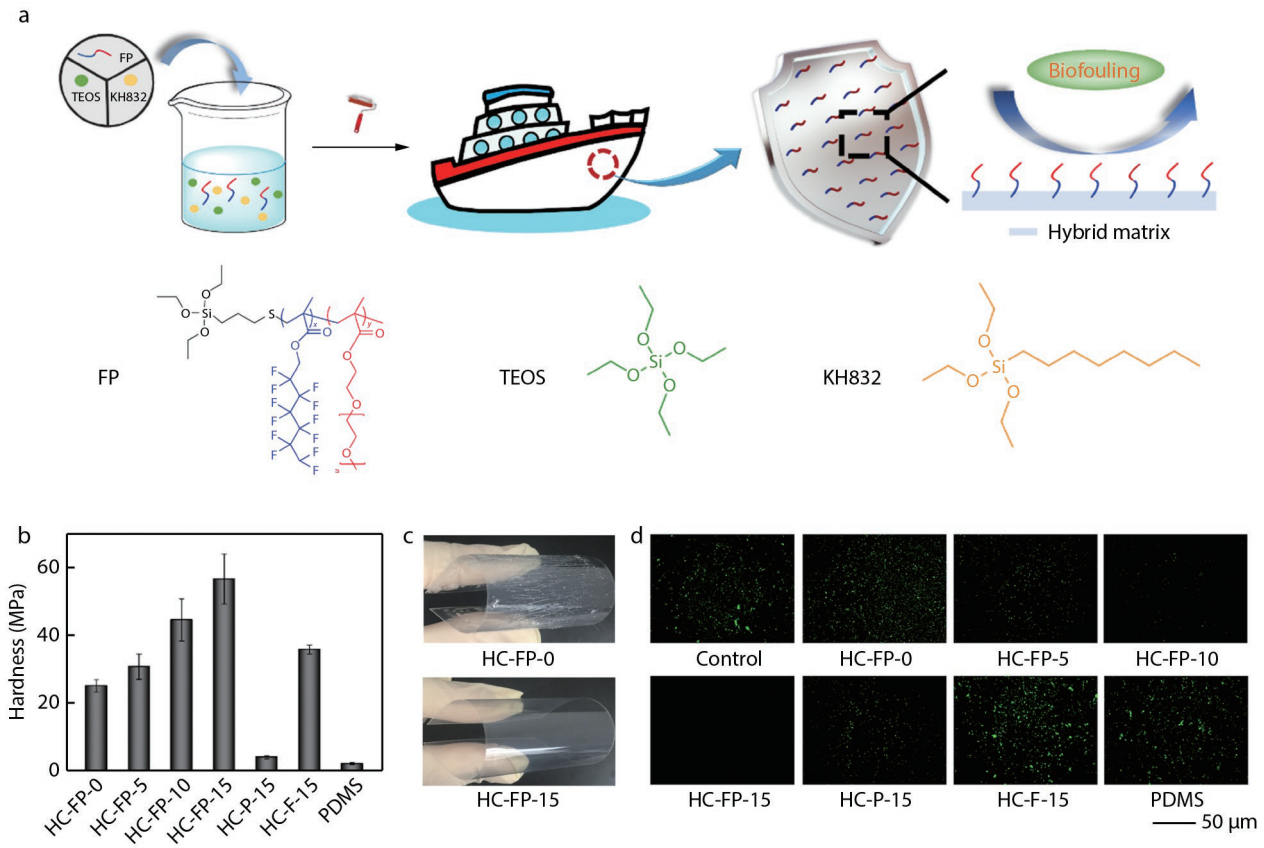


**Fig. 2** (a) Synthetic route for amphiphilic telomer FP and the hybrid coating; (b) The hardness of hybrid coatings determined by nanoindentation; (c) Flexibility test of HC-FP-0 and HC-FP-15 coated on PET; (d) Fluorescence microscopy images of *P. sp.* adhered to the hybrid coatings. (Reproduced with permission from Ref. [40]; Copyright (2017) The Royal Society of Chemistry).

