

Three-Dimensional Nitrogen and Boron Co-doped Graphene for High-Performance All-Solid-State Supercapacitors

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The supercapacitor is one important energy-storage device since it can deliver orders of magnitude higher power density, cycle efficiency, and charge/discharge rates than a battery.^[1–4] In particular, all-solid-state supercapacitors (ASSSs) have gained worldwide attention as an emerging candidate for smart and efficient energy-storage devices^[5–12] due to the increasing demand for wearable and miniaturized electronics. ASSSs have been demonstrated to deliver high power density and unlimited cycle life at fast charge/discharge processes.^[5–7,13] Nanostructured carbon materials, such as onion-like carbon,^[11] carbide-derived carbon,^[12] carbon nanotubes (CNTs),^[14–17] and graphene,^[6,7,10,18,19] possess notable features including high surface area, high electrical conductivity, and good chemical stability, and therefore they have been widely explored as thin-film electrode materials for ASSSs. However, the fabrication of ASSSs generally involves complex solution processing, high-pressure pressing, high-temperature sintering, and sputtering techniques.^[11,12,14–17] Moreover, polymer binders and conductive additives are required to enhance the adhesion between electrode materials and substrates as well as to improve the conductivity of the electrode, which unavoidably leads to decreased energy density of the devices.^[6,20] Therefore, several challenges remain in developing ASSSs, such as to: i) explore high-performance electrode materials, ii) enhance the interfacial compatibility between electrode and solid-state electrolyte, and iii) simplify the device fabrication process.

Graphene aerogels (GAs) represent a new class of ultralight and porous carbon materials that are associated with high

strength-to-weight and surface-area-to-volume ratios.^[21–24] More importantly, monolithic GAs^[21,25,26] consisting of 3D porous frameworks can provide multidimensional electron transport pathways, easy access to the solid-state electrolyte, and minimized transport distances between bulk electrode and electrolyte.^[27–30] These features strongly suggest that GAs can be qualified for use as additive/binder-free electrodes, which simplify the whole device manufacture in ASSSs.

In this work, we demonstrate a simplified prototype device of high-performance ASSSs based on three-dimensional (3D) nitrogen and boron co-doped monolithic graphene aerogels (BN-GAs). The device possesses an electrode-separator-electrolyte integrated structure, in which the GAs serve as additive/binder-free electrodes and a polyvinyl alcohol (PVA)/H₂SO₄ gel as solid-state electrolyte and thinner separator. The nitrogen and/or boron doping in carbon networks can facilitate charge transfer between neighboring carbon atoms and thus enhance the electrochemical performance of carbon-based materials.^[18,31–33] The as-prepared GAs show 3D interconnected frameworks with a macroporous architecture, which are favorable for ion diffusion and electron transport in bulk electrode. Further, monolithic BN-GAs can be easily processed into thin electrode plates with a desirable size upon physical pressing. As a consequence, the resulting BN-GAs based ASSSs exhibit not only minimized device thickness, but also show high specific capacitance ($\approx 62 \text{ F g}^{-1}$), good rate capability, and enhanced energy density ($\approx 8.65 \text{ W h kg}^{-1}$) or power density ($\approx 1600 \text{ W kg}^{-1}$) with respect to undoped (U-GAs), nitrogen doped (N-GAs), boron doped (B-GAs) GAs, or layer-structured graphene paper^[34] (GP, see Experimental Section).

Figure 1a illustrates the synthesis of BN-GAs using graphene oxide (GO)^[35–37] and ammonia boron trifluoride (NH₃BF₃) as precursors via hydrothermal reaction and freeze-drying processes (see Experimental Section). The GO nanosheets in the aqueous dispersion range in size from hundreds nanometers to several micrometers (Figure 1b,c). For comparison, U-GAs, N-GAs and B-GAs with the same doping content were also fabricated, employing dicyandiamide and boric acid as nitrogen and boron source, respectively (see Experimental Section). The size and shape of aerogel monoliths can be easily adjusted by controlling the concentration of GO, time and temperature of hydrothermal treatment, as well as the shape of used vials (Figure 1d).

The 3D morphology of as-prepared BN-GAs was confirmed by scanning electron microscopy (SEM) characterization.

