Supplementary Information

Highly active ruthenium oxide coating via ALD and electrochemical activation in supercapacitor applications

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Figure S2. High-resolution transmission electron microscopy (TEM) image of as-deposited ALD RuO_x on CNTs showing polycrystalline structure.



Figure S3. (a) Scanning electron microscopy (SEM) image of as-deposited ALD RuO_x porous Si supercapacitor electrode. The lighter regions of the pores are areas coated with RuO_x . (b) Higher magnification SEM image of ALD RuO_x conformally coating the bottom of a porous Si pore. (c)

SEM image showing the thickness of the ALD RuO_x coating on the porous Si electrode (~ 40 nm).



Figure S4. XRD measurements of ALD RuO_x deposited on planar substrates at 270 °C, 350 °C, and 400 °C. At all three temperatures the resulting films are polycrystalline and show Ru metal XRD peaks. The predominant crystal plane changes with deposition temperature: Ru(100) at 270 °C, Ru(002) and Ru(101) at 350 °C, and Ru(002) at 400 °C.



Figure S5. High-resolution XPS measurements of (a) Ru3d, and (b) O1s binding energies for ALD RuO_x deposited on vertically aligned CNTs. Ru3d measurements show a shift to higher

binding energies compared to Ru metal at take-off angles of 15°, 30°, and 75°, indicating the presence of oxidized ruthenium. The O1s binding energy is measured at 30° take-off angle.



Figure S6. XRD measurements of ALD RuO_x - CNT electrodes. Peaks at 34° and 47° match those of the uncoated CNT electrode, while peaks at 38°, 42°, and 44° correspond to Ru (100), (002), and (101), respectively.

Specific Capacitance Calculations

Specific capacitance (F/g) values were calculated from cyclic voltammetry measurements using the following equation:

$$C = \frac{\int_{E_1}^{E_2} i(E) dE}{2(E_2 - E_1)mv}; \text{ where } i(E) = \text{CV current (A)}$$
$$E_1, E_2 = \text{CV scan range (V)}$$
$$m = \text{ supercapacitor electrode mass (g)}$$
$$v = \text{CV scan rate (V/s)}$$

The integral $\int_{E_1}^{E_2} i(E) dE$ is the "total voltammetric charge" calculated from trapezoidal

integration of forward and backward sweeps of the CV curves.¹

Energy and Power Density Calculations

Power and energy density were calculated from constant current charge-discharge curves using the following equations:²

Energy density (Wh/kg):
$$E = \frac{C(\Delta E)^2}{2(3600)};$$

Power density (kW/kg): $P = \frac{3600E}{t};$ where ΔE = cell voltage range (V)
 C = specific capacitance (F/g)
 t = discharge time (s)

Specific capacitance used in the above energy density equation was calculated from the discharge slope of constant current charge-discharge curves.

ALD RuO_x-CNT Mass Estimate

The mass of vertically aligned CNTs per cm² was estimated by measuring the difference in mass of the substrates before and after CNT growth. Each before and after mass was averaged from five individual measurements taken using a Sartorius Analytic Type A2005 balance. Four CNT substrates (A through D in Figure S7) were measured to obtain the average mass of CNTs per cm² (Table S1). Substrate areas were measured from a digital image of the samples using "ImageJ" program. To find a height-normalized CNT mass (g per cm²-µm) the average height of the vertically aligned CNTs in samples A through D was estimated from cross-sectional SEM images, taking an average of 23 height measurements (Figure S8). Calculated average CNT mass is summarized in Table S2.



Figure S7. (a) CNT substrates used for mass measurements pre-CNT growth. (b) Substrate A after CNT growth.

Measurement	A (g)		B (g)		C (g)		D (g)	
	Before	After	Before	After	Before	After	Before	After
1	2.3732	2.3754	3.1266	3.1291	2.7468	2.7490	2.8441	2.8459
2	2.3733	2.3754	3.1269	3.1290	2.7466	2.7490	2.8440	2.8461
3	2.3733	2.3753	3.1267	3.1286	2.7467	2.7489	2.8441	2.8461
4	2.3737	2.3751	3.1267	3.1287	2.7469	2.7492	2.8441	2.8459
5	2.3734	2.3752	3.1266	3.1288	2.7468	2.7489	2.8440	2.8459
Average	2.3734	2.3753	3.1267	3.1288	2.7468	2.7490	2.8441	2.8460
Std. Dev.	0.0002	0.0001	0.0001	0.0002	0.0001	0.0001	0.00006	0.0001

Table S1. Mass measurements of CNT substrates before and after CNT growth.