To solve the problem, our group synthesized a silane-bearing amphiphilic fluorocarbon acrylate-PEG oligomer (FP) *via* telomerization of dodecafluoroheptyl methacrylate (DFMA), poly(ethylene glycol) methyl ether methacrylate (PEGMA), and 3-mercaptopropyl triethoxysilane (KH580), and incorporated it into a hybrid coating by a facile sol-gel reaction (Fig. 2a).[40] The hybrid coatings exhibit higher transmittance (>99%), hardness (~50 MPa), and modulus (~0.4 GPa) compared with the soft PDMS elastomers (Fig. 2b). The mechanism of fouling release was mainly determined by its low surface energy (17–24 mJ·m$^{-2}$) and low surface roughness ($R_q$<2.8 nm). Meanwhile, the soft PEG moiety of FP serves as a plasticizer to toughen the coating, thus endowing it with flexibility. As shown in Fig. 2(c), after 100 bending cycles, no cracks were observed on the surface of HC-FP-15, while numerous cracks were visible on HC-FP-0 surface. Moreover, the amphiphilic FP can self-enrich on the surface to improve the fouling resistance of the coating, which could effectively resist diatoms *Navicula incerta* as well as *Pseudomonas sp.* (*P. sp.*) and its biofilm (Fig. 2d). Furthermore, other antifouling groups, such as zwitterions[41] and quaternary ammonium salts,[42] could be covalently attached to the hybrid coating through a one-step sol-gel hybrid strategy.

It should be noted that the one-step sol–gel hybrid strategy also inevitably has some problems, such as long curing time, poor adjustment ability, and limited flexibility, and most systems need a high-temperature process to obtain a highly cross-linked network, which limits its application on various substrates.

## Step-by-Step Hybrid Strategy toward Polymer-Ceramic Hybrid Antifouling Coatings

In contrast to only using a sol-gel reaction to obtain polymer-ceramic hybrid coatings, using the R group (epoxy, acrylate, vinyl, amino, thiol, *etc.*) of the silane coupling agent, the inorganic components can connect through a polymerization process of R group.[34,43–47] Functional organic components can also be readily introduced in polymer-ceramic hybrid coatings.

In recent years, ladder-like polysilsesquioxanes (CEOS) have been reported *via* hydrolytic polycondensation of (2-(3,4-epoxycyclohexyl)ethyl) trimethoxysilane under base-catalyzed conditions.[32] The CEOS is a clear and viscous semiliquid. Next, a highly crosslinking hybrid network was obtained after UV-initiated cationic ring-opening polymerization and subsequently exposed to 85% relative humidity at 85 °C for 2 h. The hardness of hybrid coatings was up to 9 H, and no crack was observed on the surface even after bending for 10000 cycles. Hybrid coatings based on ring-opening polymerization of glycidyloxypropyl polyhedral silsesquioxane (GPOSS) have also been prepared.[48] The inorganic silicon core provides hardness, while the ether and methylene groups formed by the ring-opening polymerization of glycidyloxypropyl groups provide flexibility. Moreover, low-surface-tension liquid lubricant PDMS was incorporated into the

GPOSS coating *via* epoxy-amine reaction to fabricate an omniphobic surface. The resulting GPOSS coating was hard (>9 H) but flexible (U-shape bending). Even after 200 abrasions by steel wool or 500 times U-shape bending, water and n-hexadecane sliding capabilities remained nearly unchanged.

Note that the above coatings still lack the antifouling ability, and the photocatalytic crosslinking reaction requires complex UV irradiation, limiting the thickness and hence the application fields of the coatings. Therefore, our group presented a facile and universal step-by-step strategy for fabricating polymer-ceramic hybrid antifouling coatings.[49] We first synthesized two types of highly cross-linked epoxy-oligosiloxane nanoclusters *via* sol-gel reaction, one for the matrix and the other for fouling resistance. Then, the epoxy-oligosiloxane nanoclusters were crosslinked with various amine-terminated curing agents at room temperature without external triggers (Fig. 3a). This step-by-step strategy is simple, and the performance of coatings can be precisely regulated by the judicious design of oligosiloxane nanoclusters or curing agents.

