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Ⓢ *Supporting Information*

ABSTRACT: In this report, we show a simple route to fabricate Janus particles having magnetic nanoparticles inside them, which can respond and rotate along to magnetic fields. By solvent evaporation from the tetrahydrofran solution of polymer stabilized γ-Fe_2O_3 nanoparticles, polystyrene (PS), and polyisoprene containing water, aqueous dispersion of Janus microparticles were successfully prepared, and the γ-Fe_2O_3 nanoparticles were selectively introduced into the PS phase. We demonstrate rotation and accumulation of Janus particles by using a neodymium magnet.
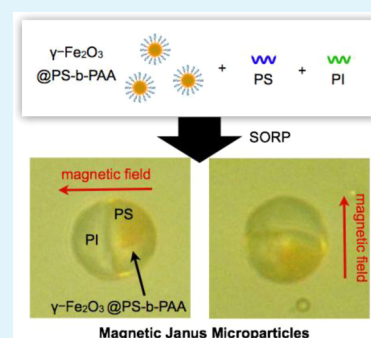
KEYWORDS: *phase separation, Janus particles, magnetic response, self-assembly, polymer particles*

1. INTRODUCTION

Electronic paper, a thin, flat, and flexible display, has attracted much attention as a next-generation display device.[1] Many fabrication techniques for electronic paper have been proposed including the use of various materials (e.g., reflective liquid crystals[2,3]), pigment electrolysis,[4,5] electrochromism,[6] and so on.[7,8] Twisting-ball-type electronic paper is a low-cost high-efficiency candidate for electronic paper.[9] Because charged spherical Janus particles whose surface or interior is colored with different dyes or pigments can be rotated by applying an electric field, the color of the pixels can be switched. The properties of Janus particles are crucial for realizing this type of device. In particular, the size, color, surface properties, and response to external fields are key factors for developing high-resolution, multicolor electronic paper that is responsive and energy-efficient.

Techniques for preparing functional Janus particles have been reported. One technique is the sputtering of metals onto spherical particles embedded in a polymer matrix;[10−12] after removing the polymer matrix, spherical particles with hemispheres covered with metal thin layers are obtained. Another technique is phase separation in monomer droplets formed in a microfluidic chamber; this method is used to prepare Janus particles on the 10 μm scale after the polymerization or cross-linking of materials.[13−15] Emulsion-based preparation methods have also reported.[16] However, such methods have drawbacks including low productivity, poor size regulation, and complex preparation processes except for the sophisticated mini-emulsion method.[17]

Accordingly, we have developed a simple polymer particle preparation method named Self-ORganized Precipitation (SORP).[18] In SORP, a good solvent is evaporated from a polymer solution containing a poor solvent of the dissolved polymer, and then the polymer molecules are precipitated as spherical particles after complete evaporation of the good solvent. By using this simple process, a wide variety of polymer materials including commodity polymers, π-conjugated polymers, engineering plastics, and biodegradable polymers can be prepared.[19,20] Particle size can be controlled from tens of nanometers to a scale of several micrometers by changing the

preparation conditions including the concentration of the solution and the mixing ratio of the good solvent to the poor solvent. Note that microphase-separated structures are formed in particles prepared from block copolymers[21−23] and that interior phase-separated structures are controlled by changing the copolymerization ratio, molecular weight, and particle size.[24−28]

Recently, we have found that the interior structures of polymer-blended particles are governed by the hydrophobicity of polymers in a blend.[29] When the difference in the Flory−Huggins solubility parameter between blended polymers is sufficiently large, a core−shell structure is formed in the interior of polymer-blended particles precipitated in water. On the other hand, a Janus-type phase-separated structure is formed in polystyrene (PS) and poly(1,4-isoprene) (PI) blended particles by SORP. Because PS and PI have similar surface free energies, the Janus-type phase-separated structure can be selected to minimize interfacial energy.

