Layer-by-Layer Assembly of High-Performance Electroactive **Composites Using a Multiple Charged Small Molecule**

Zhen Wang,[†] Liangqi Ouyang,[†] Weiqian Tian,[†] Johan Erlandsson,[†][®] Andrew Marais,[†] Klas Tybrandt,^{§,||}[®] Lars Wågberg,^{†,‡}[®] and Mahiar Max Hamedi^{*,†,‡}[®]

[†]Division of Fibre Technology, Department of Fibre and Polymer Technology and [‡]Wallenberg Wood Science Centre, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, 10044 Stockholm, Sweden

[§]Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, 60174 Norrköping, Sweden ^{II}Wallenberg Wood Science Center, Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, 60174 Norrköping, Sweden

S Supporting Information

ABSTRACT: Layer-by-layer (LbL) assembly is a versatile tool for fabricating multilayers with tailorable nanostructures. LbL, however, generally relies on polyelectrolytes, which are mostly insulating and induce large interlayer distances. We demonstrate a method in which we replace polyelectrolytes with the smallest unit capable of LbL self-assembly: a molecule with multiple positive charges, tris(3-aminopropyl)amine (TAPA), to fabricate LbL films with negatively charged single-walled carbon nanotubes (CNTs). TAPA introduces less defects during the LbL build-up and results in more efficient assembly of films with denser micromorphology. Twenty bilayers of TAPA/CNT showed a low sheet resistance of 11 k Ω , a high transparency of 91% at 500 nm, and a high electronic conductivity of 1100 S/m on planar substrates. We also fabricated LbL films on porous



foams with a conductivity of 69 mS/m and used them as electrodes for supercapacitors with a high specific capacitance of 43 F/ g at a discharging current density of 1 A/g.

INTRODUCTION

Layer-by-layer (LbL) assembly was initially developed to build functional polymeric multilayers from oppositely charged polyelectrolytes.¹ It has now evolved into a powerful tool for fabricating thin-film composites with tailored composition and structures. The choice of materials has also expanded from polymers to various types of nanomaterials such as zerodimensional (0D) particles,^{2,3} one-dimensional (1D) nanotubes or fibrils,⁴ and two-dimensional (2D) nanosheets.^{5,6} LbL assembly allows for a precise control of thickness with resolutions reaching the molecular level.⁷ This precision, along with its versatility, makes LbL an ideal method of building functional materials with a wide range of applications, such as energy storage and conversion, catalysis, optics, membranes, and biomedicine.⁸

LbL assembly is generally an entropically driven process that relies on the release of counter ions or adsorbed solvent molecules. For LbL assembly based on the release of counterions, there is limited choice of materials and counterions that are conductive, for example, carbon nanotubes (CNTs), which have found applications in energy storage and conversion,^{9,10} transparent flexible electronics,^{11,12} and sensors due to their exceptional electrical conductivity and mechanical strength.¹³ The LbL assembly of CNTs, however, mainly relies on the interactions between the functionalized, charged CNTs and polyelectrolytes such as poly(ethyleneimine) (PEI),¹⁴ or chitosan,¹⁵ which carry multiple opposite charges on a single

polymer chain. Self-assembled polyelectrolytes can form stable layers for the consecutive building up of LbL films; however, there are two major drawbacks when polyelectrolytes are used in electronic LbL composites. (i) They reside inside the composites after the assembly process and increase the inactive weight of the material, resulting in a lower volumetric or gravimetric efficiency. (ii) Their relatively large size forms an insulating spacer between individual CNTs, which results in decreased conductivity.¹⁶

To pursue the highest possible conductivity, Lee et al. functionalized the surface of multiwall CNTs with a negative and positive charge and assembled all CNT thin film using LbL assembly.¹⁷ This method, however, requires an extra chemical modification on the negatively charged CNTs, which can damage parts of the CNT and might not be generalized to other materials that are sensitive to the chemical reactions.

We hypothesized that small-molecule counterions with charged groups could be more favorable than polyelectrolytes for the LbL assembling of electronic materials. Smaller molecules can minimize the thickness of the insulating layer between the electroactive materials.^{2,18,19} The LbL formation of these types of counterions will be highly dependent on no less than four charged groups on the small molecules.²⁰ For

Received: May 27, 2019 July 14, 2019 Revised: Published: July 19, 2019



weakly charged centers, the solubility can also be of concern.²¹ The LbL assembly with small molecules with four charged sites has been demonstrated on colloidal particles²² but not for electronic materials. There is, therefore, a need to develop and understand how small molecules can be used for LbL fabrication of high-performance electronic materials. We note that the LbL assembly of conductive materials requires the use of a cationic counter phase, as the majority of electrically active and/or redox active nanomaterials are anionic such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate),²³ silicon nanoparticles,²⁴ titanium dioxide,²⁵ carboxylic acid-functionalized CNTs,¹⁷ graphene oxides,²⁶ and MXenes.²⁷ In this work, we therefore chose a cationic small molecule, tris(3aminopropyl)amine (TAPA), to compare with the widely used PEI²⁸ and to demonstrate the LbL assembly with negatively charged carboxylic acid-functionalized single-wall CNTs as a counter phase. It should be noted that the amines might have secondary interactions with CNTs via charge-transfer interactions.²⁹ In this work, however, the entropically driven charge interaction is dominant. We select TAPA (188 g/mol) as our model molecule, as it is one of the smallest units of PEI in LbL but yet maintains the minimum of 4 charges necessary for LbL buildup.²⁰ In a recently published work, we reported the use of another small molecule, tris(3-aminoethyl)amine, for the LbL assembly of 2D materials and showed that spermidine with three charges on its linear structure could not achieve the LbL assembly.¹

