Polydopamine/silver hybrid coatings on soda-lime glass spheres with controllable release ability for inhibiting biofilm formation

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ABSTRACT Filtering media is anything placed in a filter that changes the quality of water flowing through it. With the variety of media available, proper selection of filter media is of great importance for filter performance. Recycled glass is evaluated as an alternative to silica sand in media filters and is an effective medium with the advantages of lower cost than silica sand, more environmental friendliness as it is a recycled product, and ease to pulverize into different sizes for specific design requirements. However, the filtration efficiency of regenerated recycled glass is limited by the formation of biofilms on its surfaces due to the large number of microorganisms such as bacteria and algae existing in the water. In this study, hydrofluoric (HF) acid etched glass spheres (GSs) modified with polydopamine (PDA) and silver nanoparticles (PDA-Ag-HF/GSs) were fabricated on the surface of soda-lime GSs by HF etching, crystal *in situ* growth, and PDA coating. HF etching and the modification of PDA coating imparted good hydrophilicity to PDA-Ag-HF/GSs. The modification of the silver coating also rendered PDA-Ag-HF/GSs excellent antibacterial properties and reduced *Chlorella* adhesion, and inhibited microorganism growth ability by releasing Ag⁺. The catechol functional group on the PDA coating could regulate the Ag⁺ release by chelation. Good antibacterial properties, anti-algae adhesion, and controlled release of Ag⁺ indicate that PDA-Ag-HF/GS coating can effectively inhibit the formation of biofilm on the surface of the material, providing a new strategy for the formation of anti-biofilm.

Keywords: water treatment, biofilm, antibacterial, glass sphere, multifunctionality

INTRODUCTION

Water pollution is an important problem facing human beings [1]. The presence of contaminants, such as organisms [2], heavy metal ions [3], microorganisms, and radionuclide, makes wastewater treatment procedures a complex issue involving physics, chemistry, and biology [4,5]. Medium filtration has been one of the most widely used methods in water treatment due to its simple operation, low cost, high efficiency, and reliability [6,7]. Among diverse filtering media, recycled glass can effectively remove particulates, organic matter, and heavy metal ions in wastewater, markedly reducing the turbidity of water [8,9]. However, the filtration efficiency of regenerated recycled glass can be always limited by the formation of biofilms on its surfaces due to the large amount of microorganisms such as bacteria and algae existing in the water [10,11]. The presence of these biofilms severely reduces the ability of the filter media and, in severe cases, increases the risk of equipment damage. Benefiting from advances in the anti-bioadhesive technology, various surfaces with biofilm inhibition capabilities supported by different surface modification methods have received extensive attention. Among them, Ag- [12], Cu- [13], and Au-based materials can effectively inhibit the bio-adhesion of microorganisms by releasing specific substances that are harmful to microorganisms [14]. Unfortunately, the release of these substances is uncontrollable and often environmentally unfriendly [15,16]. Therefore, controlling the release of harmful substances is of great significance for the development of

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advanced water filtration media.

Dopamine (DA) has attracted much research attention as a product of biomimetic mussel adhesion chemistry [17]. Rich catechol functional groups endow DA with good adhesion, adsorption, and reduction abilities [18]. The catechol hydroxyl group can be adhered to the surface of most substrates, such as metals, ceramic, glass, and polytetrafluoroethylene by hydrogen bonding and π - π stacking [19,20]. Meanwhile, they can adsorb harmful substances in water such as heavy metal ions [21] and organic substances [22]. More importantly, the catechol functional group has a reducing ability and can form a redox balance [23]. Such excellent performances make DA widely used in many fields such as biomedicine [24] and the environment [18].

