

Layer-by-layer Assembled Heteroatom-Doped Graphene Films with Ultrahigh Volumetric Capacitance and Rate Capability for Micro-Supercapacitors

Zhong-Shuai Wu, Khaled Parvez, Andreas Winter, Henning Vieker, Xianjie Liu, Sheng Han, Andrey Turchanin, Xinliang Feng,* and Klaus Müllen*

The rapid development of miniaturized, wearable, and portable electronics have made micro-power sources on chips an important prerequisite.^[1–5] In this regard, planar micro-supercapacitors (MSCs) with short ion diffusion distances are considered to be highly competitive candidates for integrating numerous electronic devices due to their ultrahigh power density, large rate capability, and superior cycling lifetime.^[6–9] Since 2003, when Sung et al. reported the first prototype planar MSCs based on conducting polymers,^[10] tremendous attention has been focused on planar MSCs, for which a series of pseudocapacitive electrode materials, such as RuO₂,^[11] MnO₂,^[12] VS₂,^[13] and polyaniline,^[14,15] has been used. These state-of-the-art pseudocapacitive MSCs deliver a high volumetric capacitance, but generally exhibit low power density and a slow frequency response. To overcome these limitations, carbon-based MSCs utilizing activated carbon,^[16,17] carbide-derived carbon,^[3,18] onion-like carbon,^[2] carbon nanotubes (CNTs),^[19,20] and graphene^[7,8] were developed.

Graphene-based materials, such as reduced graphene oxide,^[21] CVD graphene,^[22] chemically-reduced graphene,^[7,8,23] graphene quantum dots,^[24,25] and nanohybrids of graphene/CNTs,^[26,27] graphene/polyaniline,^[28] and graphene/MnO₂,^[29] were recently exploited as advanced electrodes for planar MSCs by taking advantage of the planar device geometry and the unique structure of graphene for charge storage.^[22,30–33] In particular, graphene-based thin films for MSCs have attracted attention due to their polymer binder-free process, low macropore

volume, and good adhesion between the current collector and active material,^[7,8,23] which are essential features for achieving the high volumetric capacitance of MSCs.^[34,35] For the development of next-generation graphene-based MSCs, graphene doping with heteroatoms (e.g., N, B, S, or P) is a promising strategy to enhance the performance of supercapacitors by the introduction of pseudocapacitance.^[36–38] Despite the successful preparation of heteroatom-doped graphene sheets and porous graphene materials for supercapacitors, the fabrication of doped graphene films with a controlled thickness and uniform co-doping of different heteroatoms has not yet been reported.

Here we describe the development of large-area, highly uniform, ultrathin, nitrogen and boron co-doped graphene (BNG) films for high-performance MSCs. The BNG film was prepared using a layer-by-layer (LBL) assembly of anionic graphene oxide (GO) nanosheets and cationic poly-L-Lysine (PLL) as a nitrogen-containing precursor, followed by intercalation of H₃BO₃ within the layers and annealing treatment (Figure 1a–f). The PLL and H₃BO₃ incorporated into the assembled multilayer films not only serve as nitrogen- and boron-rich precursors, respectively, but also generate micropore fillers to promote the formation of porous, yet densely packed BNG films during the thermal treatment. All-solid-state planar MSCs were manufactured by lithographically dry-etching the as-produced BNG films on silicon wafers (Figure 1f–h), providing a pronounced pseudocapacitive behavior with ultrahigh volumetric capacitance (~488 F/cm³). This is the highest value reported to date for graphene-based supercapacitors, and an ultrahigh operation scan rate of up to 2000 V/s.

The LBL assembly is a simple and versatile bottom-up method to produce ultrathin multilayer films with a controlled thickness ranging from the nanometer to micrometer-scale through sequential immersion of a substrate into aqueous solution with pre-charged functional materials and repeated self-assembly.^[39–45] In our work, PLL with positively-charged amino acids (Figure S1 in Supporting Information) was chosen to control the deposition of negatively-charged GO nanosheets onto a surface by electrostatic attraction. Figure 1a–e illustrates the fabrication of (PLL/GO)_n multilayer films. The Si/SiO₂ wafer was initially treated by oxygen plasma to make the surface hydrophilic, and then the PLL and GO layers were repeatedly adsorbed on the modified silicon wafer to yield the multilayer (PLL/GO)_n (n ≤ 10) films.

