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Formation of gold and iron oxide nanoparticles encapsulated in boron nitride sheets

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Boron nitride nanocapsules with gold and iron oxide nanoparticles were produced by arc melting in a nitrogen gas atmosphere using a tungsten electrode and a boron-based mixture powder. High-resolution electron microscopy and electron energy-loss spectroscopy showed that the gold and iron oxide nanoparticles were encapsulated in the boron nitride sheets. The present work indicates that conducting and magnetic nanoparticles surrounded by insulating boron nitride sheets can be produced by the ordinary arc-melting method.

Nanoclusters encapsulated in carbon hollow-cage structures are intriguing for both scientific research and future device applications such as cluster protection, nanostructure devices and catalysis.[1,2] Recently, we have succeeded in the formation of carbon nanocapsules by thermal decomposition of polyvinyl alcohol with SiC clusters at 500 °C in an Ar gas atmosphere.[3,4] We have also succeeded in producing Pd intercalated onions by electron-beam irradiation.[5] These materials are expected to be useful as solid state lubricants, nano-ball bearings, and magnetic devices. However, the graphite sheets are conductive, and insulating sheets such as boron nitride (BN) are needed for the control of electrons in future nanoscale devices.

Several works on BN nanotubes have been reported recently.[6–10] Since BN nanotubes constitute a very exciting field, these works were focused on the formation of BN nanotubes. Although some BN nanocapsules have been observed in previous works,[6,9] there are few works focused on the formation of BN nanocapsules.

The purpose of the present work is to prepare BN nanocapsules with nanoclusters, which have magnetic and electronic properties. Gold and iron oxide nanoparticles were selected in the present work. Gold colloids have been used for the formation of single electron transistors[11,12] because of easy control of the cluster size.[13] In the present work, gold nanoparticles with BN sheets were selected, which are expected to behave as quantum electronic devices. Ferrimagnetic Fe_3O_4 compounds are expected to act as magnetic devices.[14] These iron oxide nanoparticles should be dispersed in a non-magnetic matrix, and BN nanocapsules are very attractive for the formation of dispersed magnetic nanomaterials. To understand the formation mechanism of the nanocapsules, high-resolution electron microscopy (HREM) and electron energy-loss spectroscopy (EELS) were carried out for microstructure analysis. These studies will give us guidelines for the design and synthesis of BN nanocapsules, which may form future nanoscale devices.

Boron particles (99%, 40 µm, 1 g, Niraco Co. Ltd.) were mixed with gold particles (99.5%, 0.5 µm, 4.56 g, Niraco Co. Ltd.) and iron oxide particles (10 nm, 1.85 g, ULVAC Co. Ltd.). Atomic ratios of B : Au and B : Fe_3O_4 were 8 : 2. The mixture powder was pressed at 15 kg mm^{-2} into pellets with the size of 1 mm height and 20 mm in diameter. The green compacts were set on a copper mold in an electric-arc furnace, which was then evacuated down to 1×10^{-3} Pa. After introducing a mixed gas of Ar (0.06 MPa) and N_2 (0.06 MPa), arc melting was applied to the samples at an accelerating voltage of 60 V and an arc current of 200 A for a few minutes. Arc melting was performed with a vacuum arc-melting furnace (ACM-01, Daia Vacuum Engineering Co. Ltd.). After the arc melting, a white or gray powder was obtained around the pellets.

Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM observation was performed with 300 kV and 200 kV electron microscopes (JEM-3000F and JEM-2010). To detect boron and nitrogen, EELS analyses were performed. The electron microscope (JEM-2010) is equipped with EELS with a model 676 PEELS (Gatan Inc.).

A HREM image of BN nanocapsules with Au nanoparticles is shown in Fig. 1(a). The particle size is in the range of 10–30 nm, and all particles are surrounded by BN sheets. An enlarged HREM image of BN nanocapsules is shown in Fig. 1(b). Lattice fringes with distances of 0.23 nm and