In this study, hydrofluoric (HF) acid etched glass spheres (GSs) filter modified with polydopamine (PDA) and silver nanoparticles (PDA-Ag-HF/GSs) with controlled release and anti-biofilm ability were prepared by an acid etching and *in situ* growth technique, as shown in Fig. 1. Firstly, the surfaces of soda-lime GSs were etched by HF to increase the surface roughness; the contact area between the filter medium and sewage could be increased in turn. Secondly, silver ions (Ag^+) were adsorbed onto the GS surfaces due to the negative charge of the surfaces, and then silver nanoparticles were grown *in situ* under hydrothermal conditions to construct a microenvironment with microbial toxicity. Finally, the chemical re-

activity of the soda-lime GSs was improved by increasing the reactive functional groups (amino and hydroxyl groups) through the induction of PDA coatings. The abundant chemical functional groups could not only inhibit the release of Ag^+ , but also reduce Ag^+ to Ag nanoparticles and maintain the dissolution equilibrium of Ag^+ .

EXPERIMENTAL SECTION

Materials

The soda-lime GSs (composition in mol%: C 11.06%, Ca 4.51%, O 51.51%, Na 10.32%, Si 22.60%) used in this study were purchased from Senno Glass Beads Co., Ltd., China. Silver nitrate (AgNO_3), sodium chloride (NaCl), and HF were purchased from Kelong Chengdu, China. DA, agar, yeast extract and peptone were purchased from Sigma, Germany. All chemicals and solvents were of reagent grade.

Methods

Hydrofluoric acid etched GSs (HF/GSs)

The soda-lime GSs were ultrasonically washed three times with ultrapure water and ethanol before use. GSs (10 g) were added into a reactor with polytetrafluoroethylene as the inner cover, and 20 mL of 20 wt% HF was added for etching. After reacting at room temperature for 10 min,

Figure 1 (a) Surface modification processes of glass sphere (GS) and (b) anti-biofilm and controlled release properties of PDA-Ag-HF/GS.

the GSs were alternately washed with water and ethanol and finally dried at 60°C to obtain HF/GSs. HF could bring about a serious safety threat due to the strong causticity and toxicity. Thus, the experiments should be carried out carefully in a fuming cupboard.

Preparation of silver-modified HF/GSs

With 10 g of HF/GSs in the beaker, 50 mL of AgNO_3 solution was added to the system. Stirring was continued for 10 min to achieve adsorption equilibrium. Finally, the reaction system was transferred to the reactor and reacted at 180°C for 5 h. The silver-modified HF/GSs (Ag-HF/GSs) were obtained after centrifugation and washing.

Preparation of PDA-modified Ag-HF/GSs

First, 10 mg of DA was added to 10 mL of HCl-tris solution, stirred and dissolved, and then 10 g of Ag-HF/GSs were added. The DA was polymerized by stirring at room temperature for 12 h. Finally, the PDA-Ag-HF/GSs were obtained by centrifugation, washing, and drying.

Characterization of the spheres

The physicochemical properties of GSs, HF/GSs, Ag-HF/GSs and PDA-Ag-HF/GSs were characterized by scanning electron microscopy (SEM, Zeiss, Ultra55), X-ray diffraction (XRD, Panalytical X'PERT PRO) and X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific, ESCALAB 250Xi). The hydrophilic and hydrophobic properties of the materials were evaluated by testing the static water contact angles (Kruss, K100) of the surfaces.

RESULTS AND DISCUSSION

Microscopic morphology of GSs

The roughness of the GS surface can be increased by HF etching. The microstructure of a GS is shown in Fig. 2a. A smooth sphere can be observed under low magnification SEM, and some particles can be seen on the surface at high magnification SEM. After HF etching, pits about 30 μm in size are clearly observed on the surface of the GS (Fig. 2b), and the pits have smooth surfaces. This is mainly because GS contains a large amount of SiO_2 that can react with HF, and after SiO_2 is etched, pits will be formed on the surface of GS. The presence of pits helps to increase the specific surface area of a GS, which is beneficial to water filtration systems [25].