The surface topography of the (PLL/GO)_n film was examined by atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements (Figure 2a–c, Figures S2–S4). A (PLL/GO)₁ film on a silicon substrate was almost completely covered by individual monolayer GO nanosheets with a

Dr. Z. S. Wu, Mr. K. Parvez, Prof. Dr. X. L. Feng,
Prof. Dr. K. Müllen
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, 55128, Mainz, Germany
E-mail: feng@mpip-mainz.mpg.de;
muellen@mpip-mainz.mpg.de

Mr. A. Winter, Mr. H. Vieker, PD Dr. A. Turchanin
Faculty of Physics, University of Bielefeld
Universitätsstr. 25, 33615, Bielefeld, Germany

Dr. X. J. Liu
Department of Physics
Chemistry and Biology
Linköping University
SE-58183, Linköping, Sweden

Dr. S. Han, Prof. Dr. X. L. Feng
School of Chemistry and Chemical Engineering
Shanghai Jiao Tong University
200240, Shanghai, P. R. China



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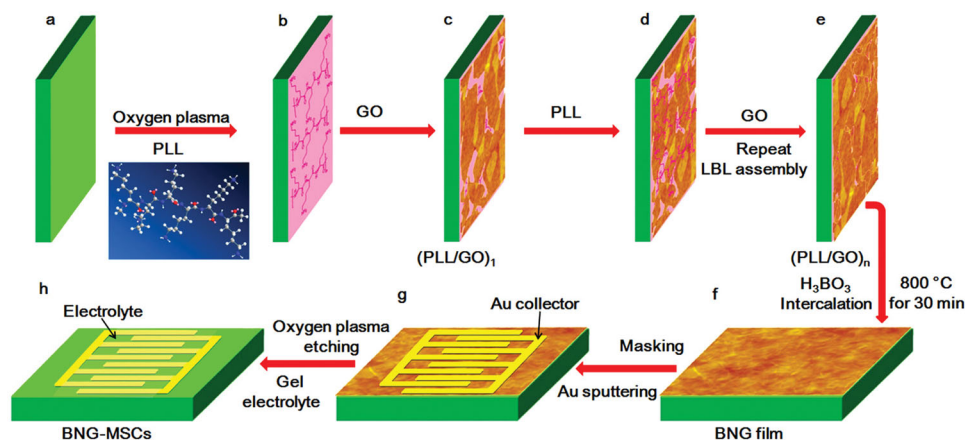


Figure 1. Schematic illustration of LBL-assembled heteroatom-doped films for planar MSCs on a Si/SiO₂ wafer. (a) Electrostatic adsorption of cationic PLL on the hydrophilic surface of silicon treated with an oxygen plasma. Inset: molecular structure of PLL with 6 units (red: N in –NH₃⁺; blue: N in –NH–; gray: C; white: H). (b) LBL assembly of anionic GO nanosheets on a PLL-adsorbed silicon wafer. (c, d) Repeated self-assembly of PLL and GO nanosheets into (PLL/GO)_n ultrathin films. (e) H₃BO₃ intercalation and annealing treatment to convert a (PLL/GO)_n film into a BNG film. (f) Lithographic micro-patterns and deposition of a gold current collector through a homemade mask. (g) Oxygen plasma etching and drop-casting of gel electrolyte on interdigital fingers. (h) All-solid-state BNG-MSCs obtained after solidification of gel electrolyte.

