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Coordination Polymer Framework-Based On-Chip Micro-Supercapacitors with AC Line-Filtering Performance

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Abstract: On-chip micro-supercapacitors (MSCs) are important Si-compatible power-source backups for miniaturized electronics. Despite their tremendous advantages, current onchip MSCs require harsh processing conditions and typically perform like resistors when filtering ripples from alternating current (AC). Herein, we demonstrated a facile layer-by-layer method towards on-chip MSCs based on an azulene-bridged coordination polymer framework (PiCBA). Owing to the good carrier mobility (5×10^{-3} cm²V⁻¹s⁻¹) of PiCBA, the permanent dipole moment of azulene skeleton, and ultralow band gap of PiCBA, the fabricated MSCs delivered high specific capacitances of up to 34.1 F cm⁻³ at 50 mV s⁻¹ and a high volumetric power density of 1323 W cm⁻³. Most importantly, such MCSs exhibited AC line-filtering performance (-73° at 120 Hz) with a short resistance–capacitance constant of circa 0.83 ms.

On-chip electrochemical energy storage devices,^[1] such as micro-supercapacitors (MSCs) and microbatteries, have attracted tremendous attention in the past few years because of the rapid development of mobile electronics, wireless sensors, and medical implants. Compared with micro-batteries, on-chip MSCs have many advantages owing to their rapid energy-harvesting features, burst-mode power delivery, and,

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201700679. in particular, compatibility with the Si industry.^[1b,2] Recent studies have focused on the thin-film fabrication of MSCs by using nanostructured functional materials such as graphene,^[1d,3] graphene-based nanocomposites,^[4] monolithic carbide-derived carbon,^[1a] mesoporous conducting polymers,^[5] and several other pseudocapacitive materials.^[6] However, most devices based on these materials require harsh processing operation steps such as the high-temperature fabrication of electrode films, metal electrode deposition, electrode gap generation by oxygen plasma, and the wet chemistry etching method. Such procedures lead to the easy cracking and delamination of active films from substrates, such as with Si wafers and Kapton films.^[1b] Therefore, the development of Sicompatible MSCs with easy and cheap fabrication procedures is essential to enable their practical applications.

Alternating current (AC) line-filtering, which can filter the AC ripple on the line-powered devices, is one of the most important tasks in the field of renewable electronic power systems such as power generation by using wind and tidal power.^[7] However, traditional aluminum electrolytic capacitors (AECs), which are widely used for this purpose, have a low energy density and large volume size. Therefore, supercapacitors, particularly MSCs, that possess an AC linefiltering ability, high energy density, and minimal size, are ideal alternatives to AECs. Traditionally, porous carbonbased supercapacitors exhibit poor AC line-filtering performance (resistance–capacitance [RC] time constant ≈ 1 s) compared with AECs (RC time constants = 8.3 ms)^[7c] because of the slow and internal response of the polarization^[7c] and limited signal propagation^[7a] from the electrodes. Recently, directly growing graphene and graphenecarbon-nanotube (CNT)-on-nickel current collectors have been reported by using chemical vapor deposition,^[7a,c] yielding short RC time constants of less than 200 µs, which can be attributed to the strong connection between the electrode and active materials. Nevertheless, the reported electrode fabrication on metal current collectors necessitates complicated processing procedures.

Herein, we demonstrate a simple, potentially up-scalable method for the room-temperature fabrication of on-chip MSCs by using a layer-by-layer (LBL) growth of an azulenebridged coordination polymer framework (PiCBA) on a Si wafer-supported Au surface. The PiCBA exhibits good carrier mobility of 5×10^{-3} cm²V⁻¹s⁻¹. The manufactured on-chip MSCs deliver a high specific volumetric capacitance of up to 34.1 F cm⁻³ at 50 mV s⁻¹, and a power density of up to 1323 W cm⁻³ (energy density of 4.7 mWh cm⁻³), for which the high intrinsic capacitance of PiCBA is supported by theoret-

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ical calculations. Notably, the as-fabricated MSCs exhibit an AC line-filtering performance $(-73^{\circ} \text{ at } 120 \text{ Hz})$ with a short RC time constant of approximately 0.83 ms, superior to that of the AECs.

