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論　文　内　容　の　要　旨

Silk is a kind of the natural filament fiber material with good mechanical properties; silk protein is not toxic and harmless and has good biocompatibility and degradability. Due to the unique advantages and broad application prospects of silk in various aspects, many scientists have aroused to explore it tirelessly. However, with the continuous progress of modern technology and the continuous deepening of research, in recent years, scientists have gradually realized that silk fibers formed by silk protein are used by silkworms as structural materials. Silk is not only biological activity in the narrow sense, but also as a protein material, in addition to specific advantages, there are inherent shortcomings, which limits the application of silk materials, thus, how to improve performance of silk and then develop new features of silk is of great significance.

In this study, with natural silk as raw material, using Hyperbranched poly(amide-amine) (HBPAA) as molecular glue, through layer-by-layer (LBL) self-assembly method, we successfully prepared graphene oxide coated silk fiber composite model. This method is simple and easy to implement. Moreover, the quantitative control of graphene oxide coating can be easily achieved by adjusting the solution concentration and adsorption times. On this basis, this study also used GO nanosheets, Ag NPs and Fe_3O_4NPs nanoparticles composite silk materials. We design and develop a coaxial cable model and multilayer composite silk nanofibers. The synergistic effect of nanomaterials will be the better, and then add the silk fiber more new features and new applications. Moreover, it is very feasible to retain the characteristics of silk fiber as far as possible in the process. The results of this study are as follows.

1. Preparation of graphene oxide-coated silk fibers through HBPAA [a molecular glue]-induced layer-by-layer self-assembly

Graphene oxide (GO)-coated silk fibers were fabricated through HBPAA-induced LbL self-assembly technology. In the experiments, GOs nanosheets were synthesized by a modified Hummers method at first. Then, a strong affinity of amine-functionalized Graphene oxide (AFGO) was designed, by coating the silk fibers with AFGO by self-assembly technique onto the silk fibers to prepare AFGO @ silk composites using self-assembly technique. The closely adhered GOs coatings were achieved by circular incubation with solutions of HBPAA and GOs, in which HBPAA serving as the “molecular glue” that could bind single or multi-layered GOs to the surface of silk fibers. Because of cationic and amphipathic characteristics of silk, it is easier to capture and fix negatively charged hydroxyl/carboxyl-contained AFGOs nanosheets with three dimensional structure and dense amino end groups, compared to linear cationic electrolytes. The developed LbL self-assembly technology may provide a controllable approach to coat GOs on the surface of biological fibers and graphene-based functional materials.

2. Graphene oxide-encapsulated Ag nanoparticle-coated silk fibers with hierarchical coaxial cable structure fabricated by the molecule-directed self-assembly

For protecting AgNP coatings from detachment, we designed the graphene oxide (GO)-encapsulated Ag nanoparticle (AgNP)-coated silk fibers with GO serving as the protective films through HBPAA-directed self-assembly. By introducing two dimensional GO nanosheets, a robust, hard, and closely-fitted protective films could be achieved on the fiber surfaces through self-stacked GOs. To design a well-defined hierarchical structure, silk fibers were hierarchically coated with HBPAA-capped AgNPs (HBPAA/AgNPs) and GOs by successively impregnating the fibers in the solutions of HBPAA/AgNPs and GOs. In such structure, HBPAA served as a “double-sided tape” not only gluing AgNPs to the fiber surfaces but also adhering GOs to the surfaces of HBPAA/AgNPs. The developed coaxial cable-structured coatings could isolate Ag nanocoatings from external stimuli, opening a potential route to improve the function persistence and biosafety of AgNP-coated bio textiles.

3. Fabrication of hierarchical structured graphene oxide-Fe3O4 hybrid nanosheets and Ag nanoparticles bimetallic composite coated silk fibers through self-assembly

It is a significant challenge to design and fabrication of well-organized hierarchical structured graphene oxide (GO)-Fe_3O_4 hybrid nanosheets and Ag nanoparticles (AgNPs) bimetallic coated silk fibers via a facile and simple assembly technology. Firstly, positively charged HBPAA-capped AgNPs and negatively charged GO-Fe_3O_4 NPs were synthesized respectively. Secondly, silk fibers were sequentially immersed in solutions of positively charged AgNPs and negatively charged GO-Fe_3O_4NPs as the building blocks. And then, we prepared novel hierarchical structured GO-Fe_3O_4NPs/AgNPs bimetallic coated silk fibers via a special electrostatic self-assembly technology using positively charged AgNPs and negatively charged GO-Fe_3O_4NPs as the building blocks The as-prepared bimetallic coated silk fibers exhibited excellent magnetic property and durable antibacterial property, which can be attributed to the high dense AgNPs assembled on the surface of silk fibers and protection from a robust, hard, and closely-fitted films of GO-Fe_3O_4NPs.

In this study, we successfully prepared GO-coated silk fibers, GO-encapsulated AgNP-coated silk fibers, and the GO-Fe_3O_4NPs/AgNPs bimetallic coated silk fibers three kinds of silk nanocomposites through the LBL self-assembly method. The method can realize quantitative controllable assembly of nanomaterials, such as graphene oxide, nanosilver, ferrosoferric oxide, etc. The as-prepared prepared silk fiber nanocomposite which not only has the good functional properties of nanomaterials but also retain the characteristics of silk fiber. Therefore, the research results of this study provide a new idea for the research of silk nanocomposites, and also find the direction for the new application of traditional silk fibers.