学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Formation and Catalytic Activity of Palladium Nanostructure Through the Spatially Oriented Biomineralization Peptide
（立体配向制御バイオミネラリザーションペプチドを介した
パラジウムナノ構造体の形成と触媒活性）

Recently, efforts to elucidate the factors governing the structure and properties of nanomaterials formed from biomineralization have been carried out. These kinds of study are very important since biomineralization is a promising biomimetic approach of forming inorganic nanomaterials that relies on peptides to control the structure. The use of biomineralization peptides (BMPep) offers several advantages over traditional methods of synthesis, such as benign reaction conditions, specific facet binding ability and self-assembly. In addition, this biomimetic approach has been successfully applied in the nanostructure formation of a wide array of relevant metals. From these investigations it has been shown that the BMPep sequence, nature of BMPep binding onto the material surface and BMPep-metal equivalence can affect the structure and catalytic activity of nanomaterials formed from biomineralization. Given that the excellent properties of biogenic materials are attributed to hierarchy and organization, manipulating the topology and valency of the BMPep may thus lead to the formation of high-performance materials (Figure 1). In addition, the interplay among several factors in the microenvironment involved in biomineralization still remains largely unknown and has not been thoroughly examined.

In this study, the effects of the presence of a buffer, as well as the BMPep topology and valency on the structure and catalytic activity of palladium nanomaterials formed from biomineralization are examined. Chapter 1 of this thesis provides a concise introduction on biomineralization and related techniques on nanostructure characterization. Chapter 2 details the effects of the buffer on palladium biomineralization. The formation of coral-like Pd nanostructures using a designed fusion peptide is presented in Chapter 3. The superior catalytic activity of the nanocorals was revealed in Chapter 4, and Chapter 5 provides the conclusions of this work. Palladium is very important in catalysis since it is involved in a wide spectrum of reactions, ranging from C-C cross coupling to functional group reductions. The effects of the presence of a buffer on the structure and catalytic activity of the Pd biomineralized products were analyzed. Buffers are very important components of biomineralization due to the sensitivity of the overall properties of the BMPep with the pH. Moreover, several buffers with different properties are available at identical pH ranges. Buffer-related structural differences were seen from the Pd nanomaterials prepared using the native Pd4 BMPep. In the presence of either Tris or HEPES buffer, smooth and spherical particles were observed wherein larger sizes were formed in HEPES buffered medium. This was in contrast to the severely aggregated particles which were

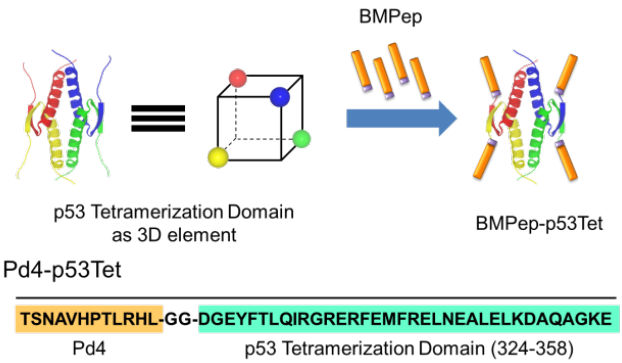

Figure 1. Design strategy of a fusion biomineralization peptide with a highly defined three dimensional orientation. The fusion peptide is composed of a BMPep conjugated with a 3D element. The BMPep used is the Pd4 peptide and the 3D element is the p53 tetramerization domain

formed in the absence of a buffer. Furthermore, the Pd nanoparticles formed under buffered conditions had greater catalytic activity towards the reduction of nitroaminophenol. These results suggest the presence of a buffer participates in the stabilization of the nanoparticle through various functional groups that can bind to metal surfaces. The bound buffer can also influence the binding behavior of the BMPep onto the nanoparticle surface. In addition, the buffer presence maintains the pH of the environment which leads to a more uniform BMPep binding due to the sensitivity of peptide conformations to the pH. Therefore, buffer selection is critical for biomineralization since it can affect both the structure and activity of the nanomaterials. Through this, the buffer can be possibly used to control the structure and activity of Pd nanomaterials which is a very simple and cost-effective way compared with other methods.