The fabrication of PiCBA film is shown in Figure 1a. The azulene-based building block, 2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (denoted as iCBA, Supporting Information) was synthesized according to a reported procedure with minor modifications.^[8] The terminal isocyanide groups of iCBA can coordinate with various metal atoms and metal ions such as Au, Pt, Pd, Co, Ni and Fe.^[9] Taking advantage of this feature, a PiCBA monolayer film was prepared through a coordination reaction between iCBA and Co ions (CoCl₂·6H₂O) at the water-air interface in a Langmuir-Blodgett trough (Supporting Information, Figure S1 and S2). After transferring the PiCBA film onto a Si wafer or copper grid, the morphology of the obtained film was studied by optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The OM and TEM images (Figure 1b and the Supporting Information, Figure S3 and 1b) indicate a uniform macroscopic lateral dimension (ca.



Figure 1. a) Synthesis of PiCBA through the coordination reaction between isocyanide and cobalt ions (R=-COOC₂H₅). b) TEM image shows a large area of a PiCBA film on a copper grid. c) N 1s core level spectra of PiCBA film and iCBA. d) Layer-dependent UV/Vis spectra of PiCBA film on a quartz wafer. Inset: Linear relationships between the absorbance at 349 nm and the layer number. e) The photoconductivity of PiCBA as a function of the pump-probe delay (excitation wavelength, 400 nm, 90 μ J-cm⁻²). f) Frequency-resolved complex-valued photoconductivity in the PiCBA film (0.45 ps after photoexcitation). Black solid and red open symbols represent the measured real and imaginary components, respectively, and lines through the data points represent best fit obtained using the Drude–Smith model.

0.1 mm²) of the obtained coordination polymer film. We identified regions at the PiCBA edge by SEM, in which the film is partially folded when transferred onto the Cu grid, demonstrating the flexible nature of the obtained PiCBA film (Figure 1b and Supporting Information, Figure S4). The AFM image and cross-sectional analysis (Supporting Information, Figure S5) reveal that the average thickness of the PiCBA film is approximately 1.1 nm, which is consistent with the calculated thickness of a single-layer PiCBA film (1.2 nm, Figure 4a). These results strongly suggest that the coordination between the isocyanide groups and Co ions renders the formation of free-standing coordination polymer frameworks.

To further analyze the chemical structure of the PiCBA film, Fourier-transform infrared (FT-IR) spectroscopy and Xray photoelectron spectroscopy (XPS) were employed. The broad peak centered at 2078 cm⁻¹ for PiCBA (Supporting Information, Figure S6) exhibits an obvious shift to lower energy compared with the N=C stretching at 2132 cm^{-1} for iCBA.^[9b,e] This can be attributed to the N=C…Co stretches^[10] caused by the electronic perturbation of the σ bond donated by the N≡C groups to the Co atoms.^[9g] This shift is direct evidence of the strong coordination between Co and isocyanide in the PiCBA film. The Co:N atomic ratio is calculated to be 1:3.6 (Supporting Information, Figures S7, S8, and Table S1), which is close to the theoretical stoichiometric ratio (Co:N = 1:4). This result strongly suggests a high degree of coordination in PiCBA films through one Co cation and four isocyanide groups.^[9f] The N 1s core level spectrum for PiCBA (Figure 1c) is deconvoluted into two peaks at 398.1 and 400.4 eV, which are assigned to the isocyanide coordinated with CoII and edge isocyanide species, respectively.[11] To study layer-dependent UV/Vis absorption spectra, multilayer PiCBA films were prepared. The linear increase in the absorbance (at 349 nm; Figure 1 d, inset) demonstrated the uniformity of each PiCBA layer (Supporting Information, Figure S9).^[12]

