Supporting Information:

Carbon nanotube coated snowman-like particles and their electro-responsive characteristics

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Experimental Section

1.1 Materials

The MWNT (CM95, purity: 95%, Iljin Nanotec Co., Korea) synthesized via a chemical vapor deposition method possesses the outer diameter of 10-20 nm and the length of 10-50 μm. Methyl methacrylate (MMA) (Duksan Chem. Co., Korea), poly(vinylpyrrolidone) (PVP) (Mw=55,000g/mole, Sigma), allyl methacrylate (AMA) (Aldrich), poly(vinyl alcohol) (PVA) (1700, DC Chemical Co., Ltd, Korea), and ethyleneglycol dimethacrylate (EGDMA) (Aldrich) were used as received without any further purification. Initiator of azoisobutyronitrile (AIBN) (Junsei Chemicals, Japan) was purified by recrystallizing three times using methanol and then dried in vacuum at room temperature before use. Methanol (99.6% DC Chemical Co., Ltd, Korea) and distilled water as the medium was employed in the polymerization.

Although the purity of MWNT is ca. 95%, in order to further improve the purity and bring chemical groups to the CNTs' surface, they were pre-treated in a 3:1 mixture of H_2SO_4 and HNO_3 at 55^oC under ultrasonication treatment for 24 h. After that, the products were washed by distilled deionized water repeatedly until the pH value of the filtrate approached to 7. Thus, the carboxylic acid functionalized MWNT was obtained, and used in this study.

1.2 Preparation of MWNT adsorbed snowman-like particles

Cross-linked PMMA seeds were prepared through a dispersion polymerization method in which the PVP was used as a stabilizer in methanol using a double layer glass reactor. When the temperature of system was heated to 60℃, the monomer solution containing contained MMA (monomer), AMA (cross-linker) and AIBN (initiator) was added. The reaction was kept for 12h. Then spherical PMMA seeds were obtained by centrifuge and washed by methanol for several times. Masses of the used materials are listed in Table S1. In the second step, PMMA seeds were dispersed in an aqueous solution which was stabilized by the PVA. Monomer solution, including MMA, EGDMA (cross-linker) as well as an initiator, was added to the seed suspension with rapid stirring. The MMA monomer to the seed particle ratio was 9:1. In the emulsion system, monomers were diffused into PMMA seed particles, resulting in the swollen particles at room temperature. After 12h, the system was heated to 75℃ and kept for 24h, in which monomer-swollen particles were polymerized to form the SL particles. The resulting non-spherical particles formed as a result of phase separation between the monomer and the swollen particle at an elevated polymerization temperature. With increasing the temperature, the equilibrium between monomer and the swollen seed particle was considered to be broken, thus, the increased elastic stress of the

cross-linked polymer chains caused the monomers to expel from the contracting seed particles, resulting in the bulge out of each particle.[1] The geometry of the particles is known to be strongly dependent on the monomer/polymer ratios, wetting properties, and mass of cross-linkers as well as temperature. Besides that, the swelling conditions such as the velocity of mechanical stirring and swelling time also are considered to play an important role in preparation of snowman-like particles because the homogenous swollen particle-seed solution is required for polymerization. The SL-particles were washed with methanol for several times by centrifuge and dried in oven at 60℃. Recipes in this process were shown in Table S2.

The fabrication process of the MWNT adsorbed SL particles is illustrated in Fig. 1. The SL particles (0.1g) were firstly dispersed in the cationic surfactant of CTAB solution by the aid of the magnetic bar with mild stirring. During this processing, we took the solution of surfactant above the CMC (critical micelle concentration) (at 25ºC, CMC=9.2×10^{-4}mol/L) to make sure all the surface of the SL particles could be wrapped by the surfactant. After 1h, the SL particles/surfactant solution was centrifuged to remove the redundant CTAB which was not stable on the surface of snowman-like particles at 6000rpm for three times (5min each time). For CNT, taking into account of its poor dispersibility under mechanical stirring, we employed an ultrasonic generator (G2806, Kyungil Ultrasonic Co., Korea) to disperse c-MWNT in de-ionized water. Due to the presence of carboxylic acid groups on the surface of MWNT, the c-MWNT solution turned to light black and relatively stable after several minutes under sonication, indicating that well dispersed c-MWNT were accomplished. Then, the products obtained from the centrifuge were added into c-MWNT solution still under the sonication treatment for 3h at 25℃ to ensure that c-MWNT sufficiently adsorbed onto the surface of SL particles. For the un-adsorbed c-MWNT, we also used centrifuge to remove them. Finally, the c-MWNT adsorbed SL particles obtained after drying processing in a vacuum oven at 60℃ for 12 h.

1.3 Measurement

Surface morphologies of the microspheres were observed by a scanning electron microscopy (SEM, Hitachi S-4300, Japan), and the doped Pt species was identified by Energy Dispersive X-ray (EDS, EX-350, Horiba, Japan) analysis. In addition, thermal properties of the composites were characterized by thermo gravimetric analysis (TGA, TA instrument Q50, USA). Moreover, the electrical conductivities of the composites were measured by a four-probe method using pressed disc-type specimens at room temperature.

