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Optical Spectroscopic and Mass Spectrometric Measurement during the Surface Modification Process of Graphite-encapsulated Magnetic Nanoparticles Using Ar/NH$_3$ Gas Mixture Plasma

Ar/NH$_3$混合ガスプラズマを用いたグラファイト被覆磁性体ナノ微粒子表面修飾過程における光学および質量分析計測

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In this research, graphite - encapsulated magnetic nanoparticles (GEMNPs) were used to introduce the amino group on the surface of particles for bio-medical application by using inductively coupled RF plasma. GEMNPs were prepared by using the DC arc discharge. To introduce amino group on the surface of nanoparticles, an RF driven Ar/NH$_3$ mixture plasma was used. To investigate the mechanismand improvement of surface modification, we used spectroscopic and mass spectrometry measurement.

1. Introduction

Because of the excellent superparamagnetic property of the graphite-encapsulated magnetic nanoparticles (GEMNPs), they could be easily controlled by magnetic force. Recently, many bio-applications with magnetic nanoparticles, such as drug delivery system (DDS) used to deliver the medicine into the body and bio-sensor to detect the biological material, have been extensively researched. To utilize the GEMNPs to bio-application, it is required to immobilize bio-molecules to surface of nanoparticles. If GEMNPs are modified by functional groups (carboxyl group, amino group, etc.), we can make it easy to immobilize bio-molecules selectively. There are many methods to surface modifications, such as wet chemical process, heating, or plasma. Among them, plasma technique is more preferable to use because it provides us a dry process at low temperature.

2. Experimental setup

The GEMNPs were made by arc discharge method. The chamber of arc discharge device was filled with CH$_4$/He mixture gas and pressure is maintained at 650 Pa. Graphite rod was used as electrode of discharge. We implanted Fe$_2$O$_3$, graphite bond and graphite powder to graphite rod as discharge electrodes. DC voltage of 20 V was supplied to electrode and flowing current was about 100 A. Iron and graphite was evaporated uniformly by arc discharge heat. After reacted with CH$_4$, they cooled by He. Then iron particles as core metal are capsulated by graphite layers. Iron particle as core metal are encapsulated by several graphite layers.

Next, to confirm their structural characterization, TEM analysis was carried out. Figure 1 shows the HR-TEM image of GEMMPs. Iron particles as core metal are capsulated by several graphite layers. The particles diameter is found to be about 10-50 nm in diameter.

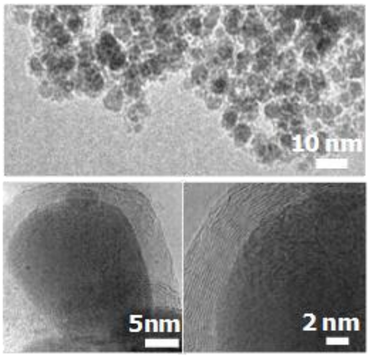

Fig. 1 TEM images of GEMNPs structure

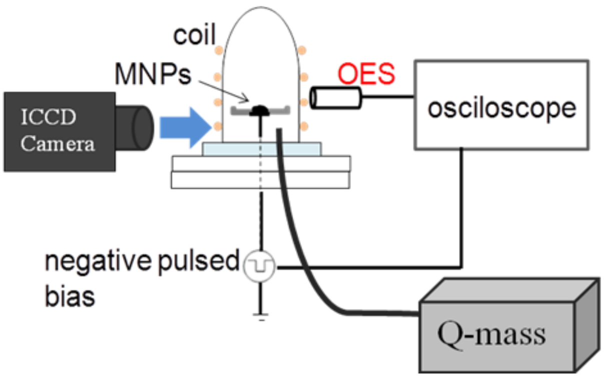

Fig. 2 RF driven inductively coupled plasma device.

We treated GEMNPs with an inductively coupled radio frequency plasma device shown in Fig. 2.

To introduce amino group on surface of the particles, NH_3 plasma was used. Sample was put on electrode plate, during the discharge negatively biased by a high voltage pulse power was supplied. We investigated the effect of negative bias on the surface modification of the particles.