EXPERIMENTAL SECTION

Materials. Tris(3-aminopropyl)amine (TAPA) was purchased from ChemCruz. Branched polyethyleneimine (PEI, 60 kDa) was purchased from Acros Organics. Single-wall carbon nanotubes (CNTs) containing 1.0–3.0 atom % carboxylic group are from Carbon Solutions, Inc. The melamine resin foam (Basotect, BASF) was generously provided by Recticel AB, Sweden. Water used in this work was ultrapure water obtained with a Milli-Q water purification system.

Solutions and Dispersions of the Building Blocks. We dissolved PEI and TAPA into water with a concentration of 1 g/L each. Afterward, we adjusted both the pH to 7.5 with hydrochloric acid (0.5 M). We examined the charge density of PEI and TAPA using a homebuilt polyelectrolyte titrator equipped with a Metrohm 716 DMS Titrino volumetric titrator and a spectrophotometer. In the titration, we used polymer potassium poly(vinyl sulphate) (KPVS, from Wako Pure Chemicals, Japan) with a charge density of 0.379 μ eq/mL to form complexes with PEI or TAPA. At the critical point of titration, excess KPVS formed complexes with ortho-toluidine blue (from Kebo AB, Sweden) and induced a color change.

We dispersed the carboxylic group-functionalized CNTs in water. The initial concentration of the added single-wall CNTs was 2 g/L. We stirred the suspension at 25 000 r.p.m. for 10 min with Ultra Turrax T25 (IKA), followed by ultrasonication (Sonics, model CV33) for 20 min at 50% amplitude in an ice bath. The suspensions were centrifuged at 20 000 r.p.m. for 1 h. We collected the supernatant and diluted it to 0.2 g/L to be used as a dispersion of CNTs without adjusting the pH.

Characterizations. We used a Hitachi S-4800 field-emission scanning electron microscope to study the micromorphology. We carried out the transmittance and absorption measurements with a Shimadzu UV-2550 spectrophotometer. Particle size distributions were determined with Malvern Zetasizer Nano ZS. The atomic force microscope (AFM) was MultiMode 8 from Bruker. We processed the AFM images with NanoScope Analysis, which gave the root mean squared (RMS) surface roughness, Rq.

We studied the buildup of the layers with quartz crystal microbalance with dissipation (QCM-D, Model E4 from Q-Sense AB). The crystals we used for QCM-D measurements were the ATcut quartz crystal sensors with a silicon oxide layer (QSX 303). We cleaned the surfaces of the crystals by rinsing with a water/ethanol/ water sequence followed by an oxygen plasma treatment for 2 min to remove the organic residues before use. The solution of PEI and TAPA were both 1 g/L in concentration and had pH of 7.5. The dispersion of CNTs was 0.2 g/L. The adsorption and rinsing times were either 15 and 20 min, which were both longer than the equilibrium time of the adsorption of each layer. The mass increase of each layer was calculated with QTool using a viscoelastic Voigt model, assuming the liquid density was 1 g/mL and the viscosity of the liquid was 1 g/(m s).

LbL Assembly. We carried out the LbL assembly onto glass slides with the assistance of a dipping robot, StratoSequence VI. Before the assembly, the glass slides were cleaned by ultrasonicating in 0.1 mol/L NaOH solution for 10 min. Afterward, we immersed the glass substrates into the solution of the cationic compound (PEI or TAPA of 1 g/L, pH 7.5) for 3 min, followed by rinsing three times with pure water for 2 min each. Then, the glass slides were immersed into the dispersion of the CNT for 3 min, followed by the same rinsing procedure. To get a uniform adsorption onto the surfaces, we spun the glass slides while immersed.

We carried out the LbL assembly on the surface of untreated melamine resin foams (MRFs) using a previously described rapid filtration procedure³⁰ to build the electrodes for supercapacitors, where the solution of PEI or TAPA (1 g/L, pH 7.5) and the dispersion of CNTs (0.2 g/L) were alternatively forced through the open pores of the MRFs with the assistance of a vacuum filtration underneath. We rinsed the MRFs with water after each deposition step to remove excessive materials that were not adsorbed.

