Directed Orientation of Asymmetric Composite Dumbbells by Electric Field Induced Assembly

Daisuke Nagao [a], *Maki Sugimoto* [a], *Ayako Okada* [a], *Haruyuki Ishii* [a], *Mikio Konno* [a,] *, *Arnout Imhof* [b], *Alfons van Blaaderen* [b,] *

[a] Department of Chemical Engineering, Tohoku University, 6-6-07 Aoba, Aramaki-aza Aoba-ku, Sendai, 980-8579 (Japan)

[b]Soft Condensed Matter Group, Debye Institute for Nanomaterials Science, Utrecht University Princetonplein 5, 3584 CC Utrecht (The Netherlands)

[a] E-mail: nagao@mickey.che.tohoku.ac.jp, konno@mickey.che.tohoku.ac.jp

[b] E-mail: A.vanBlaaderen@ uu.nl

Preparation of asymmetric composite dumbbells incorporating a silica or titania/silica core

Chemicals: Tetraethyl orthosilicate (TEOS, 95%), titanium tetraisoproxide (TTIP, 95%), ethanol (99.5%), acetonitrile (99.5%), methylamine aqueous solution (40 %), ammonia aqueous solution (25 wt%), CH_3COOH (99.7%), methyl methacrylate (MMA, 98%), styrene (St, 99%), sodium *p*-styrenesulfonate (NaSS), potassium persulfate (KPS, 95%), and sodium chloride (NaCl, 99.5%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). The inhibitors for monomers of MMA and St were removed by an inhibitor removal column. The other chemicals were used as received. Silane coupling agent 3-methacryloxypropyl-trimethoxysilane (MPTMS, 95%) were purchased from Shinetsu Chemical (Tokyo, Japan), and used as received.

Synthesis of asymmetric composite dumbbells incorporating a silica core: The silica particles (d_V = 941 nm), prepared by a seeded growth technique, were used as cores incorporated into asymmetric polymer dumbbells. Firstly, deionized water (196 g) was bubbled with nitrogen for 30 min, and then MPTMS (114 μL) and a 11.34 wt% aqueous suspension of silica particles (3.94 g) were added to the water. After 30 min of stirring, MMA (5.1 mL) and a 20 mL aqueous solution containing NaSS (0.0495 g) were added to the silica suspension. After 2 h of stirring at 35 °C, the mixed solution was heated to 65 °C and a 20 mL aqueous solution containing KPS (0.130 g) was added to initiate polymerization. The polymerization was performed at 300 rpm for 2 h at 65 ^oC. Then, the PMMA-coated silica particles were washed three times and redispersed into 30 mL deionized water.

Secondly, the suspension of the PMMA-coated particles (3.82 g) and 0.1 M NaCl solutions (5.6 g) were added to 20.7 g deionized water. After 30 min of bubbling, 0.92 mL St was added to the suspension and the mixture was stirred for 2 h at room temperature. Then, the mixture was heated to 65 ^oC and a 10 mL aqueous solution containing KPS (0.0219 g) was added. The resultant suspension was washed three times by centrifugation and redispersion in deionized water.

Synthesis of asymmetric composite dumbbells incorporating a titania/silica core: The titania/silica (d_V = 888 nm) particles incorporated in polymer dumbbells were prepared via hydrolysis and condensation of TEOS in the presence of titania particles in a mixed solvent of ethanol and acetonitrile. Concentration of titania particles (d_V = 845 nm), TEOS, water, methylamine were 0.76 wt%, 0.03 M, 0.1 M and 0.03 M, respectively. The mixed solvent of ethanol and acetonitrile had a weight ratio of 60/40. The reactions were conducted for 12 h at 35 ^oC in a glass flask reactor with a volume of 40 mL. Titania/silica particles in the resultant solution were washed by centrifugation and redispersion in deionized water.

