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Supplementary Information

Layer-by-Layer Assembled (High-Energy Carbon Nanotube/ Conductive Carbon Nanotube)$_n$ Nanocomposites for High-Volumetric Capacitance Supercapacitor Electrodes

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Experimental

Synthesis of NH_2-MWCNTs and COOH-MWCNTs

Pristine multi-walled carbon nanotubes (Sigma Aldrich, 95%) were oxidized by a mixture of H_2SO_4/HNO_3 at 70°C for 3 h to prepare COOH-functionalized MWCNTs (COOH-MWCNTs). Then, the suspensions of COOH-MWCNTs were stirred with ethylene diamine (8.0 mL) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide methiodide (800 mg) for 6 h for the preparation of NH_2-MWCNTs. The resultant suspensions were dialyzed (MWCO 12,000 – 14,000) for 3 days to remove the undesired byproducts and residuals from the functionalization process.

Synthesis of OA-Fe_3O_4

OA-stabilized Fe_3O_4 particles with diameters of approximately 8 nm were synthesized in toluene, as reported previously by Sun et al. Fe(acac)$_3$ (2 mmol), 1,2-hexadecanediol (10 mmol), OA (5 mmol), oleylamine (6 mmol), and benzyl ether (20 mL) were mixed and stirred under a flow of nitrogen. The resulting mixture was heated to 200°C for 2 h and then heated to reflux (approximately 300°C) for 1 h under a blanket of nitrogen. The black mixture was cooled to room temperature by removing the heat source. Ethanol (40 mL) was added to the mixture under ambient conditions; a black material precipitated and was separated via centrifugation. The black product was dissolved in hexane in the presence of OA (0.05 mL) and oleylamine (0.05 mL). Centrifugation (6,000 rpm, 10 min) was used to remove any undispersed residue. A black-brown hexane dispersion of 7 nm Fe_3O_4 nanoparticles was produced.

Synthesis of Anionic Octakis-Fe_3O_4 NPs

Ten milliliters of OA-Fe_3O_4 NPs (10 mg·mL^{-1}) dispersed in toluene was mixed with 10 mL of octakis aqueous solution (2 mg·mL^{-1}). After 24 h, Fe_3O_4 NPs were phase-transferred to the aqueous solution because of the high affinities between the Fe_3O_4 NP and octakis. The resulting Fe_3O_4 NP solution was isolated using a separatory funnel.

Synthesis of OA-MnO NPs

OA-MnO NPs with diameters of approximately 11 nm were synthesized as reported previously. Manganese chloride tetrahydrate (40 mmol), sodium oleate (80 mmol), ethanol (30 mL), DI water (40 mL), and *n*-hexane (70 mL) were mixed and stirred at 70°C for 12 h. The Mn-oleate complex solution was collected with a separatory funnel. Evaporation of the solution produced a pink Mn-oleate powder. Approximately 1.24 g of the resulting Mn-oleate powder dissolved in 10 g of 1-octadecene was degassed at 70°C for 1 h. The solution was heated to 300°C at a heating rate of 1.9°C·min^{-1} and then maintained at 300°C for 1 h. After the solution cooled to room temperature, hexane (20 mL) and acetone (80 mL) were added. The precipitate was removed by centrifugation. The OA-MnO NPs were then dispersed in a nonpolar solvent (i.e., toluene or hexane).

Synthesis of OA-TiO_2 NPs

An OA-TiO_2 NP solution was synthesized using *tert*-butylamine, water, titanium(IV) *n*-propoxide and OA in a 30 mL Teflon-lined stainless-steel autoclave. First, 0.1 mL of *tert*-butylamine was dissolved in 10 mL of water, and the solution was then transferred to the autoclave. Subsequently, 0.15 g of titanium(IV) *n*-propoxide (0.5 mmol) and 1.0 mL of OA were dissolved in 10 mL of toluene, and the solution then was also transferred to the autoclave containing the *tert*-butylamine solution. The autoclave was sealed and maintained at 180°C for 12 h and then cooled to room temperature. The OA-TiO_2 NPs were precipitated with methanol and further isolated by centrifugation. The purified OA-TiO_2 NPs were redispersed in toluene.

