

Supplementary Material (ESI) for Soft Matter

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Supplementary Information for:

**A comparative study on electrorheological properties of various
silica/conducting polymer core/shell nanospheres**

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1. Experimental Section

Materials: Ludox AS-40 aqueous colloidal solutions (Aldrich) were used as templates of silica nanoparticles with the diameter of *ca.* 22 nm. Iron (III) chloride (Aldrich, reagent grade, 97%) as an oxidizing agent was used without further purification. Thiophene (Aldrich, 99+%), pyrrole (Aldrich, 99+%), 3,4-ethyldioxythiophene (Aldrich, 99+%) and aniline (Aldrich, 99+%) as a monomer were used for the preparation of polythiophene (PT), polypyrrole (PPy), poly(ethyldioxythiophene) (PEDOT) and polyaniline (PANI), respectively. These monomers were used as received. 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 nanosphere was prepared using Ludox AS-40 aqueous solution as a source of 22 nm silica nanospheres. 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/conducting polymer Core/Shell Nanospheres: 22 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 various silica/conducting polymer core/shell nanospheres, overall process was the same as above procedure except the species of conducting polymer monomer, pyrrole, 3,4-ethyldioxythiophene and aniline, respectively.

Silica/conducting polymer Core/Shell Nanospheres Characterization: Photographs of transmission electron microscopy (TEM) were obtained with a JEOL EM-2000 EX II microscope. In the sample preparation, the silica/conducting polymer core/shell nanospheres diluted in ethanol were cast onto copper grid. The electrical conductivity was measured by the four-probe method using a Keithley 2400 sourcemeter at room temperature. The charge carrier mobility value were acquired by an electrophoretic light scattering (ELS) apparatus (ELS-8000, Photal, Otsuka Electronics, Japan). Ultraviolet-visible (UV-vis) spectra were taken with a Perkin-Elmer Lambda 20 spectrometer at a resolution of 1 nm, and all the cyclic voltammograms (CV) were measured at a scan rate of 50 mVs⁻¹ in the potential range of -0.3 to 1.5 V.

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. TEM images of silica/conducting polymer core/shell nanosphere

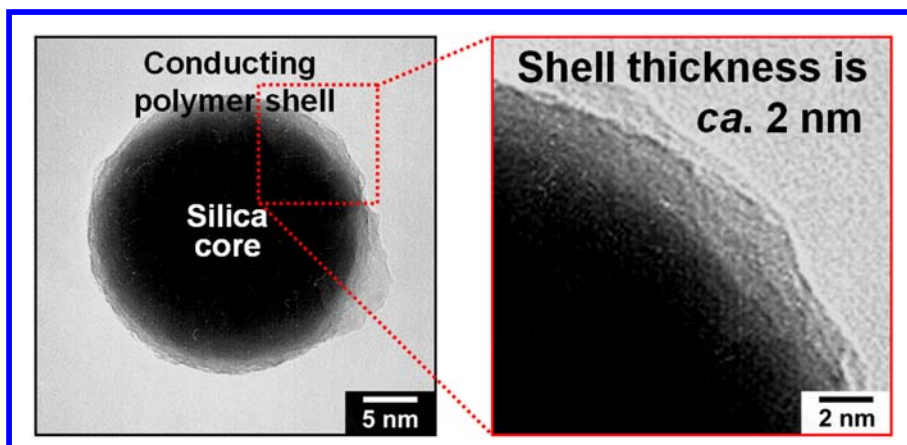


Fig. S1 A typical TEM image of silica/conducting polymer core/shell nanosphere: (left) TEM image of a single silica/polypyrrole core/shell nanoparticles. (right) The enlarged image of the area marked by the red dash box in the left image. The particles had a uniform conducting polymer layer of average thickness 2 nm.

Fig. S1 shows the transmission electron microscopy (TEM) images of the silica/conducting polymer core/shell nanosphere fabricated by seeded polymerization.

The TEM image revealed that the nanosphere had a uniform conducting polymer layer of avg. 2 nm.

3. DRIFT and EDAX spectra of the sample

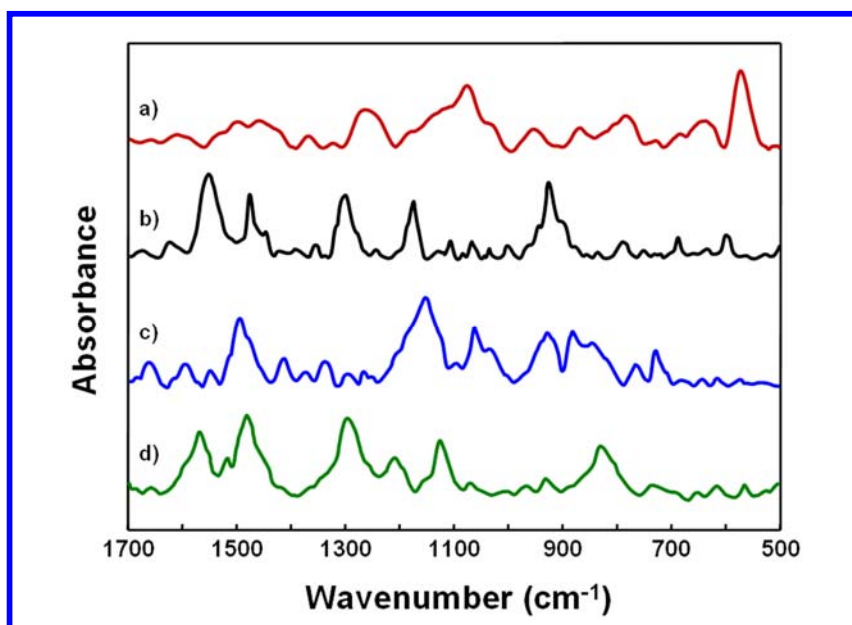


Fig. S2 DRIFT spectra in the spectral region of 1700–500 cm⁻¹; (a) silica/PT core/shell nanospheres, (b) silica/PPy core/shell nanospheres, (c) silica/PEDOT core/shell nanospheres and (d) silica/PANI core/shell nanospheres.