Fitting of the Model. The model reported by Forró et al.¹⁶ was used to fit the $R_{\rm S}$ vs *T* data for TAPA/CNT and PEI/CNT. The main equation of the model is eq 3, where $R_{\rm S}$ is the sheet resistance, $R_{\rm w}$ is the wire resistance, $R_{\rm c}$ is the contact resistance between the wires, *D* is the normalized wire density, $n_{\rm a} = 0.2027D\pi/2$ is the effective number

of contacts and
$$r_{\rm m} = \left(n_{\rm a} - 1 + R_{\rm c}\left(R_{\rm c} + \frac{R_{\rm w}}{n_{\rm a} + 1}\right)^{-1}\right) / (n_{\rm a} + 1)$$
 is the

effective wire length. By fitting to the experimental data, R_w and R_c can be determined. This requires knowledge of all other parameters, which can be obtained from the experimental observations/measurements. The average length of the CNT bundles (~1 µm), from which the effective wire length r_m can be calculated, is given by the material supplier. For thin films, the normalized wire density *D* can be related to the transmittance $T/D = K(T^{-0.5} - 1)$ (see the Supporting Information), where *K* is a material parameter. Here, *K* is determined by counting the number of wires in the AFM image (Figure S3) of (PEI/CNT)₁ of known *T*. Then, *D* can be calculated for various *T*, and the effective number of contacts n_a can be sequentially calculated from *D*. A nonlinear least-squares fit, based on the trust-regionreflective algorithm in MATLAB, was used to fit eq 1 to the logarithm of the TAPA/CNT data. The obtained R_w was then used to predict the curves for $R_c = 0$, 10⁵, 10⁶, 10⁷, and 10⁸ Ω.

Electrochemical Measurement. We evaluated the performances of the MRF-borne single-walled CNT (SWCNT) as an electrode of supercapacitor using a three-electrode connection with a BioLogic VSP potentiostat/galvanostat. The counter electrode was a piece of platinum foil; the reference electrode was a standard Ag/AgCl; and the electrolyte was 1 M sulfuric acid. The specific capacitance (*C*) was calculated according eqs 1 and 2

$$C = \frac{\int i(V) \, \mathrm{d}V}{2\nu\Delta VS} \, (\text{for CV}) \tag{1}$$

$$C = \frac{I\Delta t}{\Delta V} \text{ (for charge/discharge)}$$
(2)

where *i* and *I* are the current; ΔV is the voltage window; ν is the scan rate; *S* is the mass of PEI/CNTs or TAPA/CNTs; and Δt is the discharge time.



Figure 1. Particle size distributions of (a) TAPA and (b) PEI. Schematics showing the LbL buildup of (c) TAPA/CNT and (d) PEI/CNT. (e) Mass increase per layer of PEI/CNT and TAPA/CNT extracted from QCM-D measurements. The "n.5" bilayers (BL) with open symbols indicate the PEI or TAPA layers. (f) A photograph showing PEI/CNT and TAPA/CNT assembled on glass slides.



Figure 2. (a) Top-view SEM image and (b) an AFM height image of $(PEI/CNT)_{20}$ on a planar glass slide. (c) A top-view SEM image and (d) an AFM height image of $(TAPA/CNT)_{20}$. (e) Cross-sectional SEM image and (f) AFM section profile of $(PEI/CNT)_{20}$. (g) Cross-sectional SEM image and (h) AFM section profile of $(TAPA/CNT)_{20}$. (i) Conductivity comparison between PEI/CNT and TAPA/CNT as functions of number of bilayers. (j) Comparison of sheet resistance vs transmittance of TAPA/CNT data to theoretical predictions for various R_c . The data points from the right to the left correspond to bilayer numbers 2, 3, 5, 7, 10, 15, and 20. (k) Comparison of PEI/CNT data to theoretical predictions for various R_c values. The data points from the right to the left correspond to bilayer numbers 1, 2, 3, 5, 7, 10, 15, and 20.

RESULTS AND DISCUSSION

We adjusted the pH to 7.5 for both PEI (60 kDa) and TAPA solutions because this value has been shown to result in sufficiently charged polyelectrolytes and oligoelectrolytes²⁰ for LbL growth. We do not refer to pK values here, since polyelectrolytes have no single pK values that are naturally dependent on the ionic strength³¹ and can be altered by oppositely charged polyelectrolyte.²⁰ At pH 7.5, we measured a charge density of 18 meq/g for PEI and 21 meq/g for TAPA. TAPA has a higher charge density than PEI, presumably due to the lower influence of the neighboring charges on the polyelectrolyte chain.³² A higher charge density also leads to a gravimetric advantage of TAPA, which overcompensates the charge in the LbL formation with a lower adsorbed mass than that of PEI. The hydrodynamic diameter of the TAPA molecule, Figure 1a,b, was 0.7 ± 0.1 nm, significantly smaller than that of PEI (11.5 \pm 3.6 nm) in accordance with previous reports.³³ The high charge density and the smaller molecular size of this cationic counterion are essential for compact, ordered assemblies of consecutive CNT layers and for providing a close contact between the CNTs (Figure 1c,d).

We used a quartz crystal microbalance with dissipation monitoring (QCM-D) to study the kinetics of the growth of the first four bilayers of PEI/CNT and TAPA/CNT on the anionic silica surface. As shown in Figures 1e and S1, the assembly of TAPA/CNT exhibited a linear growth, while PEI/ CNT grew exponentially (see Experimental Section for details about the calculations). We note that for each bilayer, PEI/ CNT has a higher mass loading than TAPA/CNT. For example, in the 4th bilayer, $1.34 \pm 0.36 \ \mu g/cm^2$ of CNT was assembled by PEI, whereas 0.42 \pm 0.07 μ g/cm² for TAPA, corresponding to a ratio of the loading efficiency of around 3:1. The mass loading of PEI for this layer, however, was also higher $(0.82 \pm 0.20 \ \mu g/cm^2 \text{ versus } 0.40 \pm 0.07 \ \mu g/cm^2 \text{ of}$ TAPA). Although PEI assembled a higher amount of CNT, the loading of more insulating materials between the layers increased the overall resistance of the films and rendered the LbL assembly gravimetrically less efficient.^{30,34}

