# Solution processed sun baked electrode material for flexible supercapacitors

*Narendra Kurra[#], S. Kiruthika [#] and Giridhar. U. Kulkarni**

Chemistry & Physics of Materials Unit and DST Unit on Nanoscience
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India.
E-mail: **kulkarni@jncasr.ac.in**
Fax: +91 (80) 22082766
Phone: +91 (80) 22082814

[#]contributed equally to the work.

## Supporting Information

**Fig. S1** Schematic to make conducting nc-Pd/C by thermalising on hotplate.

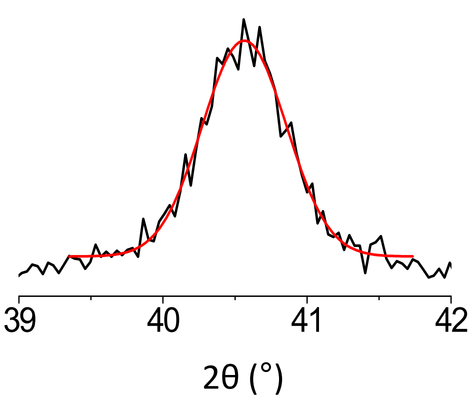


**Fig. S2** Pd (111) peak fitting.

The crystalline nature of nc-Pd/C was analyzed using X-ray diffraction technique. The XRD pattern of the film showed peaks corresponding to metallic Pd, with the estimated particle size of ~16 nm (Figure S2). The Pd nanoparticles size can be calculated from (111) peak of XRD using Scherrer formula.

$$L = k\lambda/\beta\cos\theta$$

where L = grain size

k = 0.9 (constant)

λ = wavelength (1.54Å)

β = (FWHM-FWHM for standard) * π/180

L = 158.2 Å = 15.8 nm

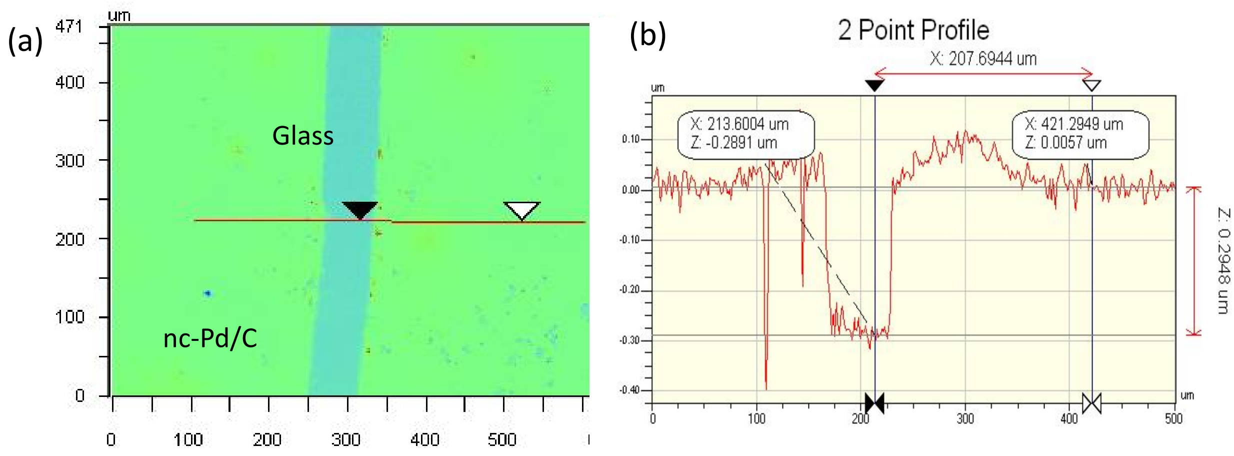


**Fig. S3** (a) The optical profile image of prepared nc-Pd/C film over glass substrate to estimate thickness of the film. (b) The z-profile of the nc-Pd/C film on glass.