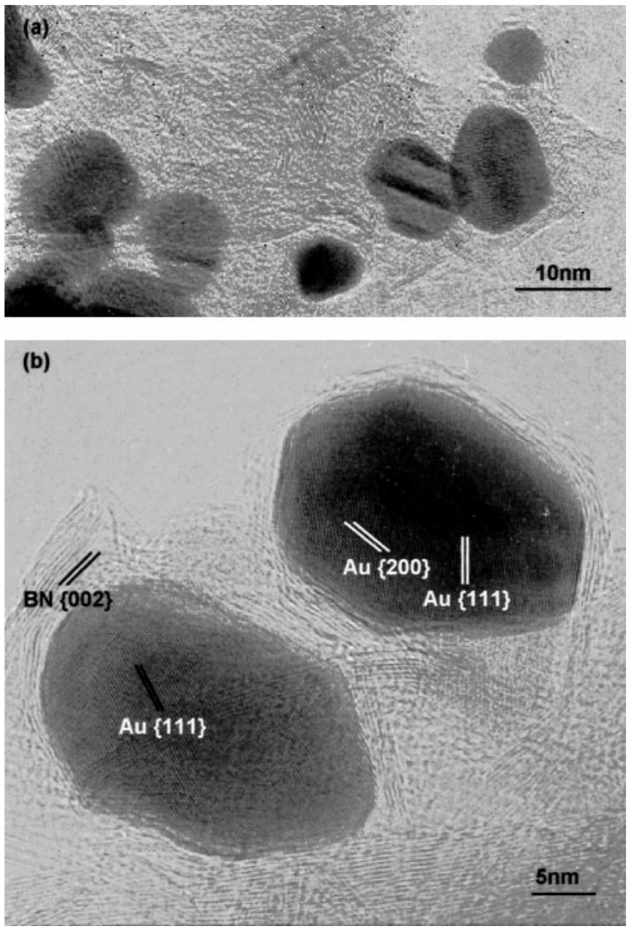

Fig. 1 (a) HREM image of arc-melting Au particles with boron particles. (b) Enlarged HREM image of the BN nanocapsules.

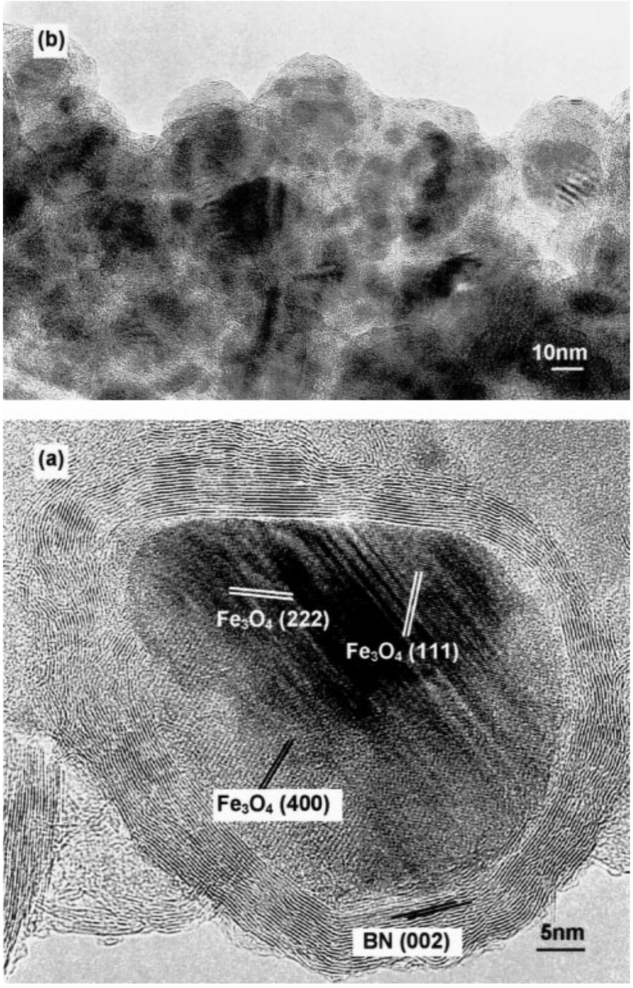

Fig. 2 (a) HREM image of arc-melting Fe_3O_4 particles with boron particles. (b) Enlarged HREM image of the BN nanocapsule.

0.20 nm, which correspond to the distances of the {111} and {200} planes of Au, are observed in the clusters. The {002} planes of BN are observed around the Au nanoparticles, which divide the Au nanoparticles. The number of BN sheets is in the range of 5–10 layers.

A HREM image of BN nanocapsules with iron oxide nanoparticles is shown in Fig. 2(a). The particle size is in the range of 10–20 nm. An enlarged HREM image of a BN nanoparticle is shown in Fig. 2(b). Lattice fringes with distances of 0.47 nm, 0.23 nm and 0.20 nm, which correspond to the distances of the {111}, {222} and {400} planes of Fe_3O_4, are observed in the clusters. The number of BN sheets is in the range of 15–20 layers, and many defects are observed.