Time-resolved terahertz spectroscopy was used to evaluate the photoconductivity within the PiCBA framework.^[13] Figure 1e shows the time-resolved real conductivity as a function of pump-probe delay (400-nm excitation and the ca. 0.6 THz probe). The signal is defined by an ultra-fast rise of approximately 100 fs followed by a decay of approximately 1 ps, consistent with the generation of quasi-free electronhole (e-h) pairs, which subsequently condense into localized states.^[14] Figure 1 f shows the frequency-resolved complex photoconductivity over the circa 2 THz probe bandwidth (at a pump-probe delay of 0.45 ps); the response can be welldescribed by the Drude-Smith model.^[14] From the data, the carrier mobility in the sample was estimated as $\mu(PiCBA) =$ $5 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This relatively large mobility (for example, similar to THz mobility estimates on conjugated polymer nanosheets^[13]) represents a lower-bound estimate as we assumed that all absorbed photons generate quasi-free charges immediately after pump excitation. In parallel, the conductivity of bilayer PiCBA films (thickness ≈ 2.0 nm) was as high as $2.4 \times 10^{-4} \, \mathrm{S \, cm^{-1}}$ (Supporting Information, Figure S10), which is the highest value to date for such synthetic and ultrathin polymer films or coordination polymer films

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and even comparable to some polymers in thick films (150–300 nm) or in bulk states.^[15]

Given its rich aromatic skeleton, ultra-low band gap (Supporting Information, Figure S11 and Table S2), good carrier mobility, and the permanent dipole moment of the azulene unit, PiCBA is a promising candidate for energy storage. Hence, the PiCBA layers were directly integrated to fabricate MSCs. First, the iCBA molecules were adsorbed onto the Au surface of the interdigitated Au-SiO₂ substrate (Supporting Information, Figure S12) through the upright η^1 coordination of the terminal isocyanide carbon atoms^[9f] (Figure 2a). Then, the substrate was rinsed in a CoCl₂



Figure 2. a–c) Schematic of LBL fabrication of a PiCBA film on Au interdigital electrodes. (i) The Au interdigital electrode was immersed in iCBA solution for 24 h, followed by rinsing in fresh CHCl₃ and then (ii) immersed in $CoCl_2$ solution for another 60 s, followed by rinsing in DI water, iCBA solution for 60 s, and fresh CHCl₃, respectively, to form the 1-layer PiCBA film. This process was repeated nine times to obtain a 10-layer PiCBA-Au electrode.

aqueous solution, deionized water, iCBA monomer solution, and fresh CHCl₃ sequentially 10 times to allow the in situ formation of 10-layer PiCBA films on the Au electrode (Figure 2b and Supporting Information, S13). The crosssection SEM images (Supporting Information, Figure S14; prepared by focused ion beam) indicated that the 10-layer PiCBA films had an estimated total thickness of approximately 30 nm, which is slightly larger than the theoretical value (2.1 nm × 11 = 23.1 nm, see calculation section) due to the possible dislocation effect (see Raman spectra in the Supporting Information, Figure S15).^[16] Finally, the H₂SO₄polyvinyl alcohol (H₂SO₄-PVA) gel electrolyte was cast on the PiCBA-Au:SiO₂ substrate and allowed to solidify overnight to form a solid–state PiCBA-Au MSC with an in-plane geometry (Figure 2c).

The electrochemical performance of the 10-layer PiCBAbased MSC was evaluated using cyclic voltammetry (CV), with scan rates ranging from 50 mV s⁻¹ to 1000 V s⁻¹ (Figure 3a and the Supporting Information, Figure S16). The PiCBA films showed an enhanced current range with a nearly rectangular CV curve, even at 100 V s⁻¹, suggesting typical double-layer capacitive behavior. The areal capacitance (C_A) and stack capacitance (C_v) for the whole in-plane PiCBAbased device were subsequently calculated based on the CV results (Figure 3b and the Supporting Information, Figure S17). The whole device exhibited a C_v of circa 34.1 F cm⁻³, at a scan rate of 50 mV s⁻¹, which is among the highest values reported for polymer-based MSCs (Supporting