Synthesis of OA-$BaTiO_3$ NPs

OA-BTO NPs with a diameter of approximately 7 nm were synthesized via a modified method based on that reported for 20 nm-diameter OA-BTO NPs by Dang et al. Titanium bis(ammonium lactate) dihydroxide (TALH) (1.2 mmol) was added to barium hydroxide octahydrate (1.2 mmol) aqueous solution (24 mL). OA (8.4 mmol), *tert*-butylamine (14.4 mmol) and 5 M NaOH solution (5 mL) were sequentially added to the mixture under stirring. The mixture was transferred to a 30 mL Teflon-lined stainless steel autoclave. The sealed autoclave was maintained at 210°C for 72 h under stirring and then cooled to room temperature. Excess ethanol was added to the resulting solution and the surfactant residue was removed by centrifugation (8,000 rpm, 10 min). The precipitated product was dispersed in toluene or hexane.

Preparation of OA-PC-MWCNT Hybrid

Approximately 10 mL of OA-PC NP (i.e., OA-Fe_3O_4 NP or OA-MnO NP) solution (10 mg·mL^{-1}) in toluene was mixed with 10 mL of NH_2-MWCNTs (1 mg·mL^{-1}) solution at room temperature for 12 h. The OA-Fe_3O_4-MWCNT hybrids formed were isolated by centrifugation and then redispersed in toluene.

Preparation of Anionic Octakis-Fe_3O_4-MWCNT Hybrid

Approximately 10 mL of anionic octakis-Fe_3O_4 NPs (10 mg·mL^{-1}) in aqueous solution was mixed with 10 mL of NH_3^+-MWCNT (1 mg·mL^{-1}) solution at room temperature for 12 h.

Buildup of LbL-Assembled (NH_2-MWCNT/OA-PC-MWCNT)$_n$ Multilayers

A toluene or hexane dispersion of the hydrophobic OA-Fe_3O_4-MWCNT (11 mg·mL^{-1}) or OA-MnO-MWCNT hybrids (11 mg·mL^{-1}) and an ethanol solution of NH_2-MWCNT (1 mg·mL^{-1} or 3 mg·mL^{-1}) were prepared. Prior to LbL assembly, the quartz or ITO substrates were cleaned with an RCA solution ($H_2O/NH_3/H_2O_2$ 5:1:1 *v/v/v*). The substrates were dipped into the NH_2-MWCNT solution for 10 min, washed twice with ethanol, and dried under a gentle nitrogen stream. The NH_2-MWCNT-coated substrates were dipped into a hydrophobic OA-PC-MWCNT hybrid solution for 30 min, followed by washing with toluene and drying with nitrogen. The substrates were then dipped into the NH_2-MWCNT solution for another 10 min. The dipping cycles were repeated until the desired number of layers was obtained.

Build-up of LbL-Assembled ($NH_3^{\pm}$-MWCNT/Anionic Octakis-Fe_3O_4-MWCNT)$_n$ Multilayers

NH_3^+-MWCNTs and anionic octakis-Fe_3O_4-MWCNTs in aqueous solution were LbL-assembled using the same method previously described for (NH_2-MWCNT/OA-PC-MWCNT)$_n$ multilayers.

Buildup of LbL-Assembled (NH_2-MWCNT/COOH-MWCNT)$_n$ Multilayers

Both MWCNTs dispersed in ethanol were built up by H-bonding interactions. The process was identical to the method used to prepare the NH_2-MWCNT/OA-PC-MWCNT multilayers.

UV-Vis Spectroscopy

UV-vis spectra of the NH_2-MWCNT/OA-Fe_3O_4-MWCNT multilayers on quartz glass were collected with a Perkin Elmer Lambda 35 UV-vis spectrometer.

Fourier Transform Infrared (FTIR) Spectroscopy

Vibrational spectra were measured by FTIR spectroscopy (iS10 FTIR, Thermo Fisher) in the transmission and attenuated total reflection (ATR) modes. The sample chamber was purged with N_2 gas for 2 h to eliminate water and CO_2 before the FTIR measurement was performed. An ATR-FTIR spectrum for the $(NH_2\text{-MWCNT/OA-}Fe_3O_4\text{-MWCNT})_n$ film deposited onto an Au-coated substrate was obtained from 300 scans with an incident angle of 80°. The acquired raw data were plotted after baseline correction, and the spectrum was smoothed using spectral analysis software (OMNIC, Nicolet).