Fig. 3 is a EELS spectrum of the BN nanocapsules with iron oxide shown in Fig. 2. Two distinct absorption features

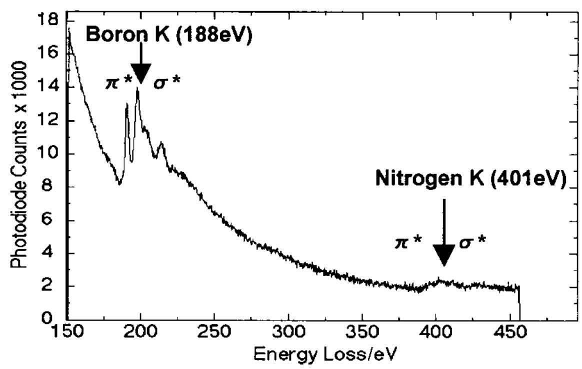

Fig. 3 EELS spectrum of BN nanocapsules.

are observed at 188 eV and 401 eV, which correspond to boron K-edge and nitrogen K-edge onsets, respectively. The fine structure of boron in the EELS spectrum shows the hexagonal bonding between boron and nitrogen, which is indicated by the presence of a sharp π^* peak and the shape of the σ^* peak. The EELS spectrum also shows the weak σ^* peaks of B and N, which indicate the spherical structure of BN nanocapsules.

The crystal structure of hexagonal BN (h-BN) is similar to that of graphite. However, from the viewpoint of electronic conductivity, BN is an insulator and graphite is a conductor. Since BN is an insulator, it is very difficult to form peculiar nano-structures such as BN nanotubes and BN nanocapsules by the arc discharge or arc melting methods.

Although some studies on the synthesis of BN nanotubes have been reported, detailed works on the synthesis and analysis of BN nanocapsules have never been reported. However, nanostructures of metal particles encapsulated in BN sheets have been observed as by-products of the synthesis of BN nanotubes in previous studies.[8,9] In these works, included metals and compounds had never been confirmed by phase identification and structure analysis. In both cases, specific conducting electrodes such as BN-packed tungsten rods and HfB_2 electrodes were prepared and used for arc discharge.

In the present work, the purpose is to form BN nanocapsules, which were prepared by the arc melting method with a metal-mixture powder. The present method has two advantages for nanocapsule production. Since the powder becomes conducting by pressing, special electrodes are not needed. In addition, ordinary arc-melting furnaces can be used. BN nanocapsules with gold and iron oxide nanoparticles were successfully prepared by the present method.

The formation mechanism of BN nanocapsules synthesized in the present work is discussed. The size of gold nanoparticles after arc melting was in the range of 10–20 nm, and they were smaller than the starting gold particles (0.5 μm). It is considered that the gold particles with a melting point of 1064 °C melted once. Because of the insolubility of boron with gold and nitrogen with gold, boron would react only with nitrogen. Boron reacts with nitrogen at temperatures over 1200 K. As a result, gold nanoparticles encapsulated in BN nanocapsules were formed. On the other hand, the size of the iron oxide nanoparticles after arc melting was in the range of 10–20 nm, and they are almost as small as the starting iron oxide nanoparticles (10 nm). It is considered that the iron oxide nanoparticles would not melt. Boron particles, which adhered to the iron oxides, would react with nitrogen gas. As a result, the iron oxide nanoparticles were encapsulated in BN nanocapsules.

BN nanocapsules are expected to have various properties. It is expected that gold nanoparticles encapsulated in BN nanocapsules enable the control of a single electron through the insulator sheets, and they can be applied to single electron transistors.[12,13] If the iron oxide nanoparticles are divided by BN sheets with a thickness of less than 3 nm, superparamagnetism is expected, and they can be applied to magnetic refrigeration.[15] In the present work, the formation processes of nanoscale insulator sheets and non-magnetic sheets around metal nanoparticles were developed, and the method is expected to be applied to nanostructure devices in the future.

In conclusion, the conducting and magnetic nanoparticles encapsulated in insulating BN sheets could be produced by the ordinary arc-melting method in the present work, and these BN nanocapsules have potential for single electron transistors and dispersed magnetic nanomaterials.

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