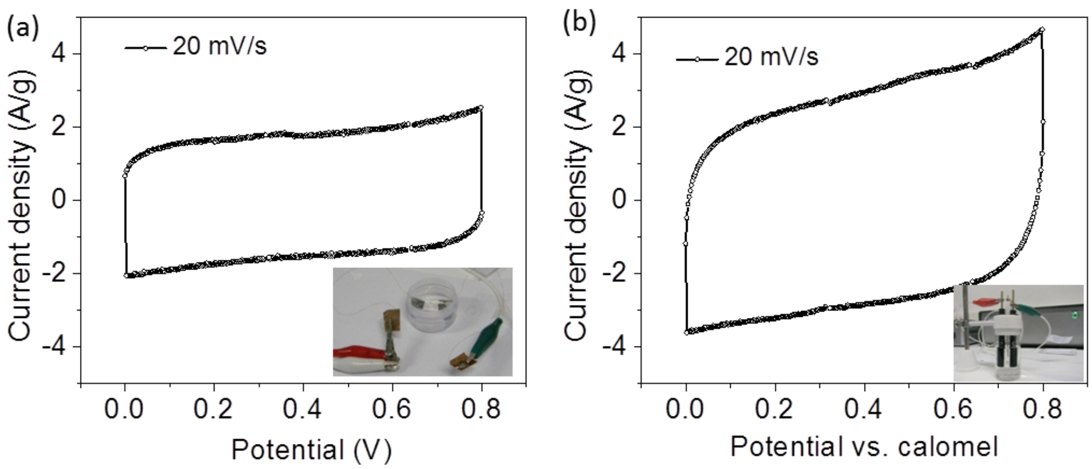


**Fig. S4** (a- b) CV curves of nc-Pd/C composite in 2-electrode vs. 3-electrode configuration at a scan rate of 20 mV/s in 1M $Na_2SO_4$ electrolyte. Inset shows the photographs for the 2 and 3-electrode configuration of the cells.

CV measurement was done in 3-electrode configuration with calomel as the reference electrode, Pt foil as counter electrode and nc-Pd/C as the working electrode.Relatively, the current density values in 3-electrode configuration are almost twice that of 2-electrode configuration.

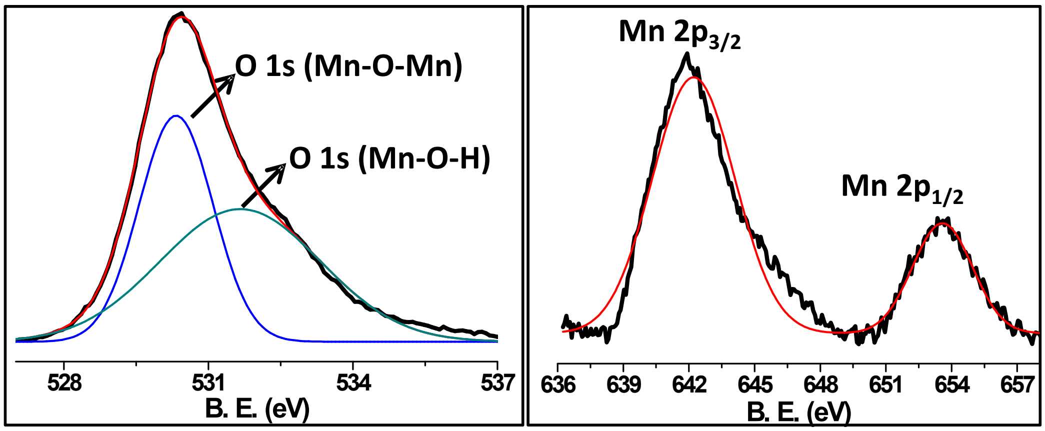


**Fig. S5** XPS core level O 1s and Mn 2p spectra for $MnO_2$. Curve fitting of the spectra was performed assuming a Gaussian peak shape after appropriate background correction.

The presence of $MnO_2$ on nc-Pd/C composite film was examined by X-ray photoelectron spectroscopy (XPS). The core level spectra of O 1s and Mn 2p are presented in Figure S5. The peaks of the O 1s spectrum at 530.3 and 531.6 eV were assigned to Mn-O-Mn and Mn-O-H, respectively, while the two peaks centered at 642.2 and 653.5 eV can be designated to the binding energy of Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively, revealing that majority of the composition is $MnO_2$.