We LbL assembled the films on glass substrates, which are basically SiO₂ surfaces carrying negative charges, using a dipcoating method, and evaluated the properties of the films of PEI/CNT and TAPA/CNT. By assuming a proportional relationship between the content of CNT and the absorbance (Abs.) at 500 nm in the UV-vis spectra (Figure S2), we found more than three times the areal content of CNT in (PEI/ $(CNT)_{20}$, with Abs. of 0.33, than that in $(TAPA/CNT)_{20}$, with the Abs. of 0.11. At the same time, the TAPA/CNT films displayed a higher transparency (Figure 1f) due to the lower amount of CNT in the film. The one-side transmittance of $(TAPA/CNT)_{20}$ is as high as 91% at the wavelength of 500 nm, with a corresponding sheet resistance of $11 \pm 2 \text{ k}\Omega/\text{sq.}$ With 20 bilayers, both $(PEI/CNT)_{20}$ and $(TAPA/CNT)_{20}$ completely covered the surface of the glass substrates (Figure 2a-d). The morphology of the two types of thin films, however, showed clear differences: the CNTs from (PEI/ $(CNT)_{20}$ were thicker than those from $(TAPA/CNT)_{20}$ due to the coating of PEI on the CNTs.35 We observe many large pores (97 \pm 28 nm averaged from 10 pores) distributed on the (PEI/CNT)₂₀ film. In contrast, (TAPA/CNT)₂₀ showed a dense and smooth surface with much smaller pores (43 \pm 9 nm). Using the AFM, we measured the RMS roughness, Rq, of 8 nm for $(TAPA/CNT)_{20}$ over an area of 5 μ m × 5 μ m, and a

considerably higher roughness of 22 nm for $(PEI/CNT)_{20}$. We also observed quite distinct morphologies from the crosssectional SEM images and section profiles from the AFM images of the two CNT composite thin films, as shown in Figure 2e–h. $(PEI/CNT)_{20}$ exhibited a more uneven surface with an average thickness of 298 ± 30 nm. In contrast, $(TAPA/CNT)_{20}$ was 82 ± 7 nm thick and showed a quite neat cross section with a highly compact structure. Figure 2e,g shows some CNTs sticking out at the cross section; these hairy structures were created during the break of the glass substrates and hence do not correspond to the structure in the unbroken films.

Compared to PEI/CNT, TAPA/CNT decreases the spacing between CNTs and showed four times higher conductivity at 20 bilayers (1100 vs 260 S/m; Figure 2i). Moreover, the conductivity of $(TAPA/CNT)_n$ remained constant with increasing number of bilayers, indicating an assembly process with little defects. The conductivity of $(PEI/CNT)_n$ decreased with the number of bilayers, suggesting that we introduced more imperfect connections among CNTs during the assembly process. To study the films further, we utilized our recently developed model,¹⁶ which describes the relation between resistance and geometry for random networks of 1D nanomaterials

$$R_{\rm S}(R_{\rm w}, R_{\rm c}) = \frac{R_{\rm w}}{D} \left[\frac{1}{2} r_{\rm m} - \sqrt{\frac{R_{\rm c} r_{\rm m}}{2R_{\rm w} n_{\rm a}}} \tanh\left(\sqrt{\frac{R_{\rm w} n_{\rm a} r_{\rm m}}{2R_{\rm c}}}\right) \right]^{-1}$$
(3)

where $R_{\rm S}$ is the sheet resistance, $R_{\rm w}$ is the nanowire resistance, R_c is the contact resistance between the nanowires, r_m is the effective nanowire length, and n_a is the effective number of contacts. As the CNTs come in the form of bundles, the unit element for the model is bundles of $\sim 1 \ \mu m$ length (specified by the supplier). The density of the CNT bundles (D) was calculated from the transmittance data based on the count of $(PEI/CNT)_1$ AFM image (Figure S3; for details, see Supporting Information). The model in eq 3 fitted the $(TAPA/CNT)_n$ data well (Figure 2j), giving an estimate of R_w = 0.62 \pm 0.32 M Ω and R_c = 0 \pm 4 Ω for the resistance of the CNT films, indicating that R_c was low enough to not affect the R_s significantly. The PEI/CNT data are more scattered, preventing a good single fit. However, as the R_w is expected to be the same, the PEI/CNT data are plotted together with the theoretical predictions for $R_c = 0$, 10⁵, 10⁶, 10⁷, and 10⁸ Ω (Figure 2k). The thicker films are consistent with a higher R_c in the range of $10^6 - 10^7 \Omega$, which strengthens the hypothesis that the connectivity of the CNTs deteriorates in thicker (PEI/ CNT) films. We attribute the more efficient assembly of the TAPA/CNT films to the smaller repulsion diameter of TAPA, which offers a more homogeneous coverage. It is also well accepted that the PEI will form an uneven structure in the LbL assembly due to its highly branched structure.³⁶ Unlike branched polyelectrolytes, most linear polyelectrolytes form smooth layers in deionized water, as in this case, but more uneven structures when the salt concentration is increased to moderate levels. Linear polyelectrolytes hence result in a rather even layer, despite a wrinkled structure in the dried state. As shown by our images (Figure 2a,b,e,f), we have an uneven structure already in deionized water, which is consistent with the characterization of the cross-linked PEI as demonstrated by Horn et al.³³

