Historical perspective

Functional architectures based on self-assembly of bio-inspired dipeptides: Structure modulation and its photoelectronic applications

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ABSTRACT

Getting inspiration from nature and further developing functional architectures provides an effective way to design innovative materials and systems. Among bio-inspired materials, dipeptides and its self-assembled architectures with functionalities have recently been the subject of intensive studies. However, there is still a great challenge to explore its applications likely due to the lack of effective adaptation of their self-assembled structures as well as a lack of understanding of the self-assembly mechanisms. In this context, taking diphenylalanine (FF, a core recognition motif for molecular self-assembly of the Alzheimer's β-amyloid polypeptides) as a model of bio-inspired dipeptides, recent strategies on modulation of dipeptide-based architectures were introduced with regard to both covalent (architectures modulation by coupling functional groups) and non-covalent ways (controlled architectures by different assembly pathways). Then, applications are highlighted in some newly emerging fields of innovative photoelectronic devices and materials, such as artificial photosynthetic systems for renewable solar energy storage and renewable optical waveguiding materials for optoelectronic devices. At last, the challenges and future perspectives of these bio-inspired dipeptides are also addressed.

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1. Introduction

In nature, many biomolecules can interact and then self-assemble into highly ordered supramolecular architectures in order to optimize their biological functions [1–4]. Among these, peptides are one of the most promising platforms, as they have the intrinsic ability to self-assemble into natural biological architectures such as elongated solid protein fibers and amyloid fibrils in all living systems [5]. Peptides, as short as dipeptides, have been of growing interest as a class of biomaterials as they can provide all molecular information needed for formation of well-ordered structures, which are found in all forms of life from simple bacteria to human cells [6]. Their functions and properties of assembled architectures are universal from the macro-scale (*i.e.*, hair, feather and fur) to micro or even nano-scale (*i.e.*, microtubules, cytoskeletal filaments and actin filaments) [7].

Among the patterns of fabricating nature well-ordered structures, self-assembly plays an extremely pivotal role in both biology and nano-technology [8–11]. Self-assembly, as one of most popular "bottom up" approaches, is a spontaneous organization for formation of highly ordered architectures based on specific interactions of molecules themselves. In general, these specific interactions include hydrogen bonds, electrostatic interactions, π–π stacking, hydrophobic forces, non-specific Van der Waals forces, ionic bonds and chiral dipole–dipole interactions [12–14]. Despite the weakness of these forces individually, the self-assembly process and final micro- or nano-architectures can be effectively manipulated, if they are acting co-operatively. In fact, a wide variety of complex functional micro- and nano-architectures were fabricated by this powerful and elegant self-assembly approach [15–18]. For instance, the formation of biological membranes through self-assembly of phospholipids, maintenance of the DNA double helix via specific hydrogen bonding interactions, protein microtubules and microfilaments as functional units for intracellular interplay, as well as the formation of amyloid fibrils relevant to a variety of neurological disorders or diseases. Therefore, it can be seen that self-assembly is ubiquitous in nature, either to accomplish the biological function of naturally occurring molecules or as part of a pathogenic process. More importantly, inspired by nature, self-assembly of bio-inspired materials has already been extended to many other promising fields (*e.g.*, material science, nano-technology, nano-manufacturing, nano-device and nano-energy) and dramatically promoted their progress [19–25].

One advantage of these bio-inspired peptides is that they are renewable. As we know, there is a huge demand for green and sustainable materials since they might be exhausted in future. Getting inspiration from nature (biomimetics) and further developing bio-energy and biomaterials is an alternative way to meet this demand [26–31]. To date, dipeptide-based architectures have been a growing research field in bio-nanotechnology and biology because of their ease of production, remarkable material properties, relative stability, functional versatility, biological modifiability and biocompatibility, all of which make them versatile and flexible materials with various applications [32–36]. Despite great advances made in dipeptide-based materials, there are still many issues to deal with for promoting their applications. Among these, manipulating their architectures to achieve a desired functionality is very critical and is still a great challenge. However, until now there have been only few articles reviewing strategies on manipulation of architectures of dipeptide-based materials and their inherent mechanism of self-assembly. In light of these, we focus mainly on advances of FF (Fig. 1a) dipeptide (recognized as the core recognition motif for molecular self-assembly of the Alzheimer's β-amyloid polypeptides) in that it always serves as a model of bio-inspired dipeptides which plays a crucial role in formation of fibril likely due to the π–π stacking in Alzheimer's disease [37–39]. Recent strategies on modulation of architectures self-assembled from FF have been systemically introduced with regard to the following two aspects: 1) architecture modulation by coupling functional groups and 2) controlled architectures by different assembly pathways. Their applications are then highlighted in certain newly emerging fields of renewable energy and materials, such as artificial photosynthetic systems for renewable solar energy storage and renewable optical waveguiding materials for optoelectronic devices [40,41]. Also, the challenge and future perspective of these bio-inspired dipeptides were pointed out at the end of this review.

2. Structural modulation and functional integration

Manipulation of self-assembled architectures is always a critical prerequisite to achieve desired functionalities. It has been reported that FF-based materials can self-assemble into various micro- or nano-architectures such as microtubes (MTs), nanotubes (NTs), nanowires (NWs), nanofibers (NFs), nanoribbons, ordered molecular chains and spherical vesicles [42–45]. During the past few decades, many strategies mainly through covalent and non-covalent ways, have been developed to manipulate the formed architectures of FF at the level of supramolecular assembly. It has been demonstrated that their architectures can be finely modulated by variation of some critical procedures, *e.g.*, architecture modulation by coupling functional groups (covalent way) and controlled architectures by different assembly pathways (non-covalent way). Adjustment of these procedures provides effective ways to control the architectures of dipeptide-based materials. In doing so, well-defined architectures or morphologies with desired functionalities are possible to be obtained for fulfilling their specific applications.

2.1. Architecture modulation by coupling functional groups

It has been reported that some bio-inspired dipeptide architectures (*e.g.*, FF NTs and MTs) can display excellent optical or electrical performance, such as light-induced ferroelectricity for information storage [46] and piezoelectricity for future generations of "green" nanopiezoelectrics [47]. To make dipeptide-based materials more functional and widespread, taking FF as a model of dipeptides, chemical modification is one of the most effective approaches to improve the properties of FF through a covalent way. It is well known that the properties of dipeptide-based materials are critical factors affecting their self-assembly performance at both micro- and nano-scale. A great deal of studies has demonstrated that the self-assembled architectures could be finely tuned through this covalent way [48–50]. In general, FF can be chemically modified via its carboxyl group or its amino group (Fig. 1a). The groups connected to FF can be either stimulus-responsive groups such as photo-responsive ones, or be functionality-directed groups (-SH, Boc, Fmoc, etc.) to fulfill their specific purpose. After chemical modification, the nature of self-assembly would be definitely altered likely due to the additional driving force provided by newly conjugated moieties. More importantly, some new optics/photonics or optoelectronics properties might also appear upon chemical modification, which are important to move forward their relevant applications.