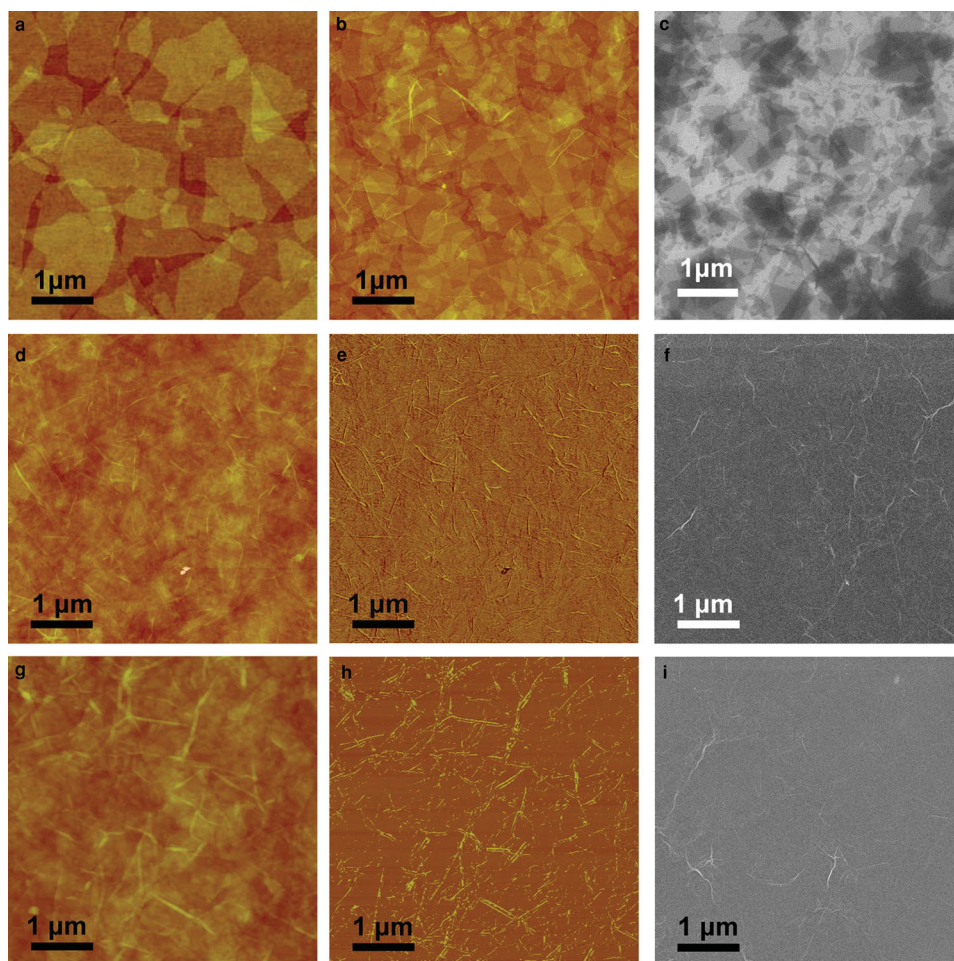


Figure 2. Surface morphology of LBL-assembled (PLL/GO)_n, NG, and BNG films. (a) AFM image of (PLL/GO)₁ film. (b) AFM and (c) SEM images of (PLL/GO)₂ film. (d) AFM height image, (e) AFM phase image, and (f) SEM image of a BNG film annealed from H₃BO₃-intercalated (PLL/GO)₁₀. (g) AFM height image, (h) AFM phase image and (i) SEM image of a NG film annealed from (PLL/GO)₁₀.

thickness of ~ 1.2 nm (Figure S2), and only a few overlapped GO nanosheets were restacked at their edges (Figure 2a). A total coverage of more than 90% was estimated for the first-layer deposited film, suggesting a highly efficient assembly of GO with PLL. The surface was fully covered by GO nanosheets after two rounds of assembly, as evidenced by the AFM and SEM visualizations (Figure 2b,c). Thus, large-area continuous $(\text{PLL}/\text{GO})_n$ films with a desirable layer number were subsequently achieved with PLL and GO nanosheets deposited in an alternating fashion (Figure S3). Notably, the resulting $(\text{PLL}/\text{GO})_n$ films had a low surface roughness (≤ 1 nm) for the entire measurement area (Figure S4). It should be mentioned that the assembling regularity of each layer, e.g., PLL layer and GO layer studied by AFM height images and 3D surface plots reveal the intimate interaction of both negative-charged GO and positively-charged PLL species during the LBL assembly process (Figures S5 and S6), which is critical for efficient self-assembly.

The structural changes of the $(\text{PLL}/\text{GO})_{10}$ film and H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$ film were investigated based on their X-ray diffraction (XRD) patterns. As shown in Figure 3a, the

XRD pattern of a $(\text{PLL}/\text{GO})_{10}$ film exhibited a sharp diffraction peak (002) at 8.3° , corresponding to a d-spacing of 10.6 \AA , which is larger than that of spin-coated GO film (8.9 \AA) without the incorporation of PLL layers.^[7] With H_3BO_3 intercalation, the characteristic (002) peak shifts to a lower angle of 7.6° , with a larger d-spacing of 11.6 \AA . In addition, a notable peak at 27.8° was observed, indicative of the presence of the H_3BO_3 (JCPDS 73–2158) in the assembled multilayer films.