D

Assembling functional materials into three-dimensional (3D) porous substrates with precise control and good structural stability remains challenging with conventional techniques. The LbL assembly, however, enables full coating of complex high-surface-area 3D substrates. We and others have formed thin films on the surface of the foams and aerogels using the filtration-assisted LbL method.^{30,37} Here, we explored the LbL assembly in a 3D porous substrate, a melamine resin foam (MRF) with a porosity of 99.4%, and compared the performances of the assembled devices composed of PEI/CNT and TAPA/CNT (Figure 3).



Figure 3. (a) Photograph and (b, c) SEM images of $(PEI/CNT)_{20}$ assembled in MRF. (d) A photograph and (e, f) SEM images of $(TAPA/CNT)_{20}$ assembled in MRF. (g) Conductivity comparison between PEI/CNT and TAPA/CNT. Electrochemistry performances of the supercapacitor electrodes of $(PEI/CNT)_{20}$ and $(TAPA/CNT)_{20}$ assembled in MRF: (h) cyclic voltammogram (CV), (i) specific capacitance at various scan rates determined by CV, and (j) galvanostatic charge/discharge profiles.

We preserved the highly porous 3D structure of the foam after the LbL assembly. Figure 3a–f shows the smooth coverage of the films on the foam scaffold without clogging the pores. In accordance to the morphology differences observed on planar substrates, we found much larger pores on $(PEI/CNT)_{20}$ (up to 131 nm in diameter) than those on $(TAPA/CNT)_{20}$ (up to 60 nm in diameter). The conductivity of the 20-bilayer composites reached 12 mS/m for PEI and 69 mS/m for TAPA (Figure 3g). In addition to the higher conductivity, the $(TAPA/CNT)_{20}$ films also contributed to a smaller increase in weight (3.1% compared to 5.5% for 20 bilayers of PEI/CNT) of the foam-based composites.

We explored the application of $(TAPA/CNT)_{20}$ in foams as 3D electrodes in a supercapacitor in an aqueous electrolyte (1

M H_2SO_4). The 3D porous structure of the composites is advantageous for extending the surface area of the electrode material and facilitating the ionic transport of the electrolyte.³⁴ At a cyclic voltammogram (CV) scan rate of 5 mV/s, as shown in Figure 3h, the $(TAPA/CNT)_{20}$ electrode exhibited more conspicuous redox peaks at around 0.4 V, which were also detected for other systems where CNT with oxygen-containing functional groups and materials with amino groups coexist.^{17,3} The anodic peak current obtained with (TAPA/CNT)₂₀ was 0.68 A/g at 0.45 V, while (PEI/CNT)₂₀ showed an anodic peak current of 0.25 A/g at 0.47 V. Moreover, the overall normalized current response to the voltage change was more significant for (TAPA/CNT)₂₀ than for (PEI/CNT)₂₀ electrode partly because of the lower resistance of the electrode. The specific capacitance of the $(TAPA/CNT)_{20}$ electrode was 86 F/g at the scan rate of 5 mV/s, which is more than twice that of the $(PEI/CNT)_{20}$ electrode of 35 F/g. Benefitting from the higher conductivity, the $(TAPA/CNT)_{20}$ electrode also showed a higher rate capability when varying the scan rate (Figure 3i and S4). The specific capacitance of (TAPA/CNT)₂₀ was 11 F/g at an ultrafast scan rate of 1000 mV/s, which is nearly 3 times higher than that of the (PEI/ $(CNT)_{20}$ electrode of 4 F/g. Figure 3j shows the charge/ discharge profiles of the supercapacitors at the current density of 1 A/g. The (TAPA/CNT)₂₀ electrode delivered a specific capacitance of 43 F/g, compared to 18 F/g delivered by the (PEI/CNT)₂₀ electrode. It also showed a smaller IR drop than the $(PEI/CNT)_{20}$ owing to the better conductivity of the $(TAPA/CNT)_{20}$ electrode.

After the electrochemical measurements, we kept the $(TAPA/CNT)_{20}$ electrode in the electrolyte for 9 months and found the electrode stayed intact in the strong acidic condition, as we observed no delamination of the CNTs from the SEM images (Figure S5), which showed the complete coverage of the $(TAPA/CNT)_{20}$ thin film on the foam. The micromorphology of the $(TAPA/CNT)_{20}$ thin film was however slightly blurred, but its pore sizes remained similar to the sample before electrochemical tests (Figure 3f). The results indicate that the $(TAPA/CNT)_{20}$ electrode was resilient to strong acid condition and was electrochemically stable.

