Electronic Supplementary Information

Phenols from green tea as dual functional coating to prepare devices for energy storage and molecular separation

Chayanika Das#, Bhanprakash Jain# and Kothandam Krishnamoorthy*

Electroless deposition of gold on anodic aluminum oxide (AAO):

Green tea was brewed in hot water for 1 h. AAO of 200 nm pore diameter (AAO_200) was immersed in the brewed green tea for 5 h. The membrane was then washed in three sets of 50 ml deionised water by dipping in for 30 min each. Washed membranes were then immersed in 0.03 M ammoniacal $AgNO_3$ solution for 8 h and washed with water. The membrane looks faint brown in colour confirming the reduction of silver ions. Finally the membrane was kept in gold plating solution (pH 9) for 48 hours at 5 °C.[1] Gold solution was changed after every 12 h.

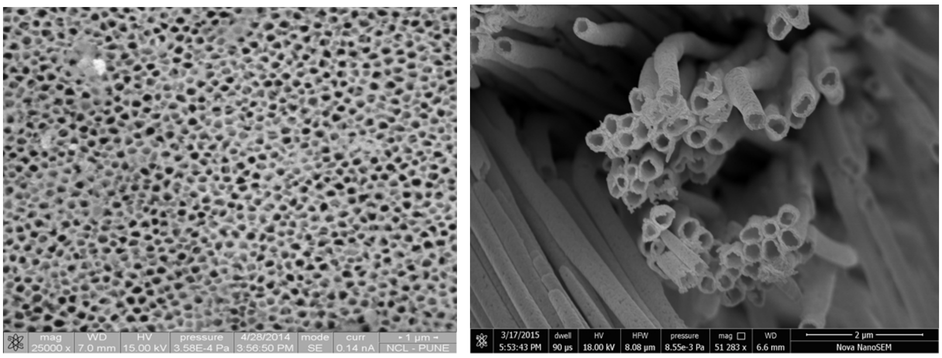

Fig. S1: Gold deposited AAO_200, top view after Ar-plasma treatment (left) and AAO dissolved (right).

Electroless deposition of gold on polycarbonate membrane (PCM):

Gold was deposited in PCM of 30 nm (PCM_30) and 600 nm (PCM_600) pore diameter. The same procedure was followed as described above with only differences being the dipping duration and the pH of the plating solution. PCM was dipped in green tea for 12 h. pH of the plating solution was 10 and deposition time was 24 h.

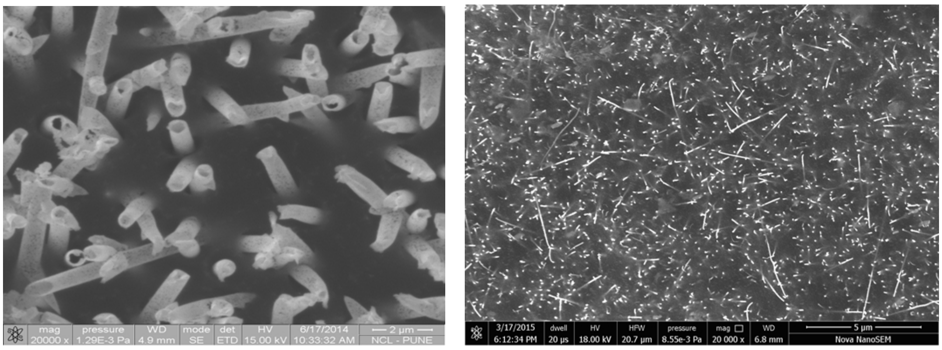

Fig. S2: Gold deposited PCM_600 (left) and PCM_30 (right) after oxygen plasma of 25 W for 5 min.

To study the effect of deposition time on the thickness of deposited gold, pore diameter was determined for PCM_30 after various deposition time 5 h, 10 h and 15 h. Pore diameter was determined by Fick's law of diffusion[1,4]. The calculated pore diameter was 20 nm, 8nm and 0 nm for 5 h, 10 h and 15 h repectively.

