Interaction between RF plasma and the graphite-encapsulated gold nanoparticle prepared by DC arc discharge method DCアーク放電法で生成したグラファイト被覆金ナノ微粒子と RFプラズマとの相互作用

 Enbo Yang¹, Han Chou² and Masaaki Nagatsu^{1,2}

 揭 恩波¹, 張 晗², 永津 雅章^{1,2}

 ¹Graduate School of Science and Technology, Shizuoka University,

 ²Graduate School of Engineering, Shizuoka University, 3-5-1, Johoku, Naka-ku, Hamamatsu 432-8561

 ¹静岡大学創造科学技術大学院

 ²静岡大学大学院工学研究科, 〒432-8561 浜松市中区城北3-5-1

We have developed a set of sophisticated plasma processing technology to fabricate and functionalize the graphite-encapsulated magnetic and gold nanoparticles. DC arc discharge plasma was used for fabricating the nanoparticles. To make the particle bio-compatible, amination using RF plasma was consequently conducted to treat and improve the surface of the as-fabricated nanoparticles. To study the role of the plasma during the surface modification for the graphite-encapsulated gold nanoparticles, characterization methods such as HR-TEM, XRD, XPS, Raman and UV-Vis spectroscopy analyses were employed to evaluate the properties of the nanoparticles.

1. Introduction

Carbon-coated metal nanoparticles have attracted many interests due to their combined properties of the carbon layers and the metal core. Previously, fabrication and surface modification of graphite-encapsulated magnetic nanoparticles have been systematically studied in our lab.[1,2] We have demonstrated the fabrication and surface modification of the graphite-encapsulated gold nanoparticles using arc discharge plasma [3] and radio-frequency (RF) inductively coupled plasma device respectively. Graphite-encapsulated gold nanoparticle is a new nano-sized material which has a gold core and several robust graphite layers covering the core. Fig. 1 shows two typical TEM images of the as-fabricated particle. From the images, it is very clear that the uniform sized graphite-encapsulated gold nanoparticles have been formed, also the graphite layers and the gold core can be seen with bigger magnification. It should be potential candidate nanoparticle aiming to the biomedical and biological applications due to its combined properties of the gold core and the carbon layers.

2. Experimental

The experiments started from the direct current arc discharge fabricating the graphite-encapsulated gold nanoparticles which was very robust and stable. To make the particle bio-compatible, plasma amination using RF plasma was consequently conducted to treat and improve the surface of the as-fabricated nanoparticles. Finally, the nanoparticles will be immobilized by some bio-molecules to confirm the capability for further biological and biomedical use. To learn more detailed properties of the graphite-encapsulated



Fig. 1 Typical TEM image for the as-fabricated graphiteencapsulated gold nanoparticles. a) in smaller magnification, b) in bigger magnification

gold nanoparticles and also optimize the plasma condition for amino group introduction, we have repeated the plasma surface modification experiments with various plasma parameters, for instance varying the treatment time, gas pressure, and power and so on.



Fig. 2 XRD pattern of the graphite-encapaulated gold nanoparticles powder on Si substrate.

To evaluate the properties of the pristine and surface modified nanoparticles, several characterizations such as HR-TEM, XRD, XPS were performed on the particles. Also Raman and UV-vis spectroscopic studies were done.

To understand the role of the plasma also the interactions between the nanoparticles and plasma during the surface modification period, we measured the optical emission spectra (OES) of the RF plasma. Confirmation of the amino groups which have been introduced onto the surface was done using fluorescence dye. Absolute amino groups population quantification was conducted using the sulfosuccinimidyl 6-[3A(2-pyridyldithio)-propionamido] hexanoate (sulfo-LC-SPDP) chemical derivatization.

3. Results and discussion

The fabrication and surface modification have been demonstrated as reported earlier [4], the size of the as-fabricated nanoparticles was around 10-30 nm in diameter with a uniform core-shell structure.

XRD analyses were conducted to confirm the crystallite structure of the fabricated particles. Figure 2 shows a typical XRD pattern for the as-fabricated nanoparticle powder. The graphite (002) and several gold crystallite structures including (111), (200), (220), (311) and (222) located at 2θ =26.6° 38.5°, 44.5°, 64.9°, 78.0° and 82.0° were identified. Signals of occurred at around 21.7° and 69.3° corresponding to SiO₂ (111) and Si (400) planes should come from the Si substrate used for placing the powder.

As for the OES, we measured the spectra of the ammonia plasma used for the nanoparticle surface modification, NH, N_2 series lines could be identified as shown in Fig. 3. This result suggested the possible atomic physical and chemical processes happened in the plasma.

The population of amino group for each particle was roughly estimated as the magnitude of 10^5 . So far, we have got the morphology information and size distribution of the particle, population of amino groups introduced for each particle and observed surface plasmon resonance phenomena from the gold nanoparticles.



Fig. 3 Typical Optical emission spectra of the ammonia plasma generated by RF power of 80 W.

To understand what happened in the plasma and the behavior of each radical and species, several kinds of plasma diagnostic methods such as measuring the electron density, atomic spectra, and species identification will be done. Currently, we are preparing the related experiments. For each part, to obtain more reproductive results and to improve the accuracy of the data, we should repeat the experiment several times. More details of the results will be presented in the preesentation during the conference.

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (Grant No. 2110010) from the Japan Society for the Promotion of Science.

References

[1] T. E. Saraswati, T. Matsuda, A. Ogino, M. Nagatsu, Diam. Relat. Mater. 20 (2011) 359.

[2] Teguh Endah Saraswati, Shun Tsumura and Masaaki Nagatsu, Jpn. J. Appl. Phys. 53 (2014) 010205.

[3] M. Nagatsu, T. Yoshida, M. Mesko, A. Ogino, T. Matsuda, T. Tanaka, H. Tatsuoka and K. Murakami: Carbon 44 (2006) 3336.

[4] E.Yang and M. Nagatsu, Jpn. J. Appl. Phys. 53 (2014) 010206.