3. Results and Discussion

After turning on the biasing, the high negative voltage caused the substrate as the powder stage was charged with the electron negative charge. The existence of high negative charges caused the ions within the plasma comes into substrate in rapid speed where the powder was placed. Because the powder was not in compact state, but in loose state, once it hit by plasma ions, the powder was spontaneously popped out and blew upwards in a very fast action (recorded in milliseconds). This phenomenon is similar with ion bombardment incident. Fig.3 is showing the mechanism of blowing up, and Fig.4 is showing the behavior of particles in blow up process taken by the digital camera.

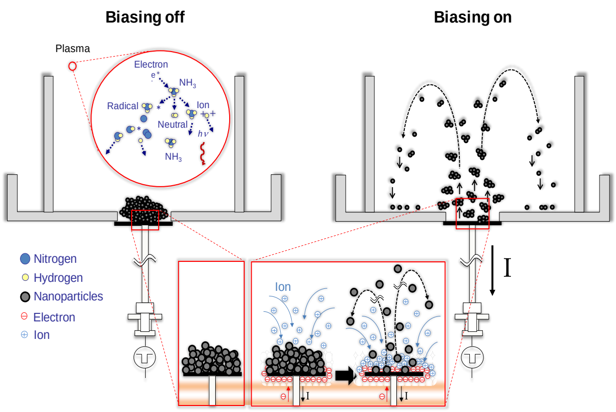

Fig. 3 Illustration of powder blowing due to ion bombardment method.

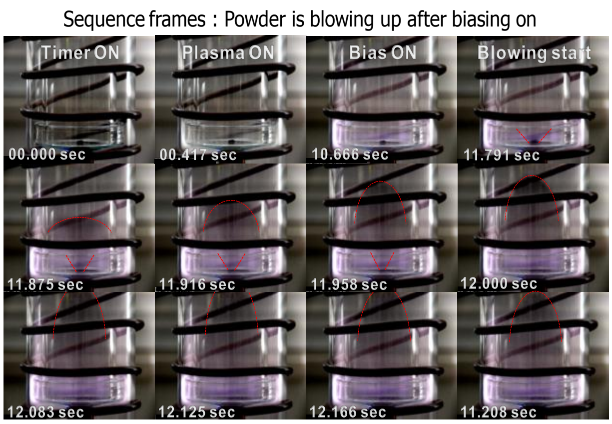

Fig. 4 Particle explosion by negative pulsed biasin***g.***

We also used OES and checked the intensity of NH line at 336.0nm during powder blowing up. Fig.5 is showing the result. We could observed forth big change from Fig.5, and we named it phase 1 to phase 4. At phase 1, because it is before the powder explosion, the intensity of NH is stable. We turned on Bias. Phase 2 is after biasing ON. We observed emission intensity decreases. This is because the powder introduced into plasma, and blocked the plasma. At Phase 3, powder moved over the region of OES measurement. So, Emission intensity increases again. At phase 4, after powder dropping down, emission intensity recovered to the first condition. From these changing, we could conclude that the powder was introduced into plasma..

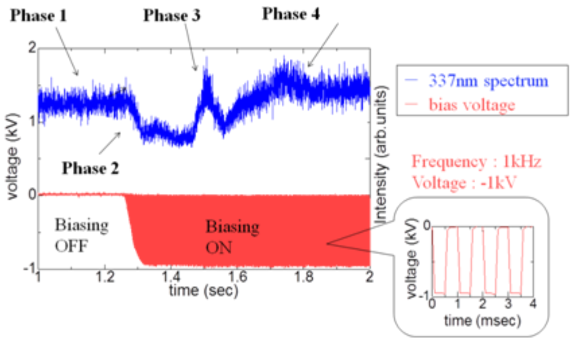

Fig. 5 Emission intensity of NH during blowing up

4. Conclusion

We have carried out surface modification of GEMNPs using negative bias technique. If the powder was introduced into plasma, the interaction effect with plasma becomes stronger. We could expect the surface functionalization of amino group can be enhanced. At first, we observed powder blowing up process used camera and OES. We also used ICCD camera and Q-mass to take the powder behavior picture and measure plasma more detail. More detail of result about interaction will be presented at the meeting.

Acknowledgements

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