Quartz Crystal Microgravimetry (QCM) Measurements

A QCM device (QCM200, SRS) was used to examine the mass of the material deposited after each adsorption step. The resonance frequency of the QCM electrodes was approximately 5 MHz. The adsorbed mass of the NH_2-MWCNTs and OA-Fe_3O_4-MWCNTs, Δm, was calculated from the change in QCM frequency, ΔF, using the Sauerbrey equation:

$$\Delta F(Hz) = -\frac{2F_0^2}{A\sqrt{\rho_q \mu_q}} \cdot \Delta m$$

where F_0 (approximately 5 MHz) is the fundamental resonance frequency of the crystal, A is the electrode area, and ρ_q (approximately 2.65 $g \cdot cm^{-2}$) and μ_q (approximately 2.95×10^{11} $g \cdot cm^{-2} \cdot s^{-2}$) are the shear modulus and density of quartz, respectively. This equation can be simplified as

$$\Delta F\ (Hz) = -\ 56.6 \times \Delta m_A,$$

where Δm_A is the mass change per quartz crystal unit area in $\mu g \cdot cm^{-2}$.

Mass Density of NH_2-MWCNT/OA-PC-MWCNT Multilayer

The mass density ($g \cdot cm^{-3}$) of the NH_2-MWCNT/OA-PC-MWCNT multilayer was calculated according to the following formula:

$$Mass\ density\ (g \cdot cm^{-3}) = \frac{Mass\ (g \cdot cm^{-2})}{Film\ thickness\ (cm)}$$

N_2 Adsorption-Desorption Isotherms

The specific surface area was obtained from the N_2 adsorption-desorption isotherms (ASAP2020, Micromeritics) at 77 K. These samples were also degassed at ~120°C at least overnight before measurement, and the specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

Electrochemical Measurements

Electrochemical tests of indium tin oxide (ITO) electrodes coated with LbL-assembled (NH_2-MWCNT/OA-Fe_3O_4-MWCNT)$_n$, (NH_2-MWCNT/anionic octakis-Fe_3O_4-MWCNT)$_n$, and (NH_2-MWCNT/OA-MnO-MWCNT)$_n$ were conducted in a three-electrode cell using a saturated calomel electrode (SCE) and a Pt wire as the reference and counter electrodes, respectively.

The LbL-assembled (NH_2-MWCNT/OA-Fe_3O_4-MWCNT)$_n$ and (NH_2-MWCNT/anionic octakis-Fe_3O_4-MWCNT)$_n$ multilayer electrodes were used as working electrodes in 1 M Na_2SO_3 electrolyte solution. Cyclic voltammetry (CV) was performed in the potential range from –0.9 to +0.1 V_{SCE} at scan rates ranging from 5 to 100 $mV \cdot s^{-1}$, and galvanostatic charge/discharge was carried out at current densities ranging from 1 to 5 A·cm^{-3}. Electrochemical impedance spectroscopy (EIS) measurements were performed at room temperature under an applied AC voltage with an amplitude of 10 mV in the frequency range from 1 MHz to 0.1 Hz. Additionally, the (NH$_2$-MWCNT/OA-MnO-MWCNT)$_n$ multilayer electrodes were measured in the potential window from 0 to +0.8 V in 1 M Na$_2$SO$_4$ electrolyte.

Calculation of Volumetric Capacitance from CV

The capacitances were calculated based on the following equation:

$$C = \frac{\int I(V)dV}{2 \times v \times \Delta V} \times \frac{1}{U\ or\ m}$$

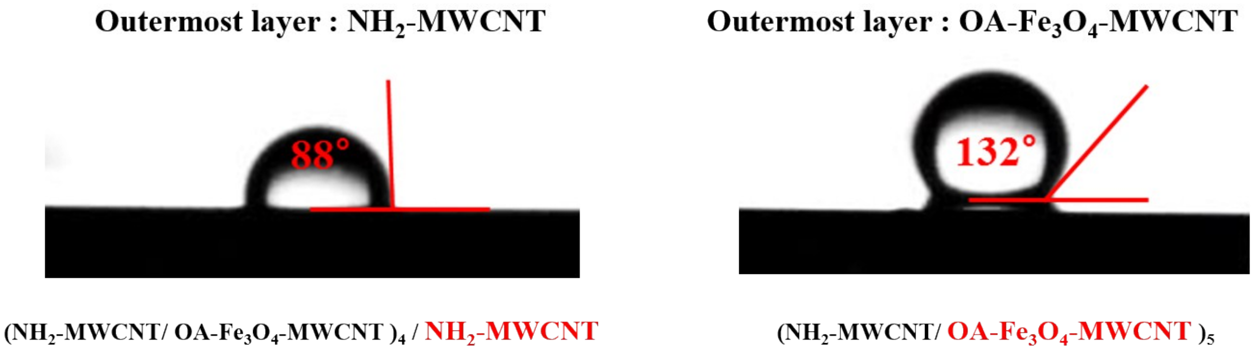
where C is the volumetric capacitance of the electrode, v is the scan rate, ΔV is the potential window, *I* is the response current, and U and m refer to the volume and mass of active material, respectively.