Thermal treatment at 800°C for 30 min in nitrogen atmosphere was subsequently performed to convert the H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$ film into a BNG film and the $(\text{PLL}/\text{GO})_{10}$ film into a nitrogen-doped graphene (NG) film. The color changed from olive green to dark green, indicating the formation of graphene films (Figure S7). Figure 2d-i shows the AFM and SEM images of the BNG and NG films, which exhibit a smooth surface morphology with good continuity and uniformity (Figure 2d,g, Figure S8). Only small wrinkles with a sub-micrometer size formed on the top surface of the BNG film (Figure 2e,f) and NG film (Figure 2h,i). A detailed comparison of the thickness of $(\text{PLL}/\text{GO})_n$ films before and after thermal annealing

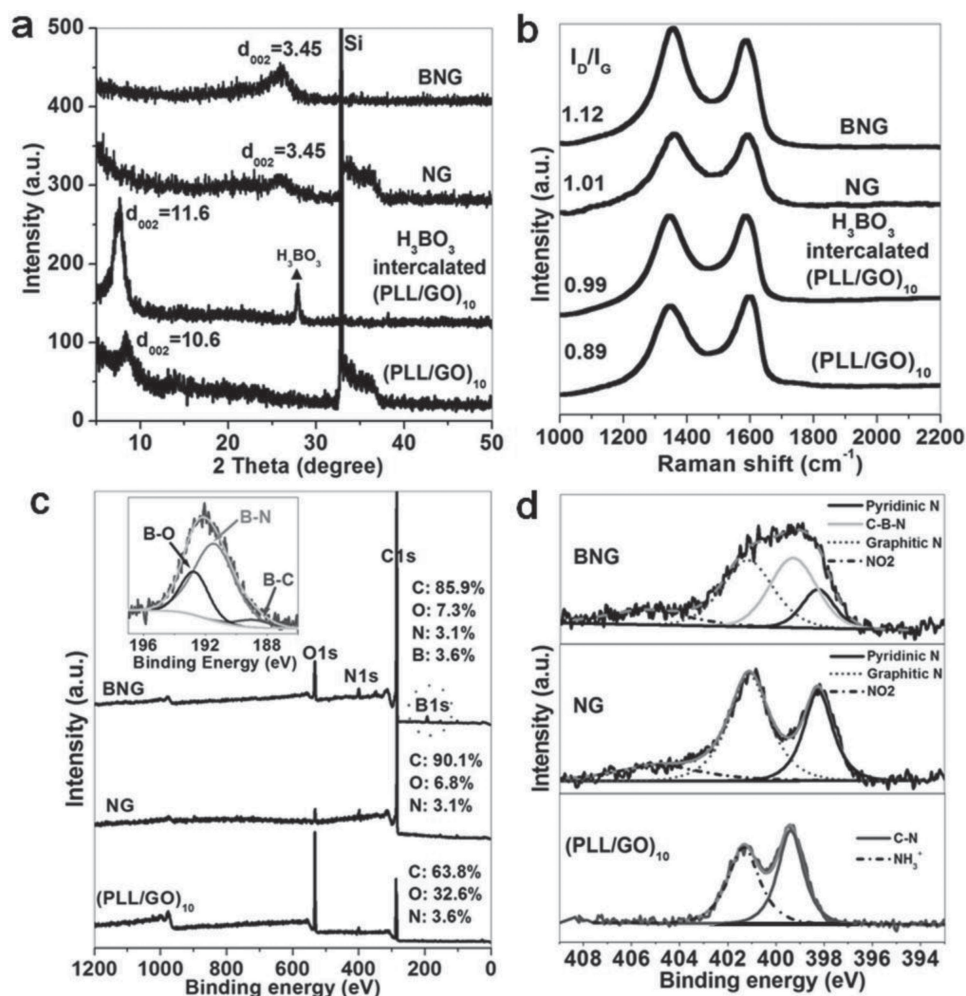


Figure 3. Structural characterization of BNG, NG, H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$, and $(\text{PLL}/\text{GO})_{10}$ films. (a) XRD patterns, (b) Raman spectra of BNG, NG, H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$, and $(\text{PLL}/\text{GO})_{10}$. (c) Overview XPS spectra (Inset: B1s XPS of BNG film) and (d) high-resolution N1s XPS spectra of BNG, NG, and $(\text{PLL}/\text{GO})_{10}$ films.

