

Nanohybridization of Single-Wall Carbon Nanotubes and Molecular Clusters

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Introduction

We have recently proposed molecular cluster batteries (MCBs) that consist of a lithium anode and cathode-active material based on polynuclear metal complexes (molecular clusters), in order to achieve both high capacity and fast charging/discharging.^[1] However, the cathodes were made by simply mixing microcrystals of molecular clusters and conductive carbon materials, and the battery reaction was associated with frictional penetration/removal of lithium ions into/from the microcrystals and with non-smooth electron transfer between the cluster molecules and the electrode. So these drawbacks brought about problems such as a slow charging/discharging rate and insufficient cyclability.

In the present work, to achieve both smooth electron transfer through SWNTs and quick lithium-ion diffusion, we examined nanohybridization between a well-known molecular cluster, polyoxometalate (POM), and SWNT.

Experimental

To graft the POM molecules onto the surface of SWNTs, acetonitrile solution (5 ml) of TBA₃[PMo₁₂O₄₀] (40 mg, 16 mmol) was added to a toluene suspension (50 ml) of the purified SWNTs (80 mg) under vigorous stirring at room temperature. After stirring until the turbidity of the solution disappeared, the solution was filtered using a membrane filter with a pore diameter of 0.1 μm. Finally, the precipitation was washed with toluene and dried under vacuum.

Mo *K*-edge XAFS spectra were recorded in a transmission mode at the beam line BL-NW10A of the Photon Factory in KEK, Tsukuba, Japan.

Results and discussion

Figure 1 shows a transmission electron microscopy (TEM) image of the POM/SWNT hybrid. The SWNT bundles are decorated by dark spots with a diameter of ca. 1.5 nm, which corresponds to the molecular size of [PMo₁₂O₄₀]³⁻. It is considered that the individual POM molecules are separately grafted onto the surfaces of the SWNTs.

Mo *K*-edge XAFS analyses were performed on both the authentic TBA₃[PMo₁₂O₄₀] and the POM/SWNT hybrid material in order to examine the structure of [PMo₁₂O₄₀]³⁻ after the nanohybridization. Fourier transforms of the $k^3\chi(k)$ functions (the k range is around 3.5–13.0 Å⁻¹) for the two samples are compared in Fig. 2. TBA₃[PMo₁₂O₄₀] exhibits four main peaks at 1.0, 1.8, 2.3, and 3.1 Å; the first three peaks are assignable to the Mo–O distances and

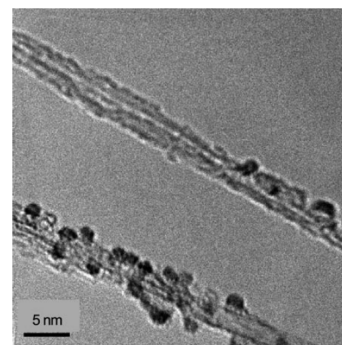


Figure 1. TEM image of the POM/SWNT hybrid material.

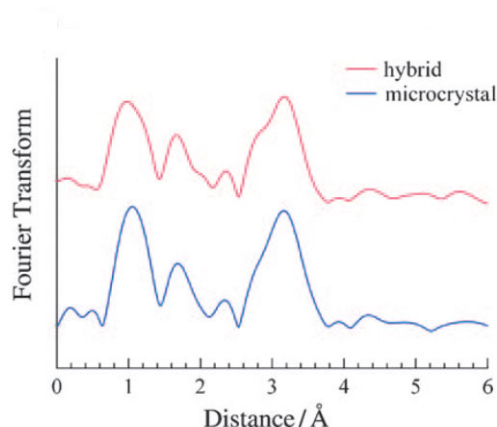


Figure 2. Mo *K*-edge EXAFS spectra of the POM/SWNT hybrid material.

the last one to Mo–Mo. The curvature and peak positions of the hybrid material completely agree with those for TBA₃[PMo₁₂O₄₀], indicating that [PMo₁₂O₄₀]³⁻ on the surface of SWNTs suffers from little structural change.

The charging/discharging measurements for the MCBs in which the cathode includes the POM/SWNT hybrid material indicate a higher battery capacity and faster charging/discharging compared with those of the microcrystalline POM MCBs. It is concluded that nanohybridization of molecular clusters with SWNTs is a promising method for improving smooth electron transport and lithium ion dispersion in battery reactions.

Reference

[1] H. Yoshikawa et al., *Chem. Commun.*, 3169, (2007)

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