Calculation of Volumetric Capacitance from Galvanostatic Charge-Discharge Measurements

The capacitances were calculated on the basis of the following equation:

$$C = \frac{I\Delta t}{\Delta V} \times \frac{1}{U\ or\ m}$$

where C is the volumetric or specific capacitance, *I* is the discharge current, Δt is the discharge time, ΔV is the potential window of discharge, and U and m refer to the volume and mass of active material, respectively.



Outermost layer : NH_2-MWCNT

Outermost layer : OA-Fe_3O_4-MWCNT

(NH_2-MWCNT/ OA-Fe_3O_4-MWCNT $)_4$ / NH_2-MWCNT

(NH_2-MWCNT/ OA-Fe_3O_4-MWCNT $)_5$

Fig. S1 Water contact angles of the (NH_2–MWCNT/OA–Fe_3O_4–MWCNT$)_n$ films according to the variation of the outermost layer.

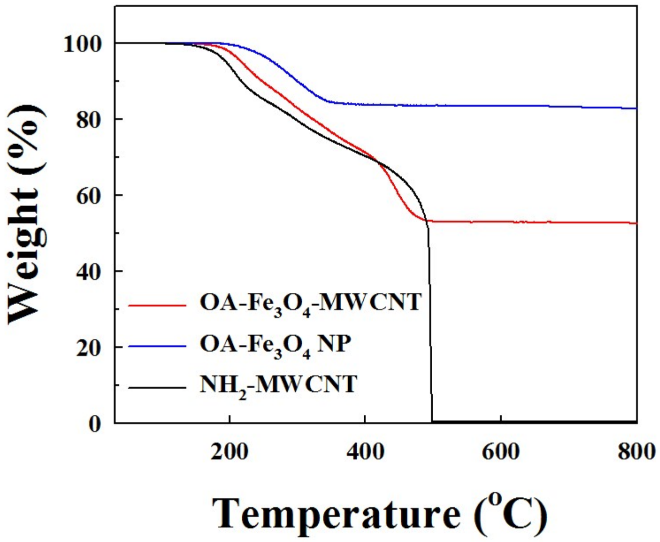


Fig. S2 Thermogravimetric analysis (TGA) of the NH$_2$–MWCNTs, OA–Fe$_3$O$_4$ NPs, and OA–Fe$_3$O$_4$–MWCNT hybrids performed at a heating rate of 10°C/min. Given that the mass ratios of pure Fe$_3$O$_4$ NPs in the OA–Fe$_3$O$_4$ NPs and OA–Fe$_3$O$_4$–MWCNTs were approximately 82% and 47%, respectively, the loading mass ratio of OA–Fe$_3$O$_4$ NPs in the OA–Fe$_3$O$_4$–MWCNTs was calculated to be approximately 57.3%.