As shown in Figs. 3(b) and 3(c), the resulting coatings exhibited excellent transmittance (>92% in the range of 400–800 nm), hardness (6–7 H), and flexibility (10 mm bending diameter). Furthermore, by introducing the antifouling oligosiloxane nanocluster-bearing amphiphilic telomer (FP) and bis(3-aminopropyl) terminated polydimethylsiloxane (APT-PDMS), the coating exhibits not only a self-cleaning ability but also excellent fouling-release performance and fouling resistance against *P. sp.*, *Escherichia coli* (*E. coli*), and *Staphylococcus aureus* (*S. aureus*) (Figs. 3d and 3e). Moreover, after abrasion for 400 cycles with steel wool, the coated glass still exhibits excellent antibacterial adhesion performance and water-sliding capability.

Based on the combination of sol-gel chemistry and epoxy-amine curing reaction, the polymer-ceramic hybrid coatings can be easily prepared using different particles to meet the requirements of different facilities. We also prepared a fouling resistant epoxy-zirconium particle (ZP) and an amine-terminated hyperbranched polysiloxane (HP), where the former is synthesized *via* the sol-gel reaction of tetrapropyl zirconate (TPOZ), 3-glycidyloxypropyltrimethoxysilane (KH560) and sulfobetaine silane (SBSi), and the latter is synthesized by 3-amino-propyltriethoxysilane (KH550) (Figs. 4a–4c).[50] The resulting coatings are transparent (>99.5% in the range of 400–800 nm), hard (7–9 H), and flexible (≤10 mm bending diameter). While the zirconia core provides the desired hardness, the flexibility is imparted by HP network. Fig. 4(d) shows that the KH550-ZP0 film was severely cracked following one rolling-up cycle due to its brittleness, but no crack was observed on the HP-ZP0 surface even after ten rolling-up cycles, indicating that the hyperbranched polysiloxane network can make coating undergo more elastic deformation. Besides, the presence of the zwitterionic group allows the