CONCLUSIONS

We demonstrated the use of a multiple charged small molecule, TAPA, for the LbL self-assembly of single-wall CNTs. We performed the LbL assembly of these electroactive composites on both planar and 3D porous substrates. The composite films formed with the efficient LbL assembly of TAPA and CNTs have five advantages over the film formed with the conventional polyelectrolyte PEI: (i) They show a more even and denser micromorphology with smaller pores (60 vs 130 nm) and a lower roughness (6 vs 18 nm over an area of $5 \times 5 \,\mu\text{m}^2$) most probably due to the smaller size of TAPA. They can form these neat films composed of less CNT but with favorable properties over both planar and 3D complex surfaces. (ii) They exhibit a higher electronic conductivity (1100 vs 260 S/m on the 2D substrates, and 69 vs 12 mS/m on the porous 3D substrates) because the small molecule forms smaller distances for electron tunneling between the CNTs. (iii) They have a higher transmittance of 91% at 550 nm (vs 75%), corresponding to a low sheet resistance of $11 \pm 2 \text{ k}\Omega/\text{sq.}$ (iv) They have an enhanced electrochemical performance, including a higher gravimetric capacitance (43 vs 18 F/g at the current density of 1 A/g) and a better rate performance due to the higher conductivity.

This work shows that the use of small molecules with multiple charges for the LbL assembly of electroactive materials is superior to the use of polyelectrolytes. We believe that numerous other multiple charged cationic and anionic small molecules³⁹ can be used for the LbL assembly of electroactive polymers, nanoparticles (0D colloids), 1D, and 2D materials^{40–44} in applications such as transparent electronics, electrochemical energy storage and conversion, sensors, catalysts, and electroactive membranes.^{45–49}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.9b01587.

Additional information and figures (PDF).

AUTHOR INFORMATION

Corresponding Author

*E-mail: mahiar@kth.se.

ORCID 💿

Johan Erlandsson: 0000-0003-1874-2187 Klas Tybrandt: 0000-0002-9845-446X Lars Wågberg: 0000-0001-8622-0386 Mahiar Max Hamedi: 0000-0001-9088-1064

Author Contributions

Z.W. designed and prepared the LbL multilayer composites, conducted characterizations of PEI, TAPA, and the devices and analyzed the data; wrote the manuscript with supervision from M.M.H. L.O. conducted the sheet resistance and conductivity measurements, designed, and drew the schematic illustrations. W.T. assisted with the acquisition of the AFM images. J.E. and L.W. contributed to the analysis of the data. A.M. took the photos of the foam samples. K.T. fit the data to a prediction model for the contact resistance. All the authors contributed to the discussion of the results and the writing of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the European Research Council (Grant 715268), the Wenner-Gren Foundation, and Knut and Alice Wallenberg Foundation (through Wallenberg Wood Science Centre at KTH) for funding. K.T. acknowledges the Swedish Government Strategic Research Area in Materials Science on Advanced Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009-00971).

REFERENCES

(1) Decher, G. Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. *Science* **1997**, *277*, 1232–1237.

(2) Ko, Y.; Kwon, M.; Bae, W. K.; Lee, B.; Lee, S. W.; Cho, J. Flexible supercapacitor electrodes based on real metal-like cellulose papers. *Nat. Commun.* **2017**, *8*, No. 536.

(3) Iler, R. K. Multilayers of colloidal particles. J. Colloid Interface Sci. 1966, 21, 569–594.

(4) Jiang, C.; Ko, H.; Tsukruk, V. V. Strain-Sensitive Raman Modes of Carbon Nanotubes in Deflecting Freely Suspended Nanomembranes. *Adv. Mater.* **2005**, *17*, 2127–2131. (5) Choi, W.; Choi, J.; Bang, J.; Lee, J. H. Layer-by-layer assembly of graphene oxide nanosheets on polyamide membranes for durable reverse-osmosis applications. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12510–12519.

(6) Lee, T.; Min, S. H.; Gu, M.; Jung, Y. K.; Lee, W.; Lee, J. U.; Seong, D. G.; Kim, B.-S. Layer-by-Layer Assembly for Graphene-Based Multilayer Nanocomposites: Synthesis and Applications. *Chem. Mater.* **2015**, *27*, 3785–3796.

(7) Xiao, F. X.; Pagliaro, M.; Xu, Y. J.; Liu, B. Layer-by-layer assembly of versatile nanoarchitectures with diverse dimensionality: a new perspective for rational construction of multilayer assemblies. *Chem. Soc. Rev.* **2016**, *45*, 3088–121.

(8) Richardson, J. J.; Bjornmalm, M.; Caruso, F. Multilayer assembly. Technology-driven layer-by-layer assembly of nanofilms. *Science* **2015**, *348*, No. aaa2491.

(9) Landi, B. J.; Ganter, M. J.; Cress, C. D.; DiLeo, R. A.; Raffaelle, R. P. Carbon nanotubes for lithium ion batteries. *Energy Environ. Sci.* **2009**, *2*, 638–654.

(10) Kwon, Y. H.; Minnici, K.; Park, J. J.; Lee, S. R.; Zhang, G.; Takeuchi, E. S.; Takeuchi, K. J.; Marschilok, A. C.; Reichmanis, E. SWNT Anchored with Carboxylated Polythiophene "Links" on High-Capacity Li-Ion Battery Anode Materials. *J. Am. Chem. Soc.* **2018**, *140*, 5666–5669.

(11) Li, D.; Lai, W. Y.; Zhang, Y. Z.; Huang, W. Printable Transparent Conductive Films for Flexible Electronics. *Adv. Mater.* **2018**, *30*, No. 1704738.