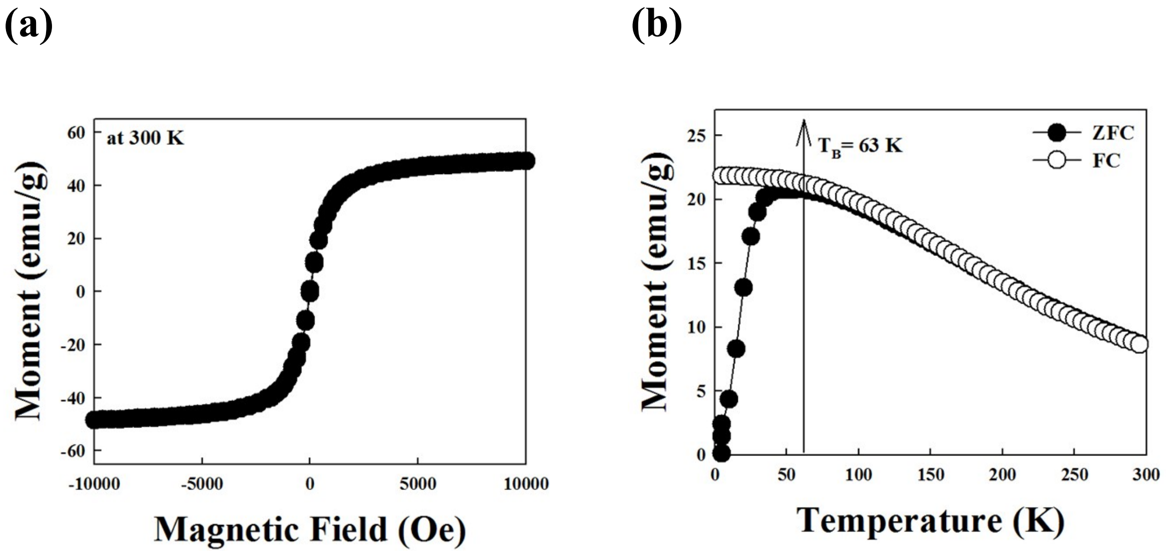


Fig. S3 (a) Magnetization curve of OA–Fe_3O_4–MWCNT hybrids examined by superconducting quantum interference device (SQUID) magnetometry at 300 K. This magnetization curve was nearly completely reversible without coercivity, hysteresis or remanence, suggesting typical superparamagnetic behavior. (b) Temperature dependence of the zero-field cooling (ZFC) and field cooling (FC) magnetization of OA–Fe_3O_4–MWCNT hybrids measured under an applied magnetic field of 150 Oe. In this case, the blocking temperature (i.e., the temperature with some deviation between FC and ZFC magnetization) of the OA–Fe_3O_4–MWCNT hybrids was fixed at approximately 63 K, corresponding to the blocking temperature of typical Fe_3O_4 NPs with a diameter of approximately 8 ± 1 nm.

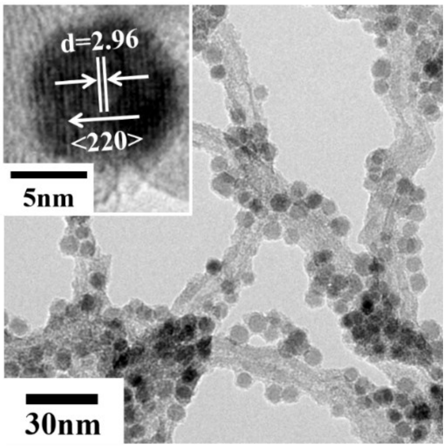


Fig. S4 HR-TEM image of anionic octakis–Fe_3O_4 NP–coated MWCNTs. For the preparation of anionic Fe_3O_4 NPs dispersed in water, OA–Fe_3O_4 NPs in toluene were phase-transferred to an aqueous medium using a ligand exchange reaction between OA and anionic octakis ligands.

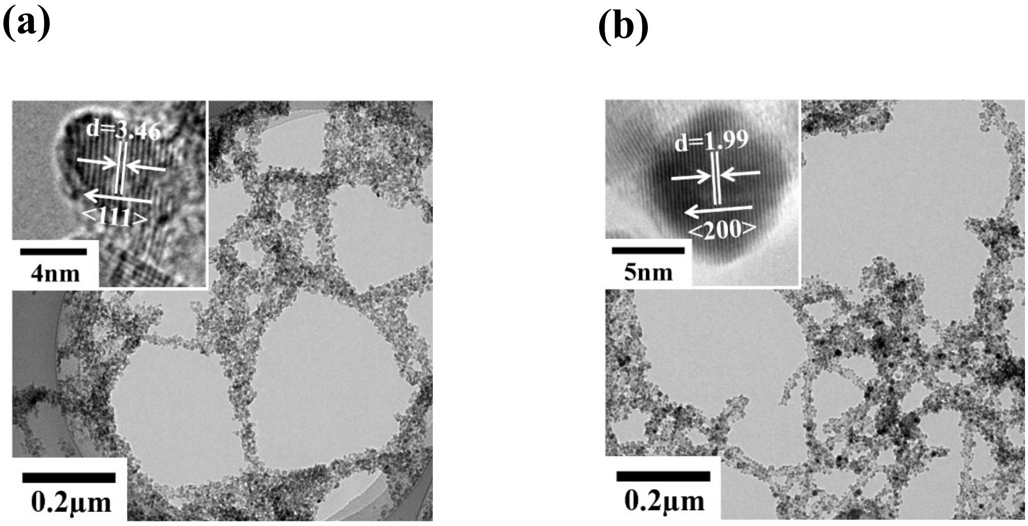


Fig. S5 HR-TEM images of (a) OA–TiO_2–MWCNT and (b) OA–$BaTiO_3$–MWCNT hybrids. The diameter of OA–TiO_2 and OA–$BaTiO_3$ NPs was measured to be approximately 4.5 and 7 nm, respectively.