Figure 3. a) CV curves of PiCBA-based MSCs in the H₂SO₄-PVA gel electrolyte at different scan rates, showing a typical double-layer capacitive behavior even at different scan rates. b) C_v evolution of the MSCs at different scan rates. c) Complex plane plot of the impedance of the PiCBA-based microdevices. Inset displays a magnification of the high-frequency region. d) Impedance phase angle on the frequency for the PiCBA-based microdevices. e) Plot of capacitance (C_v' = volumetric real capacitance and C_v'' = volumetric imaginary capacitance) versus the frequency of PiCBA-based MSCs. f) Ragone plots for PiCBA. This demonstrates that the PiCBA exhibits outstanding electrochemical energy storage with high power density compared with commercially applied Li-thin-film batteries,^[17a] electrolytic capacitors,^[17a] polyaniline (PANI) nanowires,^[17b] CNT-graphene carpets,^[17c] Ti₃C₂T_x,^[1a] and carbon onions.^[17a]

Information, Table S3). Notably, the C_v of the PiCBA films decreased gradually with increasing scan rates; for example, the capacitance remained at 7.7 Fcm⁻³ at a scan rate of 100 Vs⁻¹. Even at the ultra-high scan rate of 1000 Vs⁻¹, the PiCBA films delivered a C_v of 2.7 Fcm⁻³, demonstrating a high capacitance and rate performance of PiCBA-based MSCs.

Electrochemical impedance spectroscopy further confirmed the excellent ion transport within the in-plane device. Figure 3c shows a pronounced pure capacitance behavior of the PiCBA-based device, even for frequencies as high as 14.7 kHz, benefitting from the completely accessible surface of the PiCBA films. Figure 3c (inset) indicates displaced behavior at low impedance. Moreover, the equivalent series resistance of the whole device, calculated from the intercept of the real axis, is 70.1 Ω , which can be attributed to the internal ion-transport resistance of the PiCBA materials with the polymer-gel electrolyte.^[18] The dependence of the phase angle on the frequency indicates capacitive and inductive behavior at low and high frequencies, respectively (Figure 3d).^[7c] The phase angle of the device reached -78° at frequencies of circa 14 Hz, suggesting that the performance of the MSCs is 87% of that of an ideal capacitor (defined by a phase angle of -90°). Additionally, the characteristic frequency (f_0) of the system, corresponding to the maximum of the dispersed energy curve (obtained from the phase angle of 45°) was 3620 Hz, with a relaxation time constant τ_0 ($\tau_0 = 1/$ f_0 , the minimum time needed to discharge the energy from the whole device with an efficiency of > 50%) of approximately 0.27 ms. This value is orders of magnitude higher than that obtained for activated carbon-based MSCs (<5 Hz, $<\!200\ ms)^{[19]}$ and onion-like carbon MSCs ($<\!100\ Hz,$ <10 ms)^[17a] and much higher than that for graphene-CNT MSCs (ca. 1343 Hz and 0.74 ms).^[7a] Importantly, the whole device showed an impedance phase angle as large as -73° at a frequency of 120 Hz, indicating a high AC line-filtering efficacy.^[7a] The series-RC circuit model was then employed to further assess the RC time constant (τ_{RC}) in the PiCBA-based device. Figure 3e shows that the $\tau_{\rm RC}$ from the imaginary capacitance calculated from the Nyquist plot was as short as 0.83 ms, which is comparable to the state-of-the-art MSCs based on vertically oriented graphene (< 0.2 ms),^[7c] thermally reduced graphene oxide (2.3 ms),^[20] and graphene-conductive polymer hybrids (0.47 ms).^[7b]

To further evaluate the overall performance of the MSCs, the volumetric power and energy densities were calculated. The plot in Figure 3 f demonstrates that the PiCBA-based MSCs exhibited a high energy density of up to 4.7 mWh cm⁻³ at 50 mV s⁻¹, an order of magnitude higher than that obtained for electrolytic capacitors^[1c] and MSCs based on graphene-CNT carpets.^[7a] In addition, the device exhibited a power density of 1323 W cm⁻³, which is at least five orders of magnitude higher than that of commercial thin-film lithium batteries.^[1c] To our best knowledge, this is the first report of coordination polymer-based MSCs with such high power and energy densities (Table S3). Furthermore, the PiCBA-based MSCs showed good cycling stability, with 86% capacitance maintained after 350 cycles (Supporting Information, Figure S18).

