Characterization of Polymer-Inorganic Hybrid Materials by Dynamic Light Scattering / Gas Adsorption (Polymer Brush)

Overview

Particles having fixed the polymer brush (an organic-inorganic hybrid material) are expected to manifest both the flexibility and light weight of organic materials and the heat resistance and durability of inorganic materials. An assessment of their structure is therefore very important. Here, we propose a structural evaluation by means of gas adsorption, dynamic light scattering and streaming potential methods for the core-shell type polymer brush (PMMA-CeO_2) which is formed (as shown in Fig. 1) by fixing polymethyl methacrylate (PMMA) by cerium oxide for the purpose of better controlling the particle shapes and improving their dispersity.

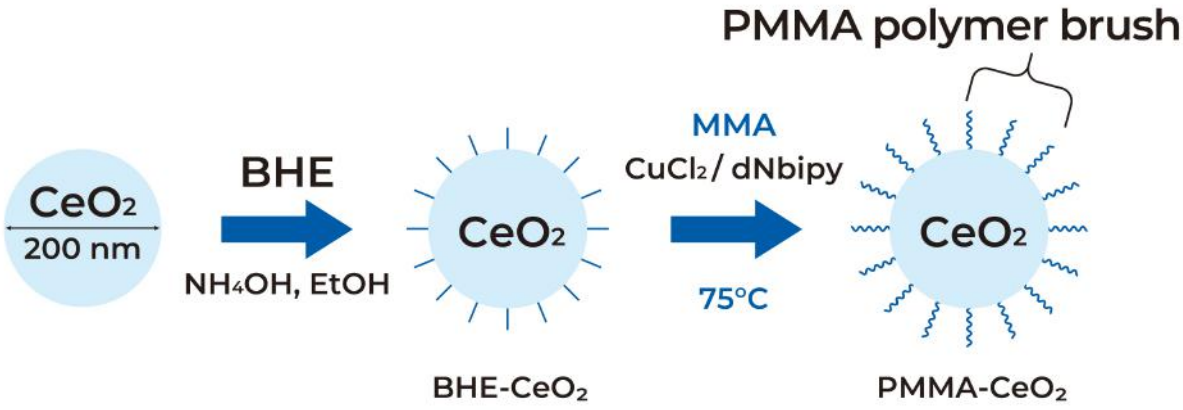

Fig. 1 Fixation of PMMA brush on CeO_2 surface

Measurement

CeO_2-PMMA particles were synthesized by atom transfer radical polymerization (ATRP) beginning on the surface after formation of CeO_2-BHE by fixation of the polymerization initiator ((2-bromoisobutyryloxy) hexyltriethoxysilane: BHE) on the CeO_2 (SEM mean particle size: ca. 200 nm). Isothermal adsorption measurement was conducted with a specific surface area/pore distribution measuring system BELSORP-miniX equipped with a free space continuous measuring system (N_2,077K). Particle size distribution was measured with a particle size distribution measuring system NANO-flex adopting the outer probe type dynamic light scattering (DLS) method. Streaming potential was measured with Stabino capable of evaluating the dispersiveness for a wide range of concentrations.

Results and Discussion

If a t-plot graph is depicted from the CeO_2 particle adsorption isotherm (Fig. 2), hysteresis is seen on the adsorbed/desorbed branch of the high relative pressure side having microspores, and the presence of space between particles can be confirmed. It is additionally shown that fixation of PMMA leads to fewer interactions between the surface and N_2 and to a change of the isotherm form from the I+IV type to the III type. Graft density (σ : chains/nm^2) is one of the important parameters of the polymer brush state. It is defined as the number of high-molecular-weight molecule chains relative to total particle surface area. The total surface area is usually calculated from the mass relative to the volume including irregularities on CeO_2 particles, i.e., the bulk density and mean particle size of SEM. The graft density thus calculated is σ=1.15 chains/nm^2. If the surface area determined by t-plot analysis of the adsorption isotherm is applied thereto, a value of 0.4 chains/nm^2 is obtained. Because the total surface area of CeO_2 determined by t-plot is 133 m^2/g, the outer surface area is 15.5 m^2/g, the mean size of micropore is 1.2 nm and the BHE molecular size is ca. 1 nm, it is likely that PMMA is mostly fixed on the outer surface.
We may therefore say that σ tends to be overestimated if it is determined with the use of particle density and that the use of the outer surface area (corresponding to the fixed surface) allows a more accurate determination.

If these parameters are evaluated by outer probe type DLS (Fig.3, Table 1), the particle size is overestimated following fixation of CeO_2, BHE and PMMA, and changes in the synthetic process can be assessed easily, thus confirming its validity. Furthermore, from the measurement of streaming potential of slurry after BHE/PMMA fixation, the retention of dispersiveness similar to the findings from visual obsevation (Fig. 4) can be confirmed. These results allow us to say that each of these evaluation methods is valid in a structural evaluation of polymer brush fixed on particles.