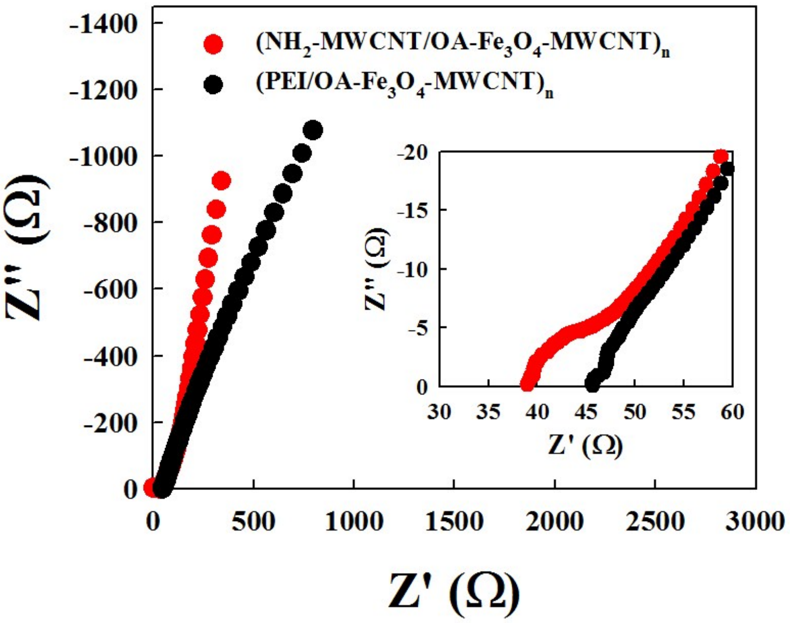


Fig. S6 Nyquist plots of the 241-nm-thick NH_2–MWCNT/OA–Fe_3O_4–MWCNT and 237-nm-thick PEI/OA–Fe_3O_4–MWCNT multilayer electrodes. EIS measurements were conducted in the frequency range from 1 MHz to 0.1 Hz at a potential amplitude of 10 mV.

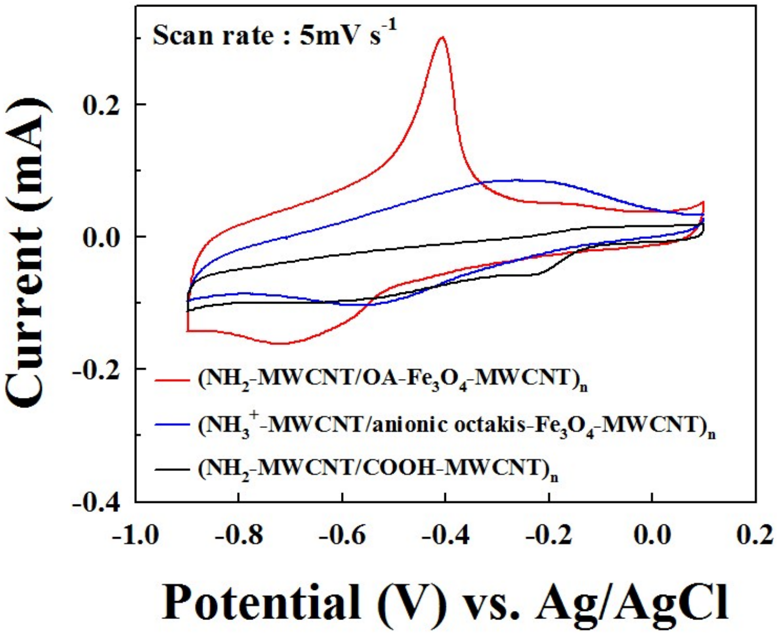


Fig. S7 CV curves of 247-nm-thick NH_2–MWCNT/COOH–MWCNT, 246-nm-thick NH_3^+–MWCNT/anionic octakis–Fe_3O_4–MWCNT, and 241 nm-thick NH_2–MWCNT/OA–Fe_3O_4–MWCNT multilayer electrodes.