GSs can induce the formation of nanoparticles and PDA coatings *in situ*. After immersion in AgNO_3 solution for hydrothermal reaction, pits of the Ag-HF/GSs were clearly observed to be coated with nanoparticles (Fig. 2c) with the diameter of 100 nm, uniformly dispersed on the inner wall. The elemental mapping at the microstructural level by SEM with energy dispersive X-ray spectrometry (EDS) (Fig. 2e) also shows that the silver distribution in the nanoparticles is uniform. This may be due to the fact that HF etches GSs, causing a large number of defects on the surfaces. Those defects facilitate the nucleation of nanoparticles and ultimately induce the growth and formation of nanoparticles. After modification by PDA coating, most of nanoparticles on the surface of PDA-Ag-HF/GSs (Fig. 2d) are embedded in the coating and the

Figure 2 The microstructure of GSs. (a–d) are SEM images of GS, HF/GS, Ag-HF/GS and PDA-Ag-HF/GS, respectively. (e) and (f) are Ag element mapping of Ag-HF/GS and PDA-Ag-HF/GS, and (g) is N element mapping of PDA-Ag-HF/GS.

particle size increases. DA has catechol functional groups that can be adsorbed on the surfaces of GSs and nanoparticles by hydrogen bonding and polymerized under alkaline conditions to form a coating of PDA. This explains the inlay of the nanoparticles and the increase in the size of surface particles. The elemental mapping also shows a uniform distribution of Ag (Fig. 2f) and N (Fig. 2g) elements on the surface of a GS, indicating successful modification of the PDA coating.

Chemical structure of the surface of GSs

Surface analysis results show that Ag nanoparticles and PDA coatings are successfully modified on the surface of the GSs. No significant diffraction peaks on the XRD pattern (Fig. 3a) can be observed, indicating that the GS is in an amorphous state. The modification process of etching and the later functional coating do not cause any change in the GS. Moreover, the survey XPS spectrum of a GS is shown in Fig. 3b, where the GS and HF/GS clearly exhibit peaks at 105, 285 and 534 eV that belong to Si 2p,

C 1s, and O 1s, respectively. For both Ag-HF/GS and PDA-Ag-HF/GS, a peak of Ag is observed around 375 eV, and the N 1s peak (401 eV) is also observed on the PDA-Ag-HF/GS.

By fitting the high-resolution spectrum (Fig. 3c and d) before and after etching, it is found that O 1s on GSs can be fitted to two peaks of 532.48 and 530.86 eV which correspond to the Si-O bond in the glass and the hydroxyl (-OH) adsorbed on the surface. However, after the HF etching, the proportion of hydroxyl oxygen (-OH) increases from 8.4% to 15.5% (Table 1), indicating that more defects have been added onto the surface of the GSs after etching, and the defects cause an increase in the content of hydroxyl oxygen (-OH). High-resolution spectrum of Ag 3d (Fig. 3e) can be fitted to two peaks of 368.24 and 374.25 eV that correspond to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively [26,27]. This finding indicates that the nanoparticles on the surface are Ag nanoparticles. It is worth noting that, because the Ag nanoparticle content is too low, almost no characteristic diffraction peak of Ag

Figure 3 Chemical compositions of the GS surface. (a) XRD spectra of GSs. (b) XPS of GSs. High-resolution O 1s spectra of (c) GSs and (d) HF/GSs. (e) High-resolution Ag 3d spectra of Ag-HF/GSs. (f–h) are the high-resolution C 1s, N 1s, and O 1s spectra of PDA-Ag-HF/GSs, respectively.