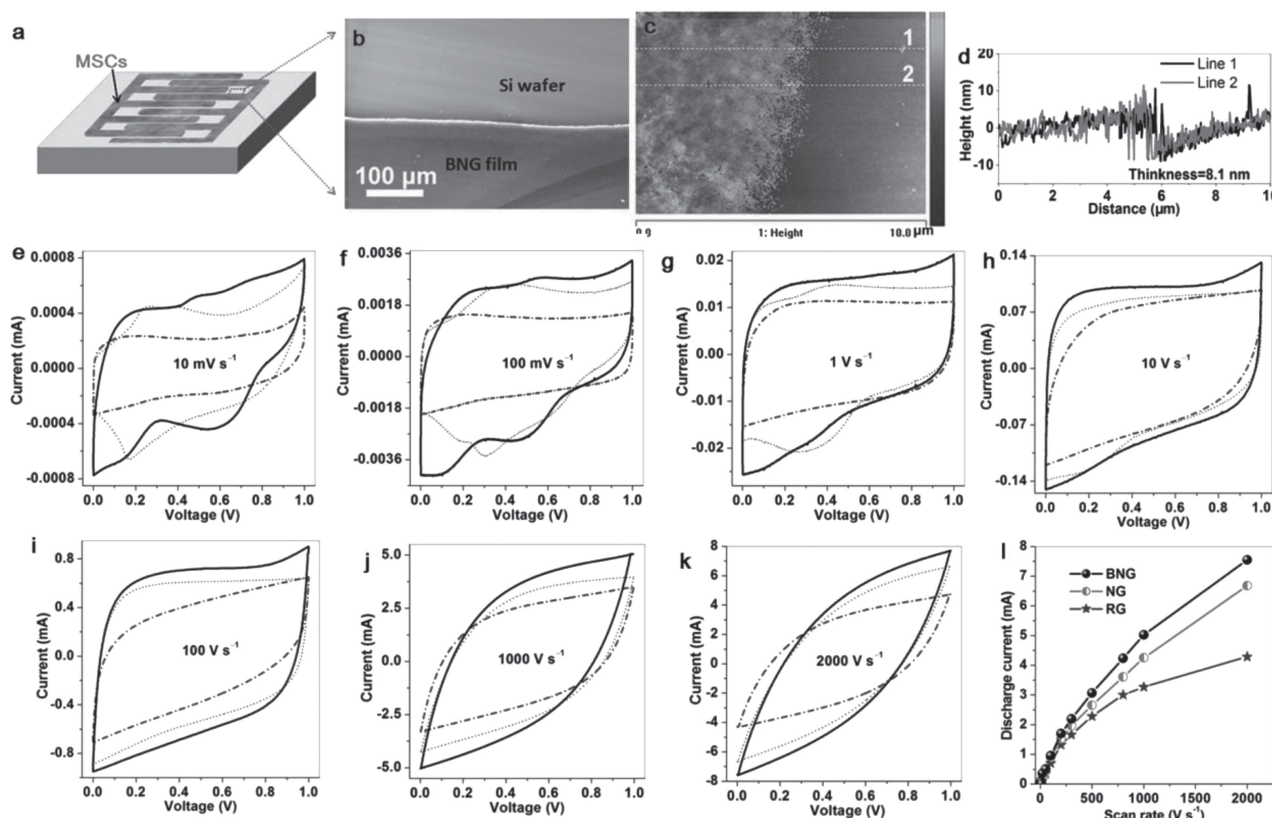


Figure 4. Electrochemical comparison of BNG-MSCs, NG-MSCs, and RG-MSCs. (a) Scheme of all-solid-state BNG-MSCs on a silicon wafer. (b) SEM image of the finger edge of a BNG film. (c) AFM image and (d) height profile of a BNG film (with a thickness of ~ 8.1 nm) annealed from a H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$ film. (e–k) CV curves of BNG-MSCs (black lines), NG-MSCs (gray, short dot lines), and RG-MSCs (dark gray, short dash dot lines) obtained at different scan rates of (e) 0.01, (f) 0.1, (g) 1, (h) 10, (i) 100, (j) 1000, and (k) 2000 V s^{-1} . (l) Plot of the discharge current as a function of the scan rate for BNG-MSCs, NG-MSCs, and RG-MSCs.