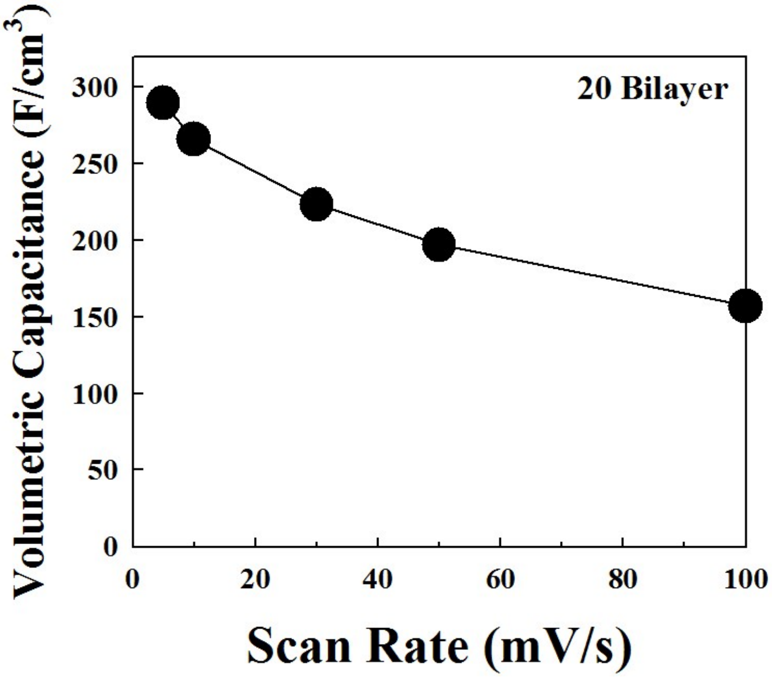


Fig. S8 Volumetric capacitances of the LbL-assembled (NH_2–MWCNT/OA–Fe_3O_4–MWCNT$)_{20}$ electrode as a function of scan rate (5 to 100 mV·s^{-1}).

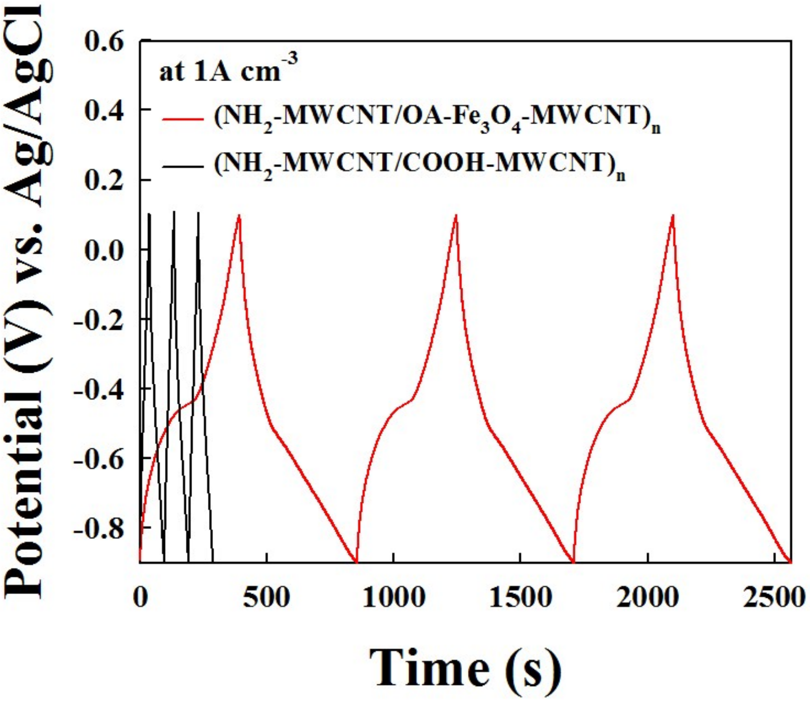


Fig. S9 Galvanostatic charge-discharge curves of the 247-nm-thick NH_2–MWCNT/COOH–MWCNT and 241-nm-thick NH_2–MWCNT/OA–Fe_3O_4–MWCNT multilayer electrodes at 1 A·cm^{-3}.