The titania/silica particles were used as cores to be incorporated into asymmetric polymer dumbbells. Firstly, deionized water (196 g) was bubbled with nitrogen for 30 min, and then MPTMS (114 μL) and a 4.57 wt% aqueous suspension of titania/silica particles (4.73 g) were added to the water. After 30 min of stirring, MMA (5.1 mL) and a 20 mL aqueous solution containing NaSS (0.038 g) were added to the titania/silica suspension. After 2 h of stirring at 35 ℃, the mixed solution was heated to 65 ℃ and a 20 mL aqueous solution containing KPS (0.130 g) was added to initiate polymerization. The polymerization was performed at 300 rpm for 2 h at 65 ^oC. Then, the PMMA-coated particles were washed three times and redispersed into 30 mL deionized water.

Secondly, the suspension of the PMMA-coated particles (9.17 g) and 0.1 M NaCl solutions (5.6 g) were added to 15.2 g deionized water. After 30 min of bubbling, 0.92 mL St was added to the suspension and the mixture was stirred for 2 h at room temperature. Then, the mixture was heated to 65 ^oC and a 10 mL aqueous solution containing KPS (0.0219 g) was added. The resultant suspension was washed three times by centrifugation and redispersion in deionized water.

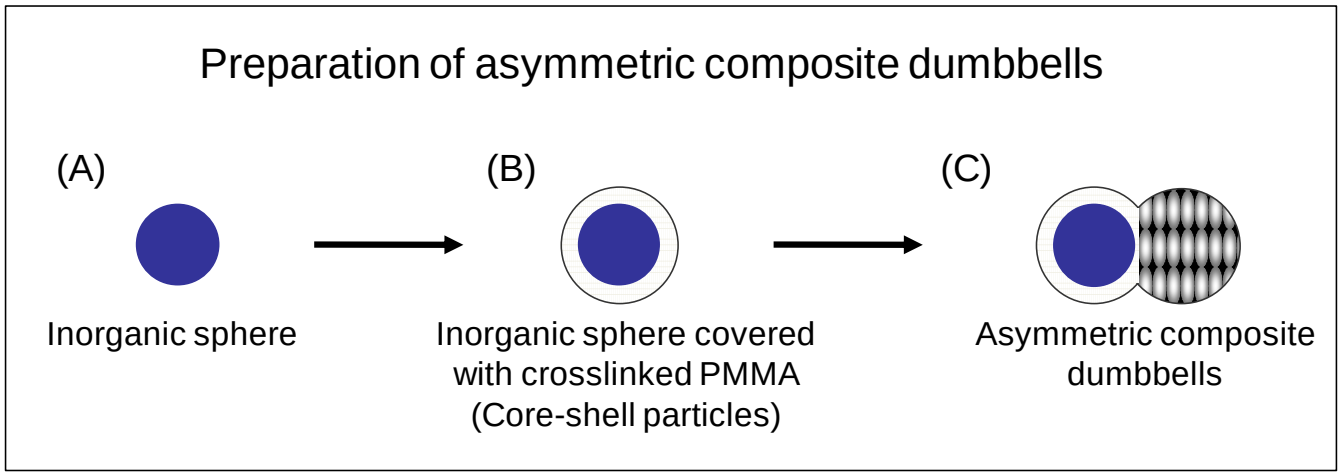

Figure S1 Schematic procedure for preparation of asymmetric composite dumbbells.

