Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting information for

'Localization of polymer-grafted maghemite nanoparticles in a hemisphere of Janus polymer particle prepared by self-organized precipitation (SORP) method'

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1. Experimantal details:

Materials:

γ-Fe_2O_3 nanoparticles (γ-Fe_2O_3 NPs; *Nano*Amor^{TM}, Purity: 96%, APS: 20-40 nm, SSA: 30 m^2/g) were purchased from Nanostructured & Amorphous Materials, In., U.S.A. and used as received. Polystyrene (PS; M_n=12.4 kg/mol, M_w/M_n=1.06), and poly(1,4-isoprene) (PI; M_n =11 kg/mol, M_w/M_n =1.06) were purchased from Polymer Source Inc., Canada. Styrene (99 %, Wako Pure Chemical Industry, Ltd. Japan) were purified by passing through a column filled with basic Al_2O_3 (70 μm, Wako Pure Chemical Industry, Ltd. Japan). 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 99%, Wako Pure Chemical Industry, Ltd. Japan) were used as received. Tetrahydrofuran (THF, HPLC grade with stabilizer, Wako Pure Chemical Industry, Ltd. Japan) was used as eluents in size-exclusion chromatography. All other solvents were purchased from Wako Pure Chemical Industry, Japan, and used without further purification.

Initiator installation and graft polymerization on γ-Fe_2O_3 nanoparticles:

Powdery ceramic NPs were prepared and spread in a quartz test tube with screw cap. The test tube was introduced into the UV-ozone etcher (TC-003/C, Meiwafosis Co., Ltd.) and exposed to

UV-ozone radiation for 45 min. After the exposure, the test tube was immediately transferred into the oxygen- and moisture- free glove box (Labmaster SP, M. Braun GmbH, Germany). Then, the beforehand prepared solution for living radical polymerization (LRP) was added to the test tube and inserted into aluminum block heater previously heated to the desired temperature. After scheduled time was passed, the test tube was removed from the glove box and the polymerization was totally quenched by adding the oxygen rich good solvent of the synthesized polymer. The NPs were washed with the good solvent of the polymer by dispersion and centrifugation method at least five times to perfectly remove the unbound polymers from the solution. The characterization of the NPs were carried out by field-emission scanning electron micrography (FE-SEM), dynamic light scattering (DLS), Fourier transfer infrared spectroscopy (FTIR), thermo gravimetry (TG) and Gel permeation chromatography (GPC).

Nitroxide mediated polymerization (NMP) of styrene:

9.6 mM of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) styrene solution was prepared and stored in the refrigerator in the moisture and oxygen free glove box. 0.5 g of UV-ozone treated NPs powder was immersed into 3 mL of the stocked solution and stirred very well. Then, the test tube with screw cap was placed in the aluminum block heater previously heated to 125 °C for 12 hours. After the polymerization, the test tube was removed from the heater and the glove box, then oxygen rich $CHCl_3$ was added to terminate polymerization and dissolve the NPs. The molecular weight of the PS synthesized had the mean number molecular weight as M_n = 52,000 g mol^{-1} with the polydispersity index (M_w/M_n) as PDI = 1.31.

Size exclusion chromatography:

Gel permeation chromatographic (GPC) analysis was carried out at 35 °C on a JASCO GPC-900 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-803L, exclusion limit: 7×10^4 and KF-805L, exclusion limit: 4×10^6), and a differential refractometer. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. The GPC system was basically calibrated by PS and PMMA standards (Polymer Standard Service, PSS-Kit, (PS): Mp. 682 - 1.67×10^6 D, (PMMA): M_p. 102 - 9.81×10^5 D).

Purification of magnetic γ-Fe_2O_3-g-PS:

2 mg of γ-Fe_2O_3-*g*-PS was dispersed in 10 mL of chloroform with ultrasonication. The dispersed powder was collected with a neodymium magnet and the supernatant was eliminated. The collected NPs washed with chloroform two or three times, and then dried at 25 °C for 3 h.

Characterization of γ-Fe$_2$O$_3$-g-PS:

The surface of γ-Fe$_2$O$_3$-*g*-PS was observed by field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Co. Ltd.). The solution of polymer grafted NPs was dropped on a carbon tape and dried. Electron micrographs were taken at an accelerating voltage of 1-2 kV. Fourier transfer infrared (FTIR) spectrometer (Jasco, FT/IR 680 plus) was employed to analyze the status of the surface of NPs. The spectra were measured at a resolution of 4 cm^{-1}. The amount of grafted PS was measured from the weight loss of the thermo gravimetry (TG, Rigaku, TG8120). The temperature dependent weight loss of γ-Fe$_2$O$_3$-*g*-PS was recorded under Ar atmosphere with temperature sweep at 10 °C/min. 10 mg of the polymer grafted NPs were used for single TG measurements. Because of the large amount of the polymer grafted NPs, 5 % of weight loss was calculated to be 0.5 mg. This amount is enough large to regard accurate measurement was done for the TG measurement. The dispersibility of γ-Fe$_2$O$_3$-*g*-PS in solvents was determined by dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern Instruments Ltd.) and also measured through our eyes (taking photographs by RICOH digital camera GX200).