is presented in Figure S9. The decreased thickness of the film after heat treatment can be attributed to the removal of oxygen-containing groups on GO and decomposition of the PLL (and H_3BO_3) precursor within the graphene nanosheets (Figure S10).

XRD patterns (Figure 3a) after thermal annealing revealed the (002) diffraction peak of both NG and BNG films at around 25.8° , with a d-spacing of 3.45 Å. This value is slightly larger than that of graphite (3.35 Å), and is likely due to the decomposition of PLL (and H_3BO_3) incorporated as micropore fillers and the residual oxygenated groups on GO remaining between the layers.

The Raman spectra showed broad D and G bands, located at 1349 and 1600 cm^{-1} for $(\text{PLL}/\text{GO})_{10}$ film, 1347 and 1586 cm^{-1} for H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$ film, 1361 and 1593 cm^{-1} for NG film, and 1359 and 1589 cm^{-1} for BNG film, respectively (Figure 3b). The I_D/I_G ratio increased from 0.89 for $(\text{PLL}/\text{GO})_{10}$ film to 1.01 for NG film, and from 0.99 for H_3BO_3 -intercalated $(\text{PLL}/\text{GO})_{10}$ film to 1.12 for BNG film. The increased I_D/I_G ratio for NG and BNG after thermal treatment can be attributed to the heteroatom doping that produces new defective sites in the sp^2 carbon frameworks.^[46–49]

X-ray photoelectron spectroscopy (XPS) was used to probe the chemical composition of the BNG and NG films (Figure 3c,d, Figure S11). The BNG film exhibited a doping content of 3.1 at% for nitrogen and 3.6 at% for boron, respectively. NG film also showed a comparable nitrogen doping content of 3.1

at%. Given that the $(\text{PLL}/\text{GO})_{10}$ film contained only ~ 3.6 at% nitrogen moieties, the doping level of heteroatoms for BNG and NG films achieved after thermal annealing is quite remarkable. This result suggests that confinement of nitrogen and boron precursors within the assembled GO films is responsible for the efficient doping process. High-resolution C1s XPS spectra revealed that the intensities of oxygen-containing groups at 286.6 (C–O), 287.3 (C=O), and 288.2 eV (O=C–O) dramatically decreased and new bonds (like C–N, N–C=O) appeared after annealing (Figure Figure S11).^[50,51] The C/O ratios of ~ 13.3 for NG film and ~ 11.8 for BNG film confirmed the restoration of the sp^2 -hybridized carbon lattices. The N1s XPS spectrum of $(\text{PLL}/\text{GO})_{10}$ film can be fitted to two distinct peaks at 399.5 and 401.3 eV (Figure 2d), which originate from the C–N (N–C=O) and NH_3^+ groups of PLL, respectively.^[52] After thermal annealing, the high-resolution N1s scan of NG film indicated the presence of multiple forms of nitrogen-containing moieties, that is, pyridinic N (398.3 ± 0.1 eV), graphitic N (401.3 ± 0.1 eV), and NO_2 (405.3 ± 0.1 eV).^[46,53–55] For the BNG film, a new C–B–N peak (399.2 eV) was clearly identified in the N1s spectrum.^[47] In the B1s XPS spectrum for BNG film (inset in Figure 3c), three bonds of B–C (189.0 eV), B–N (191.5 eV) and B–O (192.8 eV) can be unraveled.^[56–58] Energy dispersive X-ray (EDX) spectra and mapping analysis further confirmed the uniform co-doping of the nitrogen and boron moieties into the

BNG film (Figure S12). The measured electrical conductivity of BNG and NG films was ~ 230 and ~ 276 S/cm, respectively, highlighting the efficient reduction of the graphene films.

