

Bottom-Up, On-Surface-Synthesized Armchair Graphene Nanoribbons for Ultra-High-Power Micro-Supercapacitors

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ABSTRACT: Bottom-up-synthesized graphene nanoribbons (GNRs) with excellent electronic properties are promising materials for energy storage systems. Herein, we report *bottom-up-synthesized* GNR films employed as electrode materials for micro-supercapacitors (MSCs). The micro-device delivers an excellent volumetric capacitance and an ultra-high power density. The electrochemical performance of MSCs could be correlated with the charge carrier mobility within the differently employed GNRs, as determined by pump–probe terahertz spectroscopy studies.

The past decades have witnessed an urgent need for developing reliable, efficient, and eco-friendly approaches for energy storage systems (ESSs).^{1,2} Following the current trend of portable and wearable electronics, the demand for ultrathin, flexible, and powerful on-chip micro-scale ESSs has been growing rapidly.^{3–5} Among them, micro-supercapacitors (MSCs) with high charging/discharging rates, long cycle lives, high areal/volumetric capacitance, and high power densities have great potential to complement or even replace micro-batteries.^{6,7} The recently introduced graphene-based MSCs with planar interdigitated micro-electrodes combine the best of graphene's advantages, i.e., its large specific surface area and high intrinsic capacitance as well as excellent mechanical and electronic properties.^{8–13} Moreover, the open-edge-normalized capacitance of graphene-based electrode materials is higher than that of basal planes.^{14–17} In this regard, narrow graphene nanoribbons (GNRs), defined as nanometer-wide strips of graphene,^{18,19} are promising for MSC applications.

Recently, several *top-down* approaches have been demonstrated to fabricate GNRs, e.g., unzipping of carbon nanotubes,²⁰ photolithography patterning of graphene or graphene oxide,^{17,21,22} or activation of carbon nanorods from metal-organic frameworks.²³ However, it remains a formidable challenge to fabricate GNRs with well-defined width and edge structures via such top-down approaches.²⁴ In contrast, a *bottom-up* chemical approach allows for the synthesis of GNRs with precisely controlled width and edge structures in solution or on a metal surface.^{25–35} Solution-synthesized GNRs tend to aggregate and are difficult to process on different substrates,^{18,36} but the on-surface synthesis allows for the fabrication and transfer of GNR films onto an arbitrary substrate without the aggregation problem.^{34,35,37} While most of the previous on-surface syntheses of GNRs have been carried out under ultra-high-vacuum conditions, which limit the scalability of the synthesis, recent studies have demonstrated high-throughput, on-surface synthesis of GNRs using chemical vapor deposition (CVD).^{24,38–41} The CVD-grown $N = 9$ armchair GNRs showed high photoconductivity with

estimated intrinsic mobilities of $\sim 350 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³⁹ This result also marks the potential of GNRs as novel materials for electrochemical storage applications, where sufficiently high charge mobility is required.^{24,38,39} Nevertheless, the use of bottom-up-synthesized GNRs in ESSs has rarely been explored.

Herein, we report the unprecedented use of bottom-up-synthesized GNR films as MSC electrode materials. Armchair graphene nanoribbons (AGNRs) with three different widths (n -AGNRs, with $n = 5, 7,$ and 9 , indicating the width by the number of carbon atoms, see Figure 1b) were prepared by the CVD method and examined. Among the three AGNRs, we reveal that electrodes based on the narrowest 5-AGNR deliver

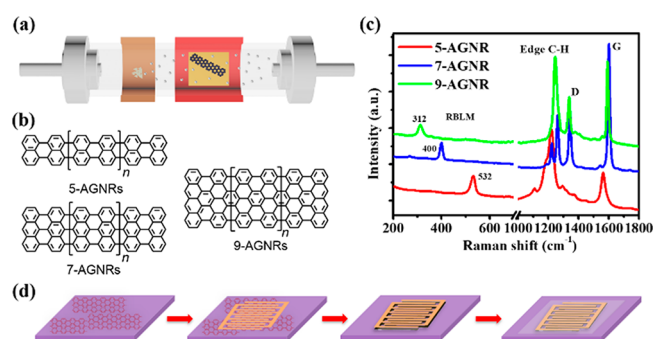
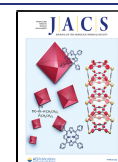


Figure 1. (a) Schematic illustration of the growth of AGNRs via CVD. (b) Molecular structures and (c) Raman spectra of 5-AGNR, 7-AGNR, and 9-AGNR. (d) Schematic illustration of the device fabrication of MSCs based on GNR films.

