HRTEM observations on composites of tin and tin dioxide nanoparticles dispersed on carbon nanotubes by single-atoms-to-clusters method

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Abstract

Nano-composites of tin and tin dioxide particles were synthesized on carbon nanotubes by the single-atoms-to-clusters (SAC) method, and their structures were investigated by high-resolution transmission electron microscopy. By changing the heat-treatment temperature during the SAC process, two different types of samples were obtained. The samples prepared around 450 K were aggregates of 2–4 nm-sized tin dioxide nanoparticles, and their size distributions on carbon nanotubes are in the range 20–40 nm. The other samples formed above 600 K had a core–shell structure of diameter 20–40 nm. The core and shell were made of tin single crystal and disordered oxidized tin, respectively. The thickness of the oxidized layers was ca. 4 nm.

Keywords: HRTEM; Nanoparticles; Carbon nanotubes; Tin; Tin dioxide; Nano-composite

1. Introduction

For improvement of lithium ion batteries, tin and oxidized tin materials have been extensively investigated due to their attractive performances: The composites of tin nanoparticles or amorphous tin oxides dispersed onto various carbon materials led to a decrease of degradation in charge capability of the lithium ion batteries [1]. Meanwhile the large surface-to-volume ratio of tin dioxide nanoparticles provided an improvement in the sensitivity of the gas-sensing devices [2]. As demonstrated by Sivashanmugam et al. [3], tin dioxide particles were usually made by precipitation from an aqueous solution and heat treatment, in which 200–300 nm size of the particles were observed in a typical SEM image. Egashira et al. [4] made tin nanoparticles on activated carbon fibers (ACF) and estimated that the sizes of the nanoparticles were 20–40 nm in diameter by using TEM and XRD. Some of the TEM images of these tin nanoparticles formed on ACF showed sintering of the particles. Caballero et al. [5] made a composite of tin nanoparticles on cellulose fibers. The size of flake-shaped aggregates was 20–30 nm in diameter. It was mentioned that the structural disorder seems to be observed in the results of a high-resolution TEM study.

In order to gain insight into the structure of nano-composites of tin and tin dioxide particles in more detail, we investigate tin and tin dioxide nanoparticles dispersed on the multi-walled carbon nanotubes prepared by using the single-atoms-to-clusters (SAC) method proposed by Kim et al. [6], which gives a unique chance to observe a structural change of nanoparticles with a single dispersion. A high-resolution transmission electron microscope (HRTEM) study is carried out on these nano-composites obtained by changing the heat treatment condition in the SAC process.

2. Experimental

Multi-walled carbon nanotubes (MWNT; Helix Material Solutions, Inc.) were heated for 2 h at 673 K in static air,
and subsequently treated with 6 M hydrochloric acid for 12 h at 343 K in order to remove row soot and/or catalyst metal. Then, the MWNT were carefully cleaned by distilled water and filtered. Finally, the purified MWNT were prepared by diffusion into the ethanol solution and then evaporating the solvent.

The next 3 steps performed ensured that the surface of the purified MWNT became thiolated. First, carboxyl groups were formed on the surface by using an acid solution (H$_2$SO$_4$, HNO$_3$, and HCl; Kanto Chemical Co., Inc.). Second, hydroxyl groups of the carboxyl groups were replaced with chloride by SOCl$_2$ (Wako). Then, the chloride was replaced with thiol by using dehydrated toluene (Aldrich) and 2-aminoethanethiol (Wako). It took 70 min, 12, and 24 h to complete the chemical reactions in each step at 343 K sufficiently, and then thiolated MWNT (S-MWNT) were obtained.

Reduction of Sn precursor and heat treatment, which are the two main processes of the SAC method, were carried out as follows. S-MWNT were diffused into deionized water by sonication. Into the solution, SnCl$_2$–2H$_2$O (Aldrich) as the Sn precursor, which was dissolved by HCl solvent (pH = 3.5), was added and stirred for 3 h. After the solution was cooled by pieces of ice for 20 min, in order to prevent unexpected sintering by excess heat of the chemical reaction, NaBH$_4$ (Kanto Chemical Co., Inc.) solution as the reducer was added and the mixture was stirred. Heat treatments were performed for 1 h at 473, 523, 573, 623, or 673 K in an H$_2$ gas flow of 100 sccm, and the samples for the present study were obtained by slow quenching.

A Hitachi H-9000NAR transmission electron microscope equipped with energy-dispersive X-ray spectroscopy (EDS) was used for the observations. EDS was carried out to check the elements included in the nano-composites synthesized. The accelerating voltage was 300 kV for obtaining a high-resolution image, and 100 kV for a wide image.

3. Results and discussion

A TEM image of the sample obtained at 473 K in the SAC process is shown in Fig. 1(a). On the surface of the MWNT, approximately 30 nm-sized aggregates are observed, consisting of 2–4 nm-sized nanoparticles. In Fig. 1(b), an HRTEM image of the aggregates is presented. The lattice of 0.32 nm spacing is clearly seen in some of the aggregates. In Fig. 1(c), the electron diffraction pattern from aggregates dispersed on the MWNT is shown. It was found that although the diffraction intensities from the aggregates denoted by ‘A’ and ‘B’ are extremely weak compared with those from the MWNT, they are identified as reflections from (0 0 1) and (1 1 2) planes with lattice spacings of 0.32 and 0.26 nm, respectively. The dark field (DF) and bright field (BF) images are also shown in Fig. 1(d), indicating that the nanoparticle denoted by the arrow is the origin of the weak diffractions. These results suggests that the nanoparticles are tin dioxide with a lattice constant of 0.319 nm for the space group of P4/nmm [7]. This is consistent with the results of EDS that the elements of aggregates consist of oxygen and tin atoms.