Next, all-solid-state planar MSCs were fabricated based on doped graphene films (Figure 4a). The fabrication scheme of the MSCs is presented in Figure 1f-g, which includes lithographic micro-patterns and deposition of a gold layer on the surface of BNG or NG film, oxygen plasma etching for removal of the exposed graphene area, drop-casting of the H_2SO_4 /polyvinyl alcohol (H_2SO_4 /PVA) gel electrolyte,^[47] and solidification of the gel electrolyte. The corresponding MSCs based on BNG and NG films were named BNG-MSCs and NG-MSCs, respectively (see details in Supporting Information). SEM and AFM images of the patterned BNG films revealed a relatively smooth edge along the fingers (Figure 4b-d).

The electrochemical performance of BNG-MSCs and NG-MSCs was first examined by cyclic voltammetry (CV) at scan rates ranging from 0.01 to 2000 V s^{-1} (Figure 4e-k). To highlight the critical role of heteroatom doping, we also fabricated planar MSCs based on reduced graphene (RG) film (denoted RG-MSCs, thickness of ~ 8.0 nm) without heteroatom doping. The CV curves of RG-MSCs are shown in Figure 4e-k for comparison. At low scan rates from 10 to 100 mV/s (Figure 4e, f),

both BNG-MSCs and NG-MSCs exhibited a large capacitive response, accompanied by strong redox peaks, indicative of the presence of a pseudocapacitive effect with heteroatom-doping.^[47] In contrast, RG-MSCs exhibited a typical electric double-layer capacitive behaviour with a nearly rectangular CV shape.^[59–61] Furthermore, BNG-MSCs had a greater capacitive response than NG-MSCs, suggesting that boron and nitrogen have synergistic doping effects.^[47,62] At high scan rates, BNG-MSCs also had a larger integration area (Figure 4g-k) and higher discharge current (Figure 4l) than NG-MSCs and RG-MSCs, confirming that co-doping indeed greatly improved the capacitive performance.^[47,62] Remarkably, BNG-MSCs allowed for operation at an ultrahigh scan rate of up to 2000 V s^{-1} (Figure 4k,l), which is three orders of magnitude higher than that of conventional supercapacitors and represents the highest value for a high-power MSCs reported to date (Table S1).

The volumetric capacitance of BNG, NG, and RG films for MSCs as a function of scan rate is compared in Figure 5a. Notably, the volumetric capacitance of BNG film for MSCs recorded at 10 mV/s was ~ 488 F cm^{-3} , higher than that of NG (~ 245 F cm^{-3}) and much higher than that of RG (~ 245 F cm^{-3}). The enhanced performance of the BNG-MSCs is likely due to the following: (1) co-doping with dual heteroatoms probably