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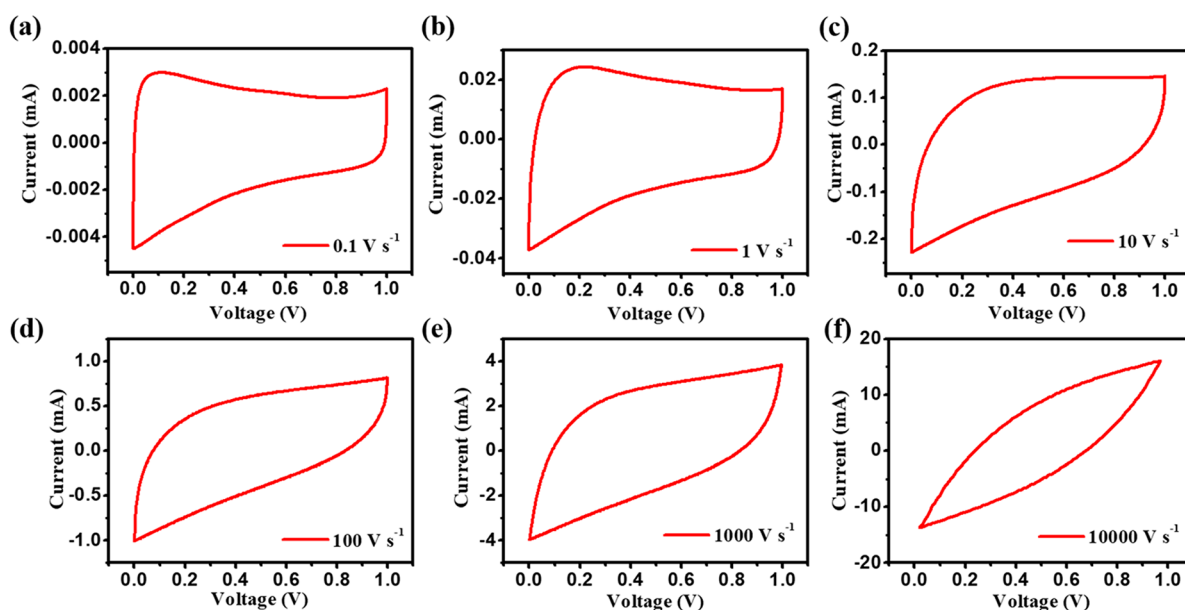


Figure 2. CV curves of a micro-supercapacitor based on 5 layers of 5-AGNR films, performed at different scan rates ranging from 0.1 to 10000 V s^{-1} , for a potential window from 0 to 1 V.

the highest MSC performance, with an excellent volumetric capacitance of 307 F cm^{-3} and an ultra-high power density of 2000 W cm^{-3} , outperforming most state-of-the-art MSCs based on graphene and other related nanomaterials. Furthermore, ultrafast terahertz (THz) spectroscopy analyses demonstrated the highest photoconductivity for 5-AGNR compared to those of 7- and 9-AGNRs, in excellent correlation with the MSC results. Such promising electrochemical performance suggests the high potential of GNRs as electrode materials for ESSs.