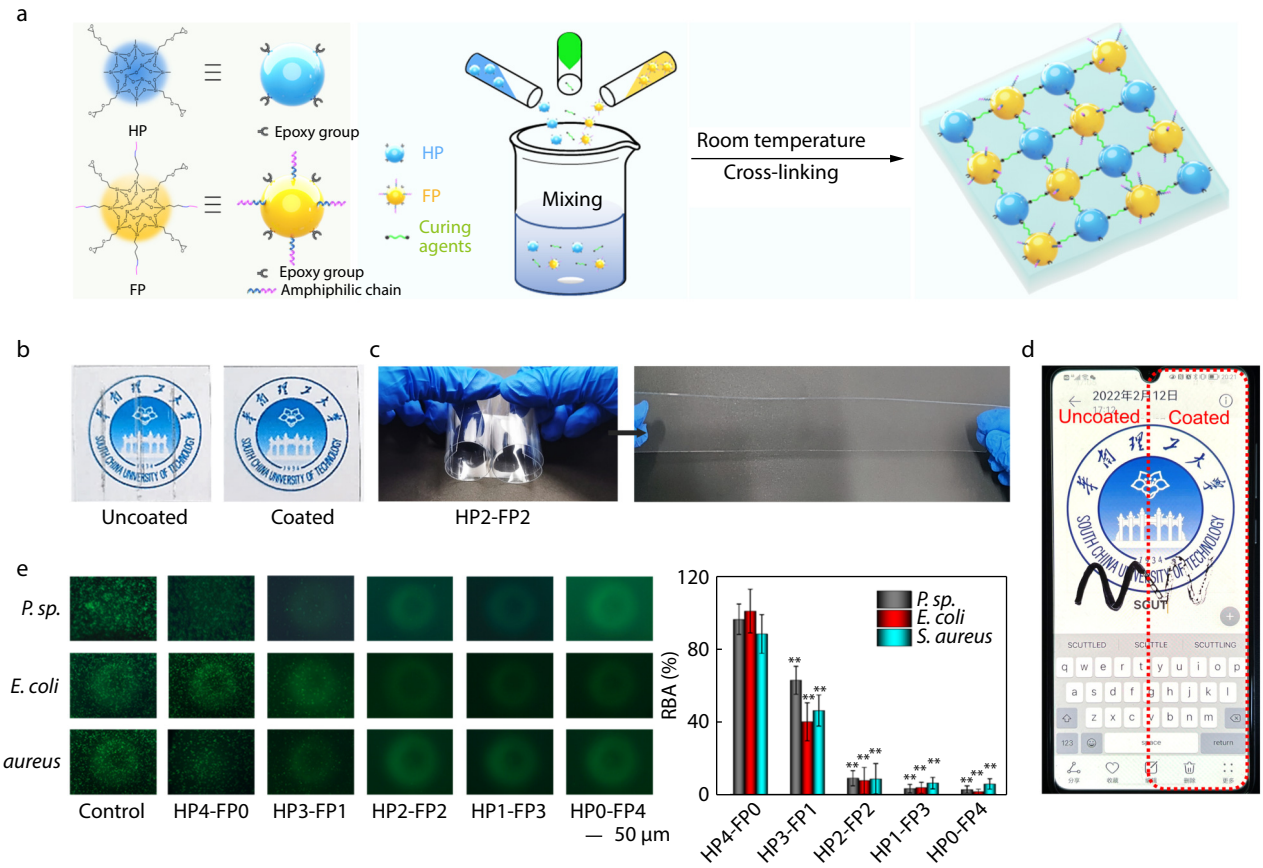


**Fig. 3** (a) Schematic illustration of the crosslinking process; (b) Wear resistance, (c) flexibility, and (d) anti-smudge of the hybrid coatings; (e) Fluorescence microscopy images of *P. sp.*, *E. coli*, and *S. aureus* on the surface of hybrid coatings and corresponding relative bacteria adhesion (RBA). (Reprinted with permission from Ref. [49]; Copyright (2022) Wiley).

