JOURNAL OF
Materials
CHEMISTRY
Communication

Chemical synthesis of silver nanoparticles encapsulated in boron nitride nanocages

Takeo Oku,* Takafumi Kusunose, Koichi Niihara and Katsuaki Suganuma

Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka, 567-0047, Japan. E-mail: Oku@sanken.osaka-u.ac.jp

Received 19th October 1999, Accepted 23rd November 1999

Silver nanoparticles encapsulated within boron nitride nanocages were produced from mixtures of boric acid, urea and silver nitrate upon reduction at 700 °C in hydrogen; this is a useful fabrication method for the mass production of boron nitride nanocapsules at low temperatures compared to the ordinary arc discharge method.

Nanoparticles encapsulated in carbon nanocage structures are anticipated to feature in both scientific research and future device applications such as cluster protection, nano-ball bearings, nano-optical–magnetic devices, catalysis and bio-technology.[1–5] However, graphite sheets are conductive, whereas insulating sheets such as boron nitride (BN) are required for the control of electrons in future nanoscale devices. Although some BN nanocapsules have been observed as by-products from BN nanotube synthesis in previous work,[6,7] there are few reports on the formation of BN nanocapsules.

In our previous work,[8] BN nanocapsules encapsulating Fe_3O_4 and Au nanoparticles were produced by an arc melting method, and the nanostructure was investigated by high-resolution electron microscopy. However, the amount of produced BN nanocapsules was very small (*ca.* 1 mg), and it was difficult to evaluate their optical, magnetic or electronic properties. Clearly, synthesis of a larger amount of BN nanocapsules was required.

The purpose of the present work was to develop a new synthetic process to provide large amounts (>1 g) of BN nanocapsules containing nanoparticles with electronic properties. Urea [$CO(NH_2)_2$] and boric acid (H_3BO_3) were selected in an attempt to prepare BN layers. A mixture of these two reagents is expected to form BN layers upon annealing in hydrogen.[9] In the present work, silver nitrate was selected as the source of silver nanoparticles, a quantum electronic material which behaves as single electron transistors.[10,11] Furthermore, since all the precursors are soluble in water, it is possible to mix them homogeneously. To understand the formation mechanism of the nanocapsules, high-resolution electron microscopy[12,13] (HREM) and energy dispersive spectroscopy (EDS) were carried out for microstructure analysis. These studies serve as a guideline for the design and synthesis of the BN nanocapsules.

The BN content was adjusted to between 70 and 95 vol%. Boric acid, urea and silver nitrate were dissolved in deionized water which was then removed using a rotatory evaporator. The dried mixtures were reduced at 300 and 700 °C in H_2 for 7 h and the samples were investigated by X-ray diffraction (XRD).

Samples for HREM were prepared by dispersing the materials on holey carbon grids and observation was performed with a 300 kV electron microscope (JEM-3000F) equipped with EDS system (EDAX). The point-to-point resolution was 0.17 nm.

A HREM image of Ag nanoparticles in a BN matrix prepared at 300 °C is shown in Fig. 1(a) with a BN content of 95 vol%. The particle size of the Ag nanoparticles in the BN matrix was *ca.* 2 nm, with a low size distribution (±0.5 nm). Lattice fringes with a distance of 0.24 nm corresponding to the {111} separation of Ag were observed in the clusters while the BN matrix was amorphous. A HREM image of Ag nanoparticles in a BN matrix prepared at 700 °C is shown in Fig. 1(b) with a BN content of 70 vol%. No clear differences were seen for the 70 and 95 vol% BN matrices. The amorphous BN is crystallized in a turbostratic BN (t-BN) structure. The size distribution of the Ag nanoparticles was in the range

