

Supporting Information for

**Enhanced Electrorheological Performance of Barium-Doped
SiO₂/TiO₂ Hollow Mesoporous Nanospheres**

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1. Experimental details

Fabrication of SiO₂/TiO₂ core/shell nanoparticles (CSNSs): Synthesis of colloidal SiO₂ via Stöber method was first step in fabrication of Ba-doped SiO₂/TiO₂ hollow nanospheres (Ba-HNSs). Tetraethyl orthosilicate (17.4 mL) was added into solution of ethanol (475 mL) and ammonia solution (23.4 mL). The mixture solution was stirred for 12 h at 60 °C. After the synthesis, 175 mL of acetonitrile was added to as-prepared colloidal SiO₂. Then, 21.6 mL of titanium (IV) isopropoxide (TTIP), 108 mL of ethanol, and 36 mL of acetonitrile were mixed. The mixed solution was reacted with the colloidal SiO₂ at 5 °C for 12 h.

Fabrication of Ba-doped SiO₂/TiO₂ hollow nanoparticles (Ba-HNSs): SiO₂/TiO₂ core/shell nanospheres were precipitated by centrifugation and supernatant was removed. The SiO₂/TiO₂ core/shell nanospheres were re-dispersed in Ba(OH)₂ aqueous solution of 500 mL (0.1 M) and treated with sonication for 3 h. Re-deposition of etched silica occurred under basic condition, resulting Ba-HNSs. After the reaction, the Ba-HNSs were isolated from the solution by centrifugation (Mega 17R, Hanil Science and Industrial) and re-dispersed in deionized water. It was repeated for washing excessive Ba(OH)₂ on surface of Ba-HNSs.

Preparation of ER fluids: Prepared Ba-HNSs were dried in a vacuum oven at 60 °C for 24 h to remove moisture. Then, the Ba-HNSs were dispersed in silicon oil (poly(methylphenylsiloxane), viscosity = 100 cSt). Concentration of ER fluid was 15 vol% and no additives were added to the ER fluid. For uniform dispersion of Ba-HNSs in the silicon oil, the ER fluid was milled for 30 min. ER fluid of HNS and commercial BaTiO₃ nanopowder (Sigma-Aldrich) was also prepared by the same method.

Electrorheological properties of ER fluids: The ER properties of the Ba-HNS and commercial BaTiO₃ nanopowder based ER fluids were examined respectively *via* rheometer (AR 2000 Advanced Rheometer, TA Instruments) with a concentric cylinder conical geometry of 15 mm cup radius, a high-voltage generator (Trek 677B), and a temperature controller. All measurements were made at a room temperature. To start a run, an ER fluid is placed between cup and rotor with a gap distance of 1.00 mm, and DC voltage is applied to the plate. An electric field was applied for 3 min to obtain an equilibrium chain-like or columnar structure before applying shear. If chain-like structure is constructed between rotor and cup, that force is equal to force of destroying chain-like structure between rotor and cup by rotating rotor. Therefore, by measuring shear rate of rotor, the shear stress (dynamic yield stress) of ER fluids can be determined.

2. Large quantity of Ba-HNS in a laboratory-scale synthesis



Fig. S1 TEM images of the HNPs fabricated by the same method for Ba-HNSs except that Ba^{2+} ions were alternated with NH_4^+ ions.

Fig. S1 displays a photograph showing ca. 13 g of Ba-HNSs prepared at once, a very large quantity in a laboratory-scale synthesis. By facile and large scale production of the nanostructure, our suggested ER system was proved to be readily applied for a practical use.