Fig. S2 depicts the DRIFT spectra of various silica/conducting polymer core/shell nanospheres in the region of 1700–500 cm⁻¹, and the spectrum provides the selective information of the conducting polymer shell. The characteristic peaks of silica/PT core/shell nanospheres (a) 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. The band 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. A DRIFT spectra of silica/PPy core/shell nanospheres (b) indicated a pyrrole ring stretching band at 1548

cm^{-1} , a conjugated C–N stretching band at 1473 cm^{-1} , a =C–H in-plane vibration band at 1301 and 1183 cm^{-1} , and a =C–H out-of-plane vibration band at 916 cm^{-1} . For the silica/PEDOT core/shell nanospheres (c), the band at 844 cm^{-1} could be ascribed to vibration mode of C–S bond in the thiophene ring. The bands at 1144 and 1065 cm^{-1} are assigned to the stretching modes of the ethylenedioxy group, and the band at 920 cm^{-1} is due to the ethylenedioxy ring deformation mode. The characteristic peak of the silica/PANI core/shell nanospheres (d) appeared at 1582 , 1484 , and 1310 cm^{-1} , due to quinone ring deformation, benzene ring deformation, and C–N stretching of a secondary aromatic amine, respectively.

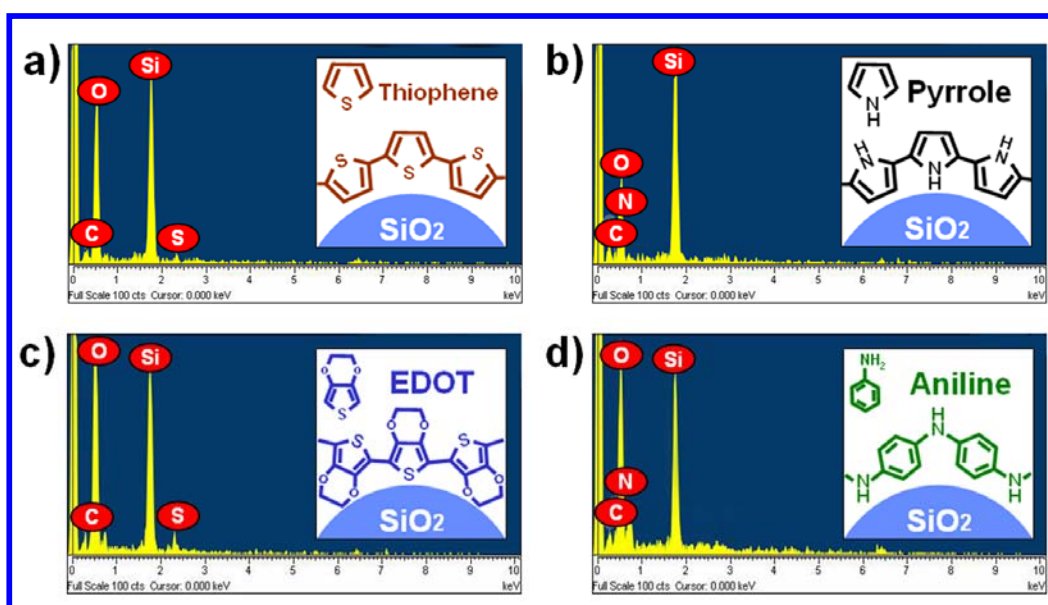


Fig. S3 The energy-dispersive analysis of X-ray (EDAX) spectrum of silica/conducting polymer core/shell nanospheres; (a) silica/PT core/shell nanospheres, (b) silica/PPy core/shell nanospheres, (c) silica/PEDOT core/shell nanospheres and (d) silica/PANI core/shell nanospheres.

In addition, the energy-dispersive analysis of X-ray (EDAX) provided the composition of the silica/conducting polymer core/shell nanospheres (Fig. S3). It mainly consisted of C, O, Si, N, and S. The Si and O peaks originated from the silica core. The elemental composition ratio (C/S or C/N) of the silica/conducting polymer core/shell nanospheres has good agreement with their theoretical values (Table S1).

Judging from these data, it can be concluded that a conducting polymer layer was successfully deposited on the surface of silica nanospheres. Namely, the silica/conducting polymer core/shell nanospheres were successfully synthesized by seeded polymerization.

Table S1. Atomic and composition ratio of various silica/conducting polymer core/shell nanospheres

Samples	Atomic ratio (%) ^a					Composition ratio	
	C	N	S	Si	O	Theoretical value	Measured value
PT	6.98	–	4.67	36.01	52.34	(C/S) 1.50	(C/S) 1.49
PPy	23.59	6.79	–	27.77	41.84	(C/N) 3.43	(C/N) 3.47
PEDOT	9.76	–	4.26	30.36	55.22	(C/S) 2.25	(C/S) 2.29
PANI	17.3	3.39	–	28.34	50.97	(C/N) 5.14	(C/N) 5.10

^a These values were acquired in the EDAX mode for 45 s, at a beam current of 10 μ A, and an accelerating voltage of 10 kV.