Figure S8. (a) Cross-sectional SEM image of uncoated CNTs grown on substrates A – D. (b) Histogram of CNT heights measured from cross-sectional SEM images.

Table S2. Summary	of calculated	l average CNT	mass per cm	2 - μ m.
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Sample	А	В	С	D
Sample area (cm ²)	13.46	16.95	14.81	16.78
Change in mass (mg) (before & after CNT growth)	1.9	2.1	2.2	1.9
CNT mass (10 ⁻³ mg/cm ² - μm)	9.7	8.6	10.4	7.9
Average CNT mass per cm ² - μm	9.1 x 10 ⁻³ mg/cm²-μm			

To determine the mass of ALD RuO_x deposited on the CNT substrates, we used TEM images (like the one shown in Figure 1c) to find the average ALD coating thickness (Figure S9). We observed an increase in CNT coating thickness with post-ALD electrochemical and thermal oxidation of the ALD RuO_x-coated CNTs (Table S3). The density of CNTs per cm² was estimated from SEM images of "CNT footprints" on the substrates after removing the CNTs from the electrode surface (Figure S10).³ Table S4 summarizes calculations of ALD RuO_x mass per cm² per unit CNT height (mg/cm²-µm). We used the density of Ru metal (12.45 g/cm³) to calculate the mass of as-deposited ALD films and the density of RuO₂ (6.97 g/cm³) for electrochemically oxidized films.



Figure S9. Histogram of uncoated CNT outside diameter as measured from TEM images.

	ALD RuO _x - CNTs	Thermally oxidized ALD RuO _x -CNTs	Electrochemically oxidized ALD RuO _x -CNTs
Average outside diameter (nm)	47.1	60.7	63.6
Standard deviation (nm)	5.1	3.0	3.2
No. of measurements	10	10	10

Table S3. Measurements of the coating thickness of as-deposited, thermally oxidized, andelectrochemically oxidized ALD RuO_x on CNTs (average outside diameter of $RuO_x + CNT$).



Figure S10. (a) SEM image of "CNT footprints" on the CVD growth substrate. (b) Corresponding "ImageJ" program count of number of CNT footprints per unit area.

Table S4. Calculations of ALD RuO_x mass on vertically aligned CNTs (detailed calculations are given for as-deposited ALD RuO_x , and the final value for electrochemically oxidized ALD RuO_x).

As-deposited ALD RuO _x				
Volume of ALD RuO _x per CNT (per μm of CNT height)	$V_{RuOx} = \pi \left[\left(\frac{d_{CNT+RuOx}}{2} \right)^2 - \left(\frac{d_{CNT}}{2} \right)^2 \right]$ = 1.55x10 ⁻¹⁵ cm ³ / µm / CNT			
Mass of RuO _x per CNT	$m_{RuOx \text{ per CNT}} = (12.45 \text{ g/cm}^3)(1.55x10^{-15} \text{ cm}^3 / \mu m)$ $= 1.92x10^{-14} \text{ g} / \mu m / \text{CNT}$			
Density of CNTs	41 CNTs/ μ m ² (average of 10 measurements; standard deviation 6.6 CNTs/ μ m ²)			
Mass of ALD RuO _x on CNTs	$m_{RuOx} = \left(1.92x10^{-14} \frac{g}{\mu m} / CNT\right) \left(41x10^8 \frac{CNTs}{cm^2}\right)$ = 0.079 mg/cm ² -\mu m			
Electrochemically oxidized ALD RuO _x				
Mass of electrochemically oxidized ALD RuO_x on CNTs	0.085 mg/cm²- μm			

ALD RuO_x - Porous Silicon Mass Estimate

Porous Si supercapacitor electrodes tested in this study have an average pore depth of 74 μ m out of a full silicon wafer thickness of 500 μ m, as measured by cross-sectional SEM image (Figure S11). In calculating the porous Si supercapacitor electrode mass, we included only the active porous region of the Si substrate. The mass of the porous region was estimated by comparing the mass per cm² of uncoated porous silicon samples vs. a pure silicon wafer (Table S5). The mass of ALD RuO_x deposited on porous Si electrodes was estimated based on the ALD film thickness measured from cross-sectional SEM images and the porous Si surface area estimated from the average diameter, depth, and spacing of the pores (Figure S12, Table S6).