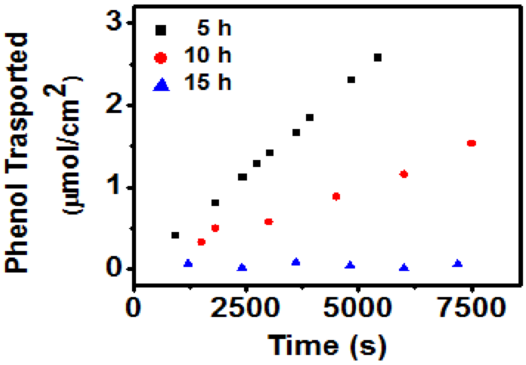

Fig. S3: Transport studies of phenol through gold coated PCM_30nm for various deposition time (5 h, 10 h and 15 h)

Electroless deposition of gold on SCs

The inner layers of a cocoon have more tightly woven silk fibers. Hence innermost layer was removed and the SCs were dipped in methanol and sonicated for fifteen minutes to loosen the layers. Green tea was brewed in hot water (100 °C) for 1 h. Silk cocoons (SCs) were immersed in this solution for 48 hrs. Then the SCs were washed with deionised water. Washed SCs were immersed in 0.03 M ammoniacal $AgNO_3$ solution for 3 h and washed with water. The colour of SCs turned from milky white to brown confirming the reduction of silver. Finally the SCs were kept in gold plating solution (pH 7.5) for 72 hours at 5 °C. Gold solution was changed after every 12 h. The resistance of the gold coated fiber in the GSCs were measured with multimeter using different fibers and the calculated conductivity values were found to vary between 1.8 x 10^3 S/cm and be 2.2 x 10^3 S/cm

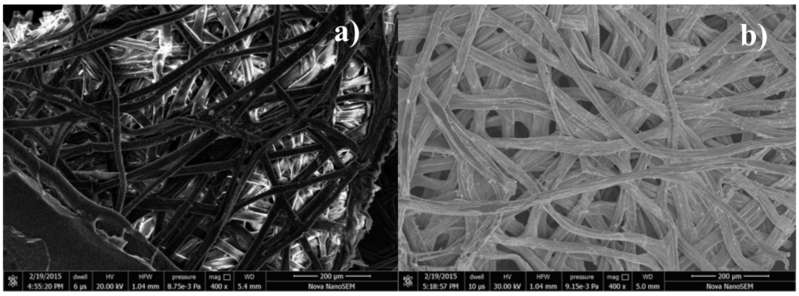

Fig. S4: SEM images of SC with evaporated gold (a) and GSC (b)

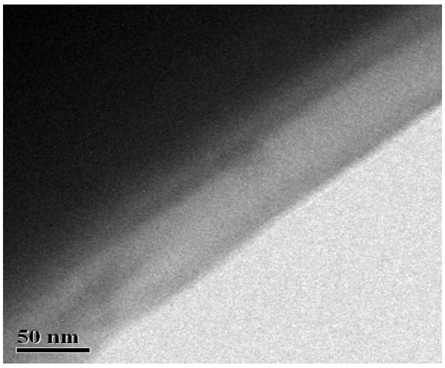

Fig. S5: TEM image of gold coated single silk fiber

Tensile strength measurement of GSC

Dumbbell shaped SCs and GSCs were studied for mechanical strength. Tensile strength tester (Linkam tensile V3.1) was used for the experiments. Calculated average Young's modulus is shown below.

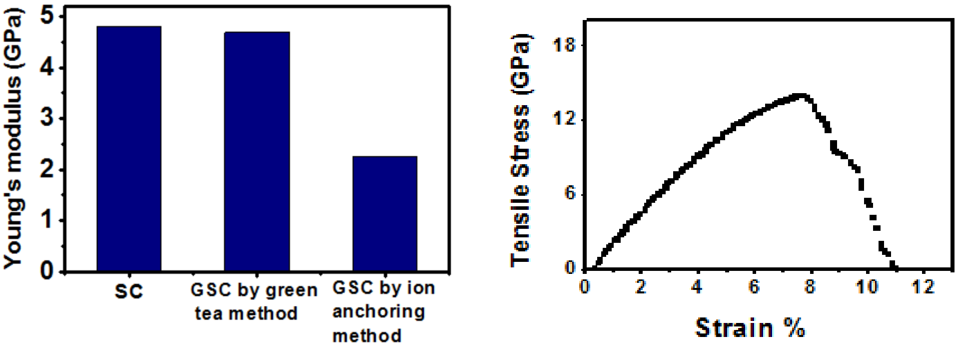

Fig. S6: Young's modulus of SC, GSC by green tea method and GSC by conventional ion-anchoring method (left); stress-strain curve of GSC by conventional ion-anchoring method

Electrochemistry (GSC)

Cyclicvoltammogram (CVs) of 1 mM ferrocene methanol (aq) was recorded using GSCs as working electrode (WE). Pt-foil was used as counter electrode (CE) and Ag/AgCl electrode as reference (RE).