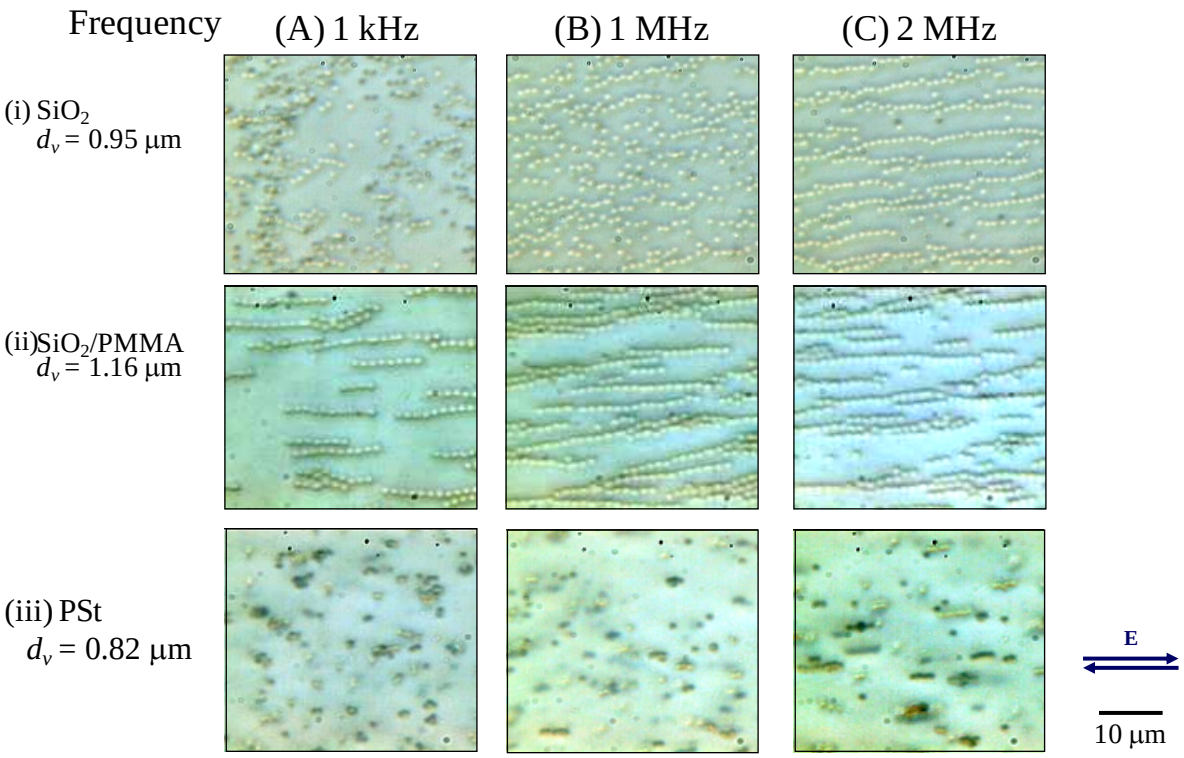

Figure S2. Optical microscope images of silica particles (i), PMMA-coated silica particles (ii) and spherical polystyrene particles (iii) under electric fields in a frequency range of 1 kHz – 2 MHz. The strengths of electric fields were V_{rms} = 17.7 for 1 kHz and 70.7 V/mm for 1 and 2 MHz.