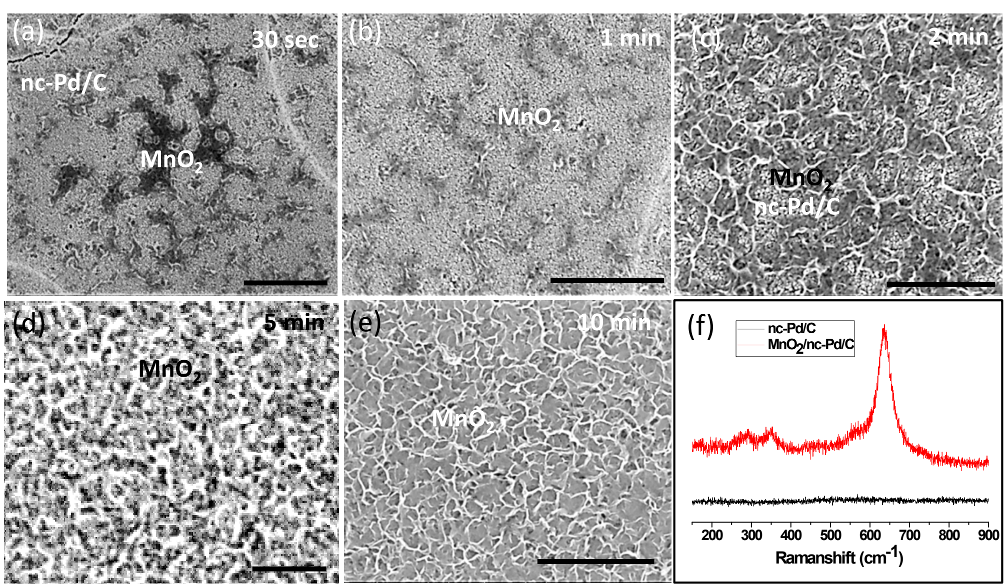

**Fig. S6** Electroless deposition of $MnO_2$ nanowall structures on the autocatalytic nc-Pd/C surface. (a-e) FESEM images of the $MnO_2$ nanowall structures after dipping in neutral permangante solution for 0.5,1, 2, 5 and10 minutes respectively. (f) Raman spectra of the $MnO_2$ in comparison with nc-Pd/C. Scale bar, 1 µm.

The growth conditions for $MnO_2$ were optimized in which 30 seconds resulted in the less dense deposits while 10 minutes dipping resulted in the formation of thicker deposits (see Figures S6a-e). It was found that the deposition time of 2 minutes resulted in the optimal coverage of $MnO_2$ where the bottom the nc-Pd/C surface is seen (see Figure S6c). The Raman spectrum of the $MnO_2$ was characterized by one sharp peak at 638 $cm^{-1}$ and weak peaks at around 290 and 347 $cm^{-1}$ respectively (see Figure S6f). The peak at 638 $cm^{-1}$ can be assigned to the symmetric Mn-O stretching vibration of the $MnO_6$ octahedra group.[51] The low-frequency bands at 290 $cm^{-1}$ and 347 $cm^{-1}$ are assigned to the bending modes of Mn-O. The Raman spectra and band frequencies of the $MnO_2$ is closely resembling that of $\gamma$-$MnO_2$.[51]

