Electronic Supplementary Material (ESI) for Materials Horizons.
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Materials Horizon

RSCPublishing

COMMUNICATION

Supplementary information

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

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Routes to 3D conformal solid-state dielectric polymers: Electrodeposition versus initiated chemical vapor deposition

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Experimental

C@SiO$_2$ fiber paper fabrication:

Strips of tissue quartz (Pall, Pallflex membrane) were cut into 4 cm × 2 cm strips and placed in a muffle furnace at 500 °C for 4 h in air. The tissue quartz strips were then stacked into an alumina boat and inserted into an alumina tube mounted in a tube furnace (MTI OTF-1200X). The samples were ramped to 1000°C at 10°C min^{-1} under an argon atmosphere. A flask fitted with a glass frit tube was filled with benzene (Alfa Aesar, ACS 99 %) and purged with argon (MFC = 100 sccm) for 1 h prior to exposure to the tissue quartz samples. Once samples were at 1000 °C, the samples were exposed to benzene-saturated argon gas at for 7 min (MFC = 100 sccm) followed by an argon purge for 10 min. The benzene/argon purge sequence was repeated two more times. At the end of the deposition, the tube furnace was turned off and allowed to cool to room temperature under an atmosphere of argon.

Poly(V3D3) deposition via electropolymerization:

Acetonitrile (Fisher Scientific, HPLC grade), and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (“V3D3”, >95%, Gelest) were used as received. Tetrabutylammonium perchlorate (“TBAP”, Fluka, ≥99.0%) was dried under vacuum at 90 °C for 24 h. All work was performed in a nitrogen drybox (Plas-Labs model 830-ABC). Deposition of poly(V3D3) was performed from a 0.1 M V3D3 + 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile solution. The C@SiO$_2$ substrates were vacuum infiltrated with an aliquot of the deposition solution and soaked for 1 h. After infiltration, electrical contact to the substrate was made with a piece of 25-µm–thick Ni foil (Alfa Aesar, 99.5%) folded over the top of the C@SiO$_2$ fiber paper. The C@SiO$_2$ fiber paper sample (deposition area: 1 cm × 2 cm) was inserted into an electrochemical cell that contained separate fritted compartments for the Ag wire reference electrode (Alfa Aesar, 1 mm, 99.999%) and the Pt wire counter electrode (Engelhard, thermocouple wire, 90% Pt 10% Rh). The deposition sequence for poly(V3D3)–C@SiO$_2$ fiber paper consisted of the following steps: (i) chronoamperometry at -0.2 V for 90 s, (ii) linear scan voltammetry from –0.2V to -0.8 V at 5 mV s^{-1}, (iii) chronoamperometry at –0.8 V for 600 s. Steps (i–iii) were repeated 5 more times. The sample was then subjected to the following steps: (iv) chronoamperometry at –0.2 V for 90 s, (v) linear scan voltammetry from –0.2 V to –1.2 V at 5 mV s^{-1}, and (vi) chronoamperometry at –1.2 V for 600 s. Steps (iv–

vi) were repeated 5 more times. Then the samples were subjected to the final sequence of (vii) chronoamperometry at –0.2 V for 90 s, (viii) linear scan voltammetry from –0.2 V to –1.8 V at 5 mV s^{-1}, and (ix) chronoamperometry at –1.8 V for 600 s. After deposition, the sample was removed from the electrochemical cell, rinsed with acetonitrile and soaked in acetonitrile for ~24 h with additional rinsing steps performed every 8–12 h. The samples were then removed from the drybox, and placed in an ambidryer at 50 °C under an atmosphere of $N_2(g)$ for 12 h. The samples were then placed in a vacuum oven and further dried for 20 h at 60 °C.

Poly(V3D3) deposition via initiated chemical vapour deposition:

Electrical contact was made to the C@SiO_2 fiber paper samples by inserting the top 2 cm of the sample into a Ni foil envelope and securing it with Ni print (MG Chemicals). The Ni foil–C@SiO_2 fiber paper assembly was then secured to a glass slide with Ni print at the Ni foil-glass interface. The assembly was further secured to the glass slide with epoxy (Torr Seal) at the edges of the Ni foil-glass slide interface. The completed assembly was then placed in a convection oven at 100 °C for 30 min to cure the epoxy.