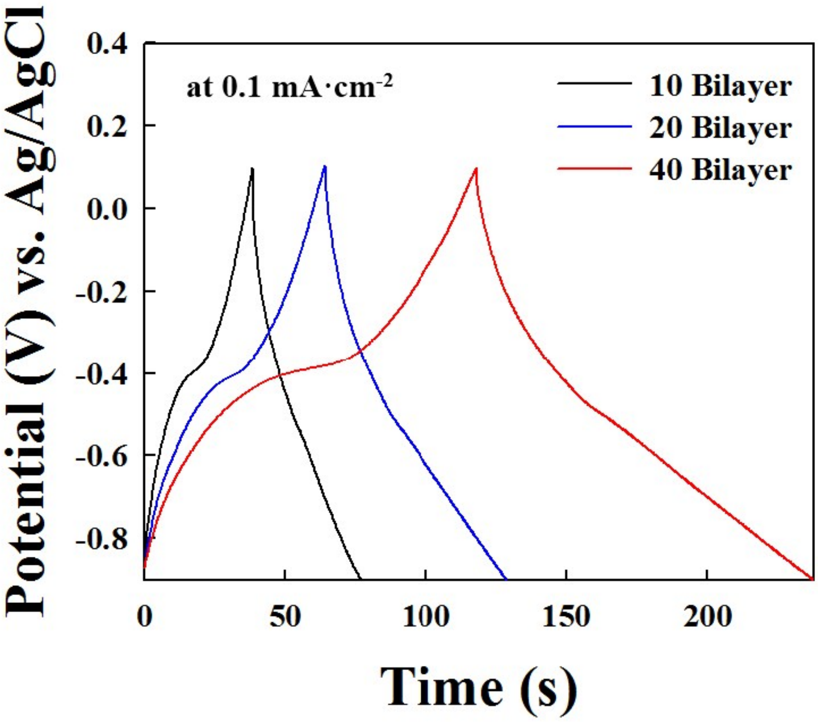


Fig. S10 Galvanostatic charge-discharge curves of the LbL-assembled (NH_2–MWCNT/OA–Fe_3O_4–MWCNT)$_n$ electrode as a function of bilayer number at a fixed current density of 1 mA·cm^{-3}.

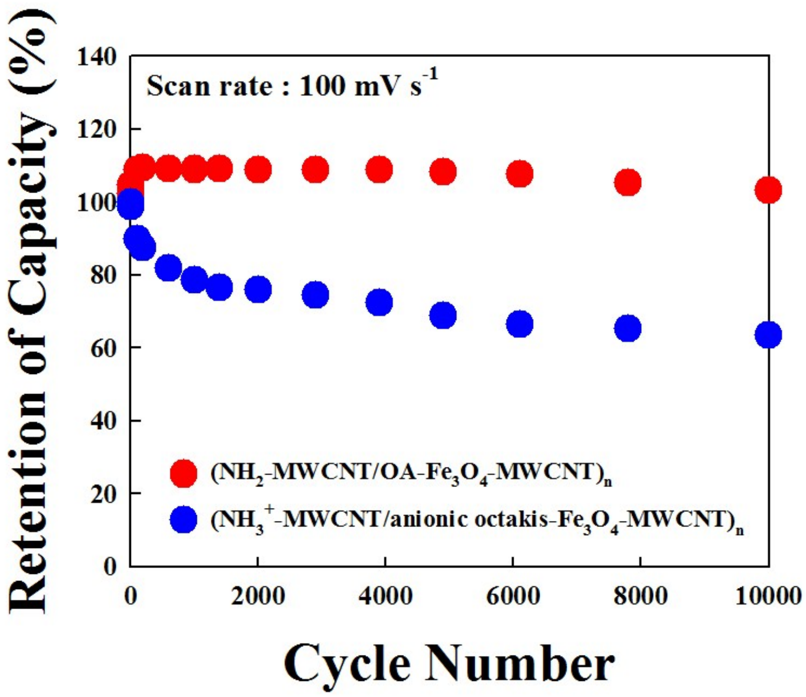


Fig. S11 Capacitance retention of the 241-nm-thick NH_2–MWCNT/OA–Fe_3O_4–MWCNT and 246-nm-thick NH_3^+–MWCNT/anionic octakis–Fe_3O_4-MWCNT multilayer electrodes.