学 位 論 文 審 査 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　WANG　Yubo

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Dispersion and Stabilization of Gold and Silver Nanoparticles by Topology Effect of Cyclic Poly(Ethylene Glycol)
（環状ポリエチレングリコールのトポロジー効果による金および銀ナノ粒子の分散安定化）

Cyclic polymers of topological effect exhibit unique physical and chemical properties such as higher glass transition temperature, reduced hydrodynamic volume, higher density, as well as higher tolerance towards temperature and salinity of micelles, by compared with their linear counterparts. On the other hand, nano-sized particles such as gold (AuNPs) and silver (AgNPs) nanoparticles are attracting much interest in industrial and biomedical applications due to the recent progress and development of nanotechnology, and the surface modifications by appropriate polymers are key techniques to stably express their characteristics. In this dissertation, cyclic poly(ethylene glycol) (c-PEG) provides polymer topology-dependent stabilization for the surface modification of AuNPs and AgNPs through physisorption, which was found that the cyclic polymers supply superior dispersion stability for the metal nanoparticles. Based on the effect of polymer topology, linear PEG with the end groups of hydroxy (HO–PEG–OH), methoxy (MeO–PEG–OMe), and thiol (HS–PEG–OMe) were compared with c-PEG to be a dispersion stabilizer for AuNPs. AuNPs dispersed by c-PEG exhibits superior stabilization in the different extreme conditions. On the other hand, the AgNPs size was significantly affected in the Tollens synthesis of AgNPs. The particle size is much smaller through the c-PEG as a dispersant than HO–PEG–OH and MeO–PEG–OMe. Furthermore, the stability of AgNPs was enhanced by cyclization in the salt tolerance tests. A novel surface modification through polymer topology towards metal nanoparticles was strictly examined and reported in this dissertation.

Chapter one introduces the background and development prospects of polymer topology effect, the potential materials of gold and silver nanoparticles, the influencing factors on the dispersion stability of metal nanoparticles, and the common dispersants for metal nanoparticles. In the last, objectives, main theme, and an outline of dissertations is carefully described.

Chapter two discusses the phenomena and principles of physisorption between AuNPs and c-PEG. By compared with linear PEG of HO–PEG–OH, MeO–PEG–OMe, and HS–PEG–OMe, c-PEG supplies strongly dispersion stability to AuNPs under the extreme conditions such as freezing, lyophilization, and heating. Especially, this method is comparable with the traditional chemisorption of HS–PEG–OMe. After heating AuNPs coated with HS–PEG–OMe at 85 ºC for 4 h, the red color caused by SPR disappeared. Surprisingly, AuNPs coated with c-PEG remained red, which indicates superior dispersion stability. Furthermore, AuNPs dispersed by cyclic PEG, but not linear PEG, maintain the superior dispersion stability in a phosphate buffer saline (PBS) solution. The strong physisorption between c-PEG and AuNPs is confirmed by DLS, ζ-potential, and FT-IR. The thicker PEG layer and reduced ζ-potential confirms the presence of cyclic PEG layer and the strong affinity between c-PEG and AuNPs. It is expected that the less entropic penalty upon adsorption is the major factor strong affinity of c-PEG to AuNPs.

Chapter three discusses the influence of size controlling and stability in the synthesis process of AgNPs by c-PEG. As a dispersant of PEG, the polymer topology of linear and cyclic polymer conversion has a significant effect on the size of the synthesized AgNPs. By compared with linear PEG of HO–PEG–OH and MeO–PEG–OMe in the same molecular weight and molar ratio, the utilization of c-PEG in Tollens' synthesis of AgNPs allows for the smaller and more narrow size. Furthermore, the synthesized AgNPs stabilized by c-PEG drastically improved stability against NaCl aqueous solution, by compared with the linear counterpart dispersant. It can be concluded that cyclized polymers endow AgNPs with superior stability and high salt resistance.

Chapter four summarizes the results about this dissertation. Based on the polymer topology effect, this methodology of c-PEG toward gold or silver nanoparticles supplies a novel approach for the colloidal stabilization, which is not suitable for other linear counterparts. It provides a new physisorption on the surface modification of nanoparticle without undergoing chemical reactions or chemisorption, retaining the original properties of the metal nanoparticles. The high stabilization, high dispersion, salt, and heat resistance of c-PEG system gives it potential for bio-medicine applications. This dissertation can be recognized to be awarded a Ph.D. degree in engineering from Hokkaido University.