(12) Hecht, D. S.; Hu, L.; Irvin, G. Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures. *Adv. Mater.* **2011**, *23*, 1482–1513.

(13) Kwon, O. S.; Song, H. S.; Park, T. H.; Jang, J. Conducting Nanomaterial Sensor Using Natural Receptors. *Chem. Rev.* 2019, *119*, 36–93.

(14) Gittleson, F. S.; Hwang, D.; Ryu, W. H.; Hashmi, S. M.; Hwang, J.; Goh, T.; Taylor, A. D. Ultrathin Nanotube/Nanowire Electrodes by Spin-Spray Layer-by-Layer Assembly: A Concept for Transparent Energy Storage. *ACS Nano* **2015**, *9*, 10005–10017.

(15) Pavinatto, A.; Mercante, L. A.; Leandro, C. S.; Mattoso, L. H. C.; Correa, D. S. Layer-by-Layer assembled films of chitosan and multi-walled carbon nanotubes for the electrochemical detection of 17α -ethinylestradiol. *J. Electroanal. Chem.* **2015**, 755, 215–220.

(16) Forró, C.; Demkó, L.; Weydert, S.; Vörös, J.; Tybrandt, K. Predictive Model for the Electrical Transport within Nanowire Networks. *ACS Nano* **2018**, *12*, 11080–11087.

(17) Lee, S. W.; Kim, B.-S.; Chen, S.; Shao-Horn, Y.; Hammond, P. T. Layer-by-Layer Assembly of All Carbon Nanotube Ultrathin Films for Electrochemical Applications. *J. Am. Chem. Soc.* **2009**, *131*, 671–679.

(18) Kim, J.; Wang, H.-C.; Kumar, J.; Tripathy, S. K.; Chittibabu, K. G.; Cazeca, M. J.; Kim, W. Novel Layer-by-layer Complexation Technique and Properties of the Fabricated Films. *Chem. Mater.* **1999**, *11*, 2250–2256.

(19) Tian, W.; VahidMohammadi, A.; Wang, Z.; Ouyang, L.; Beidaghi, M.; Hamedi, M. M. Layer-by-layer self-assembly of pillared two-dimensional multilayers. *Nat. Commun.* **2019**, *10*, No. 2558.

(20) Dieter, H. Polymeric Amines and Ammonium Salts; Pergamon Press, 1980.

(21) Linford, M. R.; Auch, M.; Möhwald, H. Nonmonotonic Effect of Ionic Strength on Surface Dye Extraction during Dye– Polyelectrolyte Multilayer Formation. *J. Am. Chem. Soc.* **1998**, *120*, 178–182.

(22) Radtchenko, I. L.; Sukhorukov, G. B.; Leporatti, S.; Khomutov, G. B.; Donath, E.; Möhwald, H. Assembly of Alternated Multivalent Ion/Polyelectrolyte Layers on Colloidal Particles. Stability of the Multilayers and Encapsulation of Macromolecules into Polyelectrolyte Capsules. J. Colloid Interface Sci. **2000**, 230, 272–280.

(23) Malti, A.; Edberg, J.; Granberg, H.; Khan, Z. U.; Andreasen, J. W.; Liu, X.; Zhao, D.; Zhang, H.; Yao, Y.; Brill, J. W.; Engquist, I.; Fahlman, M.; Wagberg, L.; Crispin, X.; Berggren, M. An Organic

Mixed Ion-Electron Conductor for Power Electronics. *Adv. Sci.* 2016, 3, No. 1500305.

(24) Wu, H.; Yu, G.; Pan, L.; Liu, N.; McDowell, M. T.; Bao, Z.; Cui, Y. Stable Li-ion battery anodes by in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles. *Nat. Commun.* **2013**, *4*, No. 1943.

(25) Li, X.; He, J. Synthesis of Raspberry-Like SiO2–TiO2Nanoparticles toward Antireflective and Self-Cleaning Coatings. *ACS Appl. Mater. Interfaces* **2013**, *5*, 5282–5290.

(26) Cong, H.-P.; Chen, J.-F.; Yu, S.-H. Graphene-based macroscopic assemblies and architectures: an emerging material system. *Chem. Soc. Rev.* **2014**, *43*, 7295–7325.

(27) An, H.; Habib, T.; Shah, S.; Gao, H.; Radovic, M.; Green, M. J.; Lutkenhaus, J. L. Surface-agnostic highly stretchable and bendable conductive MXene multilayers. *Sci. Adv.* **2018**, *4*, No. eaaq0118.

(28) Srivastava, S.; Kotov, N. A. Composite Layer-by-Layer (LBL) Assembly with Inorganic Nanoparticles and Nanowires. *Acc. Chem. Res.* **2008**, *41*, 1831–1841.

(29) Kong, J.; Dai, H. Full and modulated chemical gating of individual carbon nanotubes by organic amine compounds. *J. Phys. Chem. B* **2001**, *105*, 2890–2893.

(30) Hamedi, M.; Karabulut, E.; Marais, A.; Herland, A.; Nystrom, G.; Wagberg, L. Nanocellulose aerogels functionalized by rapid layerby-layer assembly for high charge storage and beyond. *Angew. Chem., Int. Ed.* **2013**, *52*, 12038–12042.