Table 1 Curve fitting results for the O 1s spectra of GSs and HF/GSs

Function group	Binding energy (eV)	GS (%)	HF/GS (%)
–OH	530.85	8.4	15.5
O–Si	532.48	91.6	84.5

can be observed on the XRD pattern. Finally, the fitting results of C 1s, N 1s, and O 1s of PDA-Ag-HF/GSs (Fig. 3f–h) show that the C 1s spectrum can be fitted to four peaks at 284.77, 285.94, 286.6 and 288.52 eV, corresponding to the carbon skeleton (C–C), amino group (C–N), phenolic hydroxyl group (C–OH), and carbonyl group (C=O) on PDA, respectively [24]. The peaks at 399.90 and 402.34 eV on the N 1s spectrum represent amide and the amino groups (–NH₂), respectively. The presence of C–O and C=O can also be observed at 531.1 and 533.31 eV on the O 1s spectrum, indicating that DA has polymerized on the surface and formed a PDA coating.

Wettability of the GS surface

The wettability test results show that PDA-Ag-HF/GSs have good surface wettability. As shown in Fig. 4a, when the droplets were dropped onto the surface of GSs, they were semi-circular on the surface of the glass sheet, with a water contact angle of 60°. When the surface was etched by HF, the droplets began to spread, and the water contact angle dropped to 41°. The droplets were completely spread on the Ag-HF/GS surface after the silver nanoparticles were loaded, with a contact angle of 13°. Interestingly, the spread was finally reduced on the PDA-Ag-HF/GS and the contact angle increased to 31°. This is mainly due to the fact that the modification of PDA coating reduces the roughness of the surface. The silver nanoparticles are evenly distributed on the surface, which increases the surface roughness of GS. Other research

results also demonstrated that the spread of water can be promoted with the improved roughness [28,29]. However, with the modification of PDA coating, the silver nanoparticles were embedded in the PDA coating. The relative flat PDA coating can reduce the roughness to some extent and lead to a decrement in wettability.

Silver release behavior of GSs

The cumulative release curve of Ag⁺ was used to investigate the release behavior of the coating for Ag⁺ [30]. GSs (1 g) were immersed in 80 mL of deionized water. The solution was taken out every 24 h for measuring the cumulative release concentration in it by atomic absorption spectroscopy (AAS, PerkinElmer, AA700). The cumulative release of Ag⁺ showed that the modification of the PDA coating helped to inhibit the release of Ag⁺ on Ag-HF/GSs. As shown by the ion release curve (Fig. 5), Ag ions had a rapid release rate in the first 4 days in Ag-HF/GSs without PDA coating, and the release rate decreased after 4 days, with the release concentration of 55 ppb at 5 days. With modification by the PDA coating, the release rate of Ag⁺ on PDA-Ag-HF/GSs decreased in the first 4 days, and the release concentration after 4 days was 23 ppb lower than that of the Ag-HF/GSs. This was mainly due to the fixation of Ag⁺ by the PDA coating on the GS surface. The PDA surface was rich in catechol functional groups that could adsorb Ag⁺ and reduce it to elemental Ag [31], resulting in the decrease in the release of Ag⁺.

Adhesion of *Chlorella*

Chlorella adhesion experiments were used to explore the anti-algae adhesion of GSs [32]. The GSs were placed in a suspension of *Chlorella* (8×10⁶ cells mL^{−1}) and after 24 h of culture were fixed with glutaraldehyde (2 wt.%) and freeze-dried. Finally, *Chlorella* on the surface of the GSs

Figure 4 (a) Photo images and (b) water contact angle for 5 μL droplet on the surfaces of GS, HF/GS, Ag-HF/GS and PDA-Ag-HF/GS, respectively.

Figure 5 Cumulative release of Ag⁺.

was observed by SEM. SEM images of *Chlorella* adhesion indicated that the silver-modified surface effectively inhibited *Chlorella* adhesion. As shown in Fig. 6, a large amount of *Chlorella* adhesion was observed on the surfaces of GSs and HF/GSs and a dense *Chlorella* membrane was formed. However, on the surface of the Ag-modified Ag-HF/GSs, almost no *Chlorella* adhered to the surface. Moreover, *Chlorella* adhered to the surface of PDA-Ag-HF/GSs, but the growth of the *Chlorella* was inhibited. This was mainly due to the ability of *Chlorella* to generate adhesion proteins that adhered to the surface of GSs [33,34]. However, much Ag⁺ was released on the surface of the Ag-modified surface and Ag⁺ could be bound to the surface to cause changes in the cell membrane [35]. Some studies have reported that the entry of Ag⁺ into cells could upregulate the concentration of intracellular reactive oxygen species, ultimately leading to cell apoptosis [36]. Finally, due to the abundant func-

