

Electronic Supplementary Information

One-pot synthesis of conducting polymer-coated polystyrene particles: ammonium persulfate as free radical initiator and chemical oxidant

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Materials

Unless otherwise stated, all materials were guaranteed reagent grade. Poly(*N*-vinyl pyrrolidone) [PNVP; nominal molecular weight = 360,000] and ammonium persulfate (> 95.0%: APS) were obtained from Wako Chemicals. Styrene and aluminium oxide (activated, basic, Brockmann 1, standard grade, ~150 mesh, 58 Å) were obtained from Sigma-Aldrich and were used without further purification. Pyrrole (98%) and aniline (99%) were also obtained by Sigma-Aldrich and purified by passing through a column of the activated basic alumina prior to storage at -15 °C before use. Deionized water (< 0.06 μS cm⁻¹) was prepared using a deionized water producing apparatus (Advantec MFS RFD240NA: GA25A-0715) and used for synthesis and purification of the PS latex particles and conducting polymer-coated PS particles.

Preparation of PS Seed Latex via Surfactant-free Emulsion Polymerization

Charge-stabilized anionic PS particles were prepared by the surfactant-free emulsion polymerization of styrene at 70 °C using APS initiator. Styrene (5.00 g) was added to water (45 mL) in a round-bottomed 100 mL flask fitted with a magnetic stir bar. Aqueous solution of APS (0.05 g APS dissolved in 5.00 g water) was added to the reaction vessel, followed by degassing with a nitrogen purge. Polymerization commenced after the heating of this reaction mixture to 70 °C. The reaction proceeded for 10 h with continuous stirring at 920 rpm under a nitrogen atmosphere. This latex was used for conducting polymer coating without purification.

Characterization of PS seed latex and Conducting Polymer-coated PS latexes

The chemical oxidative seeded polymerization was allowed to proceed for 24 hours. The conducting polymer-coated PS latex particles were subsequently purified by repeated centrifugation-redispersion cycles (successive supernatants were replaced with de-ionized water). For the PS extraction, the composite particles were dispersed in THF for 24 hours and were centrifugally washed five times with pure THF.

Optical microscopy

A drop of the diluted latex was placed on a microscope slide and observed using an optical microscope (Shimadzu Motic BA200) fitted with a digital system (Shimadzu Moticom 2000).

Particle size analysis

The sizes and size distributions of the latex particles were determined using a particle

size analyzer (Malvern Mastersizer 2000) equipped with a small volume sample dispersion unit (Hydro 2000SM; *ca.* 150 mL including flow cell and tubing), a HeNe laser (633 nm), and a solid-state blue laser (466 nm). The stirring rate was adjusted to 2000 rpm. The raw data were analyzed using Malvern software. The mean particle diameter was taken to be the volume mean diameter (D_v), which is mathematically expressed as $D_v = \Sigma D_i^4 N_i / \Sigma D_i^3 N_i$, where D_i is the diameter of individual particles and N_i is the number of particles corresponding to the specific diameter.

Transmission electron microscopy study

Observation of dilute dispersions dried on carbon-coated copper grids was performed using a transmission electron microscope (TEM; Jeol JEM-2000EX).

Scanning electron microscopy study

Scanning electron microscopy (SEM; Keyence VE-8800, 12 kV) was conducted with Au sputter-coated (Elionix SC-701 Quick Coater) dried samples. Some PPy-coated particles are non-spherical. This deformation from spherical morphology occurred during the chemical oxidative polymerization of pyrrole, not during centrifugal washing. Exact reason is unclear, but the nucleation of PPy on the PS seed particles may contribute this deformation. Few by-produced nanometer-sized PPy homoparticles were observed in SEM and TEM images and we believe that almost all the PPy produced was incorporated into the core-shell particles. Only the broken egg-shell capsules were observed by TEM and SEM studies on the PPy residue obtained by extraction of PS component from the composite particles, which also indicates that there are few by-produced PPy homoparticles.

Fourier transform infrared spectroscopy

The composition of the synthesized particles was studied using Fourier transform-infrared (FT-IR; Horiba Freexact-II FT-720) spectroscopy with samples dispersed in KBr discs and at 20 scans per spectrum with 4 cm^{-1} resolution.

Chemical composition

The conducting polymer loadings of the conducting-coated particles were determined by comparing the nitrogen contents determined by CHN elemental microanalysis (Yanaco CHN-Corder MT-5) with those of the conducting polymer bulk powders prepared by chemical oxidative precipitation polymerization. The CHN microanalysis of the PNVP-adsorbed PS particles after extensive centrifugal washing to remove free unadsorbed PNVP indicated that an adsorbed amount of PNVP on the PS seed particles was 6.1 wt% based on the PS particles (6.1 mg m^{-2}). Taking the N% due to PNVP on the PS seed particles into account, PPy (PANI) loading on the particles was calculated.