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DOI: 10.1002/adma.201201948

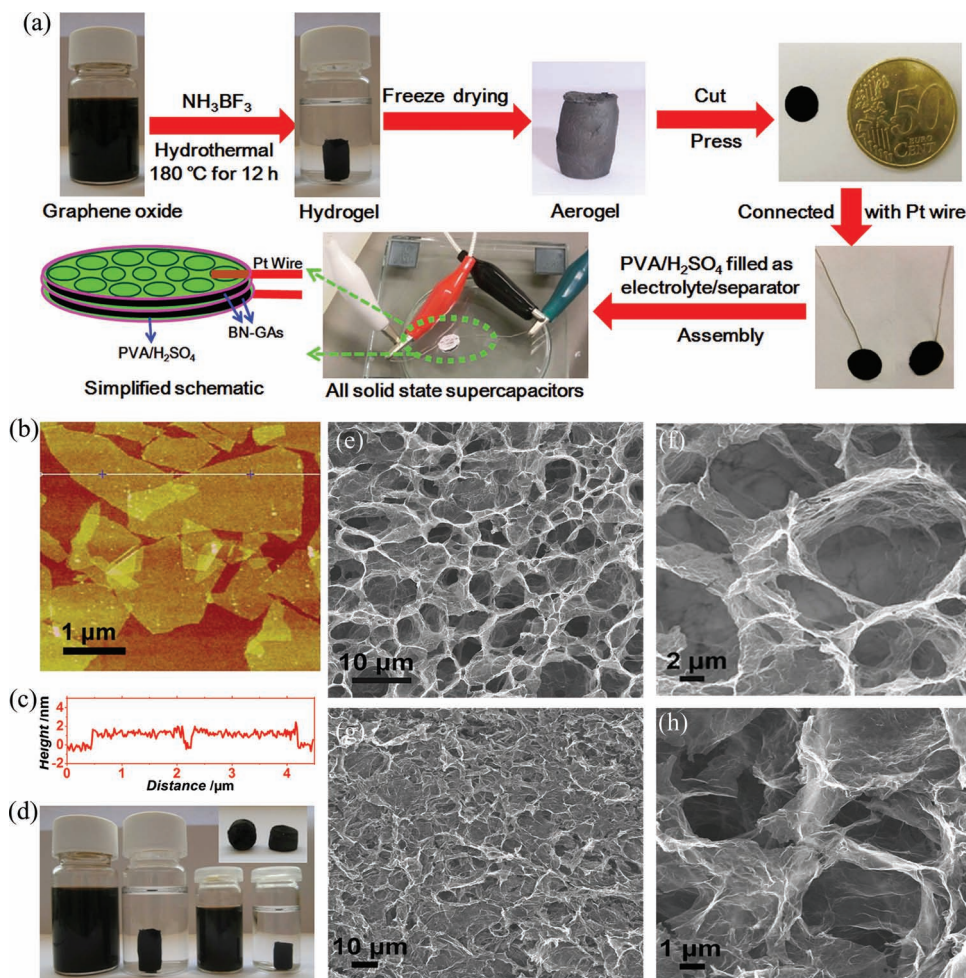


Figure 1. a) Fabrication illustration of ASSSs based on BN-GAs that were involved by a combined hydrothermal process and freeze-drying process. The as-fabricated supercapacitors with a diameter of 7 mm indicated by the dotted green ring and a simplified schematic of ASSSs based on aerogels are shown (below left). b) AFM image and c) the corresponding height profile of the GO used, with thickness of ≈ 1 nm. d) Digital images of two pairs of GO solutions with different volumes in the vials and N/B co-doped graphene hydrogels before and after hydrothermal self-assembly. Inset: digital images of the BN-GAs obtained after freeze-drying. e) Low- and f) high-magnification SEM images of the as-prepared BN-GAs. g) Low- and h) high-magnification SEM images of the as-prepared BN-GAs as binder/additive-free electrode upon physical pressing.