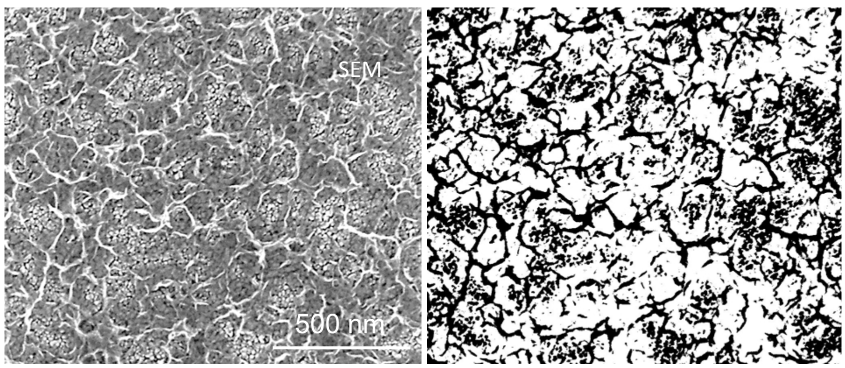


**Fig. S7** SEM image of the $MnO_2$ nanowalls on nc-Pd/C composite film and its corresponding surface coverage image.

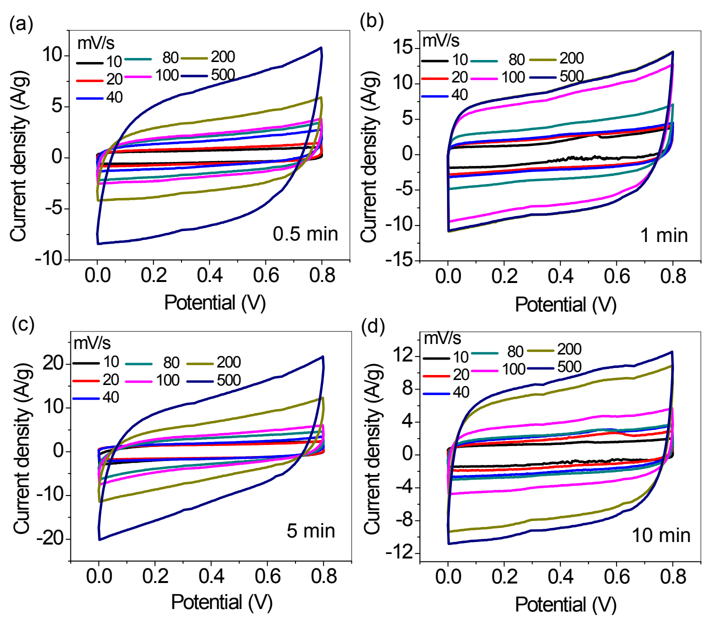

**Fig. S8** (a-d) Cyclic voltammetry curves for $MnO_2$/nc-Pd/C symmetric electrodes at different scan rates (10-500 mV/s) with different $MnO_2$ deposition times of 0.5, 1, 5 and 10 minutes, respectively.

Cyclic voltammetry (CV) measurements were performed for the $MnO_2$/nc-Pd/C composites for different mass loadings of $MnO_2$. All the electrochemical measurements were performed in two electrode configuration in 1M $Na_2SO_4$ electrolyte solution. Figure S8a shows the scan rate dependent CVs for 0.5 minute deposited $MnO_2$ on nc-Pd/C surface at different scan rates of 10-500 mV/s, with a potential window of 0 - 0.8 V. The current values of CVs for 5 minutes deposited $MnO_2$ on nc-Pd/C are found to be higher and nearly rectangular shape for CVs at various scan rates, indication for capacitive behavior of $MnO_2$/nc-Pd/C electrodes (see Figures S8a-d).

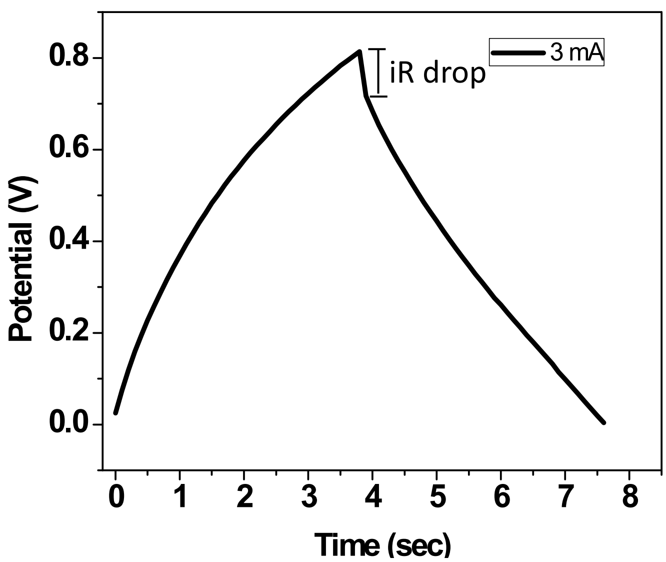


**Fig. S9** CD curve with an IR drop at the beginning of the discharge curve.

IR drop is the potential drop at the beginning of the discharge curve which is the sum of resistances of the electrodes, electrolyte and electrode-electrolyte interfaces ($\Delta V=2I_cR$ where $I_c$ is the charging current and R is the ESR).