3. A TEM image of HNPs

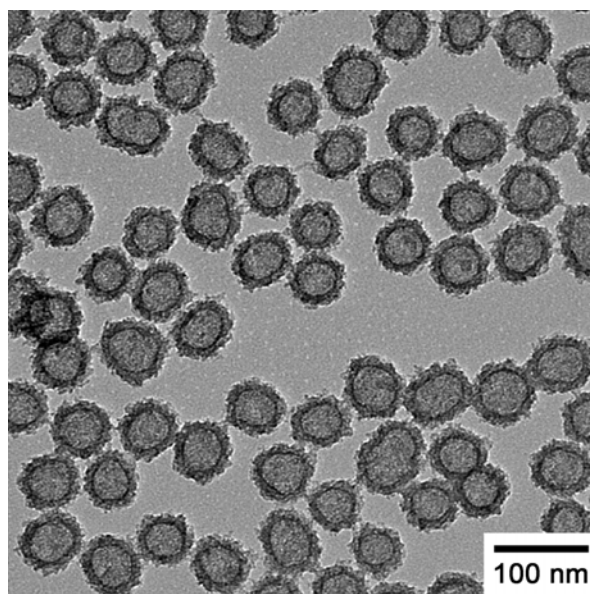


Fig. S2 TEM images of the HNPs fabricated by the same method for Ba-HNSs except that Ba^{2+} ions were alternated with NH_4^+ ions.

HNSs were fabricated by the same method for Ba-HNSs except that Ba^{2+} ions were alternated with NH_4^+ ions, and their TEM image was shown in Fig. S2. Like Ba-HNS, HNSs had spherical shape with hollow core and mesoporous shell. The particle size and large inner cavity (hollow core) of HNS were almost the same as those of Ba-HNS.

4. Atomic ratios determined by EDS analysis

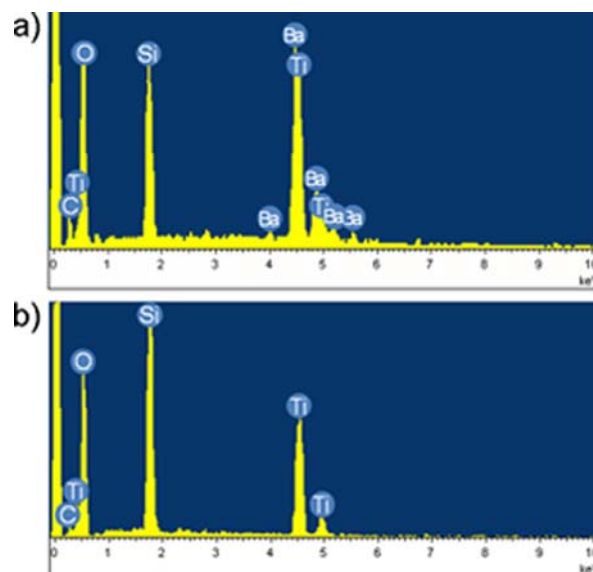


Fig. S3 Energy-disperse X-ray spectroscopy (EDS) spectra of a) the Ba-HNSs and b) the HNSs. The signal of carbon originated from the carbon tape to fix the samples.

Table S1. Elemental contents of Ba-HNS and HNS by EDX analysis.

Sample	Ti /atomic %	Si /atomic %	Ba /atomic %
Ba-HNS	36.18	33.49	30.33
HNS	50.77	49.23	0

^aCarbon and oxygen contents were excluded because they originated from carbon tape to fix Ba-HNS and HNS.

Based on the EDS results, the atomic ratio was calculated as Table S1. The atomic ratio of HNS was 50.77:49.23 for Si:Ti, while that of Ba-HNP was 36.18:33.49:30.33 for Si:Ti:Ba, respectively. Therefore, it can be concluded that a large amount of Ba was successfully doped into the Ba-HNSs.

5. X-ray diffraction spectra of HNPs

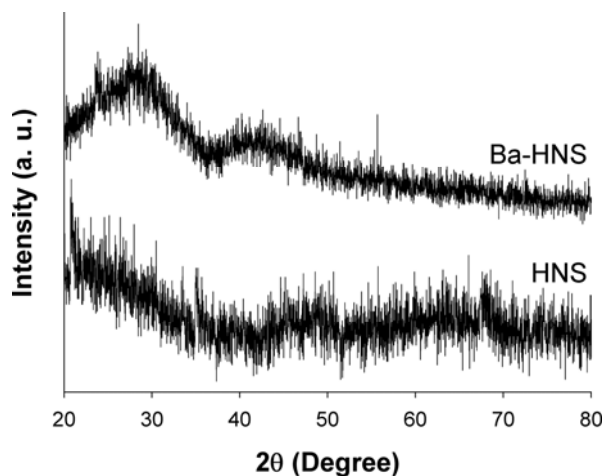


Fig. S4 XRD patterns of the Ba-HNSs and the HNSs.

