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学位論文題目	Design and fabrication of antibacterial nanocoatings on cotton and silk fibers through supramolecular self-assembly technology （超分子自己組織化技術による綿およびシルク繊維の抗菌性ナノコーティングに関する研究）
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論　文　内　容　の　要　旨

Wastewater has long been a highly important insurmountable problem in the textile industry. Since the rapid development of antimicrobial silver nanoparticle (AgNP)-coated textiles in the recent several decades, AgNP-containing wastewater produced in the finishing process has gradually posed a greater threat to the ecological environment than that by traditional organic dyes because of the former's strong antimicrobial ability. Besides, although many nanocoating technologies have been developed to coat AgNPs on the surface of biological fibers, most of them are belong to top-down approaches. The precise control of Ag content and good control of spatial arrangement of AgNPs on the fiber surface are still great challenges. To solve these problems, we developed three different supramolecular self-assembly technologies aiming to environmental-friendly coat AgNPs on biological fibers. The spontaneous arrangement of AgNPs on the fiber surface with good uniformity and mono-dispersity can be achieved by controlling supramolecular forces including electrostatic attraction and hydrogen bonding interactions and electrostatic repulsion among NPs. The specific methodologies and related conclusion are as follows.

In Chapter 2, an environmental-friendly approach has been developed for preparation of AgNP-coated cotton, silk, and calcium alginate fibers by hyperbranched poly(amidoamine) (HBPAA)-guided assembly of AgNPs on the surface of biological fibers in aqueous solution. HBPAA-functionalized AgNPs (HBPAA/AgNPs) were synthesized in aqueous media using HBPAA as the reducing and capping agent. The self-assembly of HBPAA/AgNPs were realized by incubation of biological fibers in a colloidal solution of HBPAA/AgNPs. SEM and XPS characterizations demonstrated that high density of metallic AgNPs were uniformly distributed on the fiber surface. The results of antibacterial tests indicated that the coated biological fibers exhibited high antibacterial activity against gram-positive and gram-negative bacteria.

In Chapter 3, we report an efficient and environmentally-friendly approach for the preparation of AgNP-coated silk fibers (SFs) through self-assembly of hyperbranched poly(amine-ester)s-functionalised AgNPs (HBPAE/AgNPs) on HBPAA-coated silk fibers (HBPAA/SFs) driven through strong intermolecular interactions between hydroxyl-terminated HBPAE and amino-terminated HBPAA. HBPAE/AgNPs had a particle size of 11.8 nm and were slightly negatively charged. The self-assembly process was conducted by successively impregnating the SFs with HBPAA and HBPAE/AgNPs solutions. Up to 160 mg/L of HBPAE/AgNPs could completely self-assemble onto HBPAA/SFs (2 g) at room temperature within

10 min, allowing the Ag content of HBPAE/AgNP-coated HBPAA/SFs to be precisely controlled up to 8 mg/g by simply adjusting the concentration of the AgNPs. The antibacterial activity of HBPAE/AgNP-coated HBPAA/SFs was dose-dependent and the minimum Ag content was determined as 1.5 mg/g with an inhibitory rate of over 99%. Further characterization demonstrated that the as-prepared HBPAE/AgNP-coated HBPAA/SFs have unique structural features including well-dispersed NPs on the surface and good chemical stability. The developed self-assembly technology may provide a simple, efficient, and environmentally-friendly coating strategy for the precise control of Ag content on coated fibers, which is important for the quality control of antibacterial textiles.

In Chapter 4, we designed an environmentally-friendly and energy-efficient bottom-up nanocoating strategy for cotton fibers by cooperated self-assembly of complementary AgNPs that are functionalised by amino-terminated HBPAA and hydroxyl-terminated HBPAE, respectively. HBPAA/AgNPs possess positively surface charges and dense amino end groups while HBPAE/AgNPs own slightly negatively surface charges and abundant OH end groups. Therefore, owing to intermolecular recognition and interactions between HBPAA and HBPAE, heterostructured AgNPs could cooperatively self-assemble on the surface of biological fibers. Specifically, cotton fibers were alternately incubated with solutions of HBPAA/AgNPs and HBAPE/AgNPs at room temperature and finally dried in an oven. Our SEM, FESEM, and XPS studies confirmed that heterostructured AgNPs were uniformly coated on the surface of cotton fibers, indicative of their excellent physical and good chemical stability. The coated cotton fibers also showed excellent antibacterial capability. The developed cooperated self-assembly strategy showed nearly complete uptaking of AgNPs on natural fibers and good control of Ag content, indicating its good potential for practical production.

In Chapter 5, we further applied the cooperated self-assembly technology to coat HBPAA/AgNPs and citric acid-capped Fe_3O_4 NPs (CA/Fe_3O_4 NPs) onto silk fibers. The hierarchical structured Fe_3O_4/AgNPs dual-coated silk fibers were fabricated by sequential impregnation of silk fibers with solutions of HBPAA/AgNPs and CA/Fe_3O_4 NPs. As-prepared hierarchical structured silk fibers were characterized by XRD, FESEM, and VSM. XRD and SEM characterizations demonstrated that silk fibers were hierarchically and uniformly coated by high dense AgNPs and Fe_3O_4 NPs. VSM analysis indicated that as-prepared ternary composite fibers showed good magnetic property. Besides, the supramolecular self-assembly technology can be used to design other inorganic nanoparticle coatings. As a demonstration, in chapter 5, water-soluble hydroxyl-terminated hyperbranched poly(amino-ester) (HBPAE)-capped titanium dioxide nanocrystals (TiO_2 NCs) were also synthesized for coating a cotton fabric via an amino-terminated hyperbranched poly(amidoamine) (HBPAA)-mediated self-assembly strategy to produce a controllable and uniform TiO_2 coating on the cotton surface. It was demonstrated that hydroxyl-modified TiO_2 NCs were egg-shaped and had a narrow size distribution. A TiO_2 NC-coated cotton fabric was prepared by sequential impregnation with solutions of HBPAA and TiO_2 NCs. The attachment of HBPAAs to TiO_2 NCs was evaluated by FTIR. It was shown that HBPAA were bound to the cotton surface. FESEM and XRD characterizations demonstrated that TiO_2 NCs could self-assemble on a cotton fabric efficiently and were distributed uniformly on the cotton surface.