9-AGNR, 7-AGNR, and 5-AGNR films were prepared using an ambient-pressure CVD setup, following our previous reports (Figure 1a,b).^{38,39} These AGNRs belong to three different subfamilies of AGNRs with $N = 3n$, $3n+1$, and $3n+2$, respectively, having distinct bandgaps in the order of 5-AGNR < 9-AGNR < 7-AGNR.⁴² The formation of the AGNRs was verified by Raman spectroscopy, exhibiting the typical G, D, and C–H peaks (Figure 1c).^{24,38,39,43} Importantly, different AGNRs were identified on the basis of the characteristic radial breathing-like mode (RBLM), i.e., 532 cm^{-1} for 5-AGNR, 400 cm^{-1} for 7-AGNR, and 312 cm^{-1} for 9-AGNR.^{19,38,39,44,45} AGNR films thus grown on the Au/mica substrates were then transferred onto SiO_2/Si substrates through a lift-off process with the help of poly(methyl methacrylate) (PMMA) supporting layer.^{46,47} Analyses of a transferred 5-AGNR film by transmission electron microscopy (Figure S1), atomic force microscopy, and scanning electron microscopy (Figure S2) indicated homogeneous films with $\sim 1 \text{ nm}$ thickness. For the fabrication of all-solid-state MSCs with an in-plane device geometry, 5 layers of CVD-grown AGNR films were sequentially transferred onto SiO_2/Si substrates (Figure 1d), followed by gold deposition through shadow masks acting as current collectors (Figure S3). A $\text{H}_2\text{SO}_4/\text{poly}(\text{vinyl alcohol})$ ($\text{H}_2\text{SO}_4/\text{PVA}$) gel electrolyte was employed.

Thus-fabricated AGNRs-based MSCs were analyzed by cyclic voltammetry (CV) at different scan rates to evaluate the overall electrochemical performance (Figures 2, S4, and S5). The obtained CV curves suggest that these devices can be operated from 0.1 to 10000 V s^{-1} . Notably, the maximum

operating speed for such AGNRs-based MSCs was revealed to be 4 orders of magnitude higher than that of conventional supercapacitors based on sandwiched structures, and even 1 order of magnitude higher than that of state-of-the-art, high-power MSCs based on graphene or other carbon nanomaterials (Table S1). These results mark the ultrafast charging/discharging capabilities of the AGNRs-based MSCs.¹⁰ Between the voltage window of 0 and 1 V, the CV curves are all nearly rectangularly shaped, even at a very high scan rate of 1000 V s^{-1} . This indicates a pronounced electrical double-layer capacitance from the AGNRs with preserved electronic properties, which is inherent to their graphene structure. One of the major differences between the CV curves based on different AGNRs is the charge/discharge current values, where the 5-AGNR-based MSC is superior to those based on the other two AGNRs. Especially, at a scan rate of 0.1 V s^{-1} , a maximum volumetric capacitance of 307 F cm^{-3} is achieved based on a $\sim 5 \text{ nm}$ thick 5-AGNR film electrode (results for a MSC with a different film thickness are shown in Figure S6), whereas 180 F cm^{-3} is obtained based on 7-AGNR and 200 F cm^{-3} based on 9-AGNR with the same film thickness.

Figure 3a plots the evolution of the volumetric capacitance of the three AGNR electrodes-based MSCs at different scan rates. The general electrochemical performance regarding volumetric capacitance falls in the following sequence, 5-AGNR > 9-AGNR > 7-AGNR, which exceeding the performance of most state-of-the-art graphene and other carbon materials (Table S1) and comparable to the highest values reported to date, such as 359 F cm^{-3} based on electrophoretically deposited rGO,¹³ 180 and 410 F cm^{-3} based on carbide-derived carbon,^{48,49} and 582 F cm^{-3} based on sulfur-doped graphene.⁹ The excellent volumetric capacitance might be attributed to the higher density of edge structures of AGNRs, which allows faster ion transport and more storage charges.⁵⁰ These results illustrate the great potential of GNRs as material for efficient on-chip EESs. Furthermore, the MSCs all show $\sim 10\%$ capacitance retention over a wide operating rate of 0.1 – 1000 V s^{-1} . Such excellent rate capabilities are essential for powerful MSCs. Figure 3b suggests a nearly linear correlation

