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Supplementary Information

Synthesis of hybrid nanowire arrays and their application as high power supercapacitor electrodes

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Fabrication of arrays of CNT/AuNW hybrid structures

The experimental procedure for growing CNT/AuNW hybrid structures is schematically shown in Fig 1 (article). First, a layer of Ag coating (about 200nm) was thermal evaporated onto one side of the AAO template to serve as the working electrode for the consequent electrochemical deposition. The electrodeposition was carried out to deposit Au into the nanopores, using the standard three electrode potentiostat system (Princeton EG & G 273 A). Ag/AgCl reference electrode and platinum wire counter electrode were used for the process. The length of the metal nanowire can be controlled by varying the deposition time. After the electrodeposition of the Au nanowires, CVD was carried out to grow multiwalled carbon nanotubes (MWNTs) inside the template, by the pyrolysis of acetylene at 650°C for 1 - 2 h with a flow of gas mixture containing Ar (85 %) and C_2H_2 (15 %) at a rate of 35 ml/min. Since the Au nanowires had already filled the bottom portion of the channel, the CNTs would only grow in the remaining top portion which had not been occupied during the electrodeposition step. Hybrid structures with Au Nanowire -CNT junctions were formed after the CVD. Figure S1 shows the EDX spectra. The sample was plasma etched for about 2 h to remove the amorphous carbon layer on the template surface. The length of CNT segment was ~ 40 μm, with inner diameter and wall thickness of ~ 170 nm and 15 nm respectively. The Au-segment was grown to ~ 3 μm in length. The CNT walls are not highly graphitized, due to the lower growth temperature.

Fabrication of supercapacitor electrodes and its electrochemical measurements

A supercapacitor test cell was fabricated with two CNT/AuNW electrodes separated by a thin filter paper in 6 M KOH solution. The electrodes, which were thin flexible films (~50 μm), were separated by a Whatman filter paper and were sandwiched in a Swagelok type stainless steel (SS) cell. The electrochemical properties and capacitance measurements of supercapacitor electrodes were studied in a two-electrode system by cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy using a Potentiostat/Galvanostat (EG&G Princeton Applied Research 273A).

Cyclic voltammetry measurements

The cyclic voltammetry (CV) response of the electrodes were measured at different scan rates varying from 50-1000 mVs^{-1} (Figure S2). Voltammetry testing was carried out at potentials between -0.5 V and 0.3 V using 6 M KOH aqueous electrolyte solution. The CNT/AuNW electrodes present the typical box like curve, expected for an ideal capacitor. However, CV curves are little distorted for CNT electrodes, showing significant ESR. The area of the curve also increased for CNT/AuNW electrodes, compared to CNT electrodes, indicating an enhancement of the specific capacitance for these electrodes.

Galvanostatic charge-discharge measurements

The specific capacitance of the supercapacitor electrodes was also determined by galvanostatic charge-discharge technique. Galvanostatic cycling of supercapacitor electrodes was performed at a constant current of 2 A/g. The discharge curves are linear in the total range of potential with constant slopes, showing perfect capacitive behavior.

The discharge capacitance of the electrodes (C) was calculated from the slope of the discharge curve,

$$C = \frac{I}{\frac{dV}{dt}} \quad (1)$$

where *C* is the cell capacitance in Farad (F), *I* the discharge current in Ampere (A) and d*V*/d*t* is the slope of the discharge curve in volts per second (V s^{-1}). The specific capacitance (C_{sp}) is calculated according to

$$C_{sp} = \frac{2C}{m} \quad (2)$$

where *m* is the weight per electrode of the active material. The factor of 2 comes from the fact that the total capacitance measured from the test cells is the addition of two equivalent single-electrode capacitors in series.[1] The mass of each CNT/AuNW electrode was ~ 0.26 mg.

Electrochemical impedance spectroscopy measurements

Impedance Spectroscopy measurements were carried out at a dc bias of 0 V with sinusoidal signal of 10 mV over the frequency range from 50 kHz and 10 mHz. At lower frequency, the imaginary part of impedance sharply increases, which is typical of the capacitive behavior of the electrode. The maximum power density of the supercapacitor has been calculated from the low frequency data of the impedance spectra, according to the equation,

$$P_{max} = \frac{V_i^2}{4Rm} \quad (3)$$

where V_i is the initial voltage, R is the equivalent series resistance and m is the total mass of the system. The ESR has been obtained from the *x*-intercept of the Nyquist plot. For CNT/AuNW hybrid electrodes, with a cell voltage of 0.22 V, an ESR of 480 mΩ and a total mass of 5.2 x 10^{-4} g, we obtain maximum power density of ~ 48 $kWkg^{-1}$. The obtained cell voltage is low, which might be due to the presence of functional group on the CNT surface, resulted from the dissolution of alumina template in NaOH.[2]

Table 1: Characteristics of supercapacitor electrodes[a]

Electrode	Specific capacitance (Fg^{-1})	Power density ($kWkg^{-1}$)
CNT/AuNW (present work)	72	48
CNT (present work)	38	18
SWNT[3]	80	43.3

[a] For comparison, we have included the best results from the previous works on CNT-based supercapacitors.

Reference:

1. Lee, Y. H, An, K. H., Lee, J. Y., Lim, S. C. Carbon nanotube based supercapacitors. *Encyclopedia of Nanoscience and Nanotechnology* **1**, 625-634 (2004).
2. Mattia, D., Bau, H. H., and Gogotsi, Y. Wetting of CVD films by polar and Nonpolar liquids and implications for carbon nanopipes. *Langmuir* **22**, 1789-1794 (2006).
3. Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanaike, O.; Hatori, H.; Yumura, M.; Iijima, S. *Nat. Mater.* **2006**, *5*, 987.

