HOKKAIDO UNIVERSITY

Title	Chemical and Physical Synthesis of Cationically Charged Photoluminescent Noble Metal Nanoclusters [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第12899号
Issue Date	2017-09-25
Doc URL	https://hdl.handle.net/2115/67523
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Ryan_Dula_Corpuz_abstract.pdf, 論文内容の要旨

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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　Ryan Dula Corpuz

学 位 論 文 題 名

Chemical and Physical Synthesis of Cationically Charged Photoluminescent Noble Metal Nanoclusters

(カチオン性フォトルミネセンス貴金属ナノクラスターの化学および物理合成)

Metal nanoclusters had received increasing popularity for the past decades due to its important role in both experimental and theoretical studies. It is considered as the missing link to understand the behavior of individual atoms as it forms to a more ordered nanoparticles and thus controlling the number of atoms as the cluster increases or decreases in size had been a challenge and priority among nanocluster organic chemist, physical chemist and materials scientists. To do so, several chemical and physical approaches had been developed which could be broadly classified as top down or bottom up approaches.

In most chemical synthethic methods, metal precursors are usually reduced with the use of reducing reagents like $NaBH_4$ and then capped or stabilized with ligand such as proteins, DNA, polymers, dendrimers and monomers which have functional groups that have strong affinity to coordinate with the metal atoms. Among of these ligands, phosphines and thiols are the most popular and intensively studied. In this work, the researcher focused on the latter, which is commonly referred to as cationic thiolated metal nanoclusters.

Thiol ligands which had been popularized by Brust for the synthesis of nanoparticles and had been extended by Murray and Whetten for the synthesis of metal nanoclusters could be broadly classified in to neutral, anionic and cationic. However, among of these thiols, the cationic one is the less popular and rarely found in literatures especially for the synthesis of photoluminescent noble metal nanoclusters. Thus, this study aims to synthesize a cationically charged photoluminescent noble metal nanoclusters.

Cationically charged photoluminescent metal nanoclusters had important application in the field of biomedicine. In a lot of studies, it was found that cationic species has high affinity to interact with giant DNA.

In Chapter 1, general introduction of fluorescent nanocluster systems are provided and the objective of this study is introduced.

Chapter 2 introduces a new chemical synthesis of positively charged photoluminescent gold nanoclusters. Specifically, thiocholine molecule, a short quaternary ammonium cation which is positively

charged in all pH conditions was used as stabilizing and capping ligand coupled with sodium dodecyl-sulfate (SDS) to control the electrostatic repulsion of coordinating ligands as it attach to the surface of the particle. Consequently, we are able to observe a correlation between the thiocholine-SDS concentrations with the particle size of the nanoclusters produced. At higher concentrations of thiocholine-SDS combination, we successfully produced blue photoluminescent Au monometallic nanoclusters. However, due to the difficulty of collecting a pure product with this strategy and the inherent toxicity of the reagents used ($NaBH_4$, SDS, methanol and NaOH), we report to physical synthesis by means of sputtering method to make our product useful for biomedical applications.

Chapter 3 highlights the synthesis of positively charged photoluminescent Au, Ag and Cu nanoclusters by single target sputtering in liquid polymer matrix using 11-mercaptoundecyl-*N,N,N*-trimethylammonium bromide (MUTAB) as stabilizing and capping ligand. Accordingly, photoluminescent Ag and Cu nanoclusters with blue emission and photoluminescent Au nanocluster with orange emission in both solution and solid states were generically produced in this green strategy.

Chapter 4 gives the most ambitious and novel topic, Au-Ag bimetallic nanocluster system. For the first time, we demonstrated the correlation of composition with the observed emission of a positively charged photoluminescent bimetallic Au-Ag nanoclusters synthesized by means of double target sputtering on a biocompatible polymer matrix using MUTAB as ligand. We made this possible by controlling the applied current of the metal targets. As a result, we are able to tune the emission color of the bimetallic nanoclusters from blue to near infrared regions.

Chapter 5 concludes the results obtained in this thesis.