

Supporting Information for

A comparative study on electrorheological property of various N-doped nanomaterials using ammonia plasma treatment

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1. Experimental details

Materials: Tetraethyl orthosilicate (TEOS, 98%), titanium isopropoxide (TTIP, 97%), styrene monomer ($\geq 99\%$), cetyltrimethylammonium bromide (CTAB, $\geq 99\%$), and silicone oil (poly[methylphenylsiloxane], viscosity = 100 cSt) were purchased from Aldrich Chemical Co. Ammonium hydroxide (NH_4OH , 28.0-30.0%), ethanol (95.0%), acetonitrile (CH_3CN , 99.5%), and potassium persulfate (KPS, 98.0%) were supplied from Samchun Chemical Co., Korea. Absolute ethanol (ethyl alcohol, 99.5%) was purchased from Fisher Chemical Co. Ammonia gas (NH_3 , 99.9995%) was supplied from Daesung industrial gases Co., Korea. All chemicals except styrene monomer were used without further purification. Styrene monomer was purified using an inhibitor removal column (Aldrich Chemical Co.) and stored at -5°C .

Synthesis of silica (SiO_2) spheres: Pristine SiO_2 spheres were prepared according to Stöber method.¹ In a typical synthesis of pristine SiO_2 sphere, mixture of ethanol (200 mL), DI water (32 mL), and NH_4OH solution (42.3 mL) was heated up to 60°C with stirring. Subsequently, TEOS (21.65 mL) was added to the solution and resulting mixture was stirred for 2 hours to obtain SiO_2 spheres. Resulting SiO_2 spheres were washed with ethanol and DI water for several times, and dried in an oven (100°C) for overnight to remove the remaining moistures.

Fabrication of hollow silica/titania (HST) spheres: A colloidal suspension of SiO_2 core template was fabricated by Stöber method, as previously mentioned. And then, Titania (TiO_2) shell was coated onto the SiO_2 template by sol-gel reaction to attain $\text{SiO}_2/\text{TiO}_2$ core/shell (ST/CS) spheres. Lastly, core part of ST/CS spheres was removed by sonication-mediated etching and re-deposition (SMER) method to obtain hollow $\text{SiO}_2/\text{TiO}_2$ (HST) spheres, as

described in our previous study.² In a typical synthesis of HST spheres, a mixture of absolute ethanol (36 mL), acetonitrile (12 mL), and TTIP (6 mL) was added to the as-prepared SiO₂ colloidal suspension (2.0 g of SiO₂ in 100 mL ethanol). The resulting mixture was vigorously stirred for 6 h at 0 °C to obtain ST/CS spheres. Dried ST/CS spheres (1.0 g) were well-dispersed into DI water (20 mL), and NH₄OH solution (0.1 M, 5 mL) was added to the ST/CS solution. Resulting mixture was placed into the sonicator for overnight and centrifuged several times with ethanol and DI water to obtain HST spheres.

Synthesis of silica (SiO₂) rods: Rod-like silica particles were fabricated by following the experimental method of Wand and colleagues.³ In a typical synthesis of SiO₂ rods, absolute ethanol (5 mL), DI water (120 mL), and NH₄OH solution (1.75 mL) were mixed by stirring. After that, CTAB (0.47 g) was added to the mixture and stirred for 10 min to allow the micelle formation. Subsequently, TEOS (1 mL) was injected into the resulting mixture and vigorously stirred for 2 h at room temperature. The resulting cloudy white solution was centrifuged several times with ethanol and DI water to obtain SiO₂ rods. Collected SiO₂ rod particles were dried in an oven for overnight (100 °C) to remove the moisture.

Preparation of polystyrene (PS) spheres: Monodisperse polystyrene (PS) spheres were prepared by emulsifier-free emulsion polymerization.⁴ In a typical synthesis of PS sphere, refined styrene monomer (3.75 g) and DI water (45 mL) were vigorously stirred for 30 min to attain oil in water (o/w) emulsion state. Sequentially, KPS aqueous solution (0.25 g in 5 mL) was added to the monomer containing solution and stirred for 12 h. The resulting white solution was centrifuged several times with ethanol and dried overnight to obtain PS spheres.

Plasma treatment of nanomaterials: The nitrogen doping of various nanomaterials was performed using a self-designed vacuum type plasma etcher (Korea Vacuum, Korea). The samples (2.0 g) were placed in a vacuum chamber and pressure was dropped to 200 mTorr. Subsequently, NH₃ gas (flow rate of 15 sccm) was introduced into the chamber and pressure was maintained at 400 mTorr. Approximately, 1 min was required to fully fill the chamber with reaction gas. Afterwards, NH₃ plasma treatment was operated at the power of 100 W for targeted time. Finally, vacuum chamber was vented to retrieve the plasma treated sample. Nitrogen doping level was controlled by adjusting the plasma treatment time. In addition, *ca.* 30.0 g of nanomaterials could be plasma treated by single operation under our experimental condition.