To understand the excellent capacitive performance of PiCBA, density functional theory (DFT) simulations were performed (Supporting Information). The optimization of the unit cell yields an approximately square Bravais lattice, with the symmetry of the structure slightly broken by the torsion of the azulene units (Figure 4a). Figure 4b shows the band structure and density of states (DOS). Two spin-up bands cross the Fermi level, indicating metallic behavior of the PiCBA framework in this configuration, while the narrow bandwidth is consistent with the observed mobility. Note that the splitting of the four bands close to zero energy in Figure 4a is on the order of the thermal energy and may not be observed in ambient temperature experiments. The quantum areal capacitance (Cq) extracted from the DFT calculations reaches 150 μ F cm⁻² and is clearly larger than that obtained from experiments at standard scan rates (Figure 4c); this can be explained by the limiting scenario of a disorderfree system. To include the effects of disorder on Cq, the DOS of the four bands closest to the Fermi level was broadened (Figure S18). With DOS broadening, the quantum capacitance decreased below 50 μ F cm⁻², which is closer to experimental observations. The calculations indicate that the charge densities of these bands are spread over the azulene units (Figure 4d) and the dispersion of these bands is rather small, which appears to be mainly because of the metal centers as well as partly because of the torsion between the azulene units. This result, based on unprecedented theoretical work on the energy storage abilities of azulene-containing polymer films, suggests that the PiCBA films deliver high capacitance owing to the extreme charge affinity of azulene groups.

In conclusion, we have developed an LBL approach for the room-temperature preparation of coordination polymer frameworks based on-chip MSCs. Remarkably, the fabricated on-chip MSCs delivered high specific capacitances, excellent specific volumetric power, and energy densities as well as promising AC line-filtering performance with an extremely short RC time. The coordination-polymer-framework electrode possesses a permanent dipole moment of the azulene-



Figure 4. a) Relaxed unit cell (blue square) of the PiCBA framework. The calculations reveal an almost square Bravais lattice with a = 20.948 Å, b = 20.944 Å, and $\varphi \approx 90.0^{\circ}$. b) Simulated band structure and density of states (DOS). The Fermi level crosses two spin-up bands, indicating metallic behavior of the material. c) Calculated quantum capacitance based on the two bands crossing the Fermi level for zero disorder. d) Charge density of the lower band crossing the Fermi level at the Γ point as well as close to the Brillouin zone boundary at X, namely k = (0.4, 0.0, 0.0). The charge density of the second band is almost identical at the Γ point and complementarily delocalized horizontally at (0.4, 0.0, 0.0).

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based skeleton, ultra-low band gap, and good carrier mobility, rendering it as a promising material for both energy storage and optoelectronic applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: AC line-filtering · azulene · coordination polymers · layer-by-layer methods · micro-supercapacitors

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Communications



Communications



C. Yang, K. S. Schellhammer, F. Ortmann, S. Sun, R. Dong, M. Karakus, Z. Mics, M. Löffler, F. Zhang, X. Zhuang,* E. Cánovas,* G. Cuniberti, M. Bonn, X. Feng* _____

Coordination Polymer Framework-Based On-Chip Micro-Supercapacitors with AC Line-Filtering Performance

On-chip micro-supercapacitors based on an azulene-bridged coordination polymer framework are prepared by a facile layerby-layer approach. The as-fabricated onchip micro-supercapacitors deliver high



specific capacitances, specific volumetric power, and energy densities as well as promising AC-line filtering performance with an extremely short RC time.

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