Preparation of magnetic Janus particles:

THF solutions of PS and PI (1.0 mg/mL) were also prepared. THF solutions (0.5 mL) of PS, PI, and γ-Fe$_2$O$_3$-*g*-PS were mixed in each two 12-mL vials and stirred using a vortex mixer (500 rpm.). One milliliter of Millipore-membrane-filtered (Milli-Q) water was dropped into the each mixed solution at a rate of 1 mL/min. One of the vials was then placed in a water bath at 25 °C for 2 days to evaporate THF. Another vial was then placed in a vacuum oven at 25 °C for 2 hours to evaporate THF quickly. After the complete evaporation of THF, opaque aqueous dispersions of particles were obtained.

Characterizations of magnetic Janus particles:

The surface and interior structures of the particles were observed by scanning electron microscopy (SEM, S-5200, Hitachi, Co. Ltd.) and transmission electron microscopy (TEM, H-7650, Hitachi, Co. Ltd.), respectively. PI moieties were stained with osmium tetraoxide (OsO_4) by adding 0.2% OsO_4 aqueous solution into the particle dispersion. After 2 h of staining, the stained particles were separated by centrifugation (12,000 rpm, 15 min, 5 °C) and washed with pure water to remove excess OsO4. After washing, the stained particles were redispersed in pure water. Water suspensions of the stained particles were dropped on a carbon-membrane-coated Cu grid and dried at room temperature. To prepare an ultrathin specimen for TEM, the stained particles were embedded in epoxy resin, and then the epoxy resin with particles was sliced with an ultramicrotome (Leica, EM UC7, Leica Microsystems, Germany). A 100-nm-thick specimen was obtained. The specimen was placed on a carbon-membrane-coated Cu grid.

A drop of the water suspension was sandwiched using two glass plates with a 0.03-mm-thick polyester spacer put between them. The magnetic responses of the particles were investigated with a neodymium magnet under observation by optical microscopy (Digital Microscope VHX-900, KEYENCE). The size distribution of the particles were measured by dynamic light scattering (DLS, FDLS-3000, Otsuka Electronics Co. Ltd, Japan).

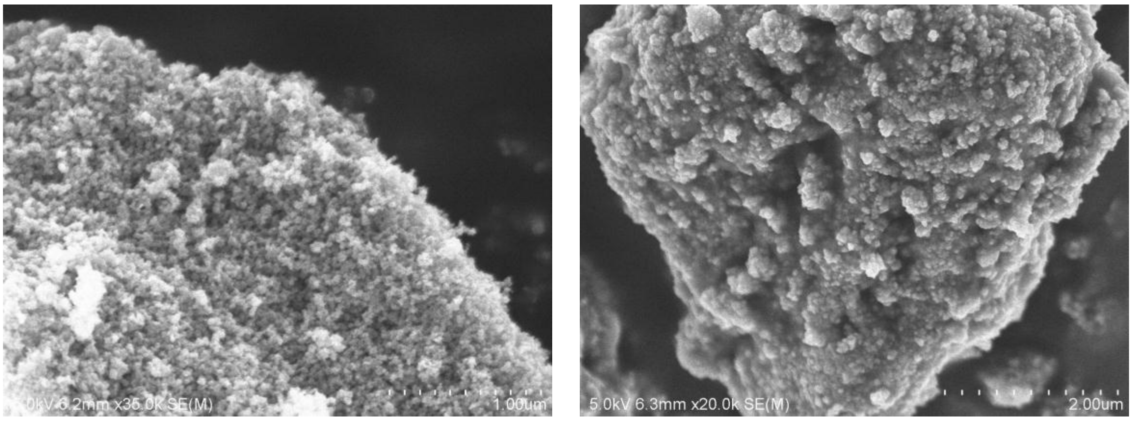

Figure S1. SEM Images of γ-Fe_2O_3 and γ-Fe_2O_3-*g*-PS. The surface and boundary of γ-Fe_2O_3-*g*-PS are much smoother than those of γ-Fe_2O_3.