As displayed in Figure 1e, an interconnected framework of ultrathin graphene nanosheets with porous structure can be discerned (Figure S1, Supporting Information). The pore size is ranging from a few hundred nanometers to several micrometers (Figure 1e,f). A similar morphology can be observed for U-GAs, N-GAs and B-GAs (Figure S2). In contrast, GP shows a layer-by-layer stacked structure of graphene sheets (Figure S3). Nitrogen adsorption-desorption analysis reveals a typical Brunauer–Emmett–Teller (BET) surface area of up to $249.0 \text{ m}^2 \text{ g}^{-1}$ for BN-GAs. The isotherm curve exhibits an type-IV behavior with pronounced adsorption, indicating the existence of a large number of mesopores and macropores in GAs (Figure S4).

The nature of the doping in the BN-GAs can be unraveled by the elemental mapping images of carbon, nitrogen, and boron in the sheets (Figure 2a–d). As expected, a homogeneous heteroatom doping in graphene was realized (Figure 2c,d). X-ray photoelectron spectroscopy (XPS) further reveals that significant

contents of nitrogen ($\approx 3.0\%$ atomic percent) and boron ($\approx 0.6\%$ atomic percent) are incorporated in BN-GAs (Figure 2e–g). The asymmetric N1s XPS peak of BN-GAs (Figure 2f) can be fitted to four peaks of pyridinic N (398.1 eV), pyrrolic N (400.1 eV), graphitic N (401.3 eV) and C–N–B (399.2 eV).^[18,31,38,39] Two peaks of B1s XPS spectra can be identified (Table S1). In addition, three distinguishable peaks (285.1 eV, 289.0 eV, and 289.9 eV) in the C 1s spectrum (Figure 2e) correspond to the chemical environment of carbon atoms bonded to carbon, nitrogen and boron in graphene.^[40] Raman spectra further provide additional evidence of the introduction of N and/or B atoms into graphene layer of GAs. With respect to the U-GAs, the upshift of D and G bands as well as increased I_D/I_G ratio of doped GAs (N-GAs, B-GAs and BN-GAs) were observed (Figure S5).^[31,41]

Cyclic voltammetry (CV) was employed to probe the electrochemical behavior of U-GAs, N-GAs, B-GAs, BN-GAs and layer-structured GP electrodes in 1.0 M aqueous H_2SO_4 electrolyte

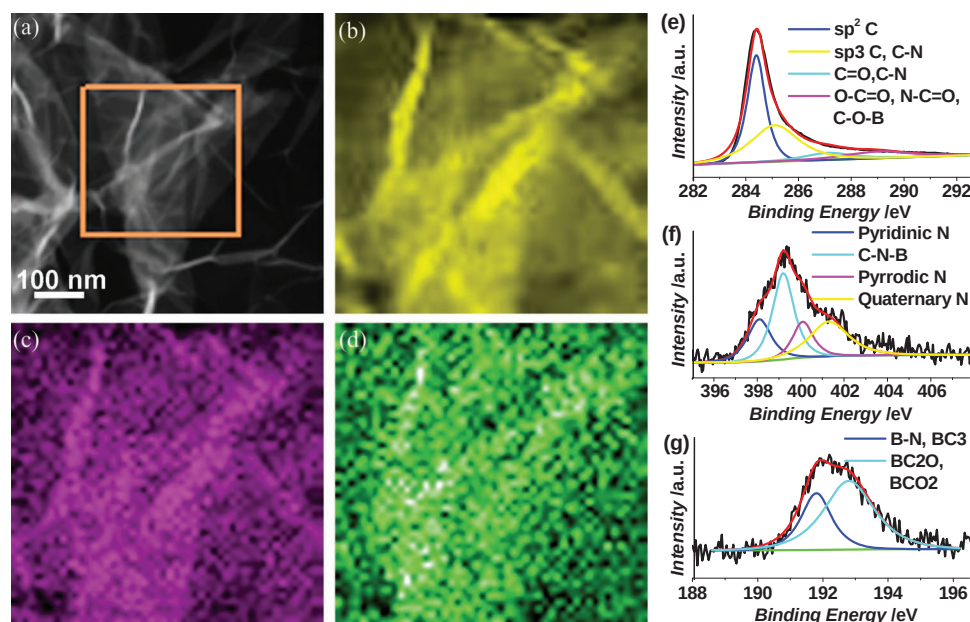


Figure 2. a) Scanning transmission electron microscopy (STEM) image and b) carbon, c) boron, and d) nitrogen element mapping images of BN-GAs taken in the square region in Figure 2a. e) C1s, f) N1s, and g) B1s XPS spectra of BN-GAs.