Well defined oxidation and reduction peaks were observed with an ΔE_p of 85 mV. The ratio of anodic to cathodic (i_a/i_c) peak current intensities was found to be less than 1. Furthermore, ΔE_p was found to increase as a function of scan rate. The peak current increased as a function of square root of scan rate indicating that the redox process is diffusion controlled.

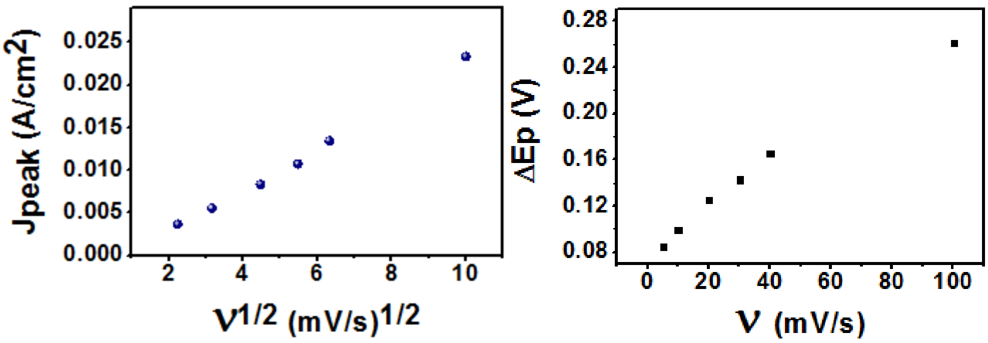

Fig. S7: Peak current density vs square root of scan rate (left) and ΔEp vs scan rate (right) obtained from the CVs of GSC

Electrochemistry (Nanoelectrode ensembles)

Gold deposited PCM_30 was used to study electrochemical behavior of two and three dimensional nano electrode ensembles (2D_NEE and 3D_NEE). The facial gold was removed from a gold deposited PCM_30 to get 2D_NEE. Gold film on one of the faces of the membrane was removed by using a Q-tip dipped in ethanol. The removal of gold film exposed 30 nm diameter gold disks embedded in the polycarbonate membrane. This electrode is known as 2D NEE. Using the gold film on one of the faces as contact, CVs of ferrocene methanol were recorded. The current density increased as a function of scan rate (ν) and the plot of $\nu^{1/2}$ vs I was found to be linear indicating diffusion controlled electrochemical process. In order to fabricate 3D NEE, the polycarbonate membrane was partially etched by oxygen plasma. The plasma etching was carried out for 5 minutes with the RF power of 25 W. Upon partial removal of polymer by oxygen plasma, gold nanowires protrude from the surface. The oxygen plasma etching results in the formation of 3D NEE. This experiment was carried out using several nanoporous (30 and 600 nm pore) polycarbonate templates. The protruding gold nanotubes can be seen in the SEM images (Fig. S2). CVs were recorded using the 3D NEE as working electrode in ferrocene methanol solution. Note that all WE area was kept constant by sticking a punched tape. The ΔE_p was found to be 69 mV, which is comparable to the ΔE_p of 2D NEE. The current density was found to scale as function of square root of scan rate confirming diffusion controlled electrochemical process. The difference, however was found in case of current density of 2D and 3D NEE. The current density of 2D NEE was found to be three times lower than the 3D NEE indicating the increase in the electroactive area of the 3D NEE.