When polymer-stabilized inorganic nanoparticles are mixed into the solution of polymer blends for particle preparation, organic−inorganic composite particles can be prepared.[30,31] Moreover, inorganic nanoparticles can be selectively introduced into a specific polymer moiety with a high affinity to polymer molecules, thereby stabilizing inorganic nanoparticles. By using this method, gold nanoparticles[32] and CdS nanoparticles[33] have been introduced into phase-separated block-copolymer and polymer-blend particles. However, gold and CdS nanoparticles only add optical properties to the nanostructured polymer particles. When the magnetic nanoparticles are introduced into these nanostructured polymer particles, a novel class of external field-responsive particles applicable to high-resolution, multi-colored, and energy-efficient pigments for electric papers will be provided.

In this study, we prepared polymer-stabilized ferromagnetic γ-Fe$_2$O$_3$ nanoparticles that are soluble in hydrophobic organic solvents by encapsulating γ-Fe$_2$O$_3$ nanoparticles in amphiphilic block-copolymer inverse micelles. Literatures have showed that magnetic Janus particles have high performance and possibilities for electric papers.[34] From the polymer-stabilized nanoparticles and polymer-blend system, Janus particles containing ferromagnetic γ-Fe$_2$O$_3$ nanoparticles were then prepared. The reactivity of the prepared Janus particles to magnetic fields is discussed.

2. EXPERIMENTAL SECTION

Materials. γ-Fe$_2$O$_3$ nanoparticles (γ-Fe$_2$O$_3$ NPs; diameter, ≤50 nm) were purchased from Aldrich, USA. Poly(styrene-*block*-acrylic acid) (PS-*b*-PAA, M_{nPS} = 16.5 kg/mol, M_{nPAA} = 4.5 kg/mol, M_w/M_n = 1.05 or M_{nPS} = 14 kg/mol, M_{nPAA} = 3.5 kg/mol, M_w/M_n = 1.06), polystyrene (PS; M_n = 12.4 kg/mol, M_w/M_n = 1.06), and poly(1,4-isoprene) (PI, $M1$ = 11 kg/mol, M_w/M_n = 1.06) were purchased from Polymer Source Inc., Canada. All other solvents were purchased from Wako Chemical Industry, Japan, and used without further purification.

Preparation of Polymer-Stabilized γ-Fe$_2$O$_3$ NPs. γ-Fe$_2$O$_3$ NPs (0.3 g) were dispersed in 30 mL of ethanol and water (1:1 v/v) with ultrasonication. The dispersed powder was collected with a neodymium magnet and the supernatant was discarded. The collected NPs washed with ethanol two or three times, and then dried at 40 °C for 5 h. γ-Fe$_2$O$_3$ NPs were stabilized with PS-*b*-PAA by a previously reported method[35,36] with modifications. Purified γ-Fe$_2$O$_3$ NPs were dispersed in 1 mL of THF solution of PS-*b*-PAA (2.0 mg/mL) with ultrasonication for 15 min. Benzene (3 mL) was slowly dropped into the THF solution with stirring using a vortex mixer (1000 rpm.). After mixing, γ-Fe$_2$O$_3$ NPs were collected using a neodymium magnet and the supernatant was discarded. The collected γ-Fe$_2$O$_3$ NPs were

washed three times with THF under ultrasonication, and then the purified γ-Fe$_2$O$_3$ NPs were collected with a neodymium magnet. The collected γ-Fe$_2$O$_3$ NPs were redispersed in THF.

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$_3$ NPs stabilized with PS-*b*-PAA 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 water bath at 25 °C for 2 days to evaporate THF. After the complete evaporation of THF, an opaque aqueous dispersion of particles was obtained. The content of PS-*b*-PAA-stabilized γ-Fe$_2$O$_3$ NPs was ca. 33 wt %. Because the density of the Fe$_2$O$_3$ is 5.24 g/cm^3, the maximum volume content of the γ-Fe$_2$O$_3$ NPs in the magnetic Janus particles is up to 5−6 vol%.

Characterization of Magnetic Janus Particles. The surface and interior structures of the particles were observed by scanning electron microscopy (SEM, S-5200, Hitachi, Co. Ltd.) equipped with a scanning electron transmission microscope (STEM) detector and transmission electron microscopy (TEM, H-7650, Hitachi, Co. Ltd.), respectively. In the case of STEM observation, scanning electron micrographs and transmission electron micrographs were simultaneously imaged by using SE and TE detectors. 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 OsO$_4$. 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, we embedded the stained particles 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.