Using published protocol, samples were coated by initiated-chemical vapor deposition (*i*CVD), using a commercial deposition chamber (GVD Corporation, Cambridge, MA). Briefly, the test substrates (C@SiO_2 FP) were placed in a heated reaction chamber while the monomer and initiator were vaporized in reaction jars and subsequently introduced into the deposition chamber under controlled flow. The monomer (1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane: V3D3, >95 %, Gelest) and the initiator (di-tert-butyl peroxide, TBPO 98 %, Aldrich) were used without further purification. Monomer and initiator were placed in separate stainless steel vessels, heated to 35 °C and 50 °C, respectively; the lines feeding the chemicals to the reaction chamber were heated 70 °C to avoid vapour condensation. The C@SiO_2 fiber paper assemblies were placed in the reaction chamber, the support stage maintained at 25 °C and chamber temperature heated to 60 °C. The flow of initiator was regulated by the computer-controlled MFC with a flow set point of 2 sccm. The monomer was then introduced to the chamber using manual regulator valve with the chamber pressure set to 370 mTorr. Thermal excitation was achieved by resistively heating Nichrome wire to 35 V (2A). Deposition was performed for either 25 min (*i*CVD1) or 40 min (*i*CVD2).

Scanning electron microscopy:

Samples were cut with a fresh razor blade and placed on SEM stubs (Ted Pella, 12.7-mm diameter, 45°/90° mount) with a piece of conductive carbon tape (Ted Pella). The samples were further secured to the SEM stubs with conductive carbon paste (SPI, LEIT-C), which also ensured good electrical contact. Samples were imaged with a Leo Supra 55 scanning electron microscope at 2 keV.

Electrochemical evaluation:

Redox Probe cyclic voltammetru. All chemicals were used as received. The samples were prepared by masking off an area of the sample with teflon tape, leaving ~1 cm × 0.3 cm exposed. Electrical connection was made with a nickel foil envelope at the top of the C@SiO_2 fiber paper sample. The sample was placed in an electrochemical cell containing deaerated 0.5 M $K_3Fe(CN)_6$ + 0.5 M KCl in H_2O with a Ag/AgCl reference electrode (WPI, DryRef) and a Pt mesh counter electrode. Cyclic voltammetry was performed from 0.7 V to –0.2 V at 1 mV s^{-1} with a Gamry Ref 600 potentiostat

Solid-state evaluation DC and AC measurements:

All measurements were performed in a nitrogen drybox (Plas-Labs, 830-ABC) with a relative humidity of 14 %. Top electrical contact (CE/RE) was made through a drop of Hg suspended from a plastic 1-mL syringe contacted to a Cu wire secured inside the syringe. Bottom electrical contact was made through a piece of Ni foil secured to the C@SiO_2 fiber paper. The top and bottom electrical leads were connected to a Gamry Ref 600 potentiostat outside of the nitrogen drybox. Electrochemical impedance spectroscopy was performed at 0 V DC with a 10 mV AC perturbation from 500 kHz to 1 Hz. Current–voltage (*i*–V) scans were collected from ± 100 mV at 5 mV s^{-1}.