These 3D NEE are effective in detecting analytes at concentrations as low as zeptomolar due to decreased capacitance.[2]

Electropolymerization of EDOT on GSCs

Electropolymerization was performed in a standard 3-electrode configuration, the above gold coated silk cocoons (GSCs) were taken as WE, Pt-foil was used as CE and a constant potential of 1.2 V vs Ag/Ag^+ was applied in a 10 mM acetonitrile solution of EDOT and 100 mM lithium perchlorate as supporting electrolyte. Before polymerization, GSCs were soaked for 30 min in monomer electrolyte solution. The polymerization was carried out for 50 (**A**), 100 (**B**) and 150 s (**C**). After polymerization, the electrodes were washed with the monomer free electrolyte to remove unreacted monomer. The quantity of polymer deposited was calculated by following equation:

$$W = \frac{Charge\ passed\ (C) \times Molecular\ weigth\ of\ EDOT}{Faraday\ constant\ \times number\ of\ electron\ released\ per\ monomer}$$

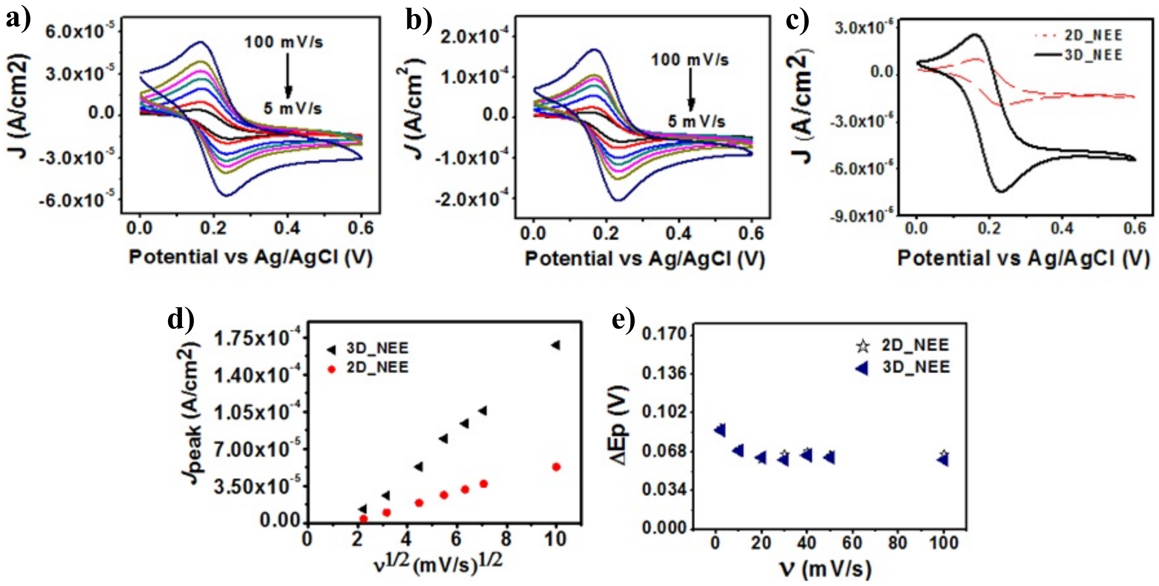

Fig. S8: CVs of ferrocene methanol with a) 2D_NEE and b) 3D_NEE as WE, c) 2D NEE and 3D NEE at scan rate 10 mV/s, d) plot of peak current density vs square root of scan rate and e) plot of ΔEp vs scan rate for 2D and 3D NEE

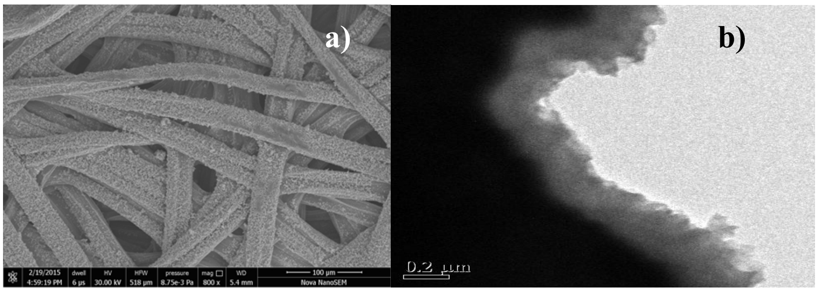

Fig. S9: SEM Images of electropolymerized PEDOT on a) GSC and b) TEM image of electropolymerized PEDOT on gold coated single fiber

