B-T-004-R1-en

Characteristics of Polymer–Inorganic Hybrid Materials (Polymer Brushes) by Gas Adsorption, DLS, and Streaming Potential Methods

Introduction

Inorganic particles immobilized with polymer brushes, which are organic–inorganic hybrid materials, are expected to exhibit the flexibility and lightness of organic materials as well as the heat resistance and durability of the inorganic materials. Therefore, understanding their structure is extremely important. In this study, we investigate the structural characterization of core–shell-type polymer brush-immobilized cerium oxide (CeO_2–PMMA, where PMMA is polymethyl methacrylate) particles (as shown in Fig. 1), which were

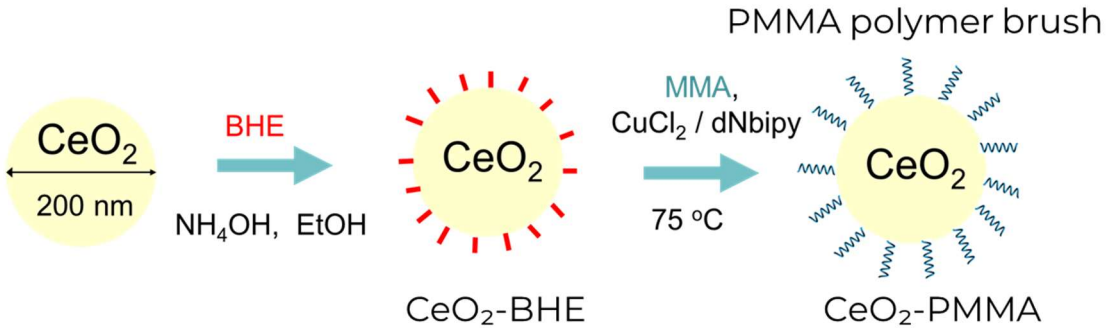

Fig. 1 Immobilization of PMMA on the Surface of CeO_2

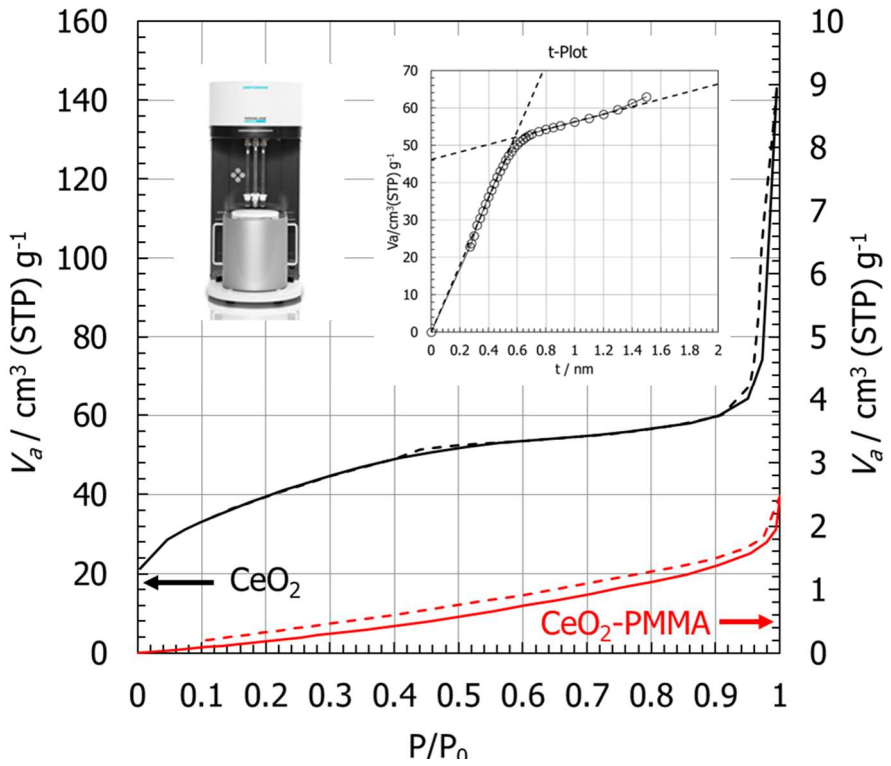

Fig. 2 Adsorption/Desorption Isotherms (N_2/77K) of CeO_2 and CeO_2–PMMA and t-Plot Analysis of CeO_2

designed to control particle morphology and improve dispersibility, using gas adsorption, dynamic light scattering (DLS), and streaming potential methods.

