Applied Surface Science 275 (2013) 409–412

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Structural analysis of nano structured carbon by transmission electron microscopy and image processing

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ARTICLE INFO

Article history:
Received 30 September 2012
Accepted 23 October 2012
Available online 1 November 2012

Keywords:
Carbon nanotube
Nano structure
Transmission electron microscopy
Image analysis
Catalyst
Battery cell

ABSTRACT

Transmission electron microscopy (TEM) is one of the highest resolution analysis methods of materials. The three dimensional recognition of the materials is difficult by TEM because the observation data is projection images through the materials. In this study, space structure of carbon nanotubes loaded with metal particles was analyzed by three dimensional TEM (3D-TEM) [1,2]. The nano structured carbons are also observed by high resolution transmission electron microscopy (HRTEM) with *Cs* corrector. Cup-stack type carbon nanotubes (CSCNTs) loaded with Pt particles (2–3 nm in diameter) prepared by GSI Creos Corporation were analyzed by these methods. Pt particles are bound selectively to the edges of hexagonal carbon layers of inside and outer surface of CSCNTs efficiently and can be expected to work well as catalysts of electrodes of fuel cell. It is sometimes difficult that the nano sized area is analyzed by selected area electron diffraction (SAD) because the selected area aperture cannot be so small. The HRTEM and image processing technique give similar results of SAD when it works and revealed to be useful to analyze nano structured carbons.

1. Introduction

Transmission electron microscopy (TEM) is one of the most high resolution analysis methods of materials. The three dimensional recognition of the materials is difficult by TEM because the observation data is projection images through the materials. In this study, space structure of carbon nanotubes loaded with metal particles was analyzed by three dimensional TEM (3D-TEM) [1,2]. The nano structured carbons are also observed by high resolution transmission electron microscopy (HRTEM) with *Cs* corrector and analyzed by image processing. The carbon nanotubes with metal particles are developed for application of electrode materials of energy devices in order to reduce expensive metals and to work effective in a minimum amount of the metal. In this study, structure of the nanocarbon is analyzed by these analysis techniques.

2. Experimental

The samples are cup-stack type carbon nanotubes (CSCNTs) loaded with Pt particles (2–3 nm in diameter). The Pt particles were deposited in the solution. The CSCNT with Pt particles was prepared by GSI Creos Corporation. This sample was developed for electrode of energy devices such as fuel cell.

3D-TEM system at Cooperative Research Facility Center (CRFC) of Toyohashi University of Technology, Japan is used.

TEM (2100FEF, JEOL) with *Cs* corrector at Institute of Carbon Science and Technology (ISCT) of Shinshu University is used for HRTEM observation. There is Seidel's 5 aberrations that reduce the resolution of TEM optically. They are astigmatism, distortion, spherical aberration, coma aberration, curvature of field. The C_s corrector can reduce all Seidel's aberrations except chromatic aberration. The phase contrast transfer function of objective lens of TEM dominant in high resolution area [3] and samples are normally observed at Scherzer focus [4] by TEM. The resolution of TEM increases to less than 0.1 nm with the C_s corrector [5].

In general, quantitative analysis of the TEM image is difficult. We have used two dimensional fast Fourier transform (2D-FFT) image processing based on atomic resolution TEM images [6,7]. The 2D-FFT was used for the frequency analysis of the TEM pictures from the analysis of the power spectrum obtained by the 2D-FFT. The result of 2D-FFT is the complex number, and the power spectrum is calculated by the sum of each square of the real part and the imaginary part. Since the TEM image itself is thought to be window, which cut down the continuous data to the rectangular, the

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http://dx.doi.org/10.1016/j.apsusc.2012.10.137

