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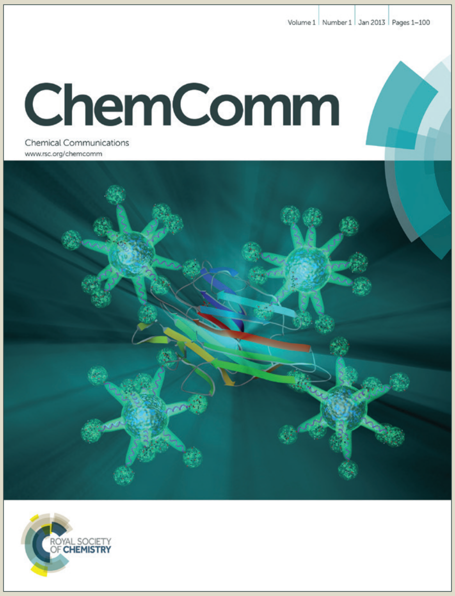

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Phenols from green tea as dual functional coating to prepare devices for energy storage and molecular separation

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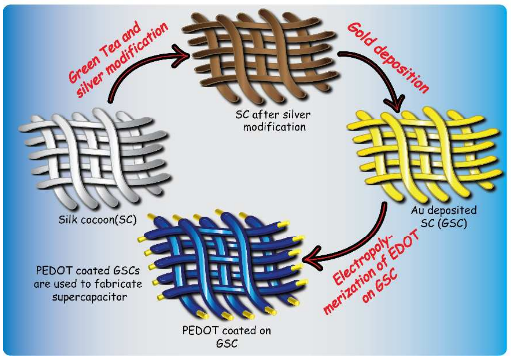
Polyphenols from green tea was used to electroless deposit gold on silk cocoons(SCs) and nanoporous aluminum oxide (AAO) templates. The gold coated cocoons were used as electrode in supercapacitors with capacitance as high as 254 F/g and specific power of 2287 W/kg. The metal coated AAO template was used for molecular separation.

Conducting substrates with woven fibers and nanopores are vital for fabrication of devices for energy storage and molecular separation.[1,2] We were interested in developing a generic method that renders the possibility of preparing substrates for above mentioned applications and beyond. To accomplish this objective, a method that allows deposition of metals on substrates irrespective of shape, size and nature is desirable. In this context, a recent report[3] that uses green tea extract to synthesize silver nanoparticles attracted our attention because Ag can be a seed for electroless deposition of metals. Furthermore, the Polyphenols (PP) in green tea adhere on variety of surfaces,[4,5] hence they are suitable for developing a generic approach to prepare conducting substrates. Herein, we like to point out that the existing electroless metal deposition (EMD) methods are not effective to deposit metals on natural substrates. The ion anchoring,[6] which is the first step in the EMD affects the mechanical strength of the natural substrates (ESI). Furthermore, the EMD requires the substrates to comprise a functionality that can be used for ion anchoring.[7]

Towards the objective of developing conducting woven electrodes, we have identified silk cocoons (SCs) as substrates. SCs have unique structure comprising very high aspect ratio micro fibers woven into a thin layer.[8] The SCs are insulators. Deposition of metal on the SCs can impart electrical conductivity. However, due to the woven structure of SCs, metal deposition by evaporation is not possible. Indeed, we found that the metal deposits only on the outer layer during metal evaporation (*vide infra*). We have tested our hypothesis of PP based EMD, by using PP present in green tea as protecting and reducing layer to prepare gold deposited silk cocoons (GSCs). The GSCs mechanical strength was found to be comparable to that of uncoated SCs. The GSCs were used as electrode to deposit poly(3,4-ethylenedioxythiophene) (PEDOT) and utilized for the fabrication of supercapacitors with specific capacitance as high as 254 F/g. The best energy and power densities were found to be 29 Wh/kg and 2303 W/kg. EMD in AAO template is more challenging,[7] but we could accomplish this task using the green tea based metal deposition procedure. The EMD results in the formation of gold nanotubes embedded AAO. This template was used for molecular separation.