Materials & Methods

CeO_2–PMMA particles were synthesized by first immobilizing a polymerization initiator (2-bromo-isobutyl-oxyhexyl-triethoxysilane: BHE) onto CeO_2 particles (average particle size by SEM: ~200 nm) to obtain CeO_2–BHE, followed by surface-initiated Atom Transfer Radical Polymerization (ATRP). The ceria particles and polymer brushes were analyzed specific surface area/pore size distribution by measuring adsorption isotherms (N_2, 77 K) using a gas adsorption analyzer (BELSORP MINI X), and various analyses including t-plot were performed to evaluate the graft density of the polymer brushes. In addition, the particle size distributions of CeO_2 slurry, CeO_2–BHE slurry, and CeO_2–PMMA slurry were measured using an external probe-type DLS particle size analyzer (NANOTRAC FLEX), and their dispersibility was evaluated by streaming potential measurements (STABINO ZETA).

Results & Discussion

The t-plot analysis of adsorption isotherms of CeO_2 particles (Fig. 2) revealed the presence of micropores. The hysteresis observed at high relative pressures indicated the existence of interparticle voids of similar size, consistent with the ~200 nm particle diameter of CeO_2. The adsorption isotherm of the polymer brush obtained by PMMA immobilization (Fig. 2) changed from type I + IV to type III, indicating weaker interactions between the polymer brush surface and N_2 molecules. The graft density (σ: chains/nm^2), an important parameter for understanding the state of polymer brushes, is defined as the number of polymer chains per unit surface area of the particles. Conventionally, the surface area used for calculating graft density is based on the mass-to-volume ratio (including surface roughness) calculated from the bulk density and average particle size by SEM. Using this method, the graft density was σ = 1.15 chains/nm^2. In contrast, using the external surface area obtained from t-plot analysis, the graft density was 0.38 chains/nm^2. The total specific surface area of CeO_2 determined by t-plot analysis was 133 m^2/g, the external specific surface area was 15.5 m^2/g,

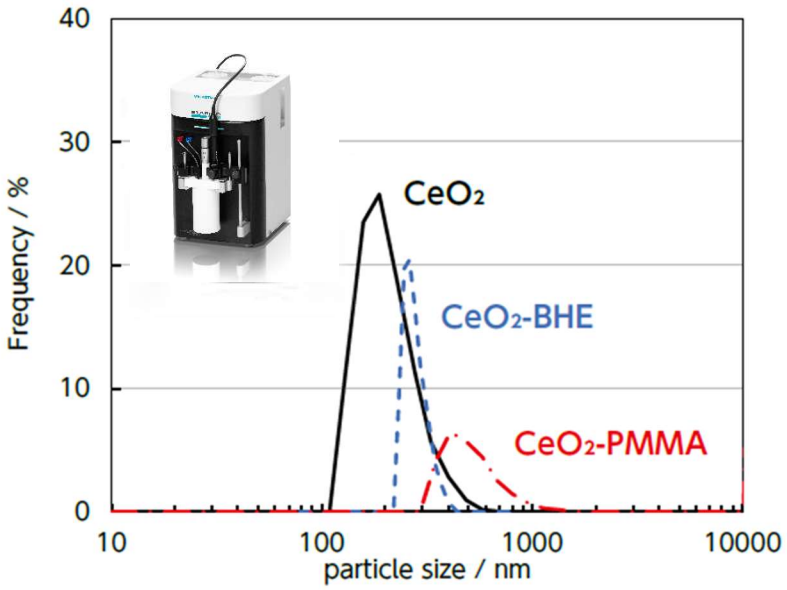

Fig. 3 Particle Size Distributions of CeO_2, CeO_2–BHE, and CeO_2–PMMA Slurries (Dynamic Light Scattering Method)