Electrochemical performance of PEDOT on GSCs

Electrochemical characterizations were performed in a standard 3-electrode configuration. The above PEDOT coated GSCs were used as WE, Pt-foil as CE, Ag/AgCl as RE and 0.5 M H_2SO_4 (aq.) as electrolytic solution. CV and cyclic charge-discharge (CCD) were performed on Multichannel Autolab MAC 80038 instrument and electrochemical impedance spectroscopy (EIS) was measured on Biologic instrument. The CVs were recorded in potential range of 0 to 0.9 V at various scan rates. The CCDs were measured at different current densities from 1 to 5 A/g. The EIS was performed in the frequency range from 50 kHz to 10 Hz. All the measurements were carried out at room temperature. The specific capacitance calculated from the slope of discharge curve. Energy density (E) and power density (P) were calculated by following equations[3]:

$$E = \frac{1}{2}CV^2 \quad \text{and} \quad P = \frac{E}{\Delta t}$$

where C is specific capacitance, V voltage range and Δt discharge time.

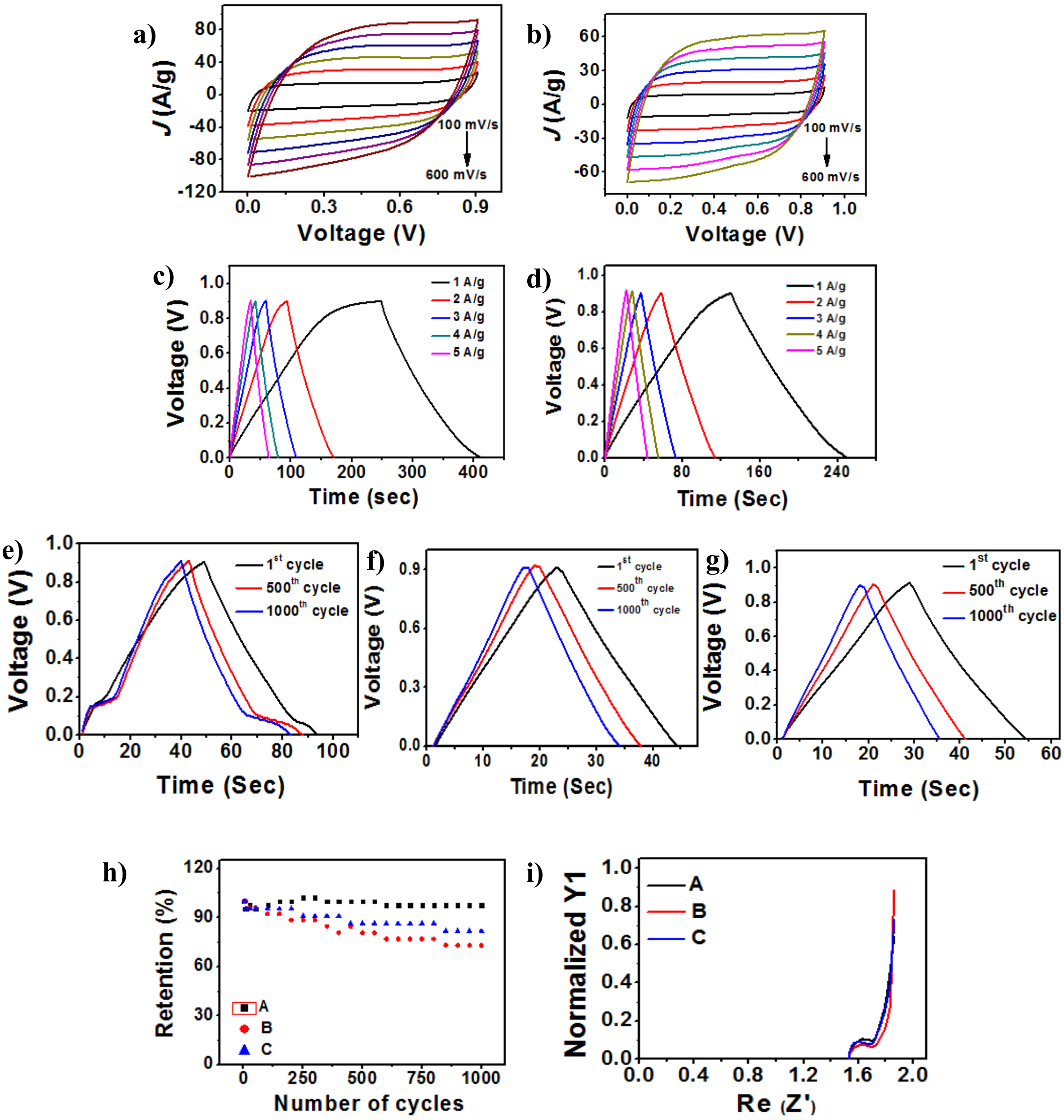

Fig. S10:Supercapacitor measurements of PEDOT on GSCs: CVs at various scan rates for a) **B** and b) **C**; charge-discharge curves at various current densities for c) **B** and d) **C**. 1st ,500th and 1000th cycles of charge-discharge for e) **A**, f) **B** and g) **C**; h) capacitance retention of 1000 charge-discharge cycles and (i) nyquist plot of **A**, **B**, **C**.

Table S1. Specific capacities of electrodes at various current densities

Electrode	1 A/g	2 A/g	3 A/g	4 A/g	5 A/g
A (0.4 mg)	254	250	244	242	237
B (1.02 mg)	186	182	176	174	173
C (1.24 mg)	143	133	130	129	125

Electropolymerization of EDOT on AAO

Before electropolymerization of EDOT the gold deposited AAO was treated with Ar plasma for 5 min at RF power of 25 W (Fig. S1) to remove surface gold. To keep the area constant a punch tape was stuck on the membrane. For electropolymerization, the above Ar-plasma treated gold deposited membrane was taken as WE, Pt-foil was used as CE and a constant potential of 1.3 V vs Ag/AgCl for 10 s was applied in a 10 mM aqueous solution of EDOT and 100 mM lithium perchlorate as supporting electrolyte. Then -0.6 V vs Ag/AgCl was applied for 10 s.