Characterization: The morphologies of HST spheres, SiO₂ spheres, SiO₂ rods, and PS spheres were characterized by TEM analysis (JEM-200CX, JEOL). Elemental mapping of nitrogen composition was analyzed by STEM-EDS (Tecnai F20, FEI) installed with an image filter (Gatan, Inc.). Atomic weight percentage of nitrogen and other elements were measured using a FE-SEM (JEOL-6700, JEOL) equipped with an EDS spectrometer (INCA energy). Dielectric properties of ER fluids were determined by dielectric interface analyzer (Solatron-1296) coupled with an impedance spectroscopy (Solatron-1260). Electrical conductivities of pristine and N-doped nanomaterials were determined by a two-point method in pellet form with a deposition of silver wire at the ends (PPMS-14, Quantum design).

Investigation of electrorheological (ER) activity: To prepare ER fluids, as-synthesized nanomaterials were completely dried in oven (110 °C) for 24 h to remove the moisture. Dried samples were well-dispersed into the silicone oil (poly[methylphenylsiloxane], viscosity = 100

cSt) using mortar and pestel followed by vigorous stirring. The concentrations of ER fluids were set to 3.0 wt% without addition of any additives. The ER activity was measured using sets of rheometer (AR2000 Advanced Rheometer, TA Instruments), insulating cup (diameter = 30 mm, height = 30 mm), a concentric cylinder conical geometry (diameter = 28 mm, height = 30 mm), and a high voltage generator (Trek 677B). The gap distance between the rotor of geometry and internal wall of cup was set to 1.0 mm. The ER measurement was started by placing ER fluids into the cup of rheometer and insertion of geometry. Afterwards, mechanical shear (5.0 s^{-1}) was applied to attain homogeneous dispersion of ER fluid. Lastly, targeted electric field strength and shear stress were applied to investigate the ER property of samples.

2. Large scale plasma treatment of nanomaterials

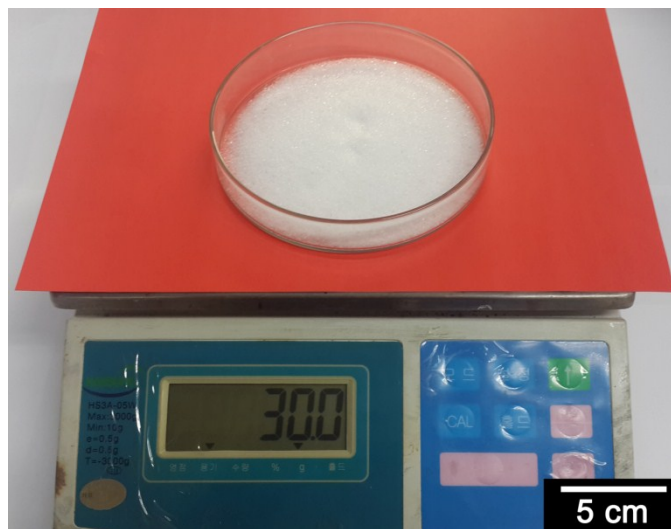


Fig. S1 Photograph of *ca.* 30.0 g of NH_3 plasma treated SiO_2 sphere sample.

Fig. S1 displays a photograph of *ca.* 30.0 g of NH_3 plasma treated SiO_2 sphere sample prepared at once, which is a very large quantity at the laboratory scale. Thus, our suggested ER system could be readily implemented at the industrial level.

3. Nitrogen compositions of NH₃ plasma treated nanomaterials

Table S1. EDS elemental analysis of various N-doped samples^a

Sample	N2 (Atomic %)					N10 (Atomic %)				
	N	Si	Ti	O	C	N	Si	Ti	O	C
HST sphere ^b	3.9	11.1	17.5	67.5	–	7.2	10.7	16.5	65.6	–
SiO ₂ sphere ^c	6.4	27.5	–	66.1	–	9.4	26.5	–	64.1	–
SiO ₂ rod ^d	10.6	25.3	–	64.1	–	16.6	23.3	–	60.1	–
PS ^e	1.7	–	–	–	98.3	3.5	–	–	–	96.5

^a Atomic weight percent was acquired by EDS mode with 45 s, 10 μ A of beam current, and 10 kV of accelerating voltage.

^b HST sphere is composed of Si, Ti, O, and N elements.

^c SiO₂ sphere is composed of Si, O, and N elements.

^d SiO₂ rod is composed of Si, O, and N elements.

^e PS sphere is composed of C and N elements.