Conductivity measurements

The electrical conductivity of the dried samples was determined for pressed pellets (13 mm diameter, prepared at 300 kg cm^{-2} for 16 min) at room temperature using the conventional four-point-probe technique with a resistivity meter (Loresta-GP MCP-T610, Mitsubishi Chemical Co.).

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted using a TGA instrument

(Perkin-Elmer Pyris 1). Dried samples were heated to 600 °C under nitrogen at a heating rate of 10 °C min⁻¹.

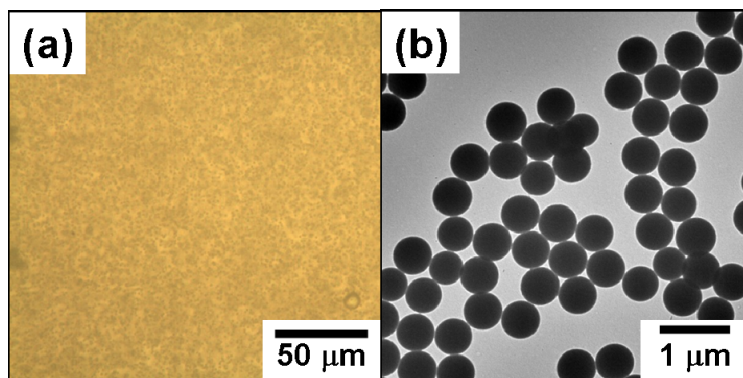


Figure S1. (a) Optical micrograph of uncoated PS seed particles dispersed in aqueous medium. (b) TEM image of the uncoated PS seed particles.

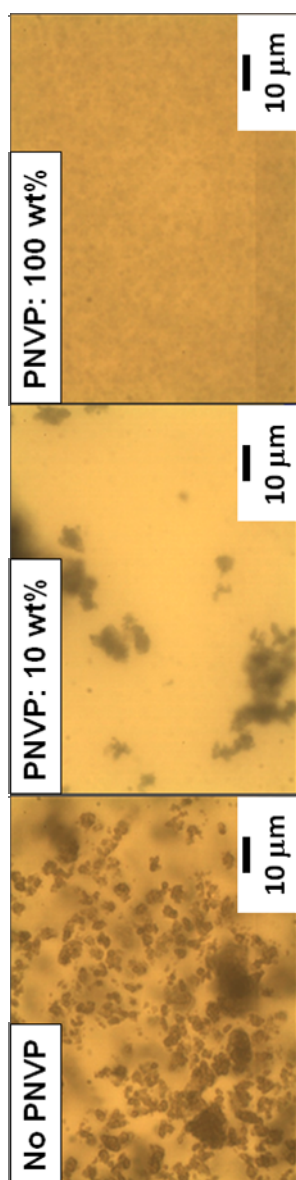


Figure S2. Optical micrographs of PPy-coated PS aqueous dispersions synthesized in the presence of various amount of PNVP.

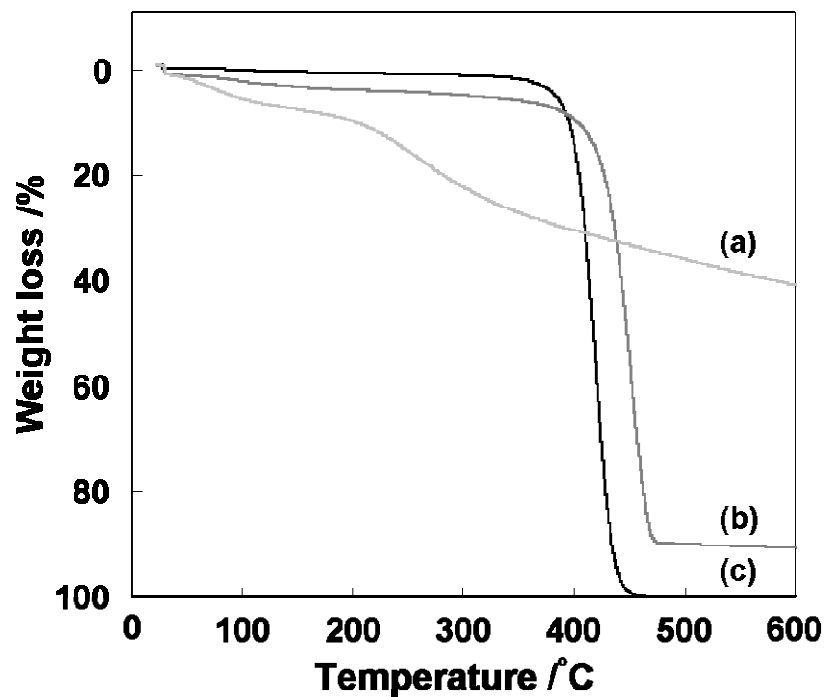


Figure S3. TGA curves of (a) PPy homopolymer bulk powder, (b) PPy-coated PS particles and (c) uncoated PS seed particles.

