Materials Science

15A/2004G266

In-situ observation of formation of metal nanoparticles and nanocomposites

Hirokazu TANAKA[1], Satoshi KOIZUMI[2], Takeji HASHIMOTO[*2], Ayano CHIBA[3], Toshiaki ITO[4], Kensuke NAKA[4], Yoshiki CHUJO[4]
[1]Mitsui Chemicals, Shiodome, Tokyo 105-7117, Japan
[2]Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
[3]Department of Physics, Keio university, Yokohama 223-8522, Japan
[4]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

Introduction

Polymer-stabilized metal nanoparticles have been of great practical interest because of the simple process of the synthesis, compared to the physical synthesis in high vacuum systems, and the various possibilities of the combination with various polymers. We study the metal nanoparticles formation stabilized by various kinds of polymers such as homopolymers, copolymers, etc. Here we report our study on the reduction process of Pd^{2+} ions at specific sites of PAMAM dendrimers and the association of the dendrimers. In other words, we focus on the reaction-induced self-assembly processes of Pd nanoparticles.

Experimental

Time-resolved SAXS measurements were conducted at the BL-15A, installed at Photon Factory, KEK, Tsukuba, Japan. We also performed time-resolved SANS measurements using the instrument SANS-J at JAEA, Tokai, Japan, to cover the lower-q range.

0.3mL of 4.0×10^{-2}M $Pd(CH3COO)_2$ / dimethyl formamide was added to 3.5mL of 2.0×10^{-4}M PAMAM dendrimer/methanol. The formation of palladium nanopartiles was induced by a temperature jump from room temperature to 50C.

Results

Figure 1 (a) shows the TEM image of the sample just after the reduction. One sees spherical aggregation of dendrimer molecules which are around 70 nm in the diameter. Sufficiently after the reduction, one sees that palladium nanoparticles in several nm scale are formed in the former sphere, as shown in Fig. 1 (b). The purpose of the time-resolved scattering measurements is not only to clarify the aggregation processes of both nanoparticles and dendrimer molecules but also to confirm the TEM results because the image can be affected by the casting process of the solution on the cupper grid. We observed the aggregation process by SAXS and SANS, as shown in Fig. 2. As one can see in the SAXS data around 0.2 - 2 nm^{-1}, the shoulder grows up with time, as shown by an arrow. This change is due to the formation of the nm-scale palladium particles. As to lower-q range covered by SANS measurements, one sees that the larger spherical templates made by dendrimer molecules are formed rather faster than the formation of the nanoparticles. These data are well reproduced by a model of two spheres, i.e., we confirmed that the spheres that can be seen in TEM image really exist in the in-situ reduction process in the solution. We analyzed the time-dependence of the SAXS and SANS data, and found that the reduction process follows an encapsulation of Pd^{2+} ions into spherical dendrimer templates which are made by a kind of chemical deposition in sub micron scale.

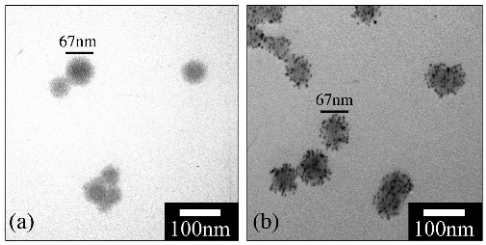

Figure 1

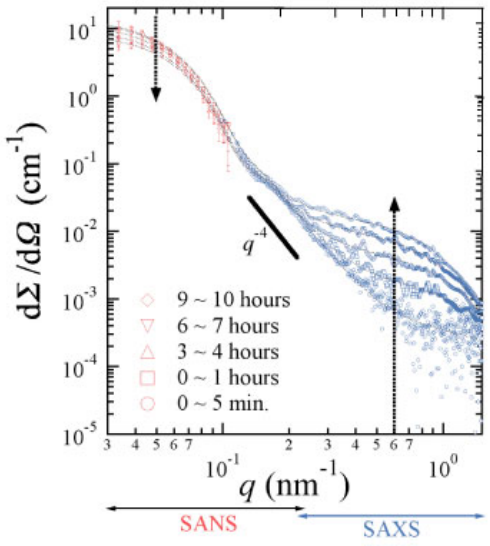

Figure 2

* hashimoto.takeji@jaea.go.jp