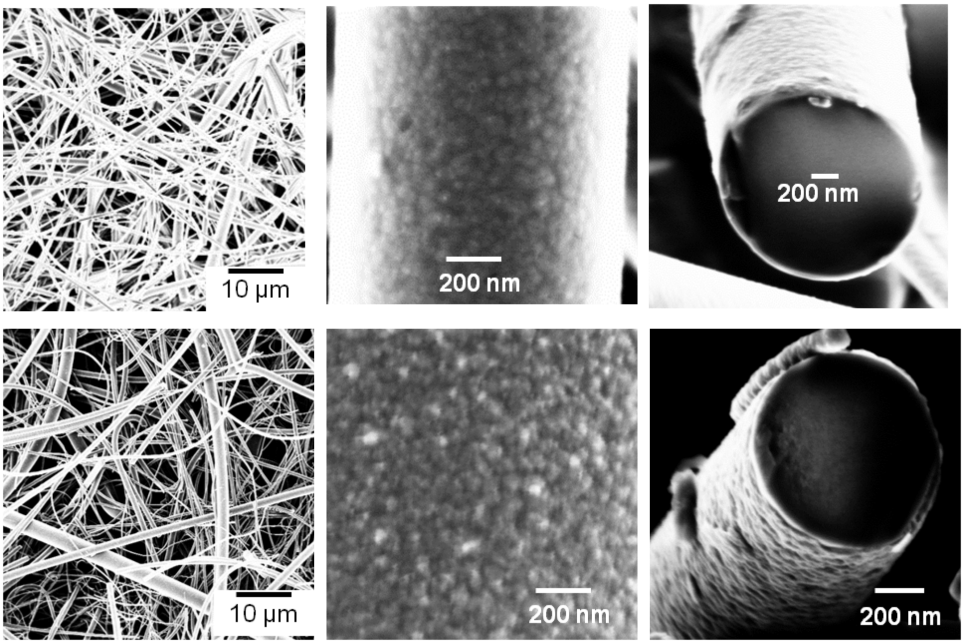

Figure S1. Scanning electron micrographs of the exterior surface (left), high resolution of a fiber surface (middle), and a cross section (right) of EP1 poly(V3D3)–C@SiO_2 FP (top row) and EP2 poly(V3D3)–C@SiO_2 FP (bottom row). Contrast and brightness settings are identical for all micrographs.

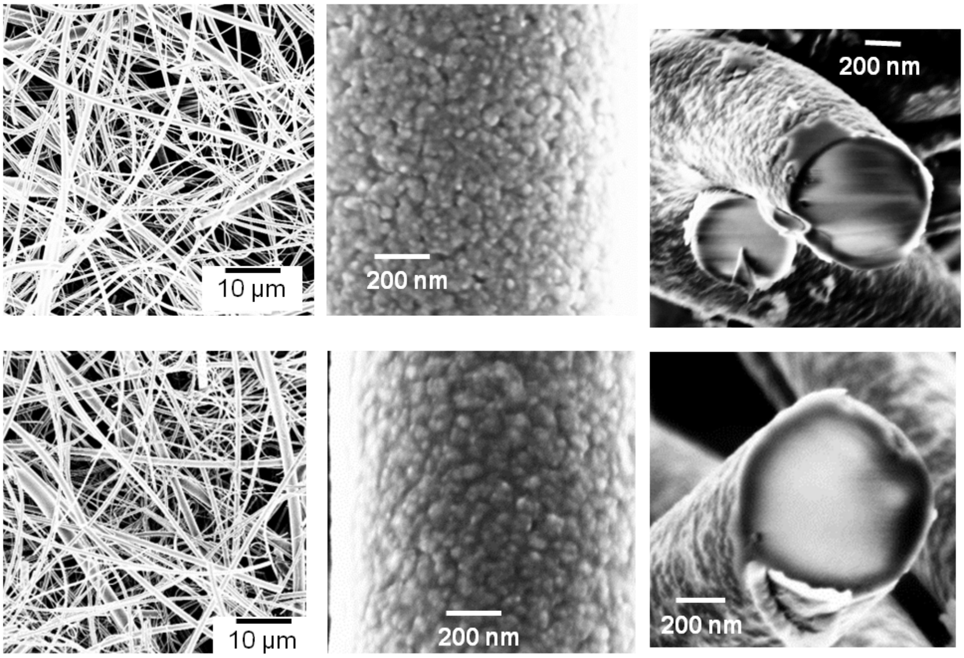

Figure S2. Scanning electron micrographs of the exterior surface (left), high resolution of a fiber surface (middle), and a cross section (right) of *i*CVD1 poly(V3D3)–C@SiO_2 FP (top row) and *i*CVD2 poly(V3D3)–C@SiO_2 FP (bottom row). Contrast and brightness settings are identical for all micrographs.

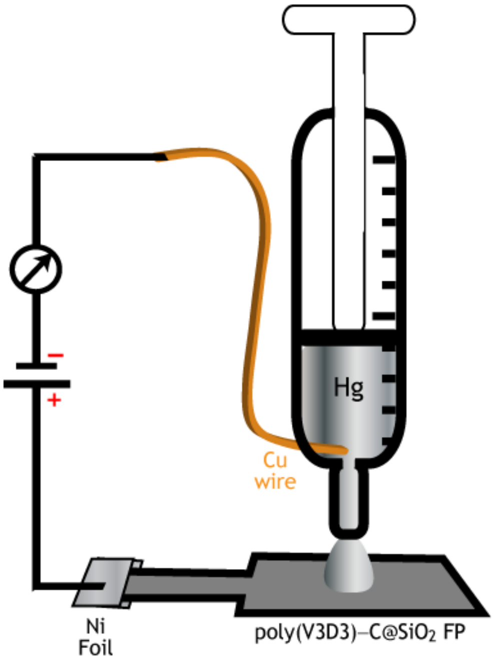

Figure S3. Schematic of the solid-state measurement setup with a liquid Hg probe.