ER property of c-MWNT adsorbed SL particles was characterized using OM (Olympus BX51, USA) by applying DC electric fields. Firstly, ER fluids were prepared by dispersing c-MWNT-SL particles in silicon oil with 10vol% under sonication about 5 min. Subsequently, we adjusted the distance of the two fixed parallel electrodes to be ca. 370 μm. Then, the ER fluids were placed between two electrodes for the observation. In addition, the ER properties of c-MWNT coating SL particle-based ER fluid was observed using a rotational rheometer (MCR 300, Physica) equipped with a

high-voltage power supply (HCP 14-12500, fug) and a CC17 geometry (gap size: 0.71mm) under various electric fields. To obtain reproducible results, the suspensions of c-MWNT coated SL particles were stirred mechanically using a vortex mixer for 2 min before placing them in a measuring system. All the measurements were carried out at 25 °C.

TGA measurement (Fig. S3) was carried out up to 600°C under the atmosphere with a heating rate of 10°C/min to study the thermal stability of the c-MWNT-SL particles and the amount of the c-MWNT adsorbed on the particle surface. The TGA profiles show that the degradation of the pure SL particles and c-MWNT-SL particles occurs from 250ºC, 265°C (0.96wt %) and 300 ºC (5.65wt %) respectively. It indicates that the introduction of a small quantity of the MWNT could improve the thermal stability of the SL particles, and the thermal stability of particles increased with increasing MWNT loading. Generally, when the heating temperature of the furnace is lower than 600ºC, CNT remains without any degradation. In Fig. S3, the residual weight is 0.96wt% and 5.65wt%, which are considered to be the quantities of the c-MWNT adsorbed on the particle surface, respectively.

The inset images of Fig. S4 are the SEM graphs in which the particles are selected randomly for the EDS analysis. As seen from the Fig. S4(a), S4(b) and S4(c) both of the spectra exhibit the same feature before and after c-MWNT coating, while the carbon peak obviously increased after c-MWNT coating, indicating that the c-MWNT was successfully adsorbed onto the SL particles surface by the aid of surfactant CTAB.

Table S1 Recipes for the preparation of monodispersed cross-linked PMMA seeds.

Ingredients	Mass(g)
MMA	104.80
AMA	0.70
PVP	28
AIBN	1.12
Methanol	565.38

Table S2 Recipes for the preparation of snowman-like particles.

Seed Dispersion		Monomer Solution	
Ingredients	Mass(g)	Ingredients	Mass(g)
PMMA seed	11.09	MMA	99.81
PVA	27.80	EGDMA	12.32
H_2O	739.33	AIBN	1.12

Table S3 Ratio of the C, O and Pt elements obtained by EDS analysis (in atomic %)

Code Name	C (%)	O (%)	Pt (%)
SL	73.60	25.73	0.67
c-MWNT(5.65wt%)-SL	81.83	17.65	0.52
c-MWNT(0.96wt%)-SL	75.33	23.97	0.70

Table S4 The optimal parameters in the CCJ model obtained from the flow curve of c-MWNT -coated particles based ER fluids at various electric field strengths.

Parameters	The different electric field strengths		
	0.5kV	1kV	1.5kV
τ_0	15	19	30
t_1	0.001	0.0011	0.012
α	0.5	0.4	0.13
η_∞	0.038	0.04	0.05
t_2	7	0.15	0.08
β	0.6	0.65	0.9999

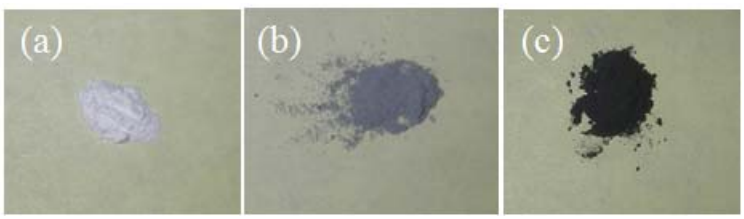

Fig.S1 Photographs of the pure SL powder before (a) and after (b) c-MWNT coating.

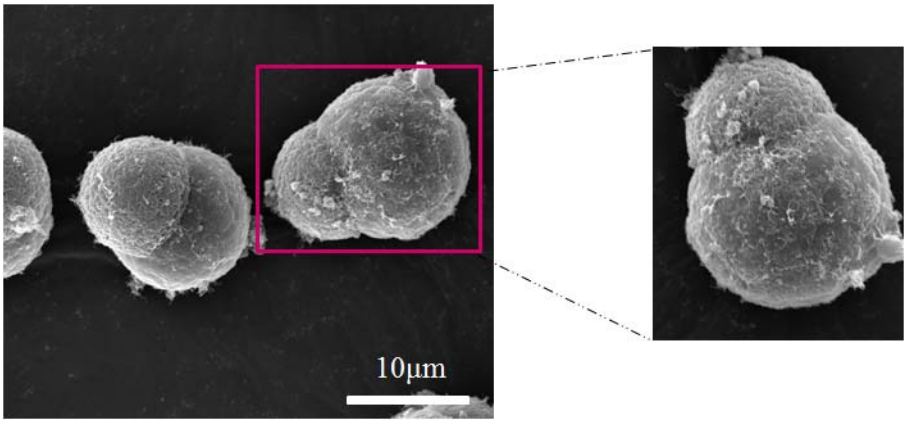

Fig.S2 SEM images c-MWNT (5.65wt %) adsorbed SL particles.