Table S1 shows the nitrogen compositions of various N-doped nanomaterials. Plasma exposure time was controlled at 2 min or 10 min to investigate the nitrogen doping level. The amount of plasma treated samples were *ca.* 2.0 g. Notably, nitrogen content increased with increasing plasma exposure time from 2 to 10 min. In addition, 10 min of exposure time was practical limit for the N-doping process. No significant increase in N-content was detected for extended treatment times of 20 and 30 min.

4. Nitrogen compositions analysis of scaled up plasma process

Table S2. EDS elemental analysis of N-doped samples treated by scaled up process^a

Sample	N2 (Atomic %)					N10 (Atomic %)				
	N	Si	Ti	O	C	N	Si	Ti	O	C
HST sphere ^b	4.2	11.6	18.1	66.1	–	7.6	10.9	16.9	64.6	–
SiO ₂ sphere ^c	6.1	26.9	–	77.0	–	9.0	26.1	–	64.9	–
SiO ₂ rod ^d	11.1	26.1	–	62.8	–	15.8	25.1	–	59.1	–
PS ^e	2.1	–	–	–	97.9	3.8	–	–	–	96.2

^a Atomic weight percent was acquired by EDS mode with 45 s, 10 μ A of beam current, and 10 kV of accelerating voltage.

^b HST sphere is composed of Si, Ti, O, and N elements.

^c SiO₂ sphere is composed of Si, O, and N elements.

^d SiO₂ rod is composed of Si, O, and N elements.

^e PS sphere is composed of C and N elements.

Table S2 shows the nitrogen compositions of plasma treated samples fabricated by scaled up process. The scaled up treatment was processed using *ca.* 5.0 g (HST and SiO₂ rod) and 30.0 g (SiO₂ sphere and PS) of samples, which is a very large quantity in laboratory scale. It is noteworthy that nitrogen contents of samples treated by scaled up process showed similar amount to normal process. This result suggested that the scaled up process was successfully operated to obtain similar quality of N-doped samples as normal process. Hence, plasma treatment method demonstrated suitability for implementation at the industrial scale.