For creating positive charge, constant potential of 0.4 V and 1.0 V vs Ag/AgCl was applied to the PEDOT coated membranes for 2 min. The electrolytic solution was 100 mM aqueous lithium perchlorate without any monomer. Pt-foil was taken as CE.

SDS (Sodium dodecyl sulphate) Treatment

Aqueous solution of 10 mM (above CMC) SDS was filtered through the positively charged PEDOT coated membranes *in vacuo.* 0.2 ml of solution was filtered four times and washed with copious amount of water.

Determination of pore diameter

Pore diameter of gold deposited nanotubes, positively charged PEDOT nanotubes as well as SDS treated nanotubes were determined by the diffusion of naphthalene by Fick's law of diffusion[4] (1):

$$J = \frac{DC_f \pi r^2 n}{l} \quad \text{...........(1)}$$

where$J$ = flux ;D = diffusion coefficient ; C_f = feed concentration ; r = radius of pore ; n = pore density ; l = membrane thickness.

Two half U-tubes (one as feed and other as reservoir) were connected with the respective membranes held in between the two tubes. The amount of molecules transported from feed to reservoir was monitored by absorbance spectroscopy. 25 ml each of 10^{-4} M naphthalene in water and blank water was taken as feed and reservoir respectively.

$$J_{200} = \frac{D C_f \pi r_{200}^{2} n}{l} \text{..........(2)}$$

$$J_{48\,h} = \frac{D C_f \pi r_{48\,h}^{2} n}{l} \text{..........(3)}$$

Where J_{200} and $r_{200}$is flux and radius of pore of AAO_200 without any modification and $J_{48\,h}$ and $r_{48\,h}$flux of gold deposited AAO for 48 h deposition time (AAO_200_48h). Assuming, only the pore size (*r*) decreases on modification, all other parameters of (1) are considered constant. For each pore size we get a *J* and a relative average *r* is thus calculated as:

$$\frac{J_{200}}{J_{48\,h}} = \frac{r_{200}^{2}}{r_{48\,h}^{2}} \text{..........(4)}$$

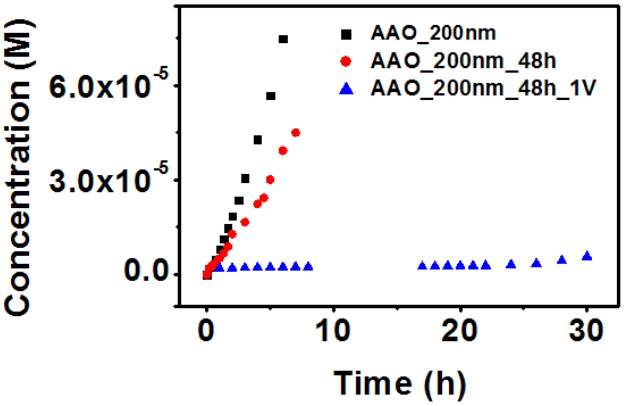

Fig. S11: Transport studies of naphthalene through AAO_200, gold coated AAO_200nm_48h and PEDOT charged at 1 V (AAO_200nm_48h_1V)