Figure 6 Adhesion of *Chlorella* on the surfaces of (a) GS, (b) HF/GS, (c) Ag-HF/GS, and (d) PDA-Ag-HF/GS.

tional groups on PDA, the adhesion of *Chlorella* could be promoted, but the released Ag⁺ also strongly affected physiological metabolism, eventually leading to the apoptosis of *Chlorella* on the surface.

Adhesion of bacteria

The antibacterial adhesion and bacteriostatic ability of GSs were investigated by *Escherichia coli* (*E. coli*) and *Bacillus*. After co-cultivation of GSs and bacteria, SEM and an absorbance experiment were used to detect the bacterial adhesion and growth [37]. The results show that the silver nanoparticle coating surface can effectively inhibit bacterial adhesion. The adhesion behavior of *E. coli* on the GS surface is shown in Fig. 7a–d. A large amount of *E. coli* adhesion can be observed aggregated on the surfaces of GSs and HF/GSs, as indicated by the red arrows. In contrast, only a small number of bacteria adhere to the Ag-HF/GSs surface and there is almost no adhesion of bacteria on the PDA-Ag-HF/GSs surface. Similar to *E. coli*, adhesion of *Bacillus* is observed on the surface of GSs and HF/GSs without Ag coating modification, as indicated by the blue arrows in Fig. 7e–h, whereas on the surfaces of Ag-HF/GSs and PDA-Ag-HF/GSs modified by Ag coating, such coating is not observed. This is mainly due to the fact that the released Ag⁺ from the silver coating can enter bacteria and interfere with the normal physiological activities of bacteria. Studies have shown that Ag⁺ can bind to bacterial cell membranes, altering the charge properties on the surface of cell membranes and disrupting the structure of cell membranes, inhibiting the formation of cell membranes during cell proliferation [38,39]. Moreover, Ag⁺ can cause the cell surface ionic membrane to lose its ability to transport and transfer energy and matter, eventually killing the cells [40,41].

Bacterial experiments show that PDA-Ag-HF/GSs also have excellent spectral antibacterial growth ability, as well as inhibiting bacterial adhesion. The culture media after co-cultivation of GSs and bacteria are shown in Fig. 7i and j. The bacterial culture medium in the blank, GS and HF/GS groups is turbid, indicating high bacterial concentration. In contrast, the color of the medium in the Ag-coated Ag-HF/GS and PDA-Ag-HF/GS groups is clear, indicating low bacterial concentration. Quantitative analysis by absorbance showed that the antibacterial rates of Ag-HF/GSs and PDA-Ag-HF/GSs for *E. coli* (Fig. 7k) were 86% and 82%, and the antibacterial rates of *Bacillus* (Fig. 7l) were 87% and 84%. The good antibacterial ability was mainly due to the release of Ag⁺ from the surface-modified Ag layer, which had spectral antibacterial properties to kill bacteria in the environment [38].

Figure 7 Adhesion of bacteria on the surface of GSs. SEM images of *E. coli* adhesion on the surfaces of (a) GSs, (b) HF/GSs, (c) Ag-HF/GSs and (d) PDA-Ag-HF/GSs. SEM images of *Bacillus* adhesion on the surfaces of (e) GSs, (f) HF/GSs, (g) Ag-HF/GSs and (h) PDA-Ag-HF/GSs. (i) and (j) are photographs of different GSs co-cultured with *E. coli* and *Bacillus*. (k) and (l) are the antibacterial ratios of different GSs against *E. coli* and *Bacillus*.