The green tea extract was prepared by brewing the tea in hot water (100 °C) for one hour. SCs were immersed in this solution for 48 hrs. The PP coated SCs were immersed in ammoniacal silver nitrate solution for three hours. The colour of SCs turned from milky white to brown indicating the formation of silver nanoparticles on the surface of the silk fibers. The silver coated SCs were immersed in gold plating solution for 72 hrs. The Ag nanoparticles reduce the Au^+ to Au and due to autocatalytic reaction, the gold deposition continued to form a thin film on top of the silk fibers (Scheme 1).The conductivity of the gold coated fiber in the GSCs were calculated using different fibers and the values were found to vary between 1.8 x 10^3 S/cm and 2.2 x 10^3 S/cm. Scanning electron microscopy (SEM) was used to image the surface of the GSCs (Fig. 1a). The SEM images indicate the formation of smooth gold film throughout the SCs. Charge accumulation was not found during the imaging that indicates that the gold coating is highly conducting and



Scheme 1. Cartoon showing supercapacitor electrode preparation using silk cocoons

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[b] *† Electronic Supplementary Information (ESI) available: [Procedures and data on the performance of devices are provided in the ESI]. See DOI: 10.1039/x0xx00000x*

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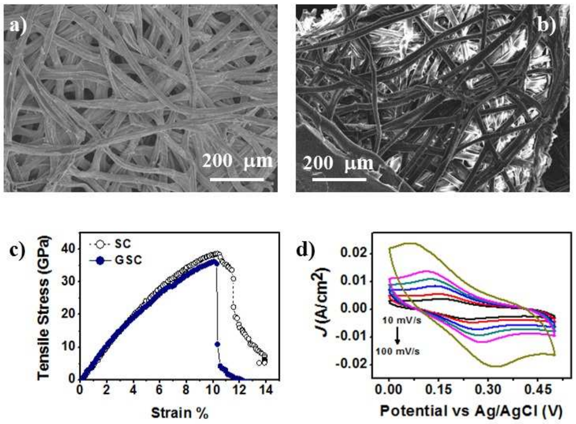

Fig. 1 SEM image of GSC (a) and SC (b). The charging of the silk fibers is visible in image b. Strain vs stress curve of SC and GSC (c). CV of ferrocene methanol recorded using GSCs as working electrode (d).

uniform. Contrary to this, charge accumulation was observed in case of SCs (Fig. 1b), despite evaporation of gold to dissipate the charges during the electron microscopy imaging. This experiment further confirms that the evaporation of metal on SCs is not an effective method to impart conductivity. The thickness of electroless deposited Au on SCs was found to be ~50 nm using TEM (Fig. S5, ESI).

Young's modulus is an important parameter that provides information about the strength of a substrate. The Young's modulus of SCs and GSCs was found to be 4.8 GPa and 4.7 GPa, respectively (Fig. 1c). This indicates that the green tea modification and subsequent electroless gold deposition didn't significantly alter the strength of the SCs. To study the suitability of GSCs as electrode, cyclicvoltammogram (CVs) of ferrocene methanol (FM) was recorded using GSCs as working electrode. Typical CV of FM was observed, which indicated the suitability of GSCs as electrode (Fig. 1d). Further discussion is provided in the ESI.

With these information in hand, we proceeded to fabricate supercapacitors using the GSCs as electrode. Conjugated polymers are pseudocapacitive materials,[1] among them PEDOT is a stable conducting polymer, hence we have chosen this polymer for supercapacitor fabrication.[9] The GSCs were used as working electrode to electrochemically deposit PEDOT by oxidizing the monomer 3,4-ethylenedioxythiophene (EDOT). The quantity of polymer deposited on the electrode was controlled by controlling the duration of the polymerization. The polymerization was carried out for 50 (**A**), 100 (**B**) and 150 s (**C**). The quantity of polymer deposited was calculated by following reported procedure (Table S1, ESI). The redox characteristics of electrode **A** was studied in 0.5 M H_2SO_4 by cycling the potential between 0 and 0.9 V. A typical rectangular cyclicvoltammogram (CV) was observed (Fig. 2a). The charge discharge experiment was carried out between 0 and 0.9 V at various current densities. The charge discharge curves are not perfectly symmetric indicating IR drop in the pseudocapacitive PEDOT (Fig. 2b). The specific capacitance calculated from the slope of discharge curve is 254 F/g while discharging the capacitor at 1 A/g. The specific capacitance didn't decrease significantly as a function of cycling. Indeed, 94% of the specific capacitance was retained at 1000 cycles (Fig. 2c). A marginal decrease in specific capacitance was observed while increasing the current density from 1 A/g to 5 A/g (Table S1, ESI). The lowest specific capacitance was 237 F/g for a current density of 5 A/g. For electrodes **B** and **C**, the CVs recorded in 0.5 M H_2SO_4 showed typical rectangular CVs (Fig. S8, ESI†). The charge discharge curves of **B** and **C** are similar to **A**. However, the best specific capacitance for **B** and **C** were 186 F/g and 143 F/g, respectively. The decrease in specific capacitance is due to the peeling off of PEDOT from the electrode during the charge discharge cycling. This is a result of the presence of thicker PEDOT film on top of GSCs in case of electrodes **B** and **C**. From this discussion, it is clear that the best performance could be obtained with 50 s polymerization that correspond to a polymerization charge of 0.65 C (0.4 mg PEDOT). For electrodes **A**, **B** and **C,** power and energy densities were calculated at various current densities. For electrode **A**, a power density of 2287 W/kg and energy density of 29 Wh/kg was observed, which is better than that observed for electrodes **B** and **C**. The Ragone plot is shown in Fig. 2d. The electrochemical impedance spectra of electrodes **A**, **B** and **C** were recorded in 0.5 M H_2SO_4 using Pt foil as counter electrode and Ag/AgCl as reference electrode. The nyquist plot of the electrodes showed a semicircle with a linear segment at low frequency indicating mass transport. The high frequency intercept of the semi circle was used to calculate the R_{ct}. The R_{ct} of all the electrodes were about 1 Ω. Thus, the resistance of the films didn't vary significantly as a function of polymerization time.