Dye separation

Each pair of dyes were 0.1 mM in phosphate buffer of pH 7.3 (PBS_7.3); 25 ml each of dye mixture and PBS_7.3 was taken as feed and reservoir solutions, respectively.

Hydrophobicity based Separation (dyes used are p-nitrophenol and p-nitrotoluene):

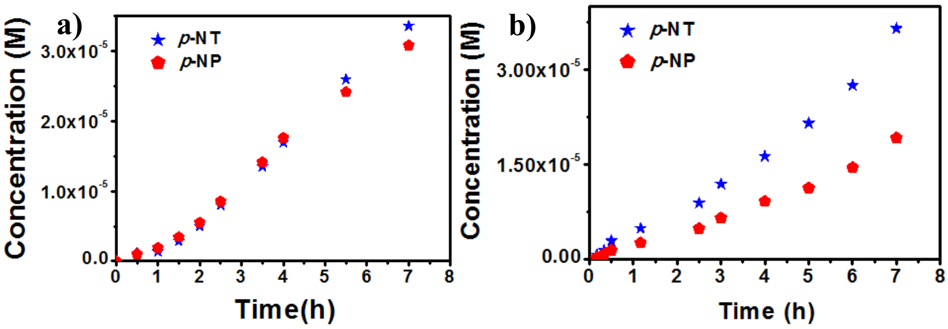

Fig. S12. Transport studies of p-NT and p-NP with a) neutral and b) positively charged PEDOT at applied potentials of 0.5 V. After oxidation, SDS was filtered through the pores to modify the tubes.

Table S2: Separation factor and pore diameter with potential variation for hydrophobicity based separation

Potential Applied (V)	Pore Diameter (nm)	Separation Factor (α)
0.0	11	1.1
0.5	9	1.8
1.0	7	8.9

*Area (punch hole) = 0.16 cm^2

Charge based Separation (dyes used Rhodamine 6G and Calcein):

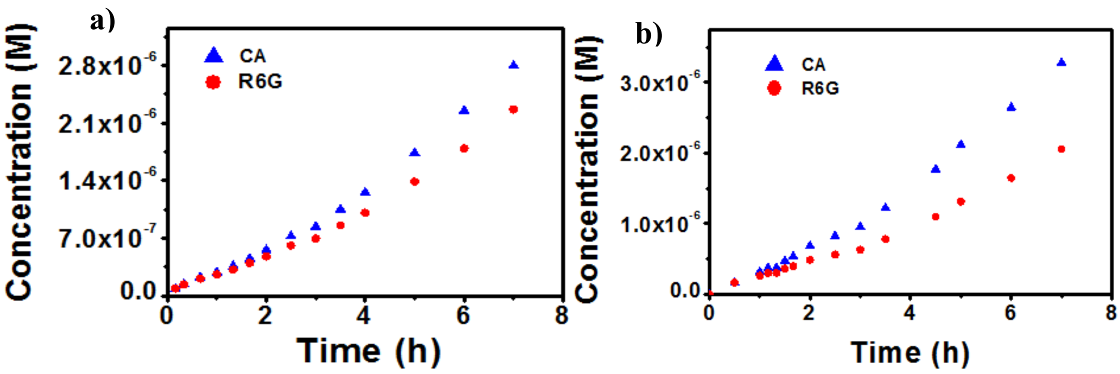

Fig. S13. Transport studies of R6G and CA with a) neutral PEDOT and positively charged PEDOT at applied potentials of 0.4 V (b)

Table S3: Separation factor (α) and pore diameter with potential variation for charged based separation

Potential Applied (V)	Pore Diameter (nm)	Separation Factor (α)
0.0	10	1.2
0.4	16.6	1.7