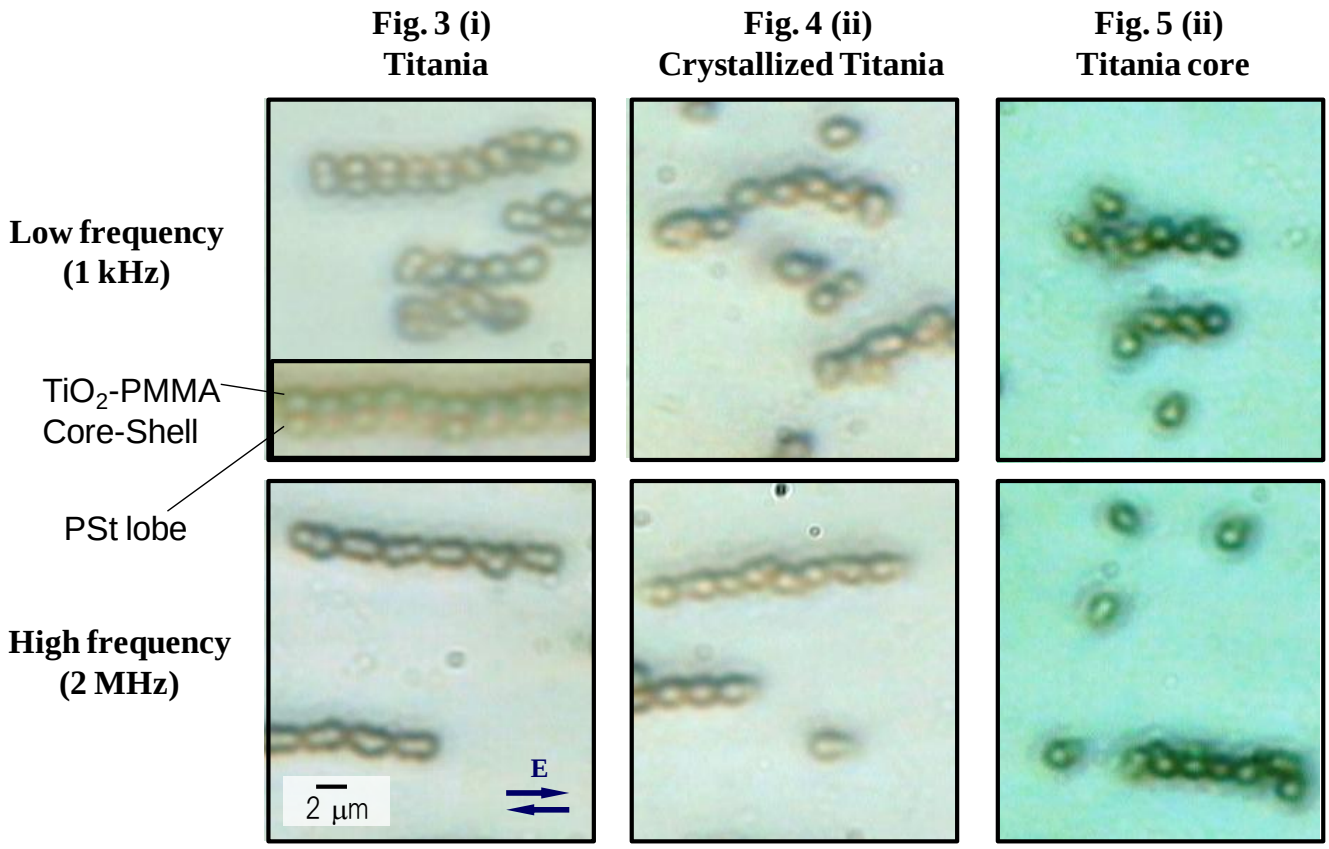

Fig. S3 OM wide views of the asymmetric dumbbells incorporating amorphous or crystallized titania spheres under electric fields at frequencies of 1 kHz and 2 MHz.