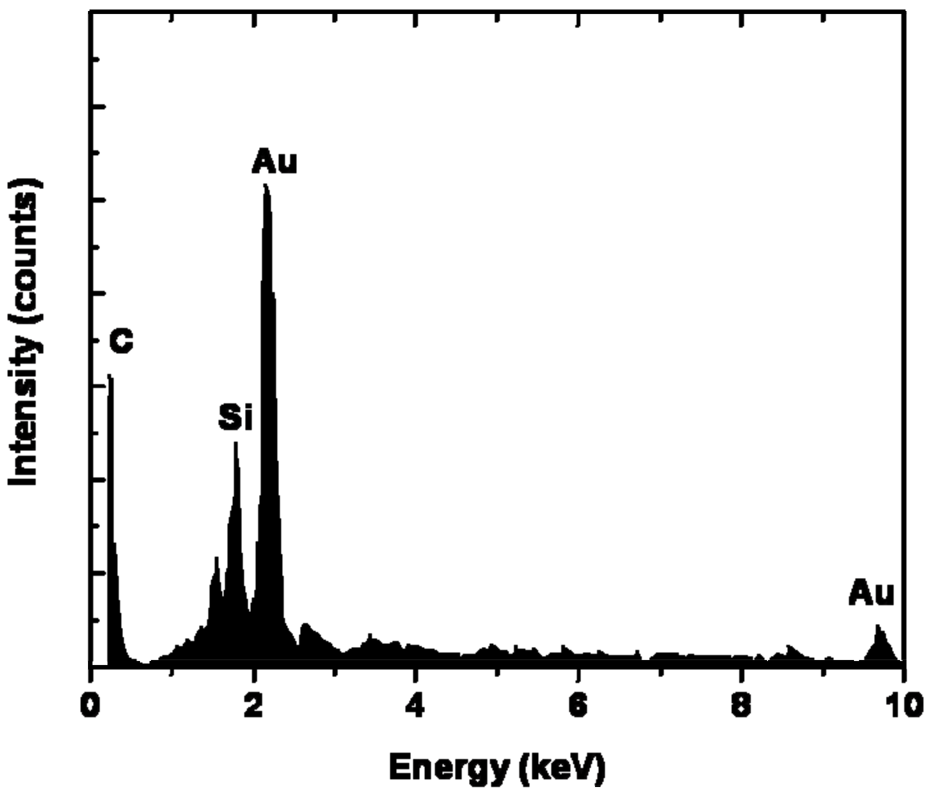

Figure S1: EDX Analysis of CNT/AuNW hybrid nanostructures dispersed on Silicon wafer.

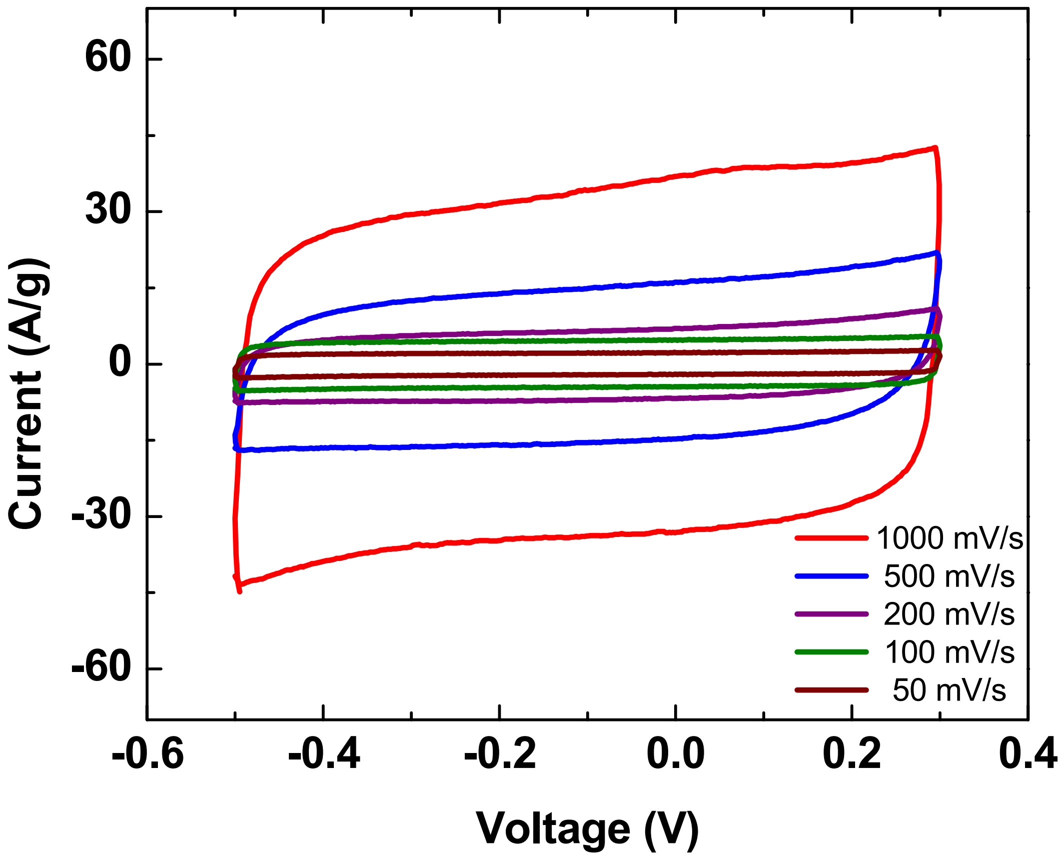

Figure S2: Cyclic voltammograms (CV) for CNT/AuNW electrodes at different scan rates using 6 M KOH aqueous electrolyte. CV at 1000 mV/s shows a rectangular curve, indicating a low ESR.