Ni-B Nanometer Particles Observed by Scanning Tunneling Microscopy*

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The samples of the Ni-B nanometer particles which were suitable for scanning tunneling microscopy (STM) have been prepared and observed. Our experimental results suggest that the vertical height of the nanometer particles imaged by the STM has strongly related to the method of the sample preparation. For the Ni-B nanometer particle the water and impurity layer adsorbed to the particle surface played an important role in the conduction mechanism. At last alcohol can be used as a tool to disperse the nanometer particles on the highly oriented pyrolytic graphite support.

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The scanning tunneling microscopy (STM) has been proven to be an excellent probing tool for structure and electronic properties of metal and semiconductor surfaces on the atomic scale.[1] One of the advantages of the STM is that it can be operated in air, gases or liquids[2] without requiring the vacuum environment which is generally used in most high resolution microscopes and surface analysis tools. In addition the STM was adopted as a high resolution microscopic method which might avoid heavy metal staining or changes occurring in the nanometer particles when they are placed in a high vacuum or under irradiation of electron beam. Although significant progress has been made in the applications of STM in the studies of material surfaces and biological structures,[3-5] there are, however, very few papers published on nanometer particles observation[6] because of the difficulties of the sample preparation and the conductivity of particle. Though the lack of a detailed understanding of the conduction mechanism on Ni-B nanometer insulator material may hinder interpretation of the images, the images can still provide some valuable insight into the shape and size of Ni-B nanometer particles. The results obtained to date indicate that this technique can provide clear images and information of the Ni-B nanometer particles.

The aim of this STM work is to investigate the size and shape of Ni-B nanometer particles prepared by chemical reduction and to discuss the suitable conduction mechanism of such nanometer insulator material.

The Ni-B nanometer particles were prepared by using KBH_4 to reduce Ni^{2+} ion in ethanol solution.[7] The substrate used in this study was highly oriented pyrolytic graphite (HOPG), which is utilized as a standard for STM calibration and as a substrate for most STM studies, and its surface structures have been well studied. The typical surface of freshly cleaved HOPG is very flat and microscopically smooth, consisting primarily of terraces separated by occasional monoatomic steps.

The specimens suitable for STM were obtained by following procedures: First a solution of 100 ppm were prepared, after oscillated by ultrasonic wave oscillator, a 3μl droplet solution which consisted of Ni-B nanometer particlés was deposited on a freshly cleaved HOPG surface, which provides a conductive surface with atomically flat crystal planes over thousands of angstroms, and the sample was allowed to dry slowly in air. We prepared the samples by two kinds of solvent: water and alcohol. No additional coating was performed.

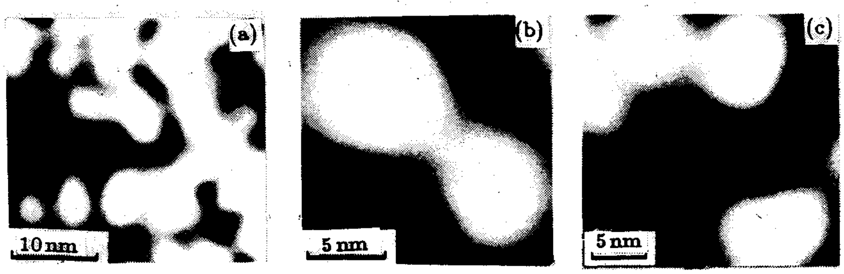

Fig. 1. Ni-B nanometer particles deposited on HOPG by alcohol and imaged in air with the STM at current setpoint 1.0 nA and tip bias 800 mV. Three images cover an area of (a) 32.8×32.8 nm, (b) 17.6×17.6 nm, (c) 25.8×25.8 nm, respectively.

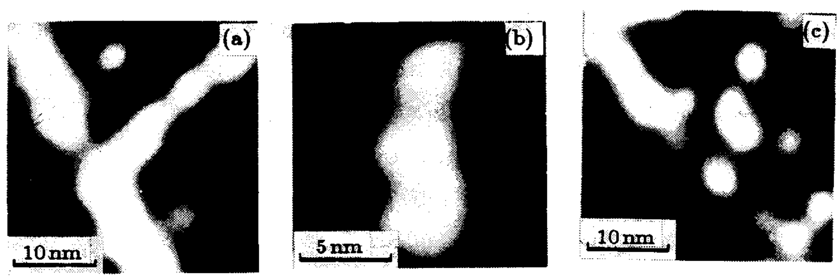

Fig. 2. Ni-B nanometer particles deposited on HOPG by water and imaged in air with the STM at current setpoint 1.0 nA and tip bias 800 mV. The scanned areas are (a) 34.3×34.3 nm, (b) 17.6×17.6 nm, (c) 34.3×34.3 nm, respectively.