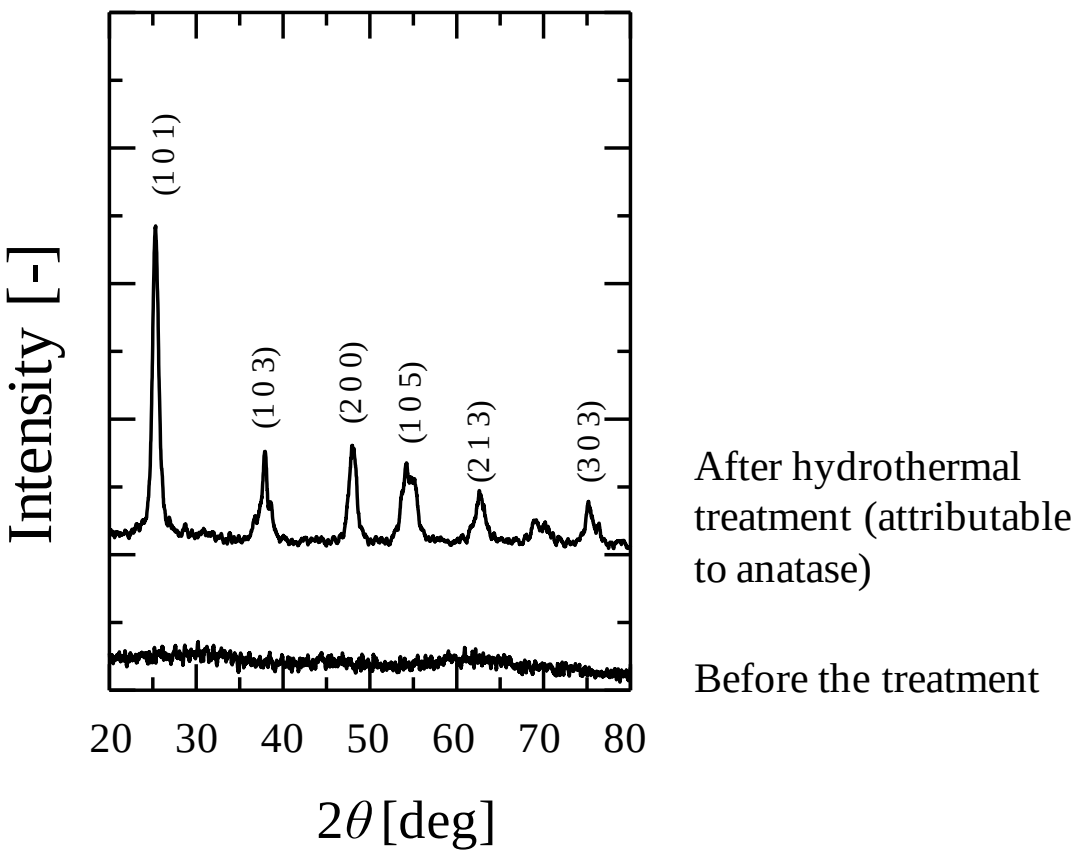

Fig. S4 XRD patters of titania spheres with and without hydrothermal treatment at 150 degree C for 3 h.

Table S1. Synthetic conditions for silica, titania and titania/silica spheres.

Inorganic spheres	Monomer	Basic catalysis	Water	Solvent	Other conditions
Silica spheres					
For seed particles [a]	[TEOS] =0.2 M	[NH_3] =1 M	11 M	Ethanol 100%	35 °C
For seeded growth [b]	[TEOS] =0.1 M	[NH_3] =0.2 M	11 M	Ethanol 100%	35 °C [CH_3COOH]=5 mM Seed Conc.: 0.078 vol%
Titania spheres [c]					
	[TTIP] =0.03 M	[CH_3NH_2] =0.03 M	0.1 M	CH_3CN: EtOH= 42: 58 (wt%)	10 °C
Titania/silica spheres					
For seeded growth [d]	[TEOS] =0.03 M	[CH_3NH_2] =0.01 M	0.33 M	CH_3CN: EtOH= 40: 60 (wt%)	35 °C Seed Conc.: 0.39 vol%

[b] Triple seeded growths stating with the seed particles [a] were performed to obtain 0.94 μm silica particles.

[c,d] Titania particles prepared with the condition [c] were silica-coated with the condition [d].

Table S2. Average dimensions of each part of asymmetric dumbbells in this study. L: length of the long axis of the dumbbell, S: PMMA-coated sphere size, P: polystyrene lobe size, D: diameter of the dumbbell neck. Figures in parenthesis are coefficients of variations for each dimension.

	L_{ave}	S_{ave}	P_{ave}	P_{ave}/ S_{ave}	$2L/(P+S)$	D_{ave}
Spheres incorporated into dumbbells						
Silica	1.8 μm (2.3 %)	1.1 μm (2.4 %)	1.0 μm (2.0 %)	0.91	1.71	0.82 μm (5.9 %)
Titania (amorphous)	2.0 μm (6.4 %)	1.2 μm (7.2 %)	1.1 μm (4.1 %)	0.92	1.74	0.95μm (7.0 %)
Amorphous-titania/silica	1.8 μm (5.5 %)	1.1μm (5.3 %)	1.0 μm (2.6 %)	0.91	1.71	0.82 μm (7.5 %)
Spheres incorporated into snowman-shaped particles						
Amorphous-titania/silica	1.6 μm (4.1 %)	1.1 μm (3.9 %)	0.69 μm (5.6 %)	0.63	1.77	0.59 μm (7.3 %)
Crystallized-titania/silica	1.8 μm (6.2 %)	1.3μm (5.9 %)	0.85 μm (5.6 %)	0.65	1.67	0.74 μm (11.9 %)
Silica	1.6 μm (2.3 %)	1.1μm (1.5 %)	0.81 μm (2.0 %)	0.74	1.68	0.69 μm (4.9 %)
Titania (amorphous)	1.6 μm (5.0 %)	1.1 μm (6.5 %)	0.81 μm (4.6 %)	0.74	1.67	0.72 μm (8.1 %)