$ESR = iR_{drop}/2i$

$= 0.097V/2(3mA)$

$= 16\ \Omega$

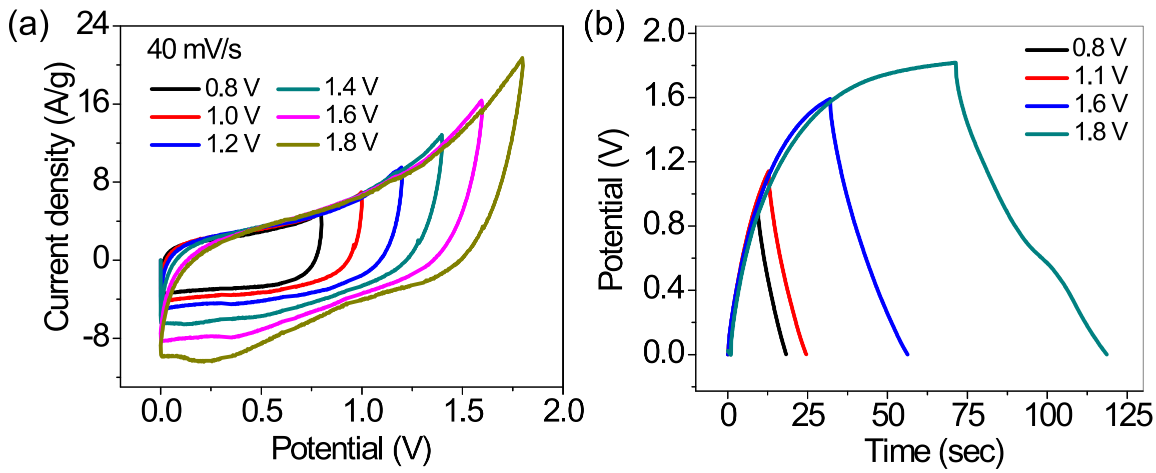


**Fig. S10** (a) CV curves of optimized (2 minutes) $MnO_2$/nc-Pd/C//nc-Pd/C ASC measured at different potential windows at a scan rate of 40 mV/s. (b) Galvanostatic charge–discharge curves at 3 A/g in different potential windows, from 0.8 to 1.8 V.

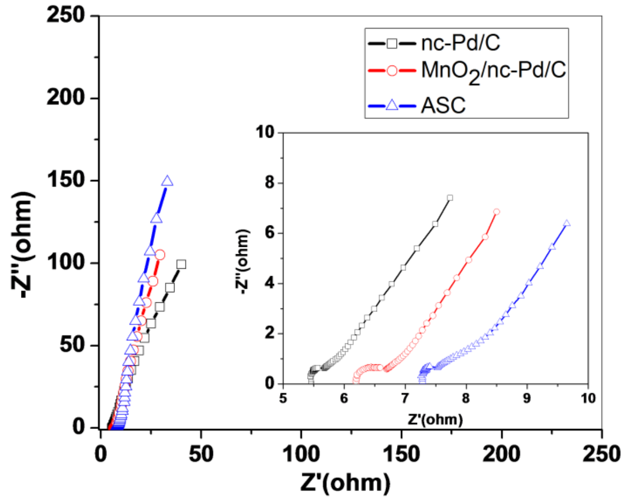


**Fig. S11** Comparison of the complex impedance plots of the symmetric (nc-Pd/C//nc-Pd/C, $MnO_2$/nc-Pd/C// $MnO_2$/nc-Pd/C) and asymmetric ($MnO_2$/nc-Pd/C//nc-Pd/C) supercapacitors.

Electrochemical impedance measurements have been performed for nc-Pd/C, $MnO_2$/nc-Pd/C and the asymmetric supercapacitor $MnO_2$/nc-Pd/C//nc-Pd/C over a frequency range of 100 kHz to 0.1 Hz at open circuit potential of 5 mV (see Figure S11). These measurements are useful in knowing the ESR, charge transfer kinetics and the ion diffusion processes involved in a supercapacitor. Impedance measurements are plotted in Nyquist plot in which the imaginary (Z'') impedance is plotted against real (Z') part, the intercept on the real axis gives the ESR value. This ESR value indicates the series resistance which includes electrolyte resistance and the electrode/electrolyte interface resistances. In the high-frequency region (shown in the inset of Figure S11), intersecting point on x-axis (Z') gives rise to ESR which is found to be in the range of 5.5 to 7.2 Ω. The presence of smaller semicircles implies better electrode–electrolyte interfacial ionic conductivity. The vertical nature of the plots from low to mid frequency regions is indicative of the capacitive behavior supercapacitors.

