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Recent progress in biomedical materials modified by polydopamine

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Abstract: *Dopamine (DA), which not only contains catechols, but also includes amino substances. Because DOPA derivative is dopamine, it's essentially the same as DOPA. According to the study of related experts, such as Lee, DA will self-react in the alkaline aerobic humid environment, and PDA nanofilms containing catechol units will be generated on the surface of the substance. The preliminary work showed that polydopamine (PDA) showed excellent advantages in adsorption and bio-compatibility in vivo. In addition, because of its excellent chemical properties, PDA can be used as a "platform" for "secondary modification", grafting a variety of functional small molecules onto the matrix, so as to improve the matrix's osteogenic, antibacterial properties. This paper briefly introduces the research progress of PDA in medical materials and other aspects in order to lay a foundation for PDA to be used more in medical materials research and development.*

Keywords: *Polydopamine; Modified organism; Applied research*

1. Introduction

In recent years, through the analysis of shell and other body forms, domestic and foreign scholars believe that 3, 4-dihydroxy-L-phenylalanine (DOPA) is an important molecule closely related to shell and other body forms. The study showed that when DOPA concentration increased, so did the amount of cytoadhesin on the cell surface. Studies have shown that the most important function of catechol group (also known as catechol) in DOPA structure is its adhesion on the surface of the substance. It can not only establish covalent bonds with the surface of the substance, but also establish non-covalent bonds, so as to achieve the adhesion effect of DOPA. The results showed that compounds containing catechol groups with similar structures to DOPA could also adsorb on the substrate.

2. Application of PDA

2.1. Surface modification of titanium and titanium alloys by PDA

In the history of biomedical materials, the first batch of medical materials used in trauma repair and plastic surgery are metal-based medical materials.[1] In the 1960s, titanium implants became commonly used in dentistry. Due to its excellent mechanical properties and corrosion resistance, it has become the most important replacement for hard tissue at present. However, due to its poor binding performance with bone defects, it is easy to cause bacterial invasion and other problems, resulting in great challenges in clinical application. At present, the research on surface modification technology of titania is mainly focused on surface modification to improve its biological activity and antibacterial activity. Based on the chemical properties of polydopamine (PDA), the secondary modification of HA and antibacterial drugs to improve the mechanical properties of materials has become the focus of current research.

2.2. Surface modification of titanium by PDA

Lee et al. constructed PDA coating on the surface of titanium implants by using the self-polymerization of DA. Our experiment found that compared with the untreated control group, the surface contact angle of titanium implants modified with PDA was reduced, and the corrosion resistance was improved.[2] The surface roughness isn't significantly reduced, and the biocompatibility is also good.At the same time, with the reductive properties of polydopamine and the coordination effect on metals, Ti

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loading was realized. The results showed that the composite membrane had good inhibition on both bacteria and bacteria. In addition, Wang et al. used the method described above to construct PDA thin film layer on the surface of porous titanium and induced HA generation on the surface of the material. In an aqueous solution of 0.9% NaCl, the electrical impedance and electrical polarization characteristics of the material were measured, and the corrosion resistance of the material was improved. At the cellular level, HA/PDA composite membrane can promote the adhesion of tumor tissue and enhance the activity of ALP, which is closely related to the formation of tumor tissue.

Previous work found that the material can effectively promote the adhesion and growth of human skin epithelium and hair cells, and can effectively redirect to EMSCs, and show good biological compatibility. Our previous study found that modified titanium matrix composite scaffolds were more conducive to osteogenesis, proliferation and osteogenesis in tissue engineering, and could slow the release of BMP2 by degrading HA. By using PDA to modify its surface, it can effectively enhance its biological activity, corrosion resistance and antibacterial properties, so as to make up for its own shortcomings, so as to extend its use as artificial bone implants and dental implants.