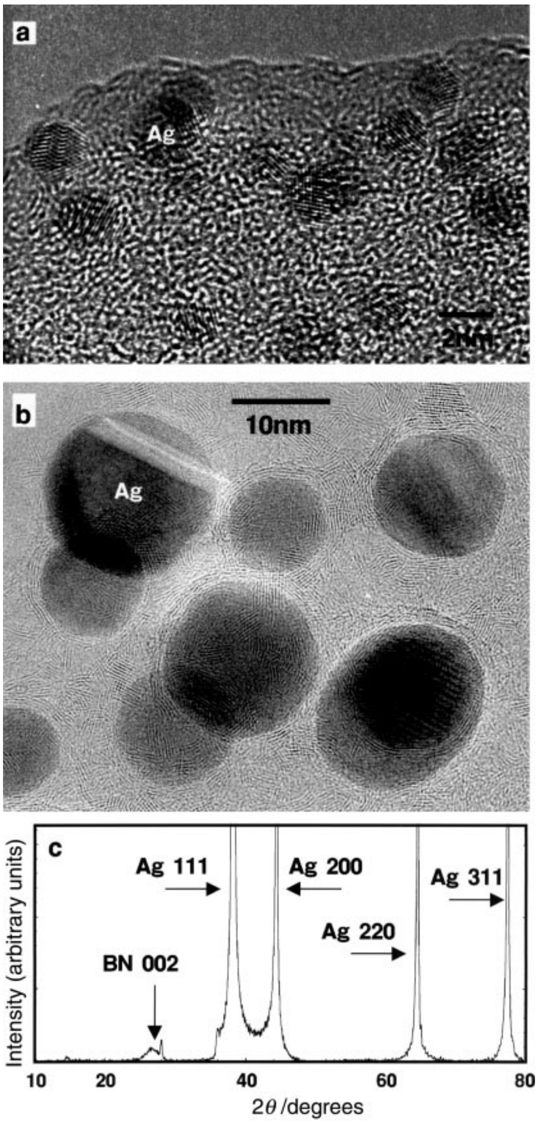

Fig. 1 HREM image of Ag nanoparticles in a BN matrix prepared at (a) 300 and (b) 700 °C. (c) XRD pattern of (b).

5–60 nm with most particles of size 10–20 nm. All Ag nanoparticles are encapsulated in BN {002} sheets, which indicates the formation of BN nanocapsules. An XRD pattern of the BN nanocapsules prepared at 700 °C is shown in Fig. 1(c). Strong 111, 200, 220 and 311 Ag reflections are observed. A weak 002 peak of BN is also observed, which indicates the formation of t-BN. Three weak undetermined peaks are observed at 0.601 nm ($2\theta = 14.72°$), 0.318 nm ($2\theta = 28.02°$) and 0.249 nm ($2\theta = 36.00°$), which can not be indexed to AgO or B_2O_3 but probably arise from oxides of some type. The grain size of the Ag nanoparticles as calculated from XRD is 34.7 nm which can be compared with the size distribution of Ag nanoparticles, 5–60 nm, as determined by HREM. However, clusters of small size would not show strong XRD peaks and only the larger Ag nanoparticles would be detected by XRD.

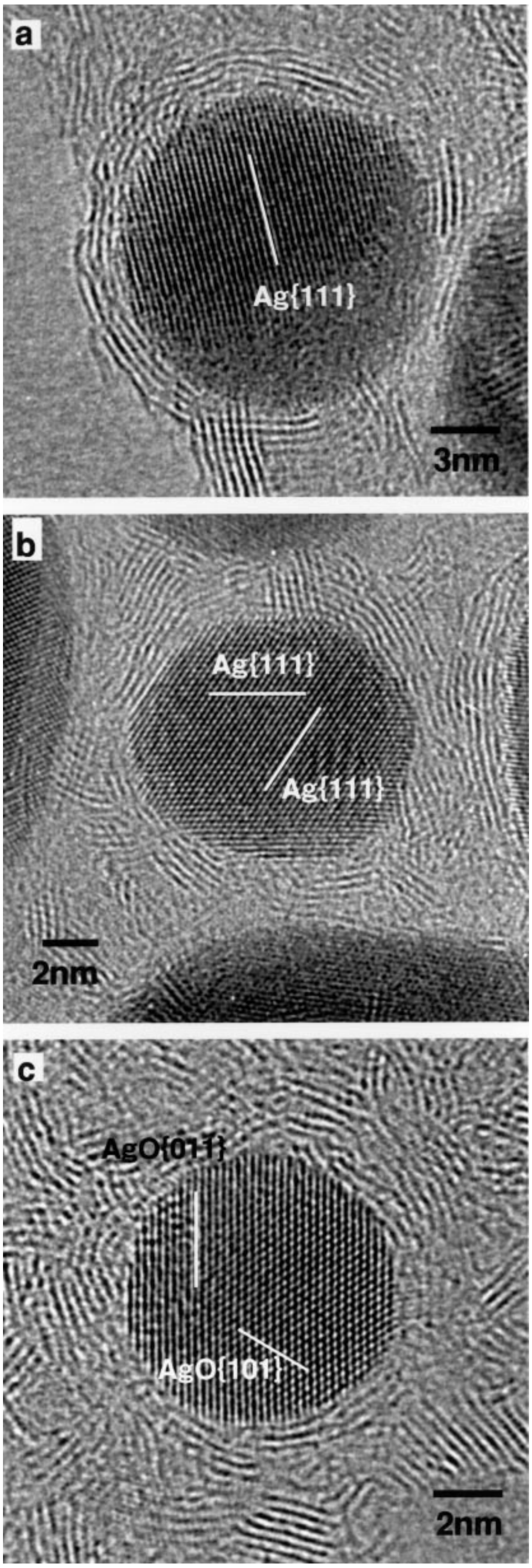

Fig. 2 HREM images of (a) a single BN nanocapsule containing an Ag nanoparticle, (b) a BN nanocapsule surrounded by four neighboring Ag nanoparticles, and (c) a BN nanocapsule containing an AgO nanoparticle.