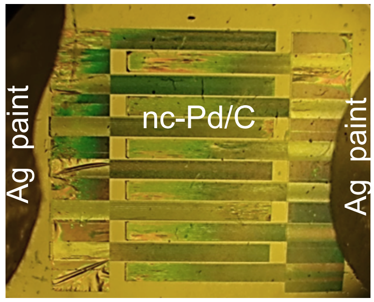


**Fig. S12** Optical micrograph showing the micro-supercapacitor of nc-Pd/C electrode on $SiO_2$/Si substrate with silver paint contact. Ionic liquid electrolyte was coated over electrode surface.

**Calculations**

Cyclic voltammetry gives a voltammogram which is a measure of charge response with respect to changing voltage, estimating capacitance of a supercapacitor. The voltammogram records the current change with respect to the changing voltages at constant scan rate (dV/dt). The capacitance can be related to current (I) and scan rate (s) by the following equation

$$\text{Cell capacitance (C)} = I/s \ldots\ldots(1)$$

The specific capacitance was calculated from the equation

$$C_s = 2(1/m_t)(I/s) \ \text{(F/g)} \ldots\ldots(2)$$

where $m_t$ is the total mass of the electrodes (0.4-0.45 mg), I is the current in mA and s is the sweep rate in mV/sec (s = dV/dt).

The voltage response can be obtained through charging or discharging the cell at a constant current. The equivalent series resistance (ESR) was calculated from the IR drop in the discharge curve. IR drop is the potential drop at the beginning of the discharge curve which arises due to the resistance of the electrodes, electrolyte and interfaces ($\Delta V = 2I_cR$ where $I_c$ is the charging current and R is the ESR).

$$\text{Energy (E)} = ½\, QV = ½\, CV^2 \ldots\ldots(3)$$

or energy density was calculated from the formula

$$E = (1/2)*(1/3.6)*C_s*(V)^2 \ \text{(Wh/kg)} \ldots\ldots(4)$$

where V is the working potential window of an electrolyte.

Power density was calculated from the following formula.

$$\text{Power (P)} = E/\Delta t \ \ (\text{kW/kg}) \ \ldots\ldots\ldots(5)$$

where Δt is the discharge time

The maximum power density was calculated from the formula,

$$P_{max} = (V)^2/4Rm_t \ldots\ldots\ldots(6)$$

**Table S1.** $C_s$, E and P for the symmetric supercapacitors nc-Pd/C//nc-Pd/C, (2 minutes) $MnO_2$/nc-Pd/C//MnO2/nc-Pd/C and the asymmetric supercapacitor (2 minutes) $MnO_2$/nc-Pd/C//nc-Pd/C.

| S(mV/s) | nc-Pd/C//nc-Pd/C Symmetric | | | (2min) $MnO_2$/nc-Pd/C//$MnO_2$/nc-Pd/C Symmetric | | | (2min) $MnO_2$/nc-Pd/C//nc-Pd/C Asymmetric | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cs (F/g) | E(Wh/kg) | P(kW/kg) | Cs(F/g) | E(Wh/kg) | P(kW/kg) | Cs(F/g) | E(Wh/kg) | P(kW/kg) |
| 10 | 142.13 | 12.5 | 1.78 | 452.3 | 39.8 | 7.24 | 191.64 | 86.23 | 3.45 |
| 20 | 68.05 | 5.98 | 2.17 | 301.6 | 26.54 | 9.65 | 150.99 | 67.94 | 5.43 |
| 40 | 42 | 3.69 | 2.69 | 223.4 | 19.66 | 14.3 | 125.01 | 56.25 | 9 |
| 80 | 33.1 | 2.9 | 4.22 | 130.9 | 11.52 | 16.75 | 114.34 | 51.45 | 16.46 |
| 100 | 28.4 | 2.5 | 4.54 | 87.27 | 7.68 | 18.96 | 99.31 | 44.69 | 17.87 |
| 200 | 19.3 | 1.69 | 6.18 | 62.37 | 5.48 | 19.95 | 81.45 | 36.65 | 29.3 |