Figure S11. Cross-sectional SEM image of an uncoated porous silicon electrode, with average pore depth, active porous region, and supporting Si substrate region indicated.

Table S5. Calculations to estimate the mass per unit area of the porous region of uncoated porous Si electrodes.

Porous Si sample area	1.429 cm ²
Porous Si sample mass	0.1703 g
Porous Si mass per unit area	0.1191 g/cm ²
Density of Si	2.33 g/cm ³
Porous Si average pore depth	74.8 μm
Silicon wafer thickness	500 μm
Mass of porous Si supporting Si substrate region (Fig. S8)	$= (500\mu m - 74.8\mu m) (2.33 \frac{g}{cm^3}) (10^{-4} \frac{\mu m}{cm})$ $= 0.0991 \frac{g}{cm^2}$
Mass of porous Si pores	$= 0.1191 \frac{g}{cm^2} - 0.0991 \frac{g}{cm^2}$ $= 0.0200 \frac{g}{cm^2}$



Figure S12. Top-view SEM image of uncoated porous Si electrode with pore diameter and center distance measurements.

	Average	Standard Dev.	# of Measurements
Pore diameter	12.9 µm	5.5 μm	30
Pore depth	74.8 µm	24.3 µm	30
Pore center-to-center distance	17.0 µm	2.7 μm	30
Surface area ratio of porous Si: planar	$=\frac{\left(\pi dh+x^2\right)}{x^2}=$	$=\left(\pi(12.9 \ \mu m)(74.8 \ (17 \ \mu))(74.8 \ (17 \ \mu)))(74.8 \ (17 \ \mu))(74.8 \ (17 \ \mu)))(74.8 \ (17 \ \mu))($	$\frac{\mu m \left(17 \ \mu m\right)^2}{m \right)^2}$
	= 11.5:1		

 Table S6. Average porous Si sample dimensions measured from SEM images.

The porous Si electrodes were not completely coated with ALD RuO_x . To calculate the approximate mass of RuO_x deposited, we used cross-sectional SEM images to estimate the average fraction of the pores that were coated with RuO_x , taking an average value based on measurements of four pores (lighter-colored regions in SEM images have RuO_x coating) (Table S7, Figure S13). Using these values, we estimate the mass of RuO_x to be approximately 0.36 mg/cm² of planar sample area (Table S8).

Table S7. Percentage of porous Si electrode pores coated with ALD RuO_x estimated from crosssectional SEM images using ImageJ area analysis.

Pore	Total area (µm²)	Uncoated area (µm ²)	Coated area (µm ²)	% Coated
1	1624	756.6	867.8	53.4%
2	2814	908.2	1906.0	67.7%
3	2229	761.9	1467.8	65.8%
4	2555	829.6	1726.4	67.5%
Average	63.6%			



Figure S13. Cross-sectional SEM images of an ALD RuO_x coated-porous Si supercapacitor

electrode with areas calculated using ImageJ (uncoated areas are outlined in yellow).

Table S8. Calculation of ALD RuO_x mass deposited on porous Si supercapacitor electrodes.

ALD RuO _x coating thickness (Fig. S2c)	40 nm
Mass of ALD RuO _x per unit planar surface area	$m = \rho_{Ru} (\text{thickness}) (\text{surface area}) (\text{fraction coated})$ $= (12.45 \text{ g/cm}^3) (40 \text{ nm}) (11.5 \text{ cm}^2 / \text{cm}^2) (0.636)$ $= 0.36 \text{ mg/cm}^2$
Total porous Si electrode mass (porous Si + ALD RuO _x)	20.36 mg/cm ²

Uncoated CNT & Porous Silicon Cyclic Voltammetry Measurements

Figure S14 shows cyclic voltammetry measurements for uncoated CNT and uncoated porous Si supercapacitor electrodes in 0.5 M H₂SO₄ electrolyte (enlarged curves from Figures 3b and 3c, respectively).



Figure S14. CV measurements of (a) uncoated CNTs, and (b) uncoated porous Si.