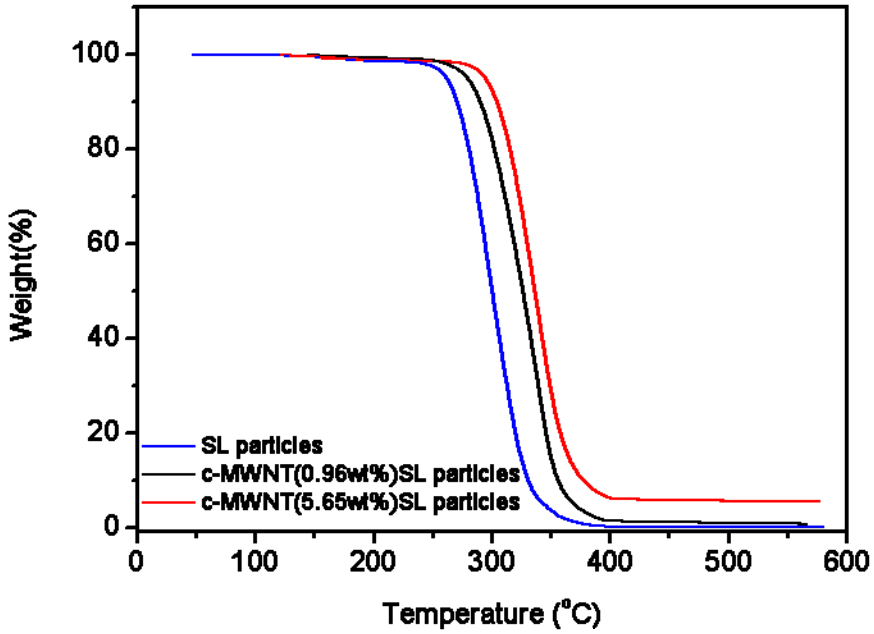

Fig.S3TGA curves of pure SL particles and c-MWNT adsorbed SL particles.

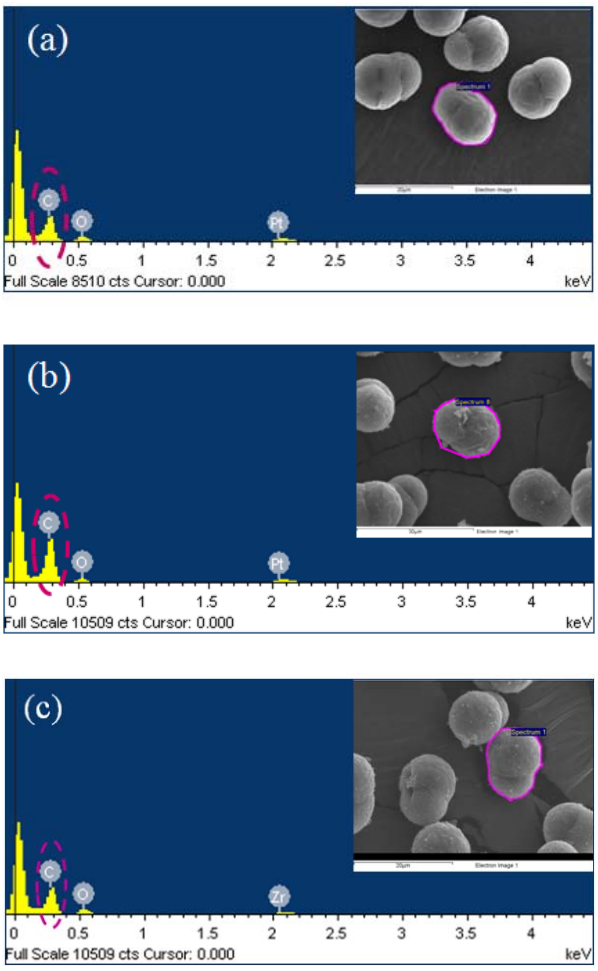

Fig.S4 EDS spectrum of pure SL particles (a), c-MWNT adsorbed SL particles (5.65wt %) (b), and c-MWNT adsorbed SL particles (0.96wt %) (c) obtained by analyzing the particles randomly selected in SEM images.

References

1. E. B. Mock, H. de Bruyn, B. S. Hawkett, R. G. Gilbert and C. F. Zukoski, *Langmuir,* 2006, **22,** 4037.