

Supplementary Material (ESI) for Soft Matter
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Supplementary Information for:

Fabrication of Silica/Polythiophene Core/Shell Nanospheres and Their Electrorheological Fluid Application

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1. Experimental Section

Materials: Ludox SM-30, HS-40 and AS-40 aqueous colloidal solutions (Aldrich) were used as templates of silica nanoparticles with the diameter of *ca.* 7, 12, and 22 nm, respectively. Iron (III) chloride (Aldrich, reagent grade, 97%) as an oxidizing agent and thiophene (Aldrich, 99 +%) as a monomer were used without further purification. Chloroform (99 %) was also obtained from Aldrich Chemical Co. For electrorheological (ER) fluid application, silicon oil (Aldrich, poly(methylphenylsiloxane), viscosity = 100 cSt) was used as a dispersing medium.

Preparation of Oxidant-coated Silica Nanospheres: Monodispersed silica nanospheres were prepared using Ludox SM-30, HS-40 and AS-40 aqueous solution as a source of 7 nm, 12 nm and 22 nm silica nanospheres, respectively. The colloidal silica suspension (25 g) was poured into a beaker, and distilled water (25 ml) was added. Mixture solution was stirred vigorously and FeCl₃ (12.5 g) was inserted in mixed solution to make the weight ratio of 0.5 FeCl₃-coated silica nanospheres. FeCl₃ was completely dissolved and allowed to dry at room temperature in order to evaporate water.

Fabrication of Silica/PT Core/Shell Nanospheres: 7 nm FeCl₃-coated silica nanospheres (10 g) were dispersed in chloroform (100 mL). Thiophene monomer (0.15 mL) was introduced into the reactor and the mixture was stirred for 4 hr at 60 °C. After

polymerization, the silica/PT core/shell nanospheres were washed with ethanol several times to remove residual reagent and dried under vacuum oven for ER fluids application. For 12 nm and 22 nm FeCl₃-coated silica nanospheres, overall process was the same as above procedure except the amount of thiophene monomer, 0.125 mL and 0.1 mL, respectively.

Silica/PT Core/Shell Nanospheres Characterization: FE-SEM images were taken with a JEOL 6700F. Photographs of energy-filtering transmission electron microscopy (EF-TEM) were obtained with a Carl Zeiss LIBRA 120. In the sample preparation, nanomaterials diluted in ethanol were cast onto copper grid. Raman spectra were recorded using a Jobin-Yvon T64000 spectrometer equipped with an Ar-ion laser beam (514.5 nm) for the optical excitation at ambient temperature. The electrical conductivity was measured by the four-probe method using a Keithley 2400 sourcemeter at room temperature.

Investigation of Electrorheological Properties: The ER properties of the silica/PT core/shell nanospheres-based ER fluids were examined via a Rheometrics Mechanical Spectrometer (RMS800, Rheometric Scientific) with a parallel plate fixture of 40 mm diameter, a high-voltage generator (Trek 677B), and a temperature controller. To start a run, an ER fluid is placed between two plates with a gap of 1.00 mm, and DC voltage is applied to the plate. An electric field was applied for 3 min to obtain an equilibrium chainlike or columnar structure before applying shear. All measurements were made at a bath temperature

of 25 ± 0.1 °C. The shear rate was varied from 10^{-1} to 10^3 s^{-1} , and yield stresses for the prepared ER fluids were mainly obtained under flow in a controlled shear rate (CSR) experiment.

2. Raman and EDAX spectra of the sample

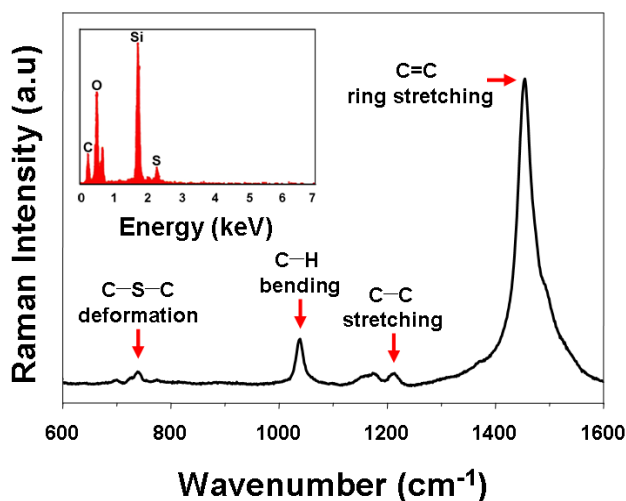


Fig. S1 Raman spectroscopy of 11 nm silica/PT core/shell nanospheres prepared using 7 nm silica nanospheres as a core material (inset: The energy-dispersive analysis of X-ray (EDAX) spectrum of 11 nm silica/PT core/shell nanospheres).