The crystallinity was analyzed by XRD. A broad decreased peak of the HNS between 20° and 40° showed the amorphous phase of SiO₂ NPs, whereas the other peaks couldn't analyzed clearly. Compared to HNS, new peaks originated from doped barium on TiO₂ and SiO₂ were shown in Ba-HNS. Therefore, X-ray diffraction (XRD) patterns confirm the existence of the doped barium on the Ba-HNSs. However, nature of both nanoparticles (HNS and Ba-HNS) is amorphous due to low reaction temperature and no calcination step, so that further analysis is needed for clarifying the molecular structure of the Ba-HNS.

6. Wide scan spectra of X-ray photoelectron spectroscopy

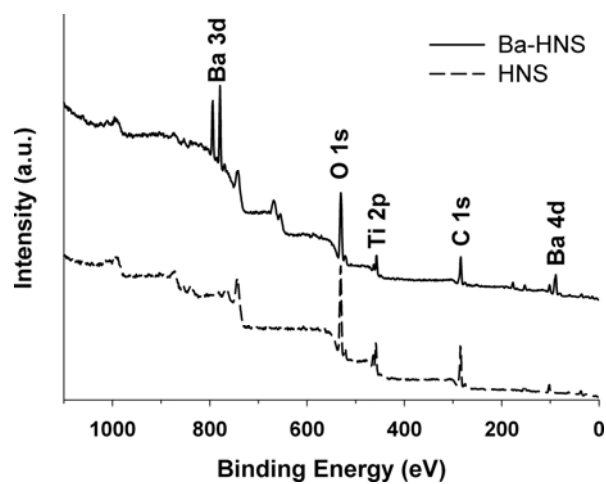


Fig. S5 Full-scale X-ray photoelectron spectroscopy spectra of the Ba-HNSs.

To further clarify molecular structure of the Ba-HNSs, X-ray photoelectron spectroscopy (XPS) was conducted. A Ba 3d photoelectron spectrum is only shown in Ba-HNSs, which implies that barium was successfully doped on the Ba-HNSs.

7. Photograph of ER fluids



Fig. S6 Photograph of ER fluids based on 25 vol% of Ba-HNSs and commercial BaTiO₃ nanopowders.

According to Fig. S6, the suspension of Ba-HNSs shows much better miscibility than that of commercial BaTiO₃ nanopowders. It was possible to increase volume fraction of the Ba-HNSs up to 25 vol%, while it was impossible for the BaTiO₃ nanopowders. Additionally, higher volume fraction of Ba-HNSs is possible than 25 vol%.

8. A TEM image of the commercial BaTiO₃ nanopowders

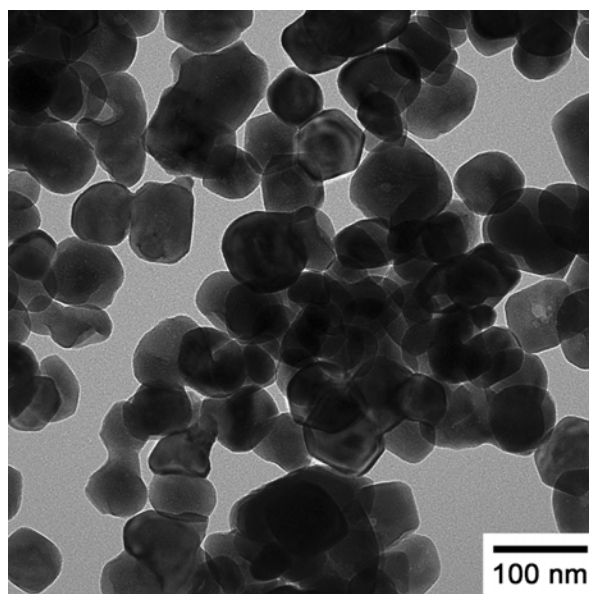


Fig. S7 TEM image of the commercial BaTiO₃ nanopowders.

Compared to the Ba-HNSs, commercial BaTiO₃ nanopowders exhibit a large amount of agglomeration and low size uniformity.