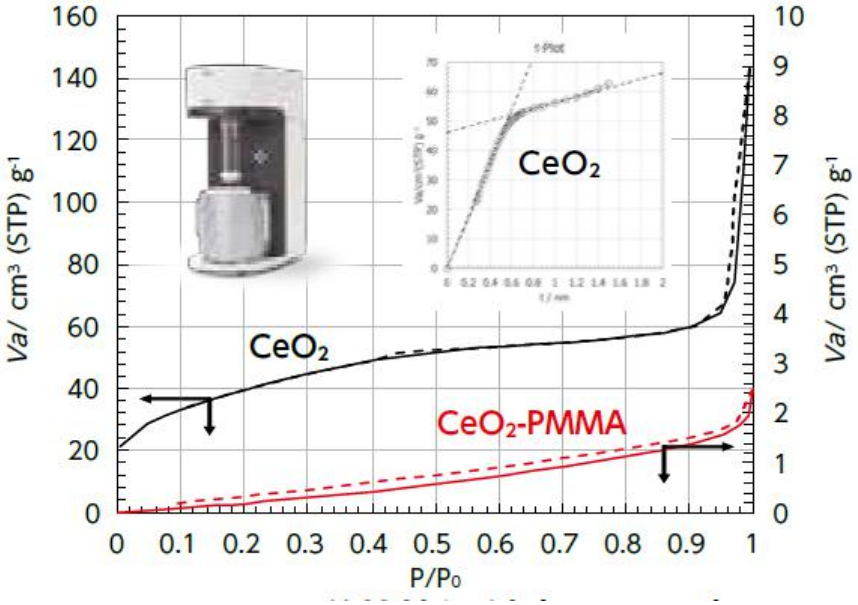

Fig. 2 Adsorption/desorption isotherm（N_2/77K）

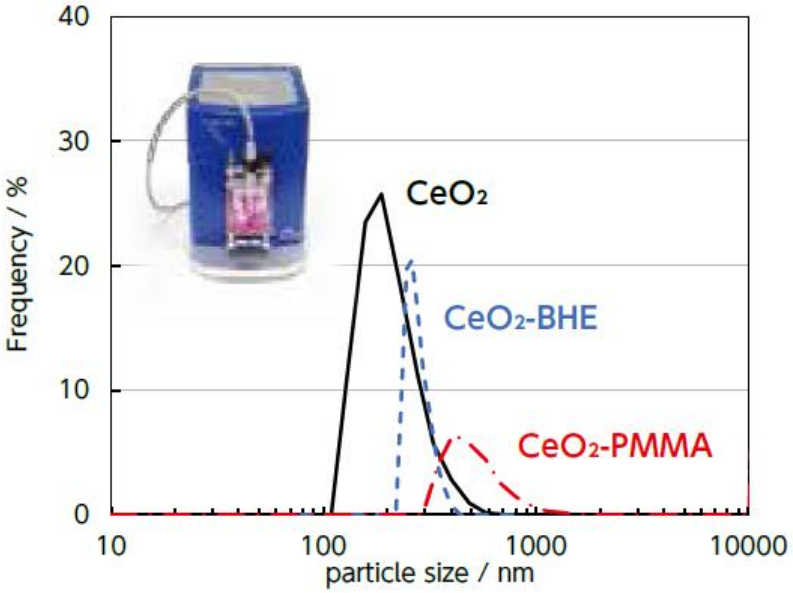

Fig. 3 Particle size distribution

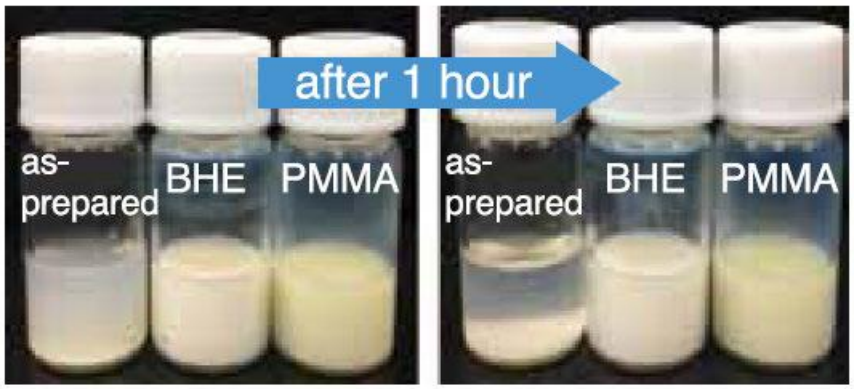

Fig. 3 Slurry dispersion

Table 1 Physical properties of each sample

	D_{50} / nm	Streaming potential / mV
CeO_2	190	data not shown
-BHE	277	-8.5
-PMMA	411	-4.3

Reference: Polymer Preprints, Japan Vol. 66, No. 28 2Pc049 Nishibori et al. (Interdisciplinary Graduate School of Engineering Science, Kyushu University)

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