and the average micropore diameter was 1.2 nm. Since the molecular size of BHE is about 1 nm, it is considered that BHE is immobilized inside the micropores of CeO_2 particles, while most of the PMMA exists on the external surface.Therefore, using the particle density and SEM-derived particle size tends to overestimate σ, on the other hand it is more accurate to use the external specific surface area corresponding to the immobilized surface, as evaluated by t-plot analysis of the adsorption isotherms.]

Furthermore, evaluation of each slurry by external probe-type DLS (Fig. 3, Table 1) showed that immobilization of BHE and PMMA on CeO_2 particles gradually increased the particle size, allowing for easy in-situ monitoring of changes during the synthesis process. Visual observation of the slurries immobilized with BHE and PMMA (Fig. 4) confirmed that both maintained good dispersibility. Streaming potential measurements of these slurries (Table 1) showed almost no change before and after stabilization (for an hour), consistent with the visual results.

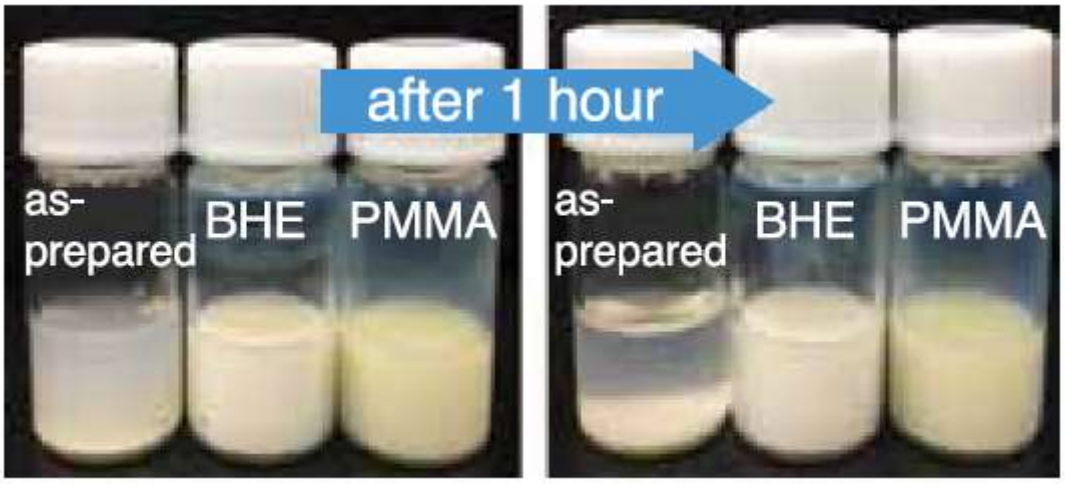

Fig. 4 Dispersion States of CeO_2, CeO_2–BHE, and CeO_2–PMMA Slurries (Visual Observation)

Table 1 Evaluation of Dispersibility of CeO_2, CeO_2–BHE, and CeO_2–PMMA (Particle Size Distribution and Streaming Potential)

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

Summary

The t-plot analysis of gas adsorption isotherms enabled the elucidation of the structure of the base particles and polymer brushes in CeO_2 and CeO_2–PMMA (polymer brushes). In particular, it was shown that using the external specific surface area obtained by t-plot analysis is effective for more accurate evaluation of graft density. Furthermore, the dispersibility of CeO_2, CeO_2–BHE, and CeO_2–PMMA slurries were evaluated by particle size distribution analysis using DLS and streaming potential measurements.

(Refernce)

K Ohno et al., *Macro1molecules*, 38, 2137 – 2142 (2005)

【Measurement instrument】

BELSORP MINI X
Pore Size Distribution Analyzer: BELSORP MINI X :: Microtrac

STABINO ZETA
STABINO ZETA - Zeta Potential Analyzer | MICROTRAC