**Note S1**

To prepare 1 L of stock solution of 100 mM Pd hexadecylthiolate, 22.45 g of Pd acetate was dissolved in 1 L of toluene solution. To that was added 30.78 mL of 1-hexadecanethiol and stirred well. In order to make two electrodes of nc-Pd/C of a supercapacitor cell, 100 µL of 100 mM Pd hexadecylthiolate was drop coated over 1 x 2.5 $cm^2$ substrate area. After thermolysis under sunlight, $MnO_2$ was deposited over nc-Pd/C by dipping the electrodes in 6 mM $KMnO_4$ solution. Details of the chemicals and the cost calculations are provided below.

**Calculations for preparing stock solution**

*(I) Pd acetate*

Mole = (Weight/Molecular Weight) * (1000/ Volume)

Mole = 100 mM

Volume = 1000 mL or 1L

Molecular weight = 224.51 g/mol

Thus, 100 mM = (Weight/ 224.51)*(1000/1000)

Amount of Pd acetate required = 22.45 g

*(II) 1-hexadecanethiol*

Mole = 100 mM

Molecular weight = 258.51 g/mol

Thus, amount of thiol = 25.85 g

Density = Mass/Volume

Density of 1-hexadecanethiol = 0.84 g/mL

Mass = 25.85 g

Thus, volume of thiol required = 30.78 mL

*(III) 6 mM $KMnO_4$ solution*

Mole = 6 mM

Volume = 5 mL

Molecular weight = 158.03 g/mol

Thus, amount of $KMnO_4$ required = 4.74 mg

(IV) 1M $Na_2SO_4$

Mole = 1 M

Volume = 5 mL

Molecular weight = 142.04 g/mol

Thus, amount of required $Na_2SO_4$ = 0.712 g

**Cost estimation for the fabrication of supercapacitor electrodes**

Cost of 25 g of Palladium acetate = $ 756

Thus, cost for 22.45 g of Palladium acetate = $ 678.9

Cost of 500 mL of 1-hexadecanethiol = $ 567

Thus, cost for 30.78 mL of 1- hexadecanethiol = $ 34.9

Cost of 20 L of toluene = $ 331.5

Thus, cost for 1 L of toluene = $ 16.58

Total cost for synthesis of 1 L of Pd hexadecylthiolate = $ 730.38

**Thus, cost of 200 µL of solution for 2 electrodes = $ 0.146**

Cost for 2 numbers of 1 x 2.5 $cm^2$ glass substrates = $ 0.009

Cost of 500 g of $KMnO_4$ = $ 9.5

Thus, cost for 4.74 mg of $KMnO_4$ = $ 0.0001

(Electrode area: 1 x 2.5 $cm^2$)

| **Electrode material** | **Cost for 200 µL of Pd hexadecylthiolate ($)** | **Substrate cost ($)** | **For heating ($)** | **External contact ($)** | **Oxide coating ($)** | **Electrolyte (5 mL of 1 M $Na_2SO_4$) ($)** | **Gel Electrolyte (1 mL of PVA/$H_2SO_4$) ($)** | **Total cost for one cell ($)** |
|---|---|---|---|---|---|---|---|---|
| nc-Pd/C | 0.146 | 0.009 | NIL (sunlight) | 0.008 | - | 0.009 | | **0.172** |
| nc-Pd/C | 0.146 | 0.009 | NIL (sunlight) | 0.008 | - | - | 0.021 | **0.184** |
| $MnO_2$ over nc-Pd/C | 0.146 | 0.009 | NIL (sunlight) | 0.008 | 0.0001 | 0.009 | | **0.1721** |

Thus, in order to fabricate $MnO_2$/nc-Pd/C based supercapacitor of 0.18 F, the cost involved is $ 0.1721. The commercially available supercapacitor of similar storage capacitance (~0.1 F) costs around $ 2.09[1].


Reference

1. http://in.mouser.com/Passive-Components/Capacit ors/Supercapacitors-Ultracapacitors/_/N-5x76s/?gclid=CI3lgsDg0rgCFcwE4godQh0A3A