2. Preparation of Fe_3O_4-*g*-PS.

It goes without saying that Fe_3O_4 having more strong magnetism than that of γ-Fe_2O_3. Therefore if γ-Fe_2O_3 NPs embedded in the magnetic Janus particle were simply replaced to Fe_3O_4 NPs, the magnetic response of the magnetic Janus particle had to be improved. We have also investigated preparation of magnetic Janus particle with Fe_3O_4. The methodology was the same as that for γ-Fe_2O_3. Firstly, Fe_3O_4-*g*-PS was prepared the same UV-O_3 assisted graft polymerization process as mentioned above. Fe_3O_4 NPs (Fe_3O_4 NPs; *Nano*Amor^{TM}, Purity: 99.5%, APS: 25 nm, SSA: 66 m^2/g) were purchased from Nanostructured & Amorphous Materials, In., U.S.A. and used as received. As synthesized Fe_3O_4-*g*-PS (2 mg) were dispersed in 10 mL of chloroform with ultrasonication. And then the dispersed powder was collected with a neodymium magnet and the supernatant was eliminated. By the operation nonmagnetic particles were removed. The images of dispersions of Fe_3O_4-*g*-PS in THF and $CHCl_3$ were depicted in Figure S2.

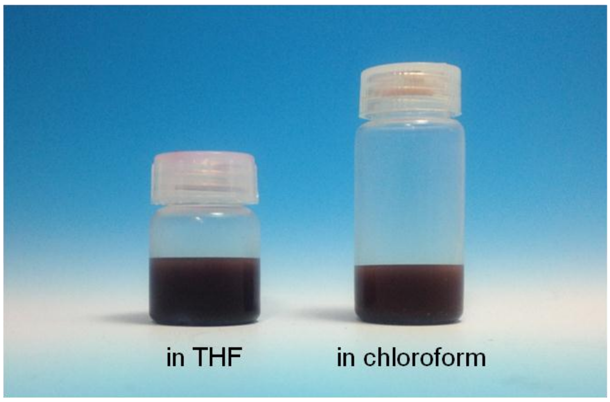

Figure S2. Images of Fe_3O_4-*g*-PS. The concentration of Fe_3O_4-*g*-PS in the dispersions were 2 wt%.

4. Preparation of Fe_3O_4-*g*-PS embedded magnetic Janus particle.

Preparation of Janus particle was carried out according to the following procedure. THF solutions of PS and PI (1.0 mg/mL) were also prepared. THF solutions (0.5 mL) of PS, PI, and Fe_3O_4-*g*-PS were mixed in a 12-mL vial and stirred using a vortex mixer (500 rpm.). One milliliter of Millipore-membrane-filtered (Milli-Q) water was dropped into the mixed solution at a rate of 1 mL/min. The vial was then placed in a vacuum oven at 25 °C for 2 hours to evaporate THF quickly. After the complete evaporation of THF, opaque aqueous dispersions of particles were obtained.

The surface and interior structures of the particles were observed by scanning electron microscopy (SEM, S-5200, Hitachi, Co. Ltd.). PI moieties were stained with osmium tetraoxide (OsO4) by above mentioned method. The SEM images of prepared Janus particles were depicted in Figure S3. As seen in Figure S3, particles were emerged. Even in the case of clear Janus structure was seen, Fe_3O_4-*g*-PS was not localized in PS hemisphere. The strong magnetic interaction between Fe_3O_4-*g*-PS would collapse the structure.

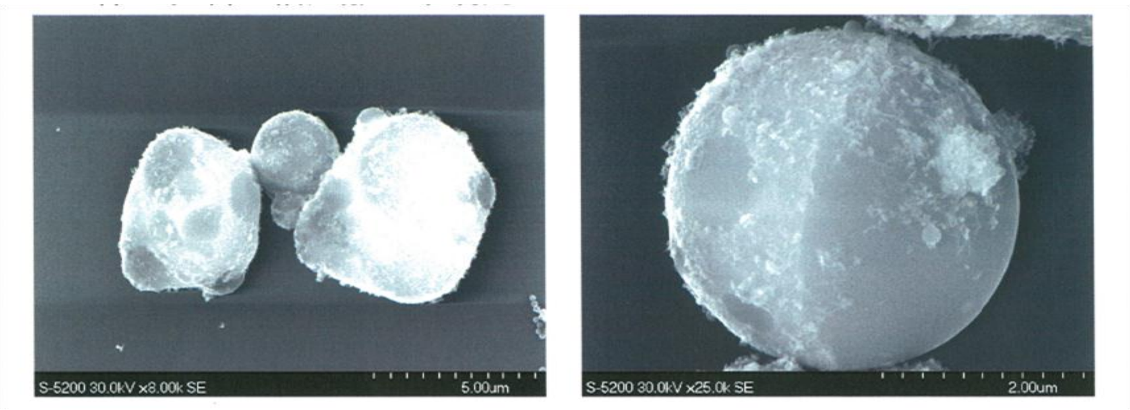

Figure S3. Bright-field SEM images of magnetic Janus particles with Fe_3O_4-*g*-PS.