Control over the spatial orientation, arrangement and valency of a Pd BMPep was achieved by conjugating it to an oligomeric peptide serving as the 3D control element. The palladium BMPep used was the twelve residue Pd4 peptide which was discovered through phage display. The tetramerization domain of the tumor suppressor p53 protein (p53Tet) on the other hand, was used as the 3D control element. The p53Tet is one of the five domains of the tumor suppressor p53 protein. The p53Tet is located at the C-terminal region and each monomer within the tetrameric assembly contains a β-strand (residues 326-333), a tight turn (residue 334), and an α-helix (residue 335-356). Two dimers are formed through the formation of a joint antiparallel β-sheet between monomers, and the two primary dimers tetramerize through hydrophobic interactions of the helices in a four-helix bundle. Upon tetramer formation, the relative position of the four N-termini of the oligomeric peptide resembles that of the tetrahedron, which is the simplest 3D object (Figure 1). Therefore by conjugating the Pd4 BMPep at the N terminus of the p53Tet, the four Pd4 BMPep segments are spatially fixed and geometrically arranged. Coral-like, 3D porous and amorphous Pd nanostructures were formed through the designed fusion peptide (Pd4-p53Tet). In addition, it was frequently observed that the filaments of the nanocorals were oriented in a tetrahedral orientation which reflects the structure of the designed fusion peptide (Figure 2). The nanocorals formed from Pd4-p53Tet exhibited high catalytic activity towards the reduction of nitrophenol as gauged from the high turnover frequency and rate constants. The catalytic efficiency of the nanocorals possibly emanates from the high 3D character of the materials since materials with a lesser defined 3D structure had weaker activity. This suggests that high-performance materials can be formed by using a 3D-controlled template in order to create materials with well-defined 3D structures.

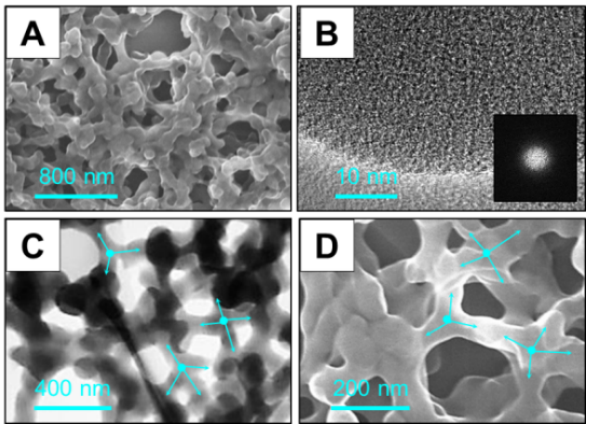

Figure 2. Representative electron microscopy images of the coral-like Pd structures derived from the Pd4-p53Tet peptide. A) SE-STEM image showing the porous nature of the Pd strucutres. B) HRTEM image focusing on a section of the filament which shows the absence of lattice lines. Inset is the SAED FFT pattern confirming its amorphous nature. C-D) STEM images showing the tetrahedral orientation of the filaments at different angles.

By and large, this study has systematically analyzed the effects of two different parameters on the structure and catalytic activity of Pd nanomaterials formed from biomineralization. The study has expanded the knowledge regarding the factors that affect the nanostructure and catalytic activity of materials formed from biomineralization. Moreover, this study has aided in the deeper understanding of biomineralization by providing new and concrete insights regarding the influence of these two parameters, namely the biomineralization peptide topology and valency, as well as the buffer. This study has brought forward the idea that biomineralization can be enhanced in terms of the structure and catalytic activity of the resulting nanomaterials by regulating the BMPep 3D structure and through careful buffer selection.