Scanning transmission electron microtomography (STEMT) of the particles was carried out using a JEM-2200FS (JEOL Co., Ltd., Japan) operated at 200 kV. A series of scanning TEM (STEM) images were acquired at tilt angles ranging from −67° to 72° at 2° intervals. The optics of the microscopy was adjusted so that the focal depth is roughly 2.2 μm.[37,38] The tilt series of TEM images were aligned by the fiducial marker method using Au nanoparticles. The three-dimensional images obtained were reconstructed by filtered back-projection.[39]

Detail surface structures and chemical composition was observed by using a field emission type scanning electron microscope (FE-SEM, Magellan 400L, FEI) equipped with electron dispersive X-ray Spectroscopy (EDX). A drop of water suspension of magnetic Janus particles was cast onto a Si substrate, and observed by FE-SEM with low acceleration voltage (1 kV) after evaporation of water at room temperature in vacuo.

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 of magnetic Janus particles was measured by dynamic light scattering (DLS) method (FDLS-3000, Ohtsuka Denshi, Japan). The hydrodynamic diameter of the prepared magnetic Janus particles was 1502 ± 830 nm. According to the literature,[18−20] the size of the Janus particles can be tailored from tens nm to μm scale by changing concentration of solutions, mixing ratio between solutions and poor solvents, and so on. The whole polymers and γ-Fe$_2$O$_3$ NPs dispersed in THF were transformed to particles.

3. RESULTS AND DISCUSSION

Figure 1 shows a schematic illustration of the preparation procedures for the PS-*b*-PAA-stabilized γ-Fe$_2$O$_3$ NPs and composite Janus particles. After encapsulation in PS-*b*-PAA, the PS-*b*-PAA-stabilized γ-Fe$_2$O$_3$ NPs dispersed in the THF
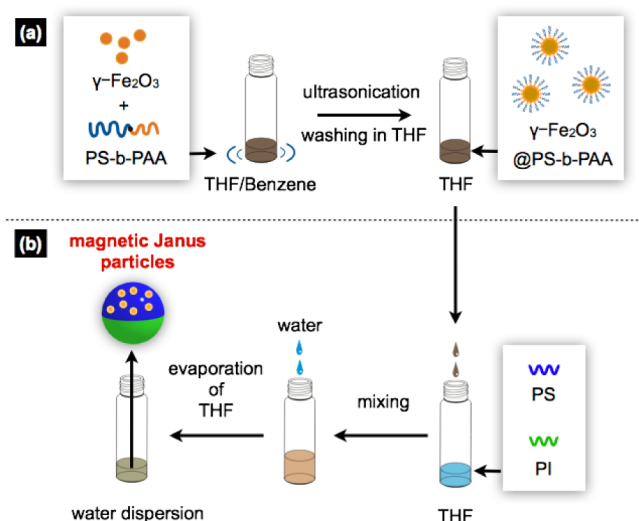
Figure 1. Schematic illustrations of (a) stabilization of γ-Fe$_2$O$_3$ NPs with PS-b-PAA and (b) preparation of magnetic Janus particles.

well (Figure 2a(i)) compared with the nonstabilized γ-Fe$_2$O$_3$ NPs (Figure 2a(ii)). Figure 2a shows a SEM image of the PS-b-
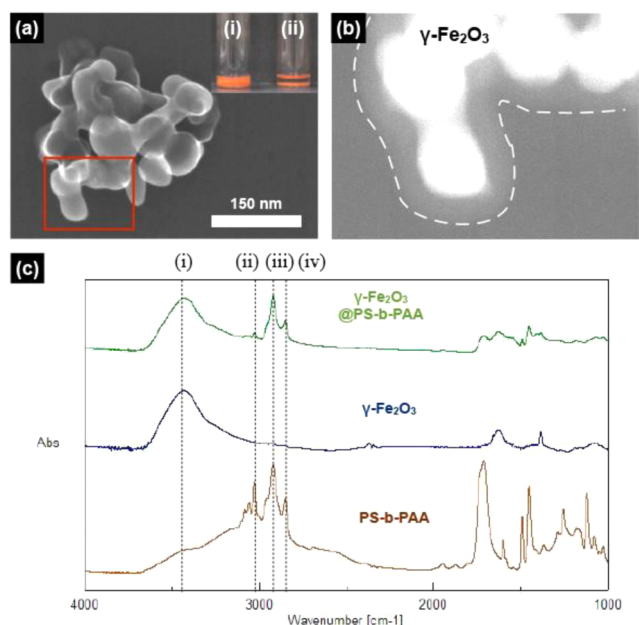