Although PDA-Ag-HF/GS owns good water wettability and the ability to inhibit microbial growth, there are still some limitations, such as relatively high cost, treatment of by-products, and dynamic antibacterial ability that need to be further optimized. Firstly, approximately 0.025 g of silver nitrate was needed to produce 10 g of PDA-Ag-HF/GS glass beads. Reducing the usage of silver nitrate will be helpful to reduce the cost of filter media. Secondly, the treatment of by-products should also be considered. During HF etching process, silicon fluoride (SiF_4) gas, precipitation of CaF_2 and silicic acid would be generated. Producing 10 g of PDA-Ag-HF/GS will generate about 20 mL wastewater with the main component of NaF. Among them, CaF_2 and silicic acid can be separated by precipitation, and NaF can also be separated into lower-level industrial raw materials. Finally, for the dynamic

antibacterial ability, the filtration process is complex involving the flow of microbial population, the flow rate of filtration solution, and the flow rate of solution. These factors will intensely affect the release of silver ions and ultimately affect the ability to inhibit microbial growth. Therefore, the best filtration procedure should be selected according to the pollutants, such as bacterial species and chemical composition in different water qualities. The ion release and long-term antimicrobial growth ability of the filter medium can finally be evaluated.

CONCLUSION

In this study, multifunctional PDA-Ag-HF/GSs were prepared on the surface of soda-lime GSs by HF etching, crystal *in situ* growth, and PDA coating modification. Among them, HF etching and the modification of PDA

coating imparted good hydrophilicity to PDA-Ag-HF/GSs. Moreover, the modification of the silver coating also gave PDA-Ag-HF/GSs excellent antibacterial properties and *Chlorella* adhesion, but inhibited microorganism growth ability by releasing Ag^+ . The catechol functional group on the PDA coating could regulate the Ag^+ release by chelation. Good antibacterial properties, anti-algae adhesion, and controlled release of Ag^+ indicate that PDA-Ag-HF/GS coating can effectively inhibit the formation of biofilm on the surface of the material, providing a new strategy for the formation of anti-biofilm.

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Author contributions Zhang HW and Tang Y designed the research. Shi Q fabricated the materials, did the characterizations, analyzed the results and drafted the manuscript with support from Zhang HP, Zhao P and Zhang Y. Zhang HP and Tang Y revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

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具有可控释放能力和可抑制生物膜形成的聚多巴胺/银杂化涂层的钠钙玻璃球

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摘要 过滤介质作为过滤装置中的关键材料可改变流经其中的水的质量。正确选择过滤介质对于过滤装置的过滤性能至关重要。再生玻璃作为介质过滤装置中硅砂的替代品, 具有比硅砂廉价、环境友好、可再生等优点, 并且可以根据特定的设计要求将其粉碎成不同的尺寸。然而, 水中存在大量的诸如细菌和藻类的微生物, 故再生的可循环玻璃介质的过滤效率受到在其表面富集的生物膜的极大限制。本研究中, 我们通过在钠钙玻璃球(GS)表面上进行氢氟酸(HF)蚀刻和原位结晶制备了用聚多巴胺(PDA)和银(Ag)纳米颗粒改性的氢氟酸蚀刻玻璃球(PDA-Ag-HF/GSs)。银晶体的原位生长、HF蚀刻和PDA涂层的改性赋予了PDA-Ag-HF/GS良好的亲水性。银涂层的改性还使得PDA-Ag-HF/GS具有出色的抗菌性能和较小的球藻附着力, 且通过释放Ag离子可抑制微生物的生长。PDA涂层上的邻苯二酚官能团可通过螯合作用调节Ag离子的释放。良好的抗菌性能、抗藻类附着力和Ag离子的受控释放表明, PDA-Ag-HF/GS涂层可有效抑制材料表面生物膜的形成, 为抗生物膜的形成提供了新的策略。