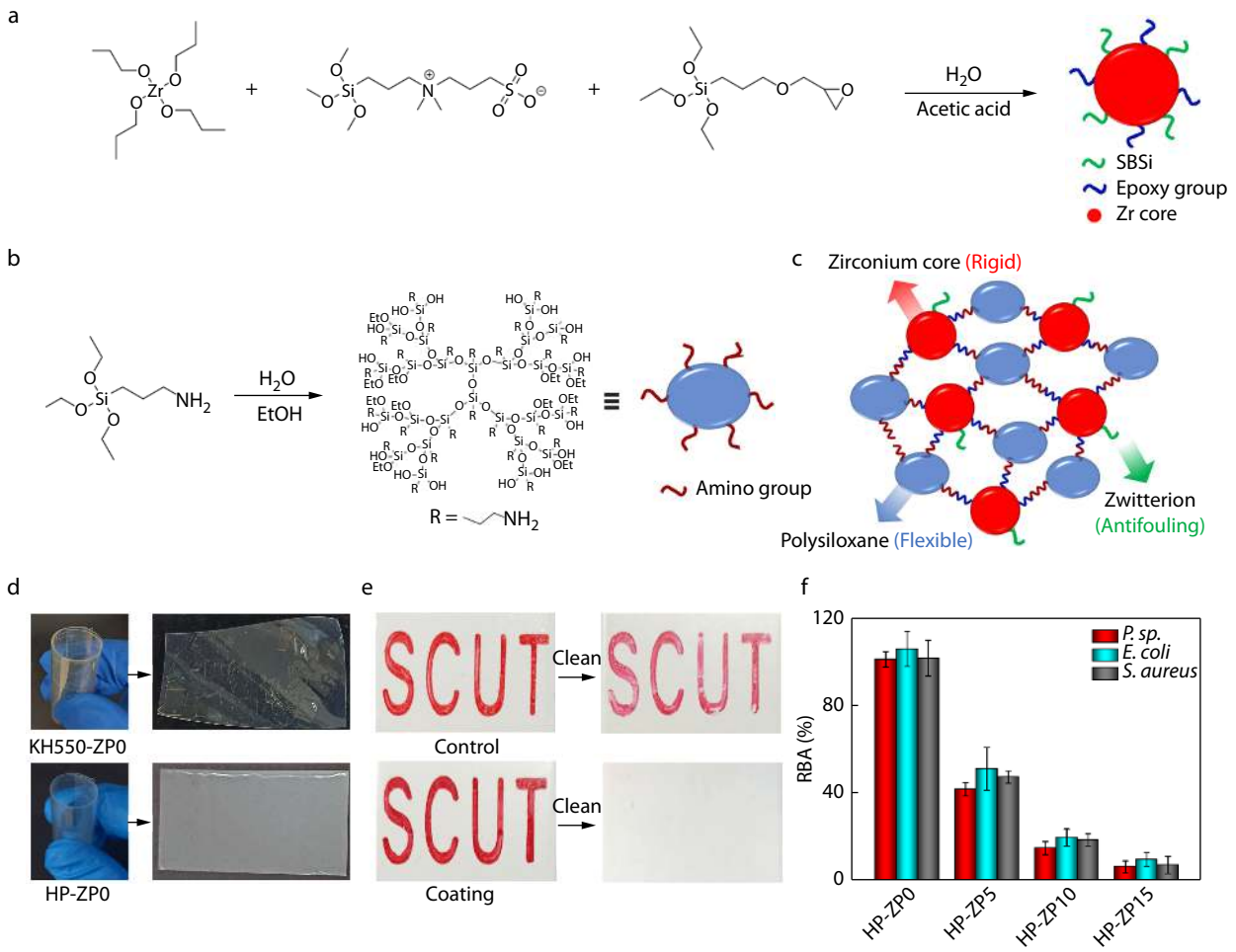


**Fig. 4** Preparation of (a) the fouling resistant epoxy–zirconium particle and (b) the amine-terminated hyperbranched polysiloxane. (c) Schematic representation of the cross-linked network of the hybrid coating. (d) Photographs of the hybrid coatings in a rolling-up test. (e) Oil repellency and (f) antibacterial ability of the hybrid coatings. (Reproduced with permission from Ref. [50]; Copyright (2021) Wiley).

coating to have excellent oil repellency and antibacterial capability against *P. sp.*, *E. coli*, and *S. aureus*. (Figs. 4e and 4f). Such a coating is expected to be used in foldable displays, optical sensors, and biomedical facilities.

## CONCLUSIONS AND PROSPECTS

In this mini-review, we summarized the advances and design strategies of polymer–ceramic hybrid antifouling coatings based on chemical hybridization, including a one-step sol-gel hybrid strategy and a step-by-step hybrid strategy. Furthermore, the effects of stereoscopic polysiloxane structures on their mechanical and antifouling properties are discussed. In particular, the step-by-step hybrid strategy can precisely and readily optimize the structure of stereoscopic polysiloxanes, the proportion of organic-inorganic components, and the form of crosslinking, which may represent the new generation of protective antifouling coatings.

Moreover, the COVID-19 pandemic has increased the demand for surface long-term fouling resistance, such as electronic displays. Numerous pathogens accumulate on the surfaces of mobile phone screens, tablets, and check-in touch screens and are spread by human contact.[51] Specifically, mobile phone is the main route of bacteria transmission in hospitals.[52] Previous strategies of surface leaching of antimicrobials are detrimental to the human body and cannot improve surface scratch resistance. The transparent polymer-ceramic hybrid antifouling coating is expected to be used in antifouling of electronic displays, especially in foldable displays. However, most reported systems have only been tested in the laboratory, and environmental stability tests under real climates were seldom carried out.

Overall, certain issues still need to be further addressed. For example, there is an urgent need to deeply understand the structure-property relationship of the hybrid antifouling coatings to improve their performance. Additionally, polymer-ceramic hybrid antifouling coatings with functions such as self-healing or anti-icing properties should be developed in the future.

## BIOGRAPHIES

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## Conflict of Interests

Guang-Zhao Zhang is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

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