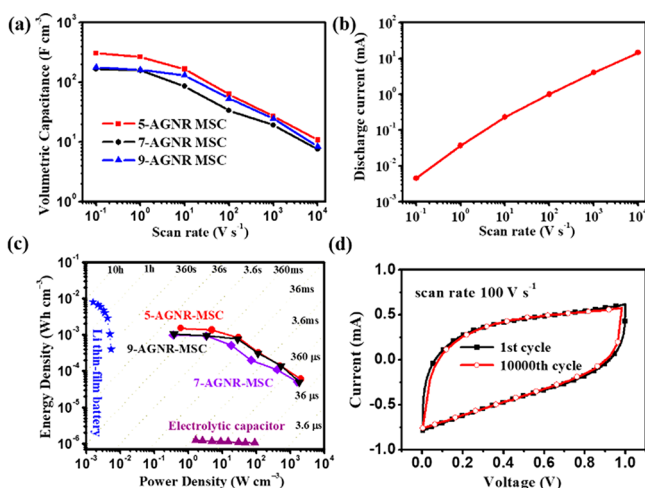


Figure 3. (a) Evolution of the volumetric capacitance versus scan rate based on 5 layers of 5-AGNR, 7-AGNR, and 9-AGNR films. (b) Discharge current of 5-AGNR-based MSC device as a function of scan rate. (c) Ragone plot of commercially available Li thin-film battery and electrolytic capacitor compared with different AGNR-based MSCs. (d) CV curves of the 1st and 10 000th cycles of a 5-AGNR-based MSC device, at a high operating speed of 100 V s^{-1} , showing capacitance retention over 95%.

between the logarithmic discharge current and scan rate from 0.1 to $10\,000 \text{ V s}^{-1}$, indicating the ultra-high-power delivery of 5-AGNR-based MSCs. Electrochemical impedance spectroscopy (EIS) of 5-AGNR MSCs is measured in a frequency range from 0.01 Hz to 100 kHz (Figure S7). The characteristics of low ESR and ultrasmall charge transfer resistance, as well as extremely short time constant, validate the excellent charge and discharge capability of the 5-AGNR MSCs.

A maximum power density of 2000 W cm^{-3} is achieved for the 5-AGNR-based MSC, larger than the values obtained for the other two AGNRs, namely 1600 W cm^{-3} for 7-AGNR and 1800 W cm^{-3} for 9-AGNR. Figure 3c shows the Ragone plot of the energy and power densities of MSCs based on the employed AGNRs. Compared with those of a commercially available lithium thin-film battery ($4 \text{ V}/500 \mu\text{Ah}$) and an aluminum electrolytic capacitor ($3 \text{ V}/300 \mu\text{F}$), the power density of AGNRs based MSCs is 2 orders of magnitude higher than that of conventional supercapacitors with sandwiched structures, and over 1 order of magnitude higher than that of aluminum electrolytic capacitors. Such comparisons with real-life ESSs clearly illustrate the huge potential of AGNRs-based MSCs, especially 5-AGNR. Meanwhile, the cycling stability study of 5-AGNR MSCs examined at a high operating speed of 100 V s^{-1} reveals capacitance retention over 95% after 10 000 cycles (Figure 3d), which further demonstrates the applicability of 5-AGNR MSCs.

To elucidate the role of electronic properties of GNRs on the MSC device performance, we employed THz spectroscopy to characterize the conductivity of photogenerated carriers in AGNRs.^{38,39} To this end, AGNR films were transferred on SiO_2 substrates, and charge carriers were optically generated in AGNRs by a laser pulse with $\sim 50 \text{ fs}$ duration and photon energy of 3.1 eV . This photon energy well exceeds the optical bandgaps of AGNRs used here (0.8 , 1.0 , and 1.6 eV for 5-, 9-, and 7-AGNRs, respectively) so that initially charge carriers appear as free carriers following photoexcitation. In the Supporting Information, we provide a detailed discussion on

the working principle of the THz spectroscopy. In Figure 4, we show the time-dependent THz conductivity σ of 5-AGNRs and