Figure 2. (a, b) SEM images of γ-Fe$_2$O$_3$ NPs in PS-b-PAA by using S-5200, Hitachi; (c) FT-IR spectra of PS-b-PAA (brown line), γ-Fe$_2$O$_3$ NPs (blue line), and γ-Fe$_2$O$_3$ NPs at PS-b-PAA (green line).

PAA-stabilized γ-Fe$_2$O$_3$ NPs. Aggregates of about 200 nm consisting of roughly 50 nm γ-Fe$_2$O$_3$ NPs were clearly imaged. When a close-up image of part of the aggregate was taken, all the γ-Fe$_2$O$_3$ NPs were found to be covered with low-electron-density materials, which implies the formation of polymer layers on their surface (Figure 2b). According to the literature, a carboxylic acid group strongly attaches to the surface of γ-Fe$_2$O$_3$, and PAA moieties in PS-b-PAA bind to the surface of γ-Fe$_2$O$_3$ NPs and form protective layers.[20] The stabilization of the γ-Fe$_2$O$_3$ NPs with PS-b-PAA was also supported by results of FT-IR spectroscopy (Figure 2c). Absorption peaks attributed to alkyl (2700−3000 cm^{-1} (ii), (iii), (iv)) and aromatic C−H bonds (3000−3200 cm^{-1} (i)) are clearly observed after the

encapsulation of the γ-Fe$_2$O$_3$ NPs with PS-b-PAA. The average thickness of the low-electron-density layers formed on the surfaces of the γ-Fe$_2$O$_3$ NPs was 15 nm, which is almost consistent with the average radius of PS-b-PAA micelles reported in the literature.[40,41] These results also support the formation of polymer layers on γ-Fe$_2$O$_3$ NPs.

After the complete evaporation of THF from the THF/water solution of the PS-b-PAA-stabilized γ-Fe$_2$O$_3$ NPs, PS, and PI, an opaque water suspension of composite particles were obtained. By using SEM equipped with a STEM detector, SEM image originated from secondary electron from the sample (SE-mode) and transmission image (TE-mode) were simultaneously obtained.

Images a and b in Figure 3 show SE-mode and dark-field TE-mode STEM images of prepared particles, respectively. The SE-
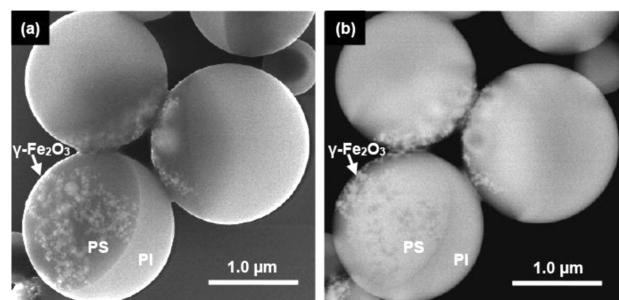

Figure 3. (a) SE-mode and (b) dark-field TE-mode STEM images of prepared magnetic Janus particles, respectively (measured by S-5200 equipped with STEM detector, Hitachi).

mode image reveals that uniform, micrometer-sized spherical particles have been formed, and the each particle has a Janus-type phase separation structure. The darker hemisphere is attributed to low electron density PS moiety, and the other hemisphere is attributed to PI moiety, which was stained with OsO$_4$. It is obvious that NPs were selectively introduced into the PS phase. From the dark-field TE mode image, the contrast was inverted comparing with the SE-mode image, and there is no NP in the PI moiety.

To confirm the chemical composition of the Janus particle, EDX spectrum of each phase was measured. Figure 4a shows a SEM image of Janus particles obtained under low acceleration voltage. Because of the low acceleration voltage, detail surface structures can be imaged without any metal coating.[47,48] Clear interface between two hemispheres were observed and the NPs were located only at the single phase. Panels b and c in Figure 4 show EDX spectra from right and left side hemispheres of the particle shown in Figure 4a, respectively. From the right hemisphere, distinctive peaks attributed to the C, O, and Os were observed. On the other hand, peaks attributed to C, O, and Fe were observed at the left hemisphere having NPs. These results also support Janus-type phase-separated particle comprising OsO$_4$-stained PI hemisphere and γ-Fe$_2$O$_3$ NP-introduced PS hemisphere.