5. Dielectric properties of various N-doped nanomaterial-based ER fluids

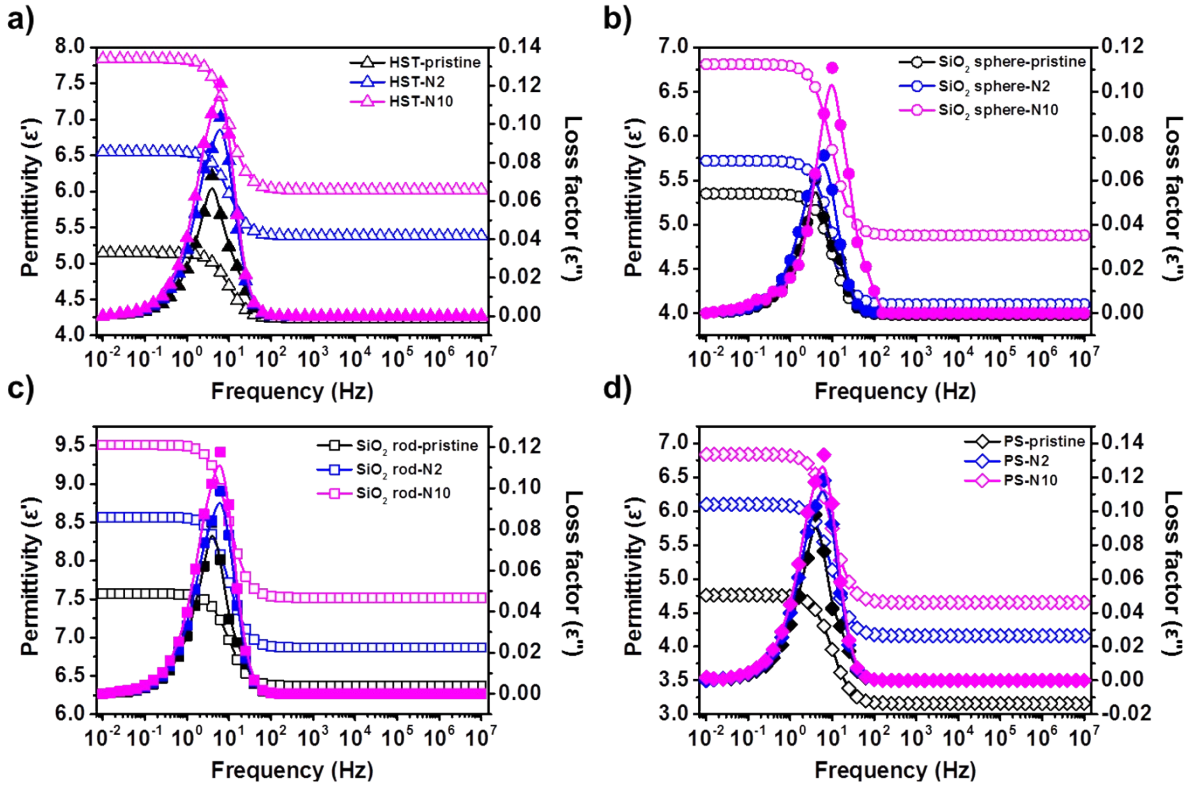


Fig. S2 Permittivity (ϵ' , open symbol) and loss factor (ϵ'' , open symbol) of pristine and N-doped ER fluids composed of a) HST spheres, b) SiO₂ spheres, c) SiO₂ rods, and d) PS spheres, respectively. All ER fluids were fabricated as 3.0 wt% in silicone oil.

Fig. S2 represents the permittivity (ϵ') and loss factor (ϵ'') of pristine and N-doped nanomaterials as a function of electric field frequency (f). Noticeably, ER fluids containing N-doped nanomaterials exhibited significantly increased dielectric property compared to pristine materials-based ER fluids. Several explanations were proposed from previous studies for enhanced dielectric property after N-doping process such as reduction of the band gap, formation of polar bonds, and creation of surface defects.⁵⁻⁷ It is known that the dielectric property of material is closely correlated with ER performance.⁸ In other word, increment in dielectric property of material can directly improve the ER performance owing to the enhanced polarization ability of material.⁹ Consequently, N-doping process effectively increased the dielectric property and ER activity of various nanomaterials.

6. Electrical conductivities of pristine and N-doped materials

Table S3. Electrical conductivities of various N-doped samples^a

	Pristine (S m ⁻¹)	N2 (S m ⁻¹)	N10 (S m ⁻¹)
HST	5.2 x 10 ⁻¹¹	7.2 x 10 ⁻¹¹	4.7 X 10 ⁻¹⁰
SiO ₂ sphere	3.6 x 10 ⁻¹¹	5.1 x 10 ⁻¹¹	2.0 X 10 ⁻¹⁰
SiO ₂ rod	1.1 x 10 ⁻¹⁰	8.1 x 10 ⁻¹⁰	3.1 X 10 ⁻⁹
PS	5.7 x 10 ⁻¹²	9.8 x 10 ⁻¹²	6.2 X 10 ⁻¹¹

^a Electrical conductivities were measured in a pellet form using a two point method.

Table S3 shows the electrical conductivities of pristine and N-doped materials. The DC conductivity of samples was measured using PPMS-14 (Quantum design) in electron transport mode. It was noticeable that N-doped nanomaterials showed slightly increased conductivities compared to pristine materials. Hence, plasma-treated samples showed increased electrical conductivity to attain larger conductivity mismatch with silicone oil medium (1×10^{-13} S m⁻¹ for 4.6 cSt to 1942.0 cSt silicone oil) compared to pristine materials.

7. Zero-field ER activity of pristine and N-doped nanomaterials

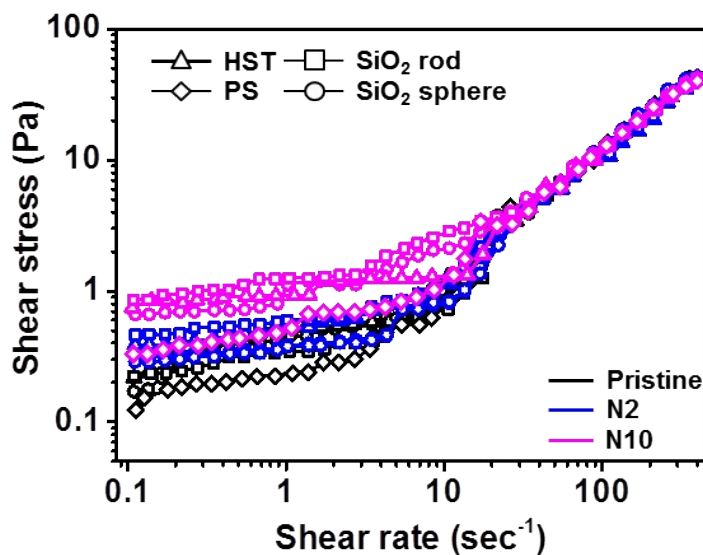


Fig. S3 Zero-field shear stress of pristine, N-2min, and N-10min-based ER fluids (3.0 wt%) as a function of shear rate.

Fig. S3 represents the zero-field ER activity of pristine, N-2min, and N-10min-based ER fluids as a function of shear rate. Particularly, shear stress of all ER fluids exhibited increasing behavior with shear rate. Also, N-doped materials-based ER fluids showed slightly high shear stress relative to ER fluids composed of pristine particles.

[Reference]

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