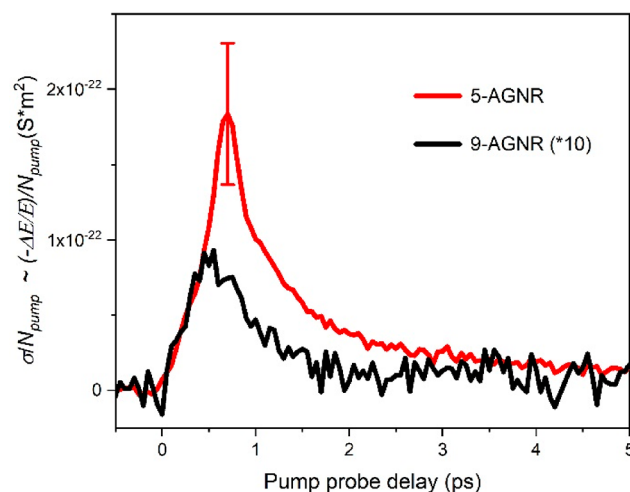


Figure 4. Photoconductivity σ due to 400 nm photoinjection of charge carriers, divided by the absorbed photon flux N_{pump} . The photoconductivity σ is proportional to the relative transmission change of the THz field $(-\Delta E/E)$ following photoexcitation. The conductivity of the 9-AGNR is scaled up by a factor of 10 for a better comparison to that of 5-AGNR. The root-mean-square variation of the peak conductivity was obtained from measurements at 6 different sample spots (see Figure S8a).

9-AGNRs normalized to the absorbed pump photon density. Following the quasi-instantaneous optical charge carrier generation, we observe a rapid decay in $\sim 2 \text{ ps}$, which has been assigned to the formation of excitons from the initially free carriers.⁵¹ Importantly, the relative magnitudes of the signals testify to a remarkably (~ 20 -fold) higher charge carrier mobility of 5-AGNRs compared to that of 9-AGNRs. Previous work employing the same approach has shown that 9-AGNRs is about 20% more conductive than 7-AGNRs.³⁹ This leads to the following trend of charge mobility μ in AGNRs: 5-AGNRs \gg 9-AGNRs $>$ 7-AGNRs ($\mu = e\tau/m^*$, with e the electron charge, τ the charge scattering time, and m^* the effective mass of the charge carriers). The charge scattering time for various GNRs has previously been determined to be in the range of 20 – 30 fs .⁵² The main difference in mobility seems, therefore, to originate from the effective mass difference of AGNRs, perfectly in line with the effective masses obtained from previous calculations (0.01 , 0.091 , and $0.21 m_0$ for 5-, 9-, and 7-AGNR, respectively).⁵³ In line with our discussion here, a recent electrical transport work based on AGNR FET devices has demonstrated that the charge carrier mobility in 5-AGNRs is 1 order of magnitude higher than that of 9-AGNRs.⁵⁴ Thus, we believe that defects do not play a major role for transport. Interestingly, the trend in charge carrier mobility in the GNR electrodes reflects the trend observed in the MSC electrochemical performances. The correlation between the charge carrier effective mass, the photoconductivity, and the volumetric capacitance illustrates the critical role of the intrinsic electronic properties of GNRs on their performance in electrochemical energy storage applications. Such correlation is perhaps not surprising: The GNRs used here are grown by CVD with a limited length up to $\sim 40 \text{ nm}$. As such, electrical transport through the GNR network may become the limiting step for charge injections. In that case, the high conductivity in

5-AGNRs will facilitate the electrical transport process and lead to a marked improvement in the electrochemical performance.

In conclusion, we have successfully used bottom-up, on-surface-synthesized AGNRs for high-performance MSCs. The AGNRs-based MSCs demonstrate promising overall performance, such as ultra-high operating speeds, volumetric capacitances, and power densities, outperforming state-of-the-art MSCs based on other graphene materials. The AGNRs-based MSC devices' performance correlates well with the charge carrier mobility indicated by THz studies, i.e., 5-AGNRs \gg 9-AGNRs $>$ 7-AGNRs. Future optimization of the CVD process for ultra-long AGNRs growth and a better design concept for metallic AGNRs, as well as a scale-up of defect-free AGNRs production via solution-phase synthesis accompanied by suitable processing approaches, may pave the way for such novel one-dimensional carbon materials being employed as practical ESSs, even in flexible and wearable forms.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c06109>.

Materials, methods, device geometry, and CV information (PDF)

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Notes

The authors declare no competing financial interest.

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