The detailed interior structures of the composite Janus particles were investigated by using a cross-sectional TEM and TEMT. Figure 5a shows a cross-sectional TEM image of prepared Janus particle. From this result, the γ-Fe$_2$O$_3$ NPs were located only at the surface of PS phase. A STEMT image of composite Janus particles is shown in Figure 5b. Clear interfaces between PS (transparent) and PI (light green) moieties are observed. The STEMT image also revealed that γ-
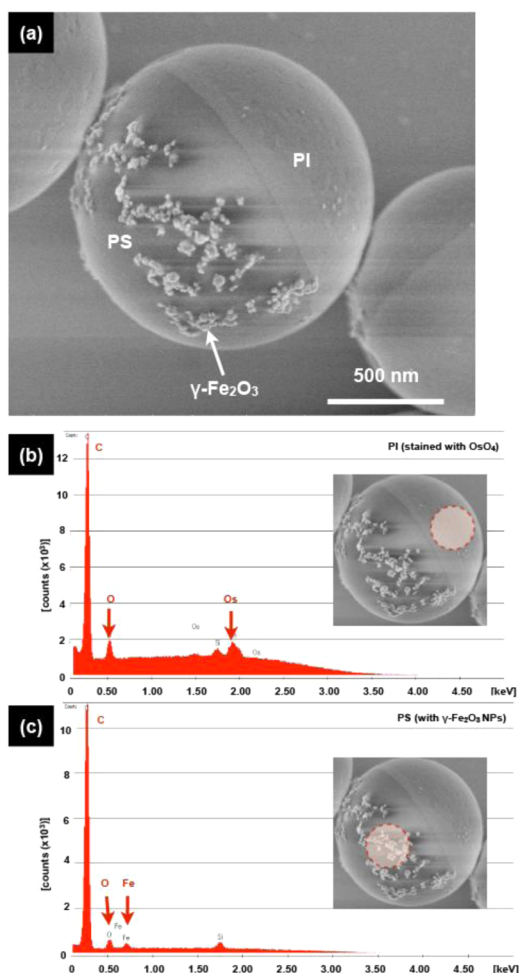
Figure 4. (a) SEM image of prepared magnetic Janus particles obtained under low acceleration voltage and EDX spectra from (b) right and (c) left hemispheres of the magnetic Janus particle shown in a. Red dotted circle in the inset images of b and c indicate measuring region of each EDX spectrum (measured by Magellan 400L, FEI).
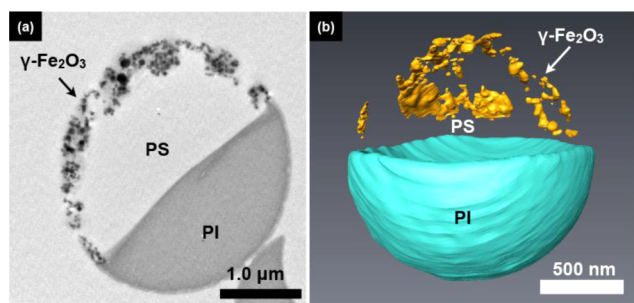

Figure 5. (a) Cross-sectional TEM image and (b) STEMT image of magnetic Janus particle (measured by Hitachi H-7650 and JEOL JEM-2200FS, respectively).

Fe_2O_3 NPs were accumulated at the surface of the particle in the PS phase (light brown dotlike structure at PS part).

The interior structures in the composite particles are strongly affected by material composition, the interfacial tension between polymers and the dispersion medium, the molecular weight and solubility parameters of polymers, and other factors.[21] Both Pikering stabilization and insoluble segregation of PS-b-PAA stabilized γ-Fe_2O_3 NPs from PS phase might induce the segregation of γ-Fe_2O_3 NPs to the water−PS

interfaces. During the formation of composite Janus particles, the solvent was changed from relatively hydrophobic THF to water. Because PAA moieties did not fully associate with the surface of γ-Fe_2O_3 NPs, a certain amount of hydrophilic PAA moieties appeared at the surface of the PS-b-PAA stabilized γ-Fe_2O_3 NPs. Some of the PS-b-PAA-stabilized γ-Fe_2O_3 NPs exhibited polarity, and the PS-b-PAA-stabilized γ-Fe_2O_3 NPs segregated to the interface between the polymer and water.