at potential interval from 0 to 0.8 V vs. saturated calomel electrode (SCE) in the three-electrode system (Figure 3). Aerogel monoliths were directly fabricated as binder/additive-free working electrodes by cutting the GAs into small thin round slices with a thickness of ≈ 1 mm and processing into these slices into thinner electrodes upon pressing (Figure 1a). Interestingly, the graphene nanosheets in aerogels became flat, compacted and crumpled after pressing, but the 3D continuous frameworks could be maintained (Figure 1g,h). Figure 3a shows the CV curves of different graphene electrodes at a low scan rate. It can be discerned that all GAs electrodes reveal a larger capacitive response than the layered GP electrode. Specifically, at a scan rate of 1 mV s^{-1} , the specific capacitance of U-GAs is about 181 F g^{-1} , while that of GP is 142 F g^{-1} . This result implies that GA monoliths enable fast electron and ion transport along all 3D directions, rather than normal to the layers as is seen for GP electrode. Furthermore, both N-GAs (190 F g^{-1}) and B-GAs (228 F g^{-1}) exhibit more pseudocapacitance contribution than that of U-GAs, indicating that heteroatom doping enhances the electrochemical activity of graphene materials.^[18] Additionally, strong synergetic effects of nitrogen and boron co-doping could be observed, which show further increased electrochemical activity and pseudocapacitance contribution (Figure 3a).^[41–43] Notably, the specific capacitance (239 F g^{-1}) for BN-GAs is superior to the reported values for pure graphene electrodes ($\approx 135\text{--}205 \text{ F g}^{-1}$) with binder and additive in aqueous electrolyte,^[44–46] graphene hydrogel (175 F g^{-1}),^[21] graphene-cellulose paper (120 F g^{-1}),^[19] and CNT buckypaper ($\approx 25\text{--}90 \text{ F g}^{-1}$)^[47,48] electrodes for supercapacitors. Moreover, the obtained capacitance also exceeds that of graphene/polyaniline composite paper (233 F g^{-1})^[34] and film (210 F g^{-1})^[49] electrodes for pseudocapacitors.

At the higher scan rate of 100 mV s^{-1} , specific capacitances of 132, 131, 115, 66, and 36 F g^{-1} could be retained for BN-GAs, N-GAs, B-GAs, U-GAs and GP, respectively (Figure 3b,c). Figure 3d further demonstrates that all of the doped GAs exhibit excellent cycling stability with close to $\approx 100\%$ capacitance retention. In contrast, $\approx 86.9\%$ of the initial capacitance was maintained for GP (Figure 3d). This result emphasizes that 3D graphene monoliths allow for a large strain accommodation from ion insertion/removal process.^[21,25]

Given their remarkable electrochemical performance, prototype ASSSs based on U-GAs, N-GAs, B-GAs and BN-GAs were built with an electrode-separator-electrolyte integrated structure. First, two thin aerogel slices, after cutting and pressing, were attached to Pt wires using a silver paste glue. Afterwards, the electrodes were directly immersed into hot PVA/ H_2SO_4 gel (80°C), which serves as both the solid-state electrolyte and thinner separator. Finally, the electrolyte-filled electrodes were solidified at room temperature and integrated into a single device (Figure 1a). It should be mentioned that the solid-state electrolyte can be easily impregnated into porous aerogel, and in that way, the thickness of the entire device can be minimized.^[5,7]

The electrochemical behavior of as-fabricated ASSSs was investigated by means of CV (Figure 4a–d). In contrast to the three-electrode system, no apparent redox peaks of ASSSs were observed in the two-electrode system (Figure 4a–d, Figure S6). The specific capacitances for these graphene-based ASSSs are compared in Figure 4e. At a scan rate of 5 mV s^{-1} , BN-GAs, U-GAs, N-GAs, B-GAs and GP deliver specific capacitances of 62, 43, 52, 55, and 29 F g^{-1} , respectively, based on the active materials mass of two electrodes. Again, the remarkable performance of BN-GAs can be attributed to the unique structural

