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Studies on Design and Characterization of Protein Cage-Based Novel Soft Materials with Controlled Nanostructures

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1. Introduction

The past twenty years have seen a convergence of chemistry, biology, and materials science. The notion of hierarchical assembly has been recognized as a common feature in biological processes, and materials scientists have long recognized that controlled hierarchical assembly at the molecular scale is an important aspect for designed functional materials. Biology has accomplished an exquisite level of control through millennia of evolution. Detailed analyses of macromolecular structures and biological processes have provided valuable advantages for materials scientists to use or mimic in a new generation of synthetic materials.

The objective of this study is to investigate the processes whereby biological units are organized into progressively more complex, higher-order structures. To achieve this purpose, we examined the some processes to make protein cages into two- dimensional (2D) and three-dimensional (3D) hierarchical structures combined with functional polymers by the controlled self-assembly.

2. Results and Discussions

The electrostatic adsorption of ferritin and apoferritin onto the surface of polyelectrolyte multilayer, which were successively prepared by the alternated adsorption of poly(diallyldimethylammonium chloride) and poly(sodium 4-styrenesulfonate). The adsorption behavior of the (apo)ferritin were quantitatively and kinetically analyzed. Then, we examined the mixed monolayer adsorption of ferritin and apoferritin onto the surface of a polyelectrolyte multilayer (precursor) film. The blended composition of ferritin and apoferritin within the monolayer is linearly dependent on their ratios in the blended solution, thus showed an ideal blend adsorption behavior. The perfectly identical structure of ferritin and apoferritin should be contributed to this ideal blend adsorption behavior. We also demonstrate that the immobilized (apo)ferritin on the substrate is able to achieve the synthesis of ferrihydrite core within the confines of the protein cage structure similar to in solution dispersed system. In addition, we applied the ferritin/apoferritin blended monolayer to the iron mineralization, and revealed that the biomineralization in this system is spatially selective manner. Then, we prepared electroactive multilayer thin films containing the ferritin as protein cages. The multilayer thin films on a solid substrate prepared by alternate adsorption of (apo)ferritin and poly(NIPAAm-*co*-CIPAAm), and we successfully prepared the stable electroactive multilayer thin films containing the (apo)ferritin. Finally, we discusses the toposelectively surface modification of (apo)ferritin with hydrophilic and biocompatible poly(ethylene glycol) to break the high symmetry of the cage structure. The self-assembly behavior of PEGylated ferritin showed that the marked difference compared to that of native cage, and the degree of assembly-induced sized change of protein cages could be controlled by manipulating of PEGylation conditions.

3. Conclusions

In this thesis, our results suggested that it will be possible to build more complex functional inorganic assembled nanomaterials with desired shape, size and dimension by using protein cage as a novel building block and functional polymers, and provide a novel protein cage-based soft nanomaterials formed by its self-assembly and hierarchical integration.

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