The magnetic response of the composite Janus particles was observed by using a neodymium magnet (Figure 6a). The
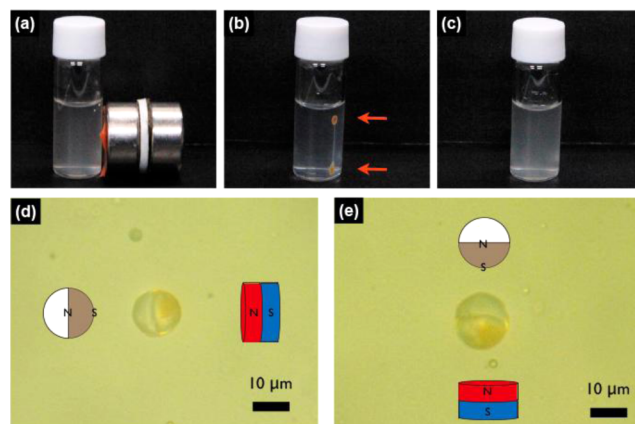

Figure 6. Photographs of aqueous dispersion of magnetic Janus particles (a) before and (b) after accumulation with neodymium magnet and (c) of redispersed dispersion. (d, e) Optical micrographs of alignment of a magnetic Janus particle along the magnetic field. The red arrows in b show accumulated magnetic Janus particles.

magnetic flux density (B) of the sample is estimated by using the following equation[42]

$$B = Br/2[(I + L)/\{(I + L)^2 + D^2/4\}2 \\ - I/\{I^2 + D^2/4\}^2]$$

where Br, I, L, and D are the remanent flux density, the distance between the sample and the magnet, and the thickness and diameter of the magnet, respectively. When the neodymium magnet was brought close to a bottle filled with an aqueous suspension of composite Janus particles (up to 2 cm, $B = 50−150$ mT), the particles accumulated around the neodymium magnet (Figure 6b). However, the accumulated particles could be redispersed by simple stirring or ultrasonication (Figure 6c). As shown in the literature,[43] the surface of particles prepared from hydrophobic polymers by SORP often has a negative charge. The polymers were precipitated from hydrophobic THF solution to water, the polymer−water interface was formed on the surface of particles after particle formation. At such a hydrophobic surface water interface, water molecules aligned on the hydrophobic surface and the structured water molecules originate surface negative charges on the hydrophobic surfaces.[44] Because a charged surface causes repulsion between particles, the prepared particles also exhibit redispersity.

When the neodymium magnet was placed 2−15 cm from the sample, the particles did not accumulate, instead they rotated along the magnetic field. Typical rotational motions of the composite Janus particles are shown in d and e in Figure 6. When the neodymium magnet was moved laterally, the brown PS and PS-b-PAA stabilized γ-Fe_2O_3 NPs headed toward the

magnet, rotating with the magnet movement. Then, when the neodymium magnet was rotated upside down (see the Supporting Information) 10 cm from the particle dispersion ($B \approx 1$ mT, which is attributed to the 5 mA electric current applied to generate a magnetic field from an electrode set 1 μm below the particle dispersion), the composite Janus particles changed from a brown phase to a noncolored phase, which was attributed to the PI moiety. From these results, composite Janus particles that respond to a magnetic field were successfully prepared.

4. CONCLUSION

We have reported a simple method for fabricating magnetic Janus particles that respond to an external magnetic field. By using the SORP method, we have also introduced TiO_2 particles to Janus particles as white pigments.[45] We found that, when colored with pigments or dyes, the particles can be suitable pixels for a novel class of electronic paper. The method can be used to produce a wide variety of organic−inorganic composite particles with nanoscale structures.[46]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Movie image of magnetic Janus particles rotating along to magnetic fields (.mov). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Author Contributions
The manuscript was written through contributions of all authors.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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