(31) Katchalsky, A.; Shavit, N.; Eisenberg, H. Dissociation of weak polymeric acids and bases. J. Polym. Sci. 1954, 13, 69-84.

(32) Dautzenberg, H.; Philipp, B. Polyelectrolytes: Formation, Characterization, and Application; Hanser Publishers, 1994.

(33) Pfau, A.; Schrepp, W.; Horn, D. Detection of a Single Molecule Adsorption Structure of Poly(ethylenimine) Macromolecules by AFM. *Langmuir* **1999**, *15*, 3219–3225.

(34) Mamedov, A. A.; Kotov, N. A.; Prato, M.; Guldi, D. M.; Wicksted, J. P.; Hirsch, A. Molecular design of strong single-wall carbon nanotube/polyelectrolyte multilayer composites. *Nat. Mater.* **2002**, *1*, 190–194.

(35) Zhou, W.; Fan, Q.; Zhang, Q.; Cai, L.; Li, K.; Gu, X.; Yang, F.; Zhang, N.; Wang, Y.; Liu, H.; Zhou, W.; Xie, S. High-performance and compact-designed flexible thermoelectric modules enabled by a reticulate carbon nanotube architecture. *Nat. Commun.* **2017**, *8*, No. 14886.

(36) Wågberg, L.; Decher, G.; Norgren, M.; Lindström, T.; Ankerfors, M.; Axnäs, K. The Build-Up of Polyelectrolyte Multilayers of Microfibrillated Cellulose and Cationic Polyelectrolytes. *Langmuir* **2008**, *24*, 784–795.

(37) Lyu, S.; Chen, Y.; Han, S.; Guo, L.; Chen, Z.; Lu, Y.; Chen, Y.; Yang, N.; Wang, S. Layer-by-layer assembled polyaniline/carbon nanomaterial-coated cellulosic aerogel electrodes for high-capacitance supercapacitor applications. *RSC Adv.* **2018**, *8*, 13191–13199.

(38) Wang, R.; Xu, C.; Du, M.; Sun, J.; Gao, L.; Zhang, P.; Yao, H.; Lin, C. Solvothermal-Induced Self-Assembly of Fe2O3/GS Aerogels for High Li-Storage and Excellent Stability. *Small* **2014**, *10*, 2260– 2269.

(39) Das, S.; Pal, A. J. Layer-by-Layer Self-Assembling of a Low Molecular Weight Organic Material by Different Electrostatic Adsorption Processes. *Langmuir* **2002**, *18*, 458–461.

(40) Zhang, Y.; Chu, W.; Foroushani, A. D.; Wang, H.; Li, D.; Liu, J.; Barrow, C. J.; Wang, X.; Yang, W. New Gold Nanostructures for Sensor Applications: A Review. *Materials* **2014**, *7*, 5169–5201.

(41) Chen, W.; Yu, H.; Lee, S. Y.; Wei, T.; Li, J.; Fan, Z. Nanocellulose: a promising nanomaterial for advanced electro-chemical energy storage. *Chem. Soc. Rev.* **2018**, *47*, 2837–2872.

(42) Oytun, F.; Kara, V.; Alpturk, O.; Basarir, F. Fabrication of solution-processable, highly transparent and conductive electrodes via layer-by-layer assembly of functional silver nanowires. *Thin Solid Films* **2017**, *636*, 40–47.

(43) Li, M.; Mangalore, D. K.; Zhao, J.; Carpenter, J. H.; Yan, H.; Ade, H.; Yan, H.; Mullen, K.; Blom, P. W. M.; Pisula, W.; de Leeuw, D. M.; Asadi, K. Integrated circuits based on conjugated polymer monolayer. *Nat. Commun.* 2018, 9, No. 451.

(44) Kang, K.; Lee, K. H.; Han, Y.; Gao, H.; Xie, S.; Muller, D. A.; Park, J. Layer-by-layer assembly of two-dimensional materials into wafer-scale heterostructures. *Nature* **2017**, *550*, 229–233.

(45) Fiori, G.; Bonaccorso, F.; Iannaccone, G.; Palacios, T.; Neumaier, D.; Seabaugh, A.; Banerjee, S. K.; Colombo, L. Electronics based on two-dimensional materials. *Nat. Nanotechnol.* **2014**, *9*, 768–779.

(46) Sun, Z.; Liao, T.; Dou, Y.; Hwang, S. M.; Park, M. S.; Jiang, L.; Kim, J. H.; Dou, S. X. Generalized self-assembly of scalable twodimensional transition metal oxide nanosheets. *Nat. Commun.* **2014**, *5*, No. 3813.

(47) Ling, Z.; Ren, C. E.; Zhao, M.-Q.; Yang, J.; Giammarco, J. M.; Qiu, J.; Barsoum, M. W.; Gogotsi, Y. Flexible and conductive MXene films and nanocomposites with high capacitance. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 16676–16681.

(48) Stratakis, M.; Garcia, H. Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes. *Chem. Rev.* **2012**, *112*, 4469–4506.

(49) Stair, J. L.; Harris, J. J.; Bruening, M. L. Enhancement of the Ion-Transport Selectivity of Layered Polyelectrolyte Membranes through Cross-Linking and Hybridization. *Chem. Mater.* **2001**, *13*, 2641–2648.