For STM we used a commercial CSTM-9000, operated in ambient condition, and the tips are made by electrochemically etching tungsten wire in a solution of 2 M NaOH with direct current (7 V). Images were obtained at constant tunnel current mode with a tip bias 800 mV and tunneling current 1 nA, scanned to give 256×256 pixels with gray scale. Figure 1 consists of three images representative of the shape of Ni-B nanometer particles deposited on the HOPG surface, prepared by ethanol solution and different degrees of aggregation of these nanometer particles could be observed in most areas of the sample, as well as a lot of isolated particles were imaged. Meanwhile the adhesion of agglomerates of particles was adequate to get a similar image for several repeated scans of the same area. All the observed Ni-B nanometer particles exhibit a spherical shape with a diameter ranging from 8 to 12 nm and the measured vertical height from 5 to 7 nm, very close to the ball-like and diameter size 10–20 nm obtained by the transmission electron microscopy technique.[7]

When the sample was prepared by aqueous solution, the significant changes in the particle size and morphology happened (Fig. 2). The particles also look globular with diameter about 5–8 nm, and the apparent height 50 nm, 5–7 times larger compared with their diameters. Great agglomerates were observed in this case. Therefore, we could easily find that the images were influenced strongly by different sample preparation such as, in our case, different solvent selection.

It is curious that the Ni-B nanometer insulator particles can be visualized by STM, which suggests that the conductivity of the Ni-B nanometer particles must have been enhanced by some unclear conduction mechanism. By now, many authors believed that if the sample which was deposited on the electric conduction substrate, such as HOPG and Au, etc., is so small that there is a sufficient electron transport through the object, which is attributed to bulk conduction, and this type of conduction mechanism has already been proposed by Lindsay *et al.*[8] as a resonant tunneling mechanism. On the other hand, the enhanced nanometer particles conductivity might be explained by their small particle size, due to their more surface atoms or higher surface energy. We think, at least, that based on the enhanced conduction mechanism mentioned above, the STM images will not be changed by different sample preparation.

However the remarkable differences of the measured vertical height between Figs. 1 and 2 suggest that there must be existing another conduction mechanism which is related to the procedures of the sample preparation. Generally, during the sample preparation the particle surface must be covered by adsorbed water and impurities and this surface contamination layer can conduct small intensity (pA order) of ionic current by ionic conductivity.[9] When the tip comes into contact with that adsorbed water layer, analogous to the tunneling current model, ionic current will be formed due to the directional migration of the positive and negative ion under the tip bias voltage in the thin adsorbed water layer, that is to say, for insulator materials, such as biological ones, STM images could be obtained by the ionic conductivity of the adsorbed water and impurity layer. Meanwhile, the positive and negative ionic concentration in the adsorbed water layer is controlled directly by the procedures of the sample preparation.

Therefore, different sample preparation will lead to different ionic concentration, in other words, different sample preparation will affect strongly the measured vertical height, which is in accord with our experimental results. Thus, we can infer that the adsorbed water and impurity layer may play an important role in Ni-B nanometer particle conduction mechanism. Moreover, because of the low ionic current intensity, the contacted area between the tip and the adsorbed water layer must be much larger than the size of the tip, and that will decrease greatly the resolution of the STM.

During the STM experiments, it was found that nanometer particles deposited on the HOPG surface, using water solvent, tend to form a chain-like agglomerates, different from the behavior of those deposited by alcohol. Maybe polarized H_2O can increase the interaction between the Ni-B nanometer particles and tend to aggregate. Choosing unpolarized solvent (i. e. alcohol) will result in good dispersing of particles on the HOPG surface and isolated particles can be imaged successfully.

In conclusion, the Ni-B nanometer particles have been imaged by the STM with a diameter 8–12 nm for sample prepared by ethanol solution, 5–8 nm for aqueous solution. The particle size and shape are easily determined from the images, and the measured vertical height by the STM is strongly related to the method of sample preparation, meanwhile the water and impurity layer adsorbed to the particle surface plays an important role in the conduction mechanism for Ni-B nanometer particle. Finally, alcohol can make such nanometer particles well disperse on the HOPG surface.

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