Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2017

Supplementary information for:

Highly conductive energy efficient electroless anchored silver nanoparticles on

MWCNTs as supercapacitive electrode

Bidhan Pandit, Babasaheb R. Sankapal*

Nano Materials and Device Laboratory, Department of Physics, Visvesvaraya National Institute

of Technology, South Ambazari Road, Nagpur-440010, Maharashtra, India.

*Corresponding Author: brsankapal@phy.vnit.ac.in; brsankapal@gmail.com

Contact No.: +91 (712) 2801170; Fax No.:- +91 (712) 2223230

S1. Electroless cycle variation

20 cycles were certified as final for all electrochemical studies in electroless reduction process. Low cycle (10 cycles) may not able to functionalize the entire surface of MWCNTs with silver nanoparticles. Moreover, increase in cycles (30 cycles) result over-deposition and agglomeration. In both the two cases except 20 cycles, the electrochemical activities are forcefully minimized. For 20 cycles, MWCNTs surface was fully covered by a single nanoparticle layer without any overgrowth, resulting fast electron transport towards maximum electrochemical activities. The whole electrochemical performance has been depicted in **figure S1**.



Figure S1 Electroless cycle variation of MWCNTs/Ag electrode (a) CV curves at cycles, (b) variation of specific capacitance with different cycle number

S2. Electrochemical characterizations

Three-electrode system consisting Ag/AgCl as reference electrode and platinum wire as counter electrode whereas MWCNTs/Ag film as working electrode was engaged to investigate all electrochemical measurements by dipping 1×1 cm² dimension of active electrode material in 0.5 M NaOH electrolyte. Based on CV studies in 0.5 M NaOH electrolyte, specific capacitance¹ of AgNPs/MWCNTs electrode was evaluated form CVs with the help of succeeding equivalence:

$$C_{s} = \frac{1}{mv\Delta V} \int_{V_{i}}^{V_{f}} I(V) dV \qquad (1)$$

where, ${}^{C_{s}}$, denotes the specific capacitance (F/g), m , signifies mass (g) deposited on SS $\int_{V_{i}}^{V} I(V) dV$, substrate, v , represents scan rate (V), ${}^{\Delta V}$, is an functional potential frame and ${}^{v}_{i}$, indicates area under the CV curve of the AgNPs/MWCNTs electrode for unit area (1 cm²) dipped in electrolyte in this study. Specific capacitance (C_{s}) from Galvanostatic charge-discharge can also be calculated as

$$C_s = \frac{I\Delta t}{m\Delta V} \tag{2}$$

where, '*I*' implies current intensity and ' Δt ' entails discharge time (t) of the experimental chargedischarge curve.

Further specific energy (E) in Wh/kg associated with specific power (P) in W/kg of electrode were evaluated from the charge–discharge dimensions using the reckoning,

$$E = \frac{1}{2} \left[\frac{C_s \Delta V^2}{3.6} \right]$$
(3)
$$P = \frac{3600 \times E}{\Delta t}$$
(4)

Here, ' Δt ' indicates discharge time (t).

S3. Electrochemical characterizations of MWCNTs electrode

MWCNTs electrode shows well-distinguished, undistorted, and rectangular CV plots through electric double layer capacitance (EDLC) and exhibits maximum specific capacitance of 126 F/g at scan rate of 2 mV/s as shown in **figure S3(a)**. The triangular charge-discharge (CD) curves also show a maximum specific capacitance of 70 F/g at current density of 1.25 mA/cm² (**figure S3(b)**). The maximum specific energy evaluated from Ragone plot is 7.9 Wh/kg as presented in **figure S3(c)**. The electrode also exhibits 94 % capacitive retention after 3000 cycles (**figure S3(d)**), showing excellent stable nature.



Figure S3 Electrochemical performance of MWCNTs electrode (a) CV curves at different scan rates ranging from 2 to 100 mV/s, (b) CD curves at different current densities ranging from 1.25 to 2 mA/cm², (c) Ragone plot related to specific energy and power, (d) Cyclic stability for 3000 cycles at 100 mV/s scan rate, inset shows CV curves for different cycle numbers

S4. Imaginary capacitance estimation to measure relaxation time constant

We have calculated $C''(\omega)$ by using following steps²

The impedance $Z(\omega)$ of supercapacitive component is related to

$$Z(\omega) = \frac{1}{j\omega C(\omega)} \tag{5}$$

Now in complex form, $Z(\omega) = Z'(\omega) + jZ''(\omega)$ (6)

Combining these two, we have,

$$C(\omega) = \frac{1}{j\omega\{Z'(\omega) + jZ''(\omega)\}} = \frac{-\{Z''(\omega) + jZ'(\omega)\}}{\omega|Z(\omega)|^2}$$
(7)

In equivalence with, $C(\omega) = C'(\omega) - jC''(\omega)$ (8)

It is derived that
$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} = \frac{Z'(\omega)}{2\pi f |Z(\omega)|^2}$$
(9)

References

- 1. S. Vijayakumar, S.-H. Lee and K.-S. Ryu, *Electrochim. Acta*, 2015, **182**, 979-986.
- 2. C. Portet, P. L. Taberna, P. Simon and E. Flahaut, J. Power Sources, 2005, 139, 371-378.