The next set of experiments was carried out using AAO template. Although electroless gold deposition on polymer substrates is well developed,[6] the same is not true in case of electroless deposition on AAO templates.[7] Electroless deposition was carried out by following the procedure mentioned above. The Au nanotubes were liberated by dissolving the AAO template in 25% phosphoric acid. The SEM images indicate the formation of continuous nanotubes of gold in the pores of AAO template (Fig. 3a). The inner diameter of the gold nanotubes embedded in the AAO template was determined using diffusion of naphthalene. Based on the Fick's law of diffusion, the inner diameter of the gold nanotubes embedded in AAO was found to be 148 nm. To impart functionality and decrease the inner diameter of the nanotubes, PEDOT was electrodeposited by applying a constant potential of 1.3 V vs Ag/AgCl. The as deposited polymer was converted to its neutral state by applying a constant potential of -0.6 V. After these steps, the pore diameter was

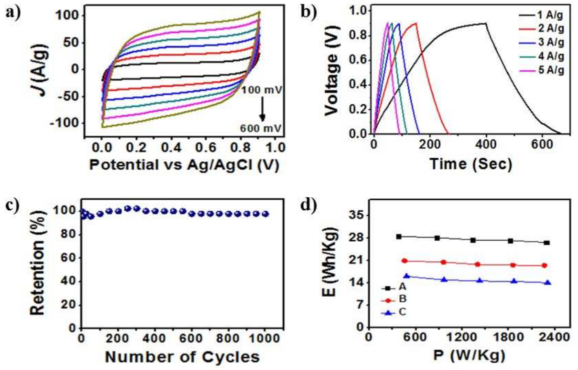

Fig. 2 CV of PEDOT deposited GSCs in 0.5 M H_2SO_4 at various scan rates (a). Charge discharge IV curves of **A** at various current densities (b). Plot of percentage specific capacity retention as a function of charge discharge cycles (c). Ragone plot showing the energy and power densities of electrodes **A**, **B** and **C** (d).

determined to be 10 nm. This template was mounted at the center of a U tube. One arm of the U tube was used as feed with two dye molecules Rhodamine 6G (cationic dye) and Calcein (anionic dye) dissolved in phosphate buffer (pH = 7.3). The reservoir had phosphate buffer of pH 7.3. Aliquots from the reservoir were withdrawn to study the transport of ions from the feed to the reservoir. By monitoring the peaks corresponding to the two dye molecules, the concentration of the transported molecules were determined. The slope of the plot of concentration vs time is rate of transport of dye molecules. The ratio of the rates is known as separation factor (α). While using PEDOT coated AAO template that was oxidized at 0 V, Calcein was preferentially transported compared to Rhodamine 6G. The separation factor was found to be 1.2. The low separation factor indicates the presence of very few positive charges on the PEDOT surface. The α increased to 1.7 while using PEDOT coated AAO template, which was oxidized by applying a potential of 0.4 V. The α further increased to 2.5 for PEDOT coated AAO, which was oxidized at 1 V (Fig. 3b). Thus, the increase in oxidation potential increased the number of positive charges on the PEDOT that facilitated the transport of complementary charge bearing Calcein.