Fig. S1 exhibits the spectroscopic analysis of the silica/PT core/shell nanospheres. The Raman spectroscopic analysis supported effective information of the PT layer. The most intense peak appeared at 1432 cm⁻¹, which was assigned to the symmetric C=C ring stretching vibrations of the conjugated polythiophene segments. The peaks at 1210 cm⁻¹ and 1069 cm⁻¹ were attributed to the C—C stretching and C—H bending vibrations, respectively. In addition, the peak at 760 cm⁻¹ was designated to C—S—C deformation. In addition, the energy-dispersive analysis of X-ray (EDAX) provided the composition of the silica/PT core/shell nanospheres (Fig. S1 inset). It consisted of C (7.37 %), O (47.07 %), Si (40.77 %), and S (4.79 %). The Si and O peaks originated from the silica core. The C/S composition ratio of the

silica/PT core/shell nanospheres (1.54) has good agreement with C/S ratio of conventional PT (1.50). Judging from these data, it can be concluded that silica/PT core/shell nanomaterials was successfully synthesized.

3. A DRIFT spectra of the sample

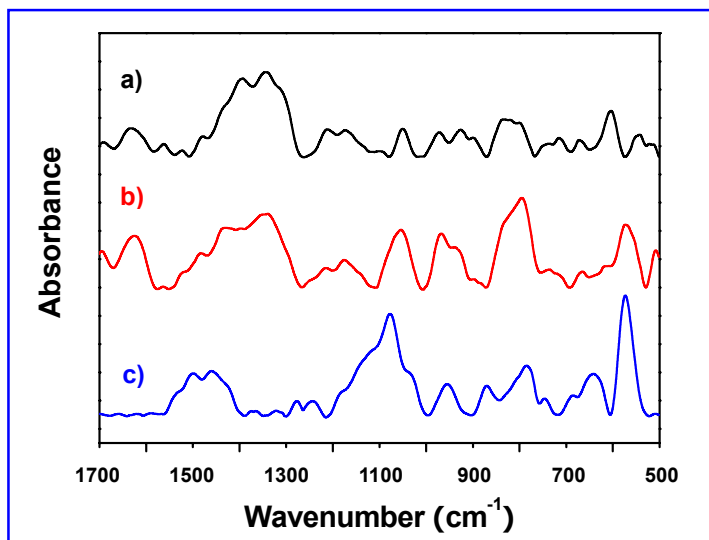


Fig. S2 DRIFT spectra in the spectral region of 1700–500 cm^{-1} ; (a) 7 nm silica nanoparticles, (b) 11 nm silica/PT core/shell nanospheres and (c) The difference spectrum (b–a).

Fig. S2 depicts the diffuse-reflectance infrared Fourier- transform (DRIFT) spectra of pristine silica nanoparticle, silica/PT core/shell nanosphere and difference spectrum in the region of 1700–500 cm^{-1} . DRIFT technique has been known as effective and powerful method for core/shell nanomaterial analysis. The difference spectrum between the silica nanoparticle and silica/PT core/shell nanosphere provides the selective information of the PT shell. The bands at 1500 cm^{-1} , 1459 cm^{-1} , 1263 cm^{-1} and 1369 cm^{-1} can be assigned to the C=C in-plane vibration mode. The characteristic peaks of silica/PT core/shell nanospheres appear at 1076 cm^{-1} , 747 cm^{-1} and 572 cm^{-1} , which are due to the C–H out-of-plane bend, asymmetric C–S–C deformation and thiophene ring deformation vibrations, respectively. Judging from these data, a PT layer was successfully deposited on the surface of silica nanoparticle.