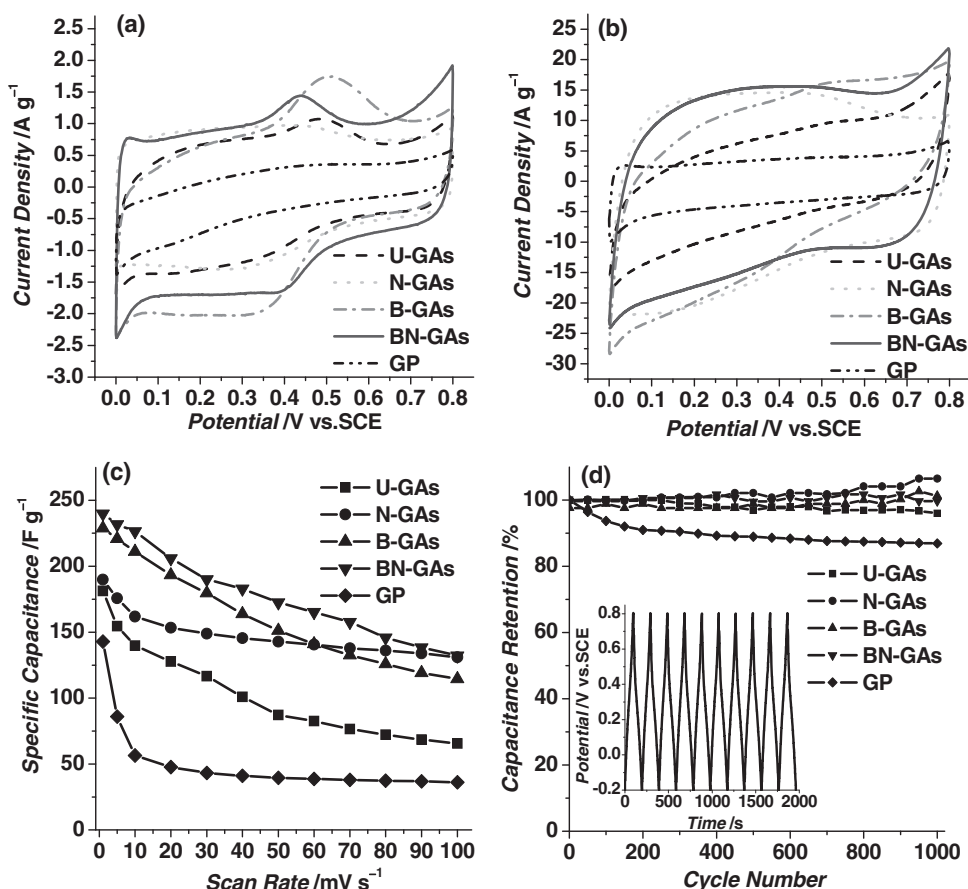


Figure 3. a) CV curves of U-GAs, N-GAs, B-GAs, BN-GAs, and GP electrodes measured at a low scan rate of 5 mV s⁻¹. b) CV curves of U-GAs, N-GAs, B-GAs, BN-GAs, and GP electrodes measured at a high scan rate of 100 mV s⁻¹. c) Specific capacitance of U-GAs, N-GAs, B-GAs, BN-GAs, and GP electrodes as a function of scan rate. d) Comparison of the cycling stability of U-GAs, N-GAs, B-GAs, BN-GAs, and GP electrodes. Inset is the charge-discharge profile of BN-GAs at 2 A g⁻¹.

feature of the aerogels and the synergistic effects of B and N co-doping.^[41–43] Further, high rate capability was obtained for BN-GAs (Figure 4e, Figure S6), with a specific capacitance of 26.2 F g⁻¹ at 100 mV s⁻¹, which is significantly larger than that of U-GAs (21.2 F g⁻¹), N-GAs (21.7 F g⁻¹), B-GAs (21.3 F g⁻¹), and GP (6.5 F g⁻¹). The power density and energy density of ASSSs were calculated by integrating the CV curves at different rates based on the Ragone plot (Figure 4f). Remarkably, a high energy density of ≈8.7 W h kg⁻¹ for BN-GAs was attained, in contrast N-GAs, B-GAs, U-GAs and GP showed lower values of ≈7.2, ≈7.7, ≈5.9 and ≈4.1 W h kg⁻¹, respectively. Power densities of approximately 1650, 1600, 1580, 1490, and 400 W kg⁻¹ were determined for BN-GAs, N-GAs, B-GAs, U-GAs and GP respectively, at less than 3.6 s. We believe that the device performance can be further improved by tailoring the content of dopants, involving additional active components in GAs, and applying organic or liquid electrolytes in devices.