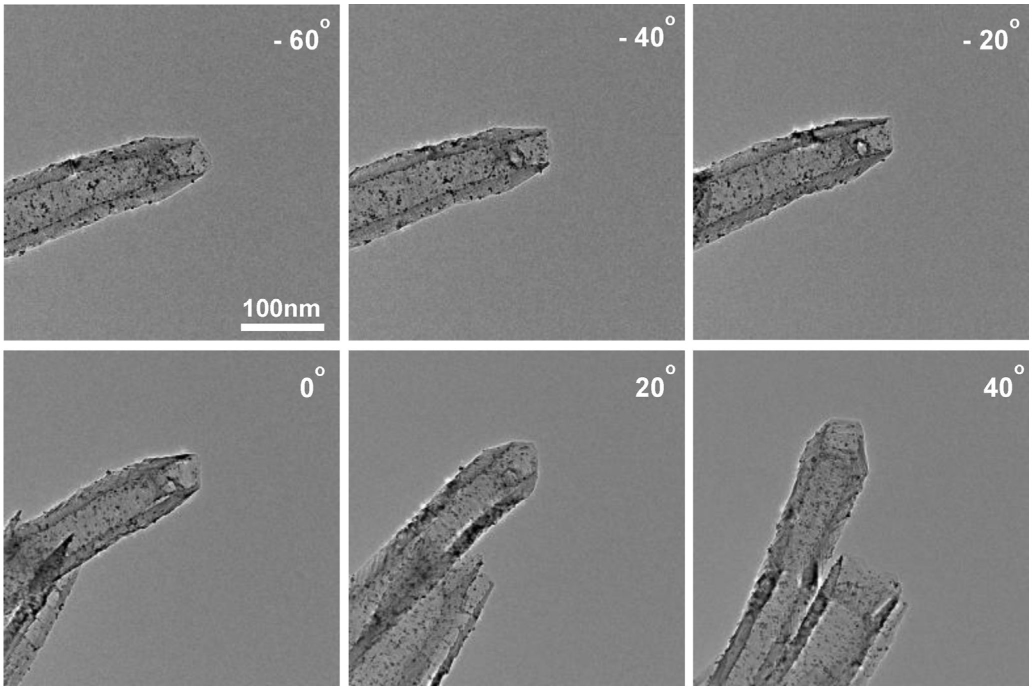

Fig. 1. These image are some of the series of TEM images obtained with tilting the sample holder for ob 3D-TEM observation when the sample holder was tilted from −60 to +60.

edge of the image is discontinuous and it affects the characteristics of resulting power spectrum. In order to remove this effect, the window treatment is performed to the original image before the 2D-FFT operation [8]. In this study, we use Hamming window for the window treatment. The 2D-FFT is the operation to the whole image, and different from the partial operation like Laplacian filter, that is, the 2D-FFT can remove periodic noises and distortions of the whole image that cannot be eliminated by the partial operation.

Small angle X-ray scattering (SAXS) system (SWXD, Rigaku) and software (NANO-Solver, Rigaku) are used for measurement of distribution of the Pt particles of the CSCNTs [9,10]. The size, aspect and state of surface of the particles or pores are estimated by SAXS [11,12].

3. Results and discussion

TEM images of CSCNTs loaded with Pt particles are shown in Fig. 1. These six TEM images were selected from over 100 images observed every 1° when the sample holder was tilted from −60 to +60°. The CSCNTs are rotated with tilting the sample holder. The three dimensional shape of the CSCNT is revealed by observation of the consecutive TEM images. The Pt catalysts are supported on the walls of CSCNT efficiently because the Pt particles adhere to the walls well separately. 3D-TEM image shown in Fig. 2 was calculated from these TEM images. The white parts correspond to Pt particles or their aggregates. The configuration of the Pt particles can be understood. Once the 3D image is created, the samples are took view from all direction and any cross section of the sample can be observed. The CSCNTs are not necessarily a cylindrical shape, not straight and have some of defective parts. The Pt particles adhere to the defective parts of CSCNTs.

When the CSCNTs are used as electrode of energy devices such as fuel cell, the Pt particles act as a catalyst. In this case, it is important that the Pt particles bind to the CSCNTs work well. The numbers of Pt particles of inside and outer surface are measured by using the over 100 tilting TEM images. The measurement result is shown in Fig. 3 and Table 1. The Pt particles of inside are marked with green dots and that of outer surface marked with red dots, respectively. The total number of Pt particles is 333 in the TEM image shown in Fig. 3. The ratios of the numbers of Pt particles of inside and outer surface are 53% and 47%, respectively, that is, the numbers of Pt particles of inside and outer surface are almost 50–50. The Pt particles on both surfaces – inside and outside – can act as catalyst when the CSCNTs are used as the electrode of energy devices.

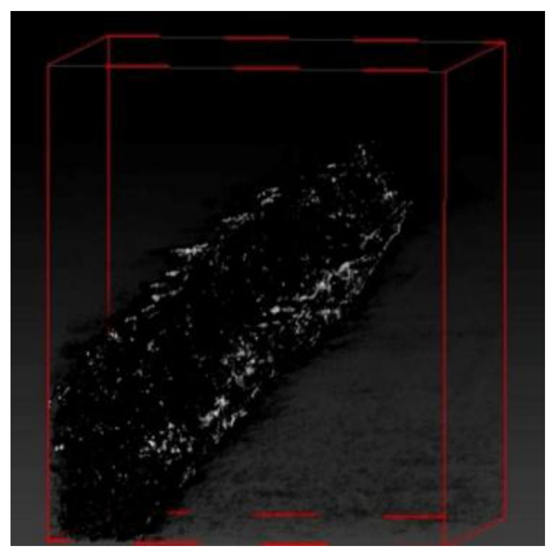

Fig. 2. 3D-TEM image of the CSCNT.

Table 1
Measurements of the number of Pt particles binding to the inside and outer surfaces of the CSCNT.

Outer surface	Inside	Total
157	176	333
47%	53%	100%