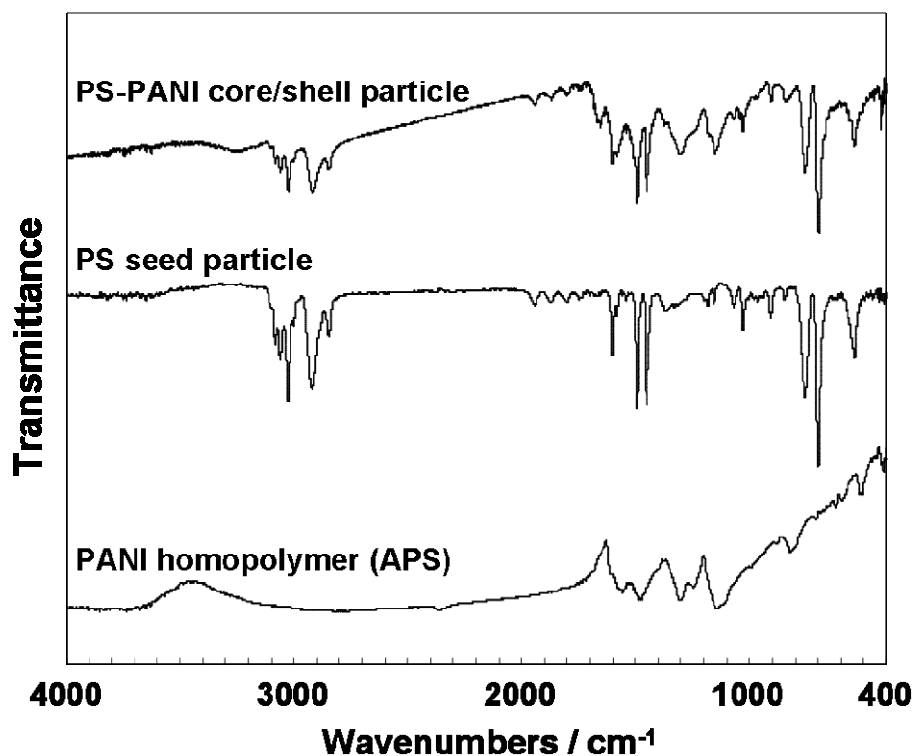


Figure S4. FT-IR spectra of PANI-coated PS particles (PNVP 100 wt% system), uncoated PS seed particles and PANI homopolymer (synthesized by chemical oxidative precipitation polymerization using APS). FT-IR studies indicated the introduction of PANI into the PS seed particles.

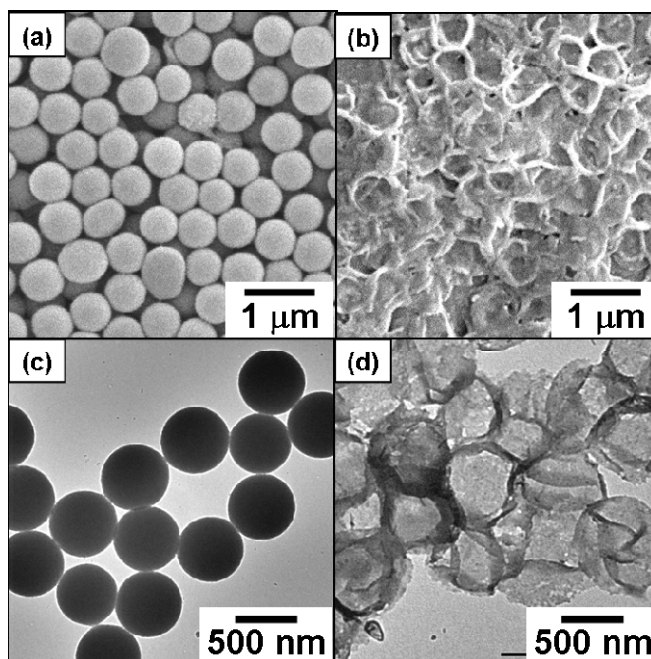


Figure S5. (a, b) SEM and (c, d) TEM images of PANI-coated PS particles (PNVP 100 wt% system) before (a, c) and after (b, d) extraction of PS component with tetrahydrofuran.

PANI-coated PS particles were also synthesized by the one-pot chemical oxidative aqueous seeded polymerization in the same manner: the APS/aniline molar ratio was adjusted to 1.25 and PNVP amount was 100 wt% based on aniline monomer. SEM and TEM studies confirmed 'broken egg-shell' morphology after extraction of PS component from the PANI-coated PS particles, which strongly suggested PS core and PANI shell structure (see Figure S5). The low conductivity of the polyaniline-coated PS latex should be due to washing (and hence de-doping) these particles with water. The PANI shell thickness was calculated to be 5.5 nm using the densities of PS and PANI of 1.05 [1] and 1.40 [2], respectively.

Reference

1. G. Natta, *J. Polym. Sci.*, 1955, **16**, 143.
2. C. Barthet, S. P. Armes, S. F. Lascelles, S. Y. Luk and H. M. E. Stanley, *Langumir*, 1998, **14**, 2032.

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