In conclusion, we have demonstrated a novel prototype device of ASSSs with an electrode-separator-electrolyte integrated structure based on 3D monolithic GAs. Aerogels built of well-interconnected ultrathin graphene sheets can provide high surface area, 3D macroporosity and high electrical conductivity,

which are favorable for enhancing solid-state ion and electron transport in supercapacitors. To the best of our knowledge, such a type of simplified ASSSs has not been reported. Monolithic GAs materials may have the potential for other efficient, light, minimized energy-storage devices.

Experimental Section

Synthesis of BN-GAs: GO was prepared from natural graphite flakes using a modified Hummers method, the details of which were described elsewhere.^[35–37] BN-GAs was prepared by a combined hydrothermal assembly and freeze-drying process. In a typical procedure, a 10 mL GO (1.5 mg mL⁻¹) aqueous dispersion containing 1.2 mmol ammonia boron trifluoride (NH₃BF₃) was first treated by sonication for 5 min. The resulting stable suspension, sealed in a Teflon-lined autoclave, was hydrothermally treated at 180°C for 12 h. Finally, the as-prepared sample was freeze-dried overnight, followed by vacuum drying at 60 °C for several hours. For comparison, the U-GAs, N-GAs and B-GAs were also prepared using the same procedure with the addition of the appropriate dopants as needed. For example, dicyandiamide (C₂H₄N₄) and boric acid (H₃BO₃) were employed for N-GAs and B-GAs, respectively. GP can be readily fabricated by vacuum filtration of stable black reduced graphene supernatant in N-methylpyrrolidone, followed by air drying and peeling from the filter.^[34]