1.0	15	2.5

*Area (punch hole) = 0.16 cm^2

Electroless deposition of palladium

SC, AAO_200 and PCM_100 after green tea and silver modification was dipped in Pd plating bath for an hour. 10 ml of Pd bath contains $PdCl_2$ (0.002 g), HCl (0.004 ml), NH_4OH (1.6 ml), NH_4Cl (0.27 g) and Na_2HPO_2 (0.1 g). pH of the bath was adjusted to 8.5 by HCl. Temperature of the bath was maintained at 60 °C

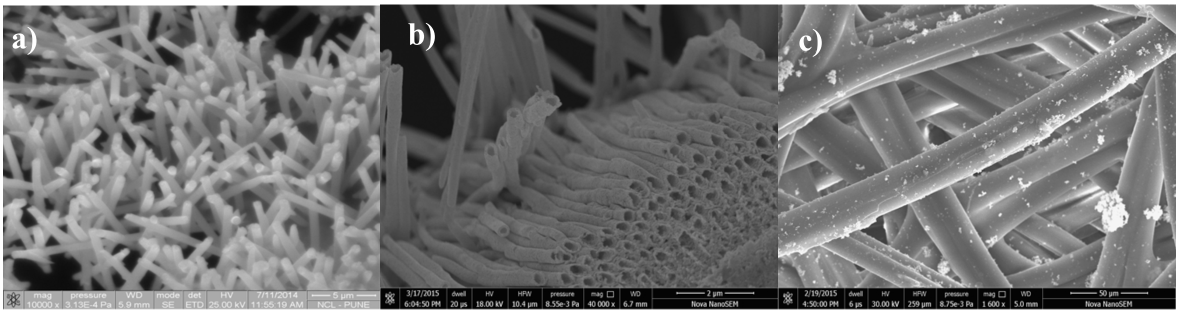

Fig. S14: Palladium deposited a) PCM_600, b) AAO_200 and c) SC

Electroless deposition of nickel

SC, AAO_200 and PCM_100 after green tea modification was dipped in $PdCl_2$ solution (0.002 g $PdCl_2$, 2 drops of HCl and 50 ml water) for an hour and washed with water. Then dipped in Ni bath for 3 h. 10 ml of Ni bath containsNiSO4 (0.0.875 g), citric acid (0.375 g), sodium acetate (0.125 g) and Na_2HPO_2 (0.5 g). pH of the bath was adjusted to 8.5 by HCl. The bath was kept at room temperature.

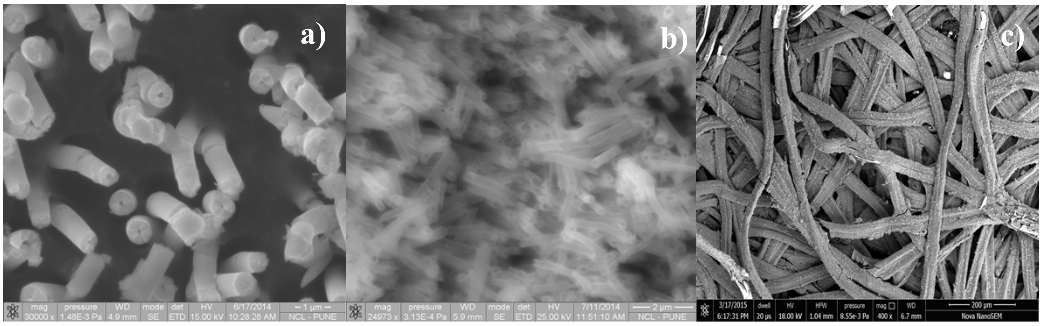

Fig. S15: Ni deposited a) PCM_600, b) AAO_200 and c) SC

References

1. C. Das and K. Krishnamoorthy, *Chem. Commun.*, 2014, **50**, 5905-5908.
2. R. Gasparac, B. J. Taft, M. A. Lapierre-Devlin, A. D. Lazareck, J. M. Xu and S. O. Kelley, *J. Am. Chem. Soc.*, 2004, **126**, 12270-12271.
3. J. W. Park, S. J. Park, O. S. Kwon, C. Lee and J. Jang, *Chem. Mater.* 2014, **26**, 2354-2360.

4. K. Yamada, R. Gasparac and C. R. Martin, *J. Electrochem. Soc.,* 2004, **151**, E14-E19.