In the case of the sample obtained at 623 K, a different type of 20–40 nm-sized nanoparticles was dispersed on the MWNT as shown in Fig. 2(a). The shape of the nanoparticles is almost spherical, which is clearly different from the aggregates shown in Fig. 1(a). In Fig. 2(b), an HRTEM image of the nanoparticle is shown. It is confirmed that a core–shell type structure exists in every nanoparticle which is distributed around approximately 30 nm size. A dark-contrast core region is surrounded by a rather transparent shell, whose thickness is approximately 4 nm. The lattice spacing of the core is 0.29 nm. Furthermore, the electron diffraction pattern from some particles dispersed on the MWNT is also shown in Fig. 2(c). The diffraction spots denoted by ‘A’, ‘B’, ‘C’, ‘D’ and ‘E’ correspond to the spacing of 0.29, 0.17, 0.15, 0.12, and 0.11 nm, respectively. These are assigned to reflections from (2 0 0), (3 0 1), (1 1 2), (3 1 2), and (5 0 1) planes of tin metal with a lattice constant of 0.5831 nm for the body-centered tetragonal which belongs to the space group of I4$_1$/amd [7]. The fact that the signal of an oxygen component could not be detected in the EDS measurements on the core–shell samples, in contrast to the case of the aggregates mentioned above, indicates an occurrence of the transformation from the aggregates to the core–shell structure by an increase of the heat-treatment temperature. Actually, the core–shell type structure was also observed for the samples obtained at 673 K. In Fig. 2(d), DF and BF images of the same region are shown. The DF image was formed by using the diffraction spot denoted by ‘C’ in Fig. 2(c). All contrasts disappear except one particle in the DF image, and the bright contrast appears only at the core of the particle, but not at the shell. Judging from the HRTEM and DF/BF images, the shell region seems to have some structural defects, and the core region of the nanoparticle is presumably occupied by a single tin crystal. This indicates that the tin metal structure is stable above ca. 600 K and covered by oxidized tin, which might be imperfectly oxidized and include a small amount of oxygen atoms, which could not be detected by EDS due to the chemical instability of the tin metal surface in air.

These two different types of nano-composites, i.e. fully and partially oxidized tin nanoparticles dispersed to MWNT, is expected to be effective stemming the degradation of the anode of lithium ion batteries during the repetition of charging and discharging [8]. On the other hand, many 2–4 nm-sized nanoparticles of tin dioxide obtained at low temperatures presumably improves the sensitivity of gas-sensing devices, because of the considerable large surface-to-volume ratio [2].
Fig. 1. (a) TEM image of tin dioxide aggregates dispersed on carbon nanotubes prepared by the SAC method at 473 K. The size of the aggregates is approximately 20 nm. (b) HRTEM image of aggregates on MWNT composed of 2–4 nm-sized tin dioxide nanoparticles. The lattice spacing is 0.32 nm, corresponding to the (0 0 1) plane of the tin dioxide crystal. (c) The electron diffraction pattern from aggregates dispersed on MWNT. The spots denoted by the letters ‘A’ and ‘B’ are assigned to 0 0 1 and 1 0 1 reflections with the lattice spacings of 0.32 and 0.26 nm, respectively. (d) Dark field (DF) and bright field (BF) images of aggregates dispersed on MWNT in the same region. The nanoparticle denoted by an arrow corresponds to the weak diffractions denoted by the letters ‘A’ and ‘B’ in Fig. 1(c).
4. Conclusions

We successfully synthesized nano-composites of tin and tin dioxide nanoparticles dispersed on carbon nanotubes through a chemical process, i.e. the SAC method developed by one of the authors, and found that those nanoparticles had two different structures by HRTEM observations. One type of the nanoparticles was the 2–4 nm-sized tin dioxide, and the other type was 20–40 nm-sized tin covered with oxidized tin. These experimental results indicate that there takes place a transformation between the two types around 600 K.

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Fig. 2. (a) TEM image of 20–40 nm-size particles dispersed on carbon nanotubes prepared by the SAC method at 623 K. (b) The HRTEM image of the core–shell structure observed in the case of samples processed at 623 K. The lattice spacing of 0.29 nm in the core region corresponds to (2 0 0) of the body-centered tetragonal crystal structure of metallic tin. (c) The electron diffraction pattern from the nanoparticles dispersed on MWNT. The diffraction spots denoted by letters ‘A’, ‘B’, ‘C’, ‘D’, and ‘E’ are corresponding to 2 0 0, 3 0 1, 1 1 2, 3 1 2, and 5 0 1 reflections of metallic tin nanoparticles, respectively. (d) The DF and BF images of nanoparticles dispersed on the MWNT. The bright contrast in the DF image is only due to the core of the nanoparticle.

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