2.3. PDA promotes surface mineralization of ceramic materials

Because of its excellent biocompatibility and bone conduction properties, it has become a hot topic in medical research in recent years. Because of the deep understanding of biological materials, it has been widely used in medical materials, such as artificial bone, tooth root and bone filling material. There are mainly two types of bioceramics.[3] One is in human body, and the other is chemically bonded with surrounding living tissues in human body. Bioceramics modified by PDA can not only enhance its hydrophilicity[4] and promote the formation of nano-hydroxyapatite on its surface, but also enhance its growth and growth on its surface, thus enhancing its binding to bone.

Liu et al. mixed calcium phosphate bone cement (CPC) with 40 mg/ml dopamine (DCPD), 25 mg/ml dopamine (DCPD), 8.5% hydroxyapatite (HA) and 8.5% calcium carbonate ($CaCO_3$).[5] The phase, functional group and composition of PDA-CPC in SBF were studied by XRD, FTIR and XPS. We found that in the early stage of PDA-CPC, PDA can transform DCPD, alpha-CP and other molecules into HA, and construct a NanoHA similar to normal bone on the surface of PDA-CPC, so as to realize effective regulation of biological tissues. Zain et al. constructed PDA coating on yttrium stabilized zirconia (YSZ) through the self-polymerization of DA, and soaked it in SBF solution. The experimental results showed that the hydrophilicity of YSZ membrane could be improved by polydopamine coating. In addition, the spontaneous polymerization of dopamine on YSZ results in the formation of a large number of benzoquinone functional groups and the complexation with Ca^{2+}, thus accelerating the calcification on YSZ.

3. Application of polydopamine in biomedical materials

Medical polymers and their composites are a new kind of high-tech synthetic materials that can repair, replace and regenerate biological tissues.[6] With the development of biomedicine, materials science and biotechnology, biomedical polymers and polymer composites have been widely used in the medical field. However, the biocompatibility of polymers and polymer composites has been greatly limited. Good biocompatibility is the key to ensure that the interface between medical device and human tissue is in a relatively stable state and improve the service quality and life of medical device. PDA modification technology is a new way to solve this problem.

Gao et al. combined BMP-7 (BMP-7) with polycaprolactone static spinning nanowires (PCL) by using PDA-assisted monomolecular membrane modification technology. Our previous study found that polycaprolactone prepared by electrostatic field spinning significantly enhanced the adhesion, proliferation and osteogenic induction of BMSCs, and showed higher biological properties. Zhu et al. fixed bovine blood albumin (BSA) on the surface of porous polyethylene (PE) film in a similar manner. The results of Fourier transform infrared ray and X-ray photoelectron spectroscopy show that PDA and BSA have binding sites on the interface of nanoparticles. The hydrophilicity of polyethylene film can be improved obviously. The results of adsorption tests on blood clots showed that the anticoagulant activity of BSA-modified polyvinyl alcohol/polytetrafluoroethylene (PDA) was better than that of unmodified polyvinyl alcohol (BSA). In the same manner, liver protein (HEP) and BSA (BSA) were grafted onto the porous membrane interface of polysulfone (PSF) using PDA chemistry. The hydrophilicity of the modified polyamide film was obviously improved by water contact Angle measurement. After surface treatment of HEP and BSA, it was found that the surface treatment of PSF films with HEP and BSA had

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significantly improved platelet adhesion and anticoagulant properties, and the surface treatment effect was good. In addition, Sureshkumar et al. Modified silver nanoparticles (Nano-Ag) onto polymethacrylic acid (PMMA). The results show that the modified nano-composite membrane not only has high biocompatibility, but also has strong inhibition to bacteria.