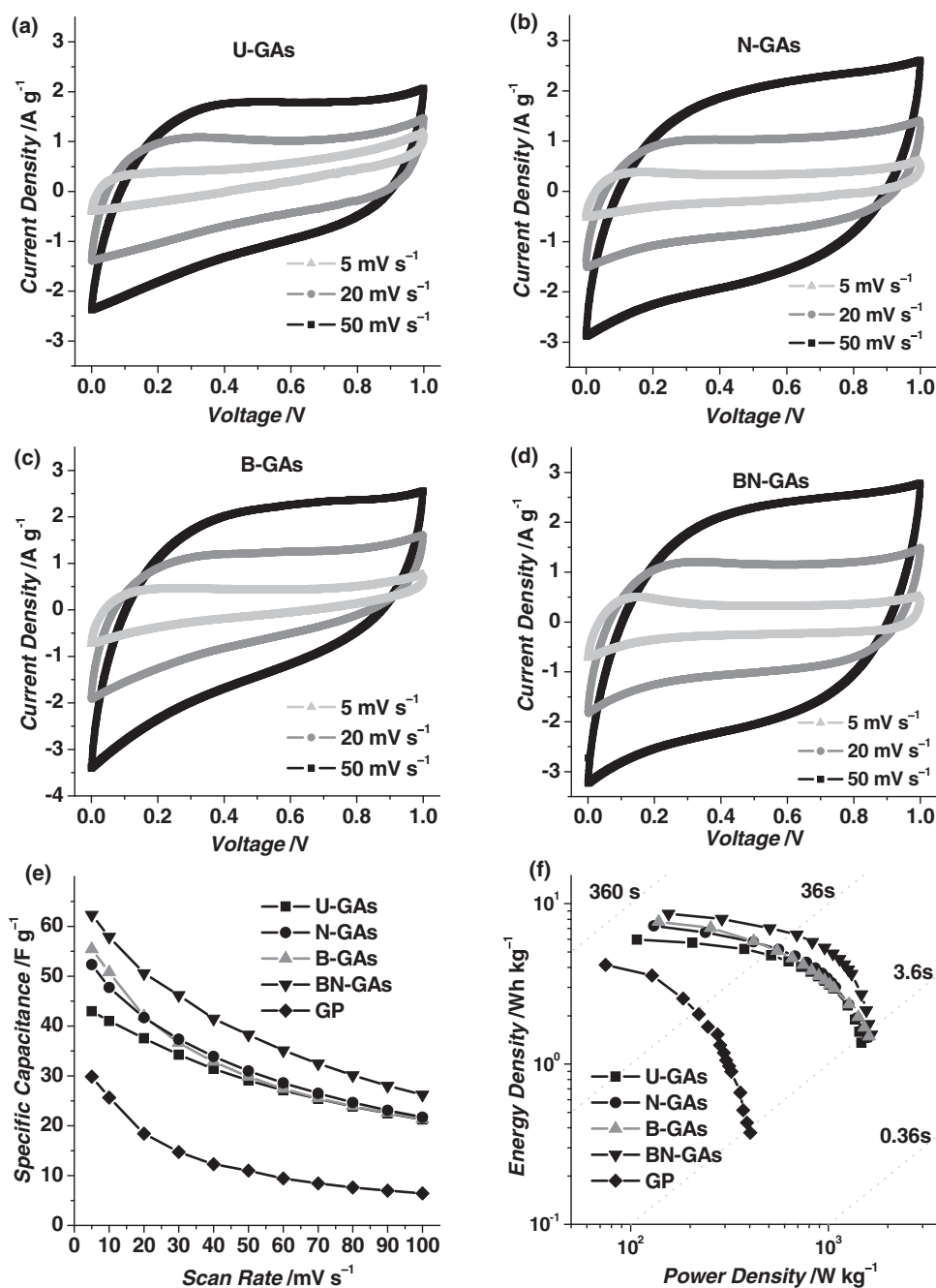


Figure 4. a–d) CVs of a) U-GAs, b) N-GAs, c) B-GAs and d) BN-GAs based ASSSs measured at the scan rates of 5, 20 and 50 mV s⁻¹. e) Specific capacitance of U-GAs, N-GAs, B-GAs, BN-GAs, and GP based ASSSs based on two-electrode mass as a function of scan rates from 1 to 100 mV s⁻¹. f) Ragone plot of ASSSs based on U-GAs, N-GAs, B-GAs, BN-GAs and GP, based on two-electrode mass of active materials.

Materials Characterization: All of the samples were characterized by SEM (Gemini 1530 LEO), STEM and element mapping (Philips Tecnai F20), atomic force microscopy (AFM) (Veeco Dimension 3100), Raman spectra (Bruker, 532 nm) and XPS (Omicron Multiprobe equipped with the monochromatic Al K source, electron analyzer resolution of 0.9 eV). Nitrogen adsorption and desorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA).

Electrochemical Measurements: Monolithic U-GAs, N-GAs, B-GAs and BN-GAs were cut into small slices with a thickness of about 1 mm and diameter of about 7–10 mm, and pressed into a flat thin electrode

upon physical pressing. Electrochemical measurements were carried out on an EG&G potentiostat/galvanostat Model 2273 instrument. In a three-electrode system, the cell was equipped with monolithic GAs or GP attached to a platinum mesh network as the working electrode, a platinum plate as the counter electrode and a SCE as a reference electrode, using 1 M H₂SO₄ as aqueous electrolyte. In the case of ASSSs, two slices of aerogel monoliths or GP were glued with a platinum wire by conducting silver paste, and then were immersed in a hot clear solution of PVA/H₂SO₄ gel electrolyte for 5 min. The gel electrolyte was fabricated by mixing 6 g H₂SO₄ and 6 g PVA in 60 ml deionized water

and thus heat up to 80°C for 1 h under vigorous stirring. The resulting electrolyte-filled electrodes were solidified for 12 h at room temperature. Finally, as-prepared two electrodes were symmetrically integrated into one ASSS under a pressure of about 5 MPa for 5 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the Max-Planck Society through the program ENERChem, DFG Priority Program SPP 1355, DFG MU 334/32-1, DFG Priority Program SPP 1459, and ESF Project GOSPEL (Ref Nr: 9-EuroGRAPHENE-FP-001), EU Project GENIUS, EU Project MOLESOL, BMBF LiBZ Project, and ERC grant on NANOGRAPH.

Received: May 15, 2012

Published online: July 16, 2012

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