Separation of molecules based on hydrophobicity is more challenging.[10,11] We have chosen *p*-nitrophenol (*p*-NP) and *p*-nitrotoluene (*p*-NT) with small log P difference.[11] The oxidized PEDOT is hydrophilic, hence it is not effective in separating molecules based on their hydrophobicity. Therefore, to convert the hydrophilic PEDOT into hydrophobic ones, we have disassembled sodium dodecyl sulfonate (SDS) micelles by following the procedure reported by us.[11,12] Depending on the number of positive charges on the PEDOT, the number of SDS molecules sticking on the PEDOT was found to vary. This variation imparts different degree of hydrophobicity inside the nanopores. While using AAO template decorated with PEDOT oxidized at 0 V and modified with SDS, the α between *p*-NT and *p*-NP was found to be 1.1. Thus, the separation of molecules is insignificant. On the other hand, the α increased to 1.8, while the PEDOT was oxidized at 0.5 V and modified with SDS. The α further increased to 8.5, while the PEDOT was oxidized at 1 V with subsequent SDS modification (Fig. 3c). This proves that the gold deposited AAO modified with PEDOT and SDS is an efficient template based molecular separator. To demonstrate the efficacy of this green tea based metal deposition method, palladium and nickel nanostructures were also prepared using SCs, AAO and polycarbonate templates. The palladium nanotubes liberated from the AAO templates are shown in Fig. 3d. The SEM images of nanostructures prepared in AAO template using the green tea approach are shown in ESI† (Fig. S14 and Fig. S15, ESI†). Indeed, we were able to fabricate 2D and 3D Au nanoelectrode ensembles (NEE) using this approach. The details of the electrode fabrication and analysis of the performance of the electrode are provided in the ESI†.

PP extracted from green tea was used as protective as well as reducing layer to deposit gold on silk cocoons (GSCs). The GSCs were used as large area electrodes in supercapacitors. The supercapacitor fabricated using PEDOT deposited GSCs exhibited capacitance of 254 F/g and specific power of 2287 W/kg. Thus, the electrodes prepared from natural resources can be an effective alternate to carbon based electrodes.

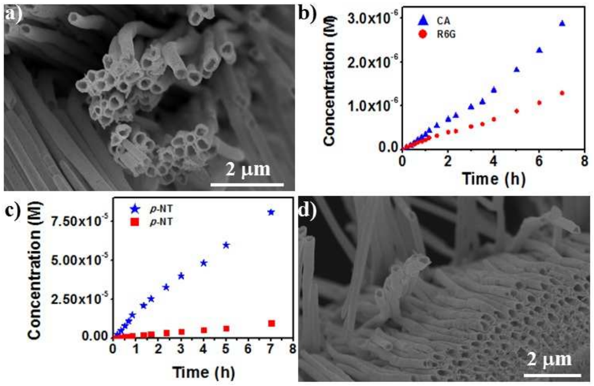

Fig. 3 (a) SEM image showing Au nanotubes liberated from AAO template. (b) Plot showing the differential transport of calcein and rhodamine 6G through PEDOT coated Au nanotubes embedded in AAO template. The potential applied on the electrode was 1 V (c) Time vs concentration plot showing differential transport of *p*-nitro toluene and *p*-nitro phenol through SDS modified PEDOT nanotubes in AAO template. Prior to SDS modification, a potential of 1 V was applied on PEDOT. (d) SEM image showing electroless deposited palladium nanotubes liberated from AAO templates.

Furthermore, the green tea based electroless deposition method was used to deposit metals in the nanopores of polycarbonate and AAO templates. The nanoporous membranes efficiently separated molecules based on charge and hydrophobicity. The same approach was used to prepare nanostructures and 2D and 3D NEE that are useful in electroanalysis.

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Notes and references

1. L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C. K. Tee, Y. Shi, Y. Cui and Z. Bao, *Proc. Natl. Acad. Sci. U.S.A*, 2012, **109**, 9287-9292.
2. S. B. Lee and C. R. Martin, *J. Am. Chem. Soc.*, 2002, **124**, 11850-11851.
3. T. S. Sileika, D. G. Barrett, R. Zhang, K. H. A. Lau and P. B. Messersmith, *Angew. Chem. Int. Ed.*, 2013, **52**, 10766-10770.
4. H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426-430.
5. H. Lee, N. F. Scherer and P. B. Messersmith, *Proc. Natl. Acad. Sci. U.S.A*, 2006, **103**, 12999-13003.
6. V. P. Menon and C. R. Martin, *Anal. Chem.*, 1995, **67**, 1920-1928.
7. P. Kohli, J. E. Wharton, O. Braide and C. R. Martin, *J. Nanosci. Nanotech*, 2004, **4**, 605-610.
8. H. Tao, D. L. Kaplan and F. G. Omenetto, *Adv. Mater*., 2012, **24**, 2824-2837**.**
9. G. A. Sotzing, J. R. Reynolds and P. J. Steel, *Adv. Mater.*, 1997, **9**, 795-798.
10. A. Asatekin and K. K. Gleason, *Nano Lett.*, 2011, **11**, 677-686.
11. C. Das and K. Krishnamoorthy, *Chem. Commun.*, 2014, **50**, 5905-5908.

12. K. Dutta, R. Y. Mahale, A. Arulkashmir and K. Krishnamoorthy, *Langmuir*, 2012, **28**, 10097.