HOKKAIDO UNIVERSITY

Title	Use of Coated Electrode in Microwave-Induced Plasma-in-Liquid Process to Synthesize Metal Nanoparticles [an abstract of dissertation and a summary of dissertation review]
Author(s)	Cempel, David
Citation	北海道大学. 博士(工学) 甲第13202号
Issue Date	2018-03-22
Doc URL	http://hdl.handle.net/2115/69934
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/4.0/
Type	theses (doctoral - abstract and summary of review)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	David_Cempel_abstract.pdf (論文内容の要旨)

Instructions for use

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

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　David Cempel

学 位 論 文 題 名

Use of Coated Electrode in Microwave-Induced Plasma-in-Liquid Process to Synthesize Metal Nanoparticles
(金属ナノ粒子を合成するために用いられるマイクロ波液中プラズマ法におけるコート電極の利用に関する研究)

Metal nanoparticles (NPs) are under immense interest for their unique optical, electrical, and catalytic properties. In various applications, e.g. electronics, photodynamic therapy, therapeutic agent delivery, sensors, probes, diagnostics, catalysis, and cancer treatment, green synthesis of pure metal NPs are highly in demand.

Microwave induced plasma in liquid process (MWPLP) has become a green and effective method for the preparation of metal NPs. This thesis aims to create highly pure metal and alloy NPs with size and composition control and improve the understanding of the NP formation using MWPLP. Yttrium oxide (Y_2O_3) coated stainless steel electrode have been introduced to obtain highly pure NPs via preventing the loss of electrode materials. MWPLP with coated electrode is advantageous compared with conventional methods in terms of high purity of the obtained NPs and non-necessity to use toxic solvent and reducing agents (alcohol, $NaBH_4$, N_2H_4, citrate, polyol, etc.) thereby lower impact on the environment. The MWPLP also eliminates complicated purification and separation of NPs from liquid dispersion. Microwave generated non-equilibrium plasma in water at reduced pressure thermally decomposes water molecules and provide various highly reactive chemical species (e.g. solvated electron (e^-_{aq}) and hydrogen (H●) radicals), which can reduce metal ions, M^{n+}. The reduction of metal ions by reactive species formed in plasma discharge can occur as follows:

M^{n+} + nH● → M_0 + nH^+

M^{n+} + ne^-_{aq} → M_0

at low pH or via below reaction:

M^{n+} + ne^-_{aq} → M_0

at high pH.

Composition and size of NPs can be controlled by adjusting the conditions of the synthesis (reaction time, pH, type and amount of precursor and protecting agent).

In the chapter 2, the time-dependent formation and growth of gold NPs during MWPLP with L-arginine as bio-compatible protecting agent was investigated together with the effect of the solution pH on formation of gold NPs. We were able to obtain highly pure Au NPs with bimodal size distribution for pH in range of 3.5 – 12.0. The fraction of small sized Au NPs became significant at pH 6.0 and 12.0 while that of big sized Au NPs was dominant at pH 3. This change in the size distribution of Au NPs was governed by different reduction rate of gold ions at different pH.

In chapter 3, the synthesis of highly uniform and small sized Ag NPs via MWPLP was studied. Ag

NPs are widely used for their high optical extinction, anti-bacterial, and lower cost than Au NPs. Small sized Ag NPs show improved anti-bacterial activity but it is very challenging to produce monodispersed Ag NPs with small size. Moreover, it is necessary to protect such small Ag NPs from aggregation caused by their high surface energy. Here, the influence of different precursor ($AgNO_3$ and $[Ag(NH_3)_2]^+$) and various amount of L-arginine as the stabilizing agent on the formation of Ag NPs in MWPLP was investigated. L-arginine was chosen because as one of the essential amino acids, it's highly biocompatible and non-toxic. As a result, a strong influence of L-arginine on NP size, and of silver diamine complex on the uniformity of the synthesized Ag NPs was observed. In particular, uniform, small sized (with the average diameter ca. 5 nm) and highly pure Ag NPs were obtained by using $[Ag(NH_3)_2]^+$ and large amount of L-arginine during MWPLP. The obtained Ag NPs were effectively stabilized by functional group contributed by L-arginine as was confirmed by FT-IR.

Au/Ag alloy bimetallic NPs have been intensively investigated due to their tunable plasmonic properties and their applications in optics and biosensing. In the fourth chapter, green synthesis of noble metal Au/Ag alloy NPs via MWPLP was studied. Suitable metal source, i.e. $HAuCl_4$ and $[Ag(NH_3)_2]^+$ and high reaction pH, i.e. 11 were chosen to overcome the formation of AgCl and single metal NPs. Consequently, Au/Ag alloy NPs were obtained by MWPLP without addition of any protecting or reducing agents. It was confirmed by STEM-EDX mapping that Au-Ag alloy NPs were successfully synthesized after 140 minutes reaction duration. Moreover, Au/Ag alloy NPs of different compositions were obtained via varying the input ratios of Au and Ag precursor.

The formation of Au/Ag alloy NPs was investigated via time dependent NP composition and sizes' study. In the beginning period of the plasma discharge only small Au NPs with tendency to aggregation could be observed, this can be attributed to the fastest reduction rate of Au^{3+} ions in comparison with Ag^+ ions. After 60 min Ag NPs were observed followed by alloying of Au and Ag.

It is impressive that using MWPLP we can synthesize Au/Ag alloy NPs without addition of any protecting agent.

The fifth chapter contains conclusions of this thesis. Preparation of highly pure metal and metal alloy NPs, controlling their composition, and understanding of their formation have been achieved using MWPLP process with coated electrode. Investigation of metal sources, pH, protecting agents are important to obtained optimal conditions for making Au, Ag, and Au/Ag alloy NPs. The method developed here can contribute to the progress in nanotechnology and its applications.