Using PDA as intermediate, carboxymethyl chitosan (CMC) and osteogenic polypeptide (BFP) were grafted into PEEK/CF/n-HA. The experimental results show that polyether ether ketone/carbon fiber /n-HA can be coated on its matrix, and can be effectively grafted with CMC and BFP. The results show that the modified composite membrane has better hydrophilic properties and higher hydrophilic properties. Through cell culture of MSCs, it was found that the adhesion, proliferation and osteogenic ability of modified MSCs were significantly enhanced, as well as the surface antibacterial activity and osteogenic ability. In vivo experiments showed that the modified material showed good osteogenic effect both in vivo and in vitro. Based on the adhesion and chemical activity of PDA, the functional modification of PDA can significantly improve the biocompatibility of polymer and its composites.

4. Other applications of PDA

Dopamine can oxidize and self-polymerize under acidic and high humidity conditions to produce dopamine nanoparticles. Through the complexation and reduction of polydopamine, silver nanoparticles with excellent bacteriostatic performance were produced. Wu et al. placed dopamine hydrochloride solution in a solvent mixed with ethanol, deionized water and ammonia gel to complete the chemical reaction, and thus obtained PDA nanoparticles.[7] Then, the PDA/cationic gap nanocomposites were obtained by dissolving PDA in the newly prepared cationic gap $(NH_3)_2$ solvent. In vitro cytological experiments, the system showed higher chemical stability. The results showed that the compound granules showed good antioxidant effects on Escherichia coli and Staphylococcus aureus. In addition, polydopamine can also act as a transitional substance by grafting silver particles onto the interface of the nanomaterial. Our previous studies have shown that PS/Ag has no significant killing effect on human renal epithelial cells (HEK293T) in vitro, but its bacteriostatic effect in vivo remains unclear. Pda-mediated silver carrying particles can significantly improve its clinical application, and its clinical application also shows a good prospect. Because of its excellent mechanical properties, excellent biocompatibility and potential antibacterial activity, it has shown broad development potential in dental implant and bone repair. How to enhance its antibacterial activity and enhance its integration with bone tissue is the focus of current research. Zhang et al. through the mechanism of oxidative self-polymerization of dopamine, synthesized PDA-modified Graphene Sodium Rice Tablets (PDA-GNS). [8] Then they were mixed with the newly synthesized $[Ag(NH_3)_2]$ ionic solution under magnetic field agitation for 1 hour, and then the newly synthesized dopamine aqueous solution was added to the system for 30 hours of agitation, and finally Ag nanoparticles (Ag-PDA-GNS) were obtained. Through in vitro bacteriostatic test, it was found that the nanoparticles showed good bacteriostatic effect against two kinds of Gram-negative or positive bacteria. The preliminary work showed that PDA could significantly improve its film forming ability on Graphene Oxide and showed high film forming ability, showing great potential in implant and scaffold materials.

Because of its excellent mechanical properties, it has been widely used in the repair of dental defects. At present, bond failure has become an important factor affecting its application effect. Lietal firstly prepared PDA film on the glass fiber matrix by using the self-polymerization of dopamine, and then binding properties between the glass fiber matrix and epoxy material before and after the PDA modification were compared. It is found that the modified film has better hydrophilic properties. The results show that the binding ability of the modified fiber matrix and resin is obviously improved. The results show that the functionalization of o-diphenol in PDA can make it form a good interfacial bond with epoxy resin, but its mechanism still needs further study.

5. Conclusion

To sum up, the adhesive performance of PDA is excellent, the molecular chain of phenylenediamine and amine functional primitive, not only can give PDA excellent hydrophilicity, adhesion and biological compatibility, but also can be used as a secondary modification of the "carrier", will be a variety of active small molecules grafted onto the carrier. PDA modification can significantly improve the bonding strength, corrosion resistance and antibacterial properties of oral and orthopaedic implants and promote osteogenesis. Dopamine (DA) is a new biological modification method, because of its simple preparation method, wide range of applications, low cost, and has important application prospects in materials,

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medicine and other aspects. Through further exploration of PDA molecules, we will further elucidate the self-polymerization and functional group mechanism of PDA molecules, which will lay a foundation for the further development of PDA molecular modification in medicine and other aspects.

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