XPS measurement of hydrated, as-deposited ALD RuO_x

High-resolution XPS measurement of O 1s binding energy provides evidence for in-situ formation of hydrated ALD RuO_x. Figure S15 provides O 1s measurements for ALD RuO_x deposited at 350 °C on a planar substrate. The cumulative fit closely matches measured values and is composed of three peaks with binding energies (BE) centered at 529.5 eV, 530.8 eV, and 532.4 eV. These three peaks correspond to oxygen atoms present as O^{2-} , OH⁻, and H₂O, respectively.^{4,5} Curve fits of the three peaks closely resemble that of hydrous RuO₂ measured by Mun *et al.*, with a prominent OH⁻ peak and substantial presence of H₂O (note that measured values of H₂O are limited by the ultrahigh vacuum conditions used in XPS).⁵



Figures S15. High resolution XPS measurements of O 1s binding energy for as-deposited ALD RuO_x, with Gaussian-Lorentz curve fits. Background intensity is estimated using a Tougaard fit. Experimental error for the high resolution XPS measurements is less than \pm 0.2 eV.

Planar ALD RuO_x Life Cycle Testing

Planar ALD RuO_x electrodes were tested for 3000 CV cycles to determine their durability with repeated charging and discharging. CV curves for cycles 10 and 3000 are significantly different due to irreversible electrochemical oxidation of as-deposited ALD RuO_x during CV scans (after 3000 cycles, the planar ALD RuO_x shows characteristic RuO₂ CV peaks at 0.5 and 0.85 V vs. Ag/AgCl) (Figure S16a). While capacitance increases with repeated cycling, there is considerable delamination of the ALD RuO_x film, resulting in a maximum life of about 3000 charge-discharge cycles (Figure S16b).



Figure S16. Life-cycle testing of planar ALD RuO_x supercapacitor electrode. (a) CV curves of a planar ALD RuO_x electrode after 10 and 3000 cycles. (b) Capacitance increase of the planar ALD RuO_x electrode over 3000 cycles (inset: Photo of the electrode after 3000 cycles shows delamination of the ALD RuO_x).

Thermal & Electrochemical Oxidation of ALD RuOx- CNTs

SEM images of ALD RuO_x-CNTs after thermal and electrochemical oxidation (Figure S17) showing vertically-aligned CNTs and ALD coatings are preserved through the oxidation steps.



Figure S17. SEM images of ALD RuO_x supercapacitor electrodes: (a) as-deposited, (b) thermally oxidized, and (c) electrochemically oxidized.



Figure S18. XRD measurements of ALD RuO_x films on a planar Si electrode. The as-deposited film ("ALD RuO_x ") shows a strong Ru(100) peak, while thermally oxidized ("Thermal ox.") and electrochemically oxidized ("Electrochem ox.") films show $RuO_2(210)$ and amorphous mixed $RuO_2(110)/RuO_2(101)$ crystal structures, respectively.

Electrochemical Oxidation of ALD RuO_x-Porous Silicon Electrodes

SEM images of electrochemically oxidized ALD RuO_x -porous Si electrodes (Figure S19) show damage to the ALD film compared to as-deposited ALD RuO_x (Figure S3). A close-up view of the electrochemically oxidized ALD RuO_x film on porous Si (Figure S19c) shows a different texture than the as-deposited film (Figure S3c).



Figure S19. SEM images of electrochemically oxidized ALD RuO_x porous Si electrodes.



Figure S20. Constant current charge-discharge measurements of: (a) planar, as-deposited ALD RuO_x , (b) electrochemically oxidized planar ALD RuO_x (9 min oxidation time), (c) as-deposited ALD RuO_x -CNTs, (d) electrochemically oxidized ALD RuO_x -CNT electrodes (9 min oxidation

time), and (e) uncoated CNTs. Measurements were conducted with a symmetrical two-electrode set-up in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte.



Figure S21. Capacitance of as-deposited ("ALD RuO_x ") and electrochemically oxidized ("Electrochem ox.") planar ALD RuO_x electrodes at CV scan rates of 10 mV/s to 20 V/s.



Figure S22. Life cycle testing of electrochemically oxidized ALD RuO_x-CNT electrodes, showing a gradual, 19% decrease in specific capacitance after 1500 cycles.

References

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