Fig. 2(a) shows an HREM image of a single BN nanocapsule containing an Ag nanoparticle prepared at 700 °C. The BN nanocapsule size is *ca.* 10 nm and lattice fringes of Ag{111} are observed. {002} planes of BN are observed around the Ag nanoparticle, surrounded by four BN layers. Fig. 2(b) shows a BN nanocapsule surrounded by four BN nanocapsules. The Ag nanoparticles are separated by BN {002} layers. BN nanocapsules containing AgO nanoparticles were sometimes observed as shown in Fig. 2(c). The incident beam is along the [11$\bar{1}$] direction of the AgO. Ag oxides were not detected by XRD, owing to their small size and amount.

EDX spectra of Ag nanoparticles in BN matrices prepared at 300 and 700 °C are shown in Fig. 3(a) and (b), respectively. After annealing at 300 °C, a large amount of oxygen is detected, and the intensity of the nitrogen signal is weak while a Cu peak arises from the HREM grid. After annealing at 700 °C, the oxygen peak is reduced and the nitrogen peak becomes as intense as the boron peak, which indicates the formation of boron nitride. Although oxygen atoms remain in the sample, no carbon is detected. As observed in the HREM images, the BN structure is highly disordered and oxygen would be incorporated in the BN matrix.

The overall formation mechanism of BN nanocapsules synthesized in the present work is probably described by eqn. (1):

$$2H_3BO_3 + CO(NH_2)_2 + AgNO_3 + H_2 \rightarrow Ag + 2BN + 6H_2O\uparrow + CO\uparrow + NO_x\uparrow$$

After annealing at 300 °C, silver clusters and amorphous BN with low nitrogen content were formed, and oxygen would be

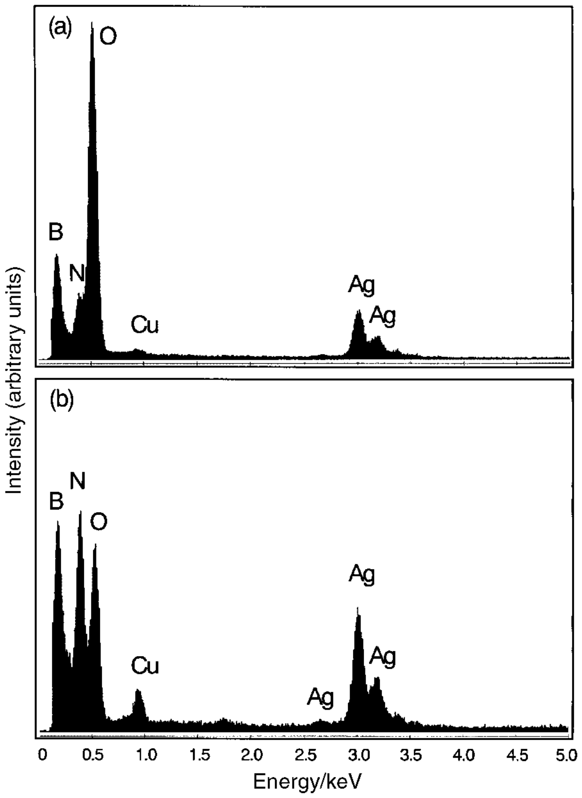

Fig. 3 EDX spectra of Ag nanoparticles in a BN matrix prepared at (a) 300 and (b) 700 °C.

included in the BN matrix. After annealing at 700 °C, t-BN layers were formed around the silver nanoparticles as a consequence of the reduction by H_2 and crystallization of the BN matrix.

As well as obtaining a large amount of BN nanocapsules we have also succeeded in preparing these at a "low" temperature of 700 °C. Previous BN nanocapsules produced by arc-discharge or arc-melting methods required *ca.* 3000 °C and it was difficult to control the formation of BN nanocapsules. Use of a lower temperature allows better control of BN nanocapsule formation.

Formation of the BN layer around the nanoparticles is also useful for cluster protection. In the present work, AgO nanoparticles were also observed to be encapsulated in BN nanocapsules after annealing at 700 °C despite the fact that AgO ordinarily decomposes at *ca.* 100 °C.

In conclusion, HREM observation and EDS analysis indicate the formation of silver nanoparticles encapsulated in BN nanocapsules, which were produced by a new chemical process using H_3BO_3, $CO(NH_2)_2$ and $AgNO_3$. This type of chemical process is useful for large-scale production of BN nanocapsules containing nanoclusters.

Acknowledgements

This work was partly supported by The Shinsedai Foundation, and by a Grant-in-Aid for Scientific Research, Ministry of Education, Science, Sports and Culture, Japan.

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