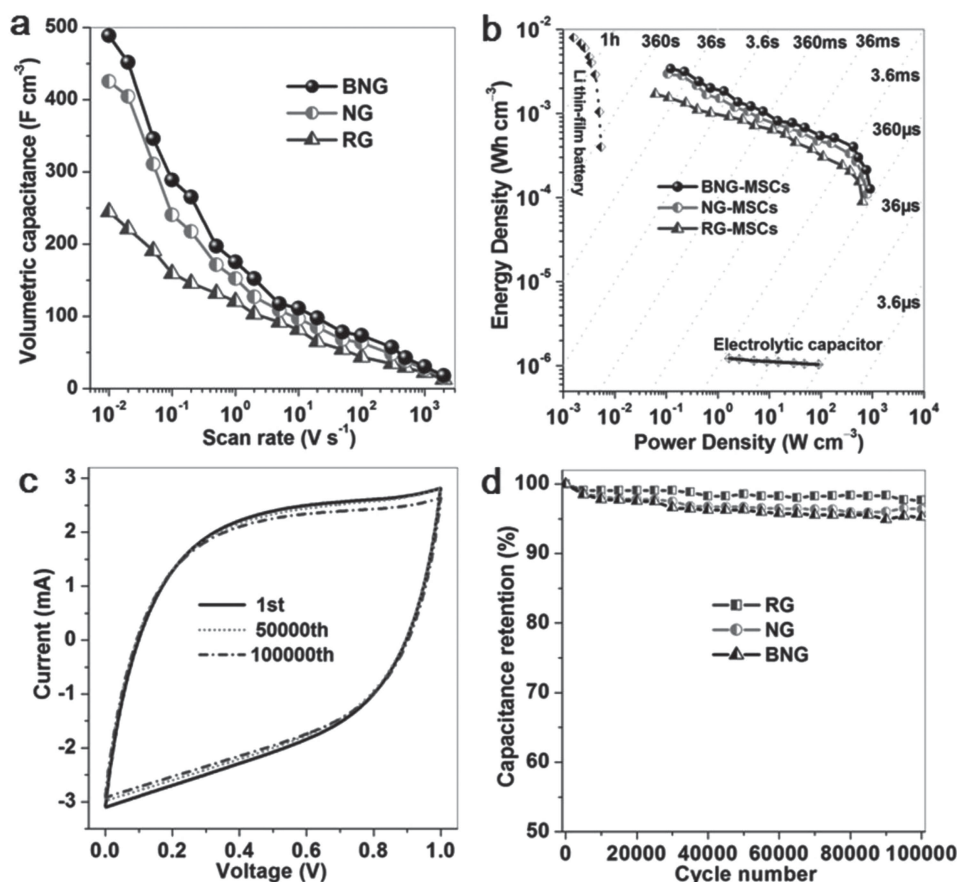


Figure 5. Electrochemical characterization of BNG-MSCs, NG-MSCs, and RG-MSCs. (a) Comparison of the volumetric capacitance of BNG, NG, and RG films for MSCs. (b) Ragone plot of BNG-MSCs, NG-MSCs, and RG-MSCs in comparison with lithium thin-film batteries ($4\text{V}/500\ \mu\text{Ah}$)^[2] and an electrolytic capacitor ($3\text{V}/300\ \mu\text{F}$).^[31] (c) The 1st, 50000th, and 100000th CV curves of BNG-MSCs measured at 500 V s^{-1} . (d) Cycling stability of BNG-MSCs, NG-MSCs, and RG-MSCs.

creates new electrochemically active moieties (e.g., B-N-C) with a synergistic effect that provides additional pseudocapacitance contributions;^[47–49,63] and (2) the new binding environment of neighboring B and N atoms directly incorporated into the graphene lattice is favorable for improving the interface wettability of the electrode with the electrolyte, resulting in a thickened electrochemical double layer.^[47,57,62]

The energy and power densities were estimated on the basis of the CV measurements of MSCs (Figure 5b). Based on the above-described volumetric capacitance and working voltage (1.0 V), the energy density $E_{\text{electrode}}$ and power density $P_{\text{electrode}}$ were calculated to be ~ 16.9 mWh/cm³ and ~ 4560 W/cm³ for BNG film, values higher than those of a NG film (14.7 mWh/cm³ and 3960 W/cm³) and a RG film (8.5 mWh/cm³ and 3220 W/cm³). By taking into account the whole volume of a packaged MSC,^[2,3,7] a remarkable energy density E_{device} of ~ 3.4 mWh/cm³ for BNG-MSCs was achieved, comparable to that of high-energy lithium thin-film batteries (1–10 mWh/cm³).^[2] More importantly, BNG-MSCs delivered a maximum power density P_{device} of ~ 910 W/cm³, which is much higher than that of reported MSCs (~ 495 W/cm³, Table S1),^[7] and comparable to that of high-power electrolytic capacitors (10¹–10³ W/cm³).^[31] The cycling stability of BNG-MSCs was demonstrated for 100000 cycles at a scan rate of 500 V s⁻¹ (Figure 5c,d). The CV shapes (Figure 5c) and $\sim 95.2\%$ of the initial capacitance (Figure 5d) were maintained, indicating the superior cycling stability.

In summary, we demonstrated an efficient LBL self-assembly and intercalation protocol for constructing large-area, ultrathin, uniform heteroatom-doped graphene films. The fabricated MSCs based on a boron and nitrogen co-doped graphene film exhibited a remarkable pseudocapacitive behavior with an ultrahigh volumetric capacitance of ~ 488 F/cm³, and an outstanding rate capability of up to 2000 V/s. The described LBL fabrication provides the opportunity to incorporate metal or metal oxide nanostructures into doped-graphene films, which hold great potential for other thin-film energy storage and conversion devices, such as metal-free electrocatalysts for oxygen reduction reactions in fuel cells^[54] and lithium battery applications.^[64]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. The authors thank G. Gläßer for the kind help with SEM and EXD measurements.

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