

Supporting Information

Structure evolution and thermoelectric properties of carbonized polydopamine thin films

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Supporting Information

EXPERIMENTAL METHODS

PDA Coating

In this study, PDA thin films were coated onto fused silica substrates (26013, Ted Pella Inc., Redding, CA) and silicon wafer with native oxide layer (21620-6, Ted Pella Inc., Redding, CA). After being ultrasonically cleaned in acetone and then deionized water, the substrates were immersed into 50 mM tris buffer (BP1761, Thermo Fisher Scientific Inc., Waltham, MA) containing 13mM dopamine chloride (H8502, Sigma-Aldrich, St. Louis, MO). The pH value of the tris buffer was adjusted to 8.5 using HCl (SA48, Thermo Fisher Scientific Inc., Waltham, MA). Coating was conducted at room temperature without mechanical stirring. After 48 hours, the substrates were removed from the solution, cleaned with deionized water, and dried overnight at 60°C in an oven.

Heat Treatment

Substrates with PDA coating were heat treated under flowing Ar using a tube furnace (GSL-1500X, MTI, Richmond, CA). In a typical heat treatment run, the sample was heated with a heating rate of 10°C/min, held at peak temperature for an hour, then cooled to room temperature with a nominal cooling rate of 10°C/min.

TGA

Thermogravimetric analysis (TGA) (Pyris 6, Perkin Elmer, Waltham, MA) was conducted on precipitated PDA powders during the coating process. Approximately 50 mg of oven-dried

powder was heated between 50°C and 1000°C with a heating/cooling rate of 20°C/min. Testing was conducted in a running N₂ environment with a purging speed of 20 ml/min.

SEM and EDS

Scanning electron microscopy (SEM) was performed using FEI Quanta450 FEG SEM (FEI Inc. Hillsboro, OR). Samples prepared on Si/SiO₂ were examined using an accelerating voltage of 30 kV under the high-vacuum mode; while samples on the fused silica substrates were examined using an acceleration voltage of 10 kV in the low-vacuum mode using the water vapor. All energy dispersive x-ray spectroscopy (EDS) analyses were performed using an acceleration voltage of 10 kV and a working distance of approximately 10 mm.

AFM

Thicknesses of the PDA and cPDA thin films on SiO₂ substrate were determined by atomic force microscopy (AFM). The AFM (MMAFMLN-AM, Veeco Metrology, Horsham, PA) was operated in the tapping mode. Prior to AFM experiments, thin film samples were scratched using a stainless steel razor blade. Film thicknesses were determined by scanning across the scratches. At least six scans were made on each sample. Film roughness was obtained on 10µm x 10µm areas without scratches.

XRD

X-ray diffraction (XRD) was conducted on thin film samples prepared on fused silica substrates on a Bruker D8 Discover diffractometer (Bruker, Billerica, MA) using Cu K α radiation (wave length = 0.154 nm). The θ -2 θ scans were performed in the range of 5° < 2 θ < 80° at a resolution

of 0.01 deg/step and a scan rate of 3 sec/step. Scans from blank substrates were also conducted and used as the background.

TEM and SAED

PDA and carbonized PDA powder samples were collected on Cu grids and examined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) using JEM-1400 TEM (JEOL, Tokyo, Japan) under an accelerating voltage of 120 kV.

Neutron Scattering and Data Analysis

Neutron scattering experiments were conducted at room temperature for 25 min on powdered samples sealed in 2-mm diameter quartz capillaries using the Nanoscale-Ordered Materials Diffractometer (NOMAD) instrument at Oak Ridge National Laboratory. The structural factor, $S(Q)$, was obtained by normalizing diffraction data against a solid vanadium rod and subtracting the background developed for the NOMAD instrument. Pair distribution function (PDF) was obtained by the Fourier transform of $S(Q)$ at the maximum intensity of $Q_{\max} = 31.4 \text{ \AA}^{-1}$. The fitting of PDF was performed at $r < 20 \text{ \AA}$, using the PDFgui software [S3].

Raman Spectroscopy

Raman spectroscopy was performed on thin film samples prepared on Si/SiO₂ substrates using a Horiba LabRAM HR Evolution Raman spectrometer (Horiba, Japan) with a laser excitation wavelength of 532 nm, and 1800 g/mm diffraction grating providing spectral resolution of $\sim 2 \text{ cm}^{-1}$. Laser light was focused on $\sim 1 \text{ \mu m}$ diameter focal spot with Olympus MPlan N 100x objective lens. Excitation intensity was maintained below damage threshold of the samples. At least two scans were performed for each spot. Spectra were collected for at least 3 spots per

sample in order to check homogeneity of the samples. Scans were conducted within the spectral range of 100 cm^{-1} to 3000 cm^{-1} . Background scans were performed on blank Si/SiO₂ substrates before and after scanning the samples.

While other wavelengths are available, the current study selected a 532-nm laser that yielded the most clearly defined G and D bands without damage the samples, which helped to trace the evolution of the G band position and the intensity ratio between the G and the D bands. While G band is always present in different carbon materials, D band may or may not appear in Raman spectra using different excitation lasers. At longer excitation wavelengths, blue shift of the D peak may occur while G peak may experience small shift, if any. Additional peaks may also appear depending on the laser wavelength.

Electrical Conductivity and Seebeck Coefficient Measurements

Gold electrodes were sputtered through a mask on PDA and cPDA films. Electrical resistance was measured using a digital multimeter (Model 2750, Keithley, Cleveland, OH) and conductivity was calculated from the film dimensions. The Seebeck coefficient was measured using a custom system (Figure S1). A temperature difference, ΔT , measured by two type K thermocouples, was applied across the sample using a heater/cooler module, which in turn resulted in a thermal voltage, ΔV . The Seebeck coefficient, S , was calculated as the slope of the ΔV versus ΔT curve when ΔT varied from -5°C to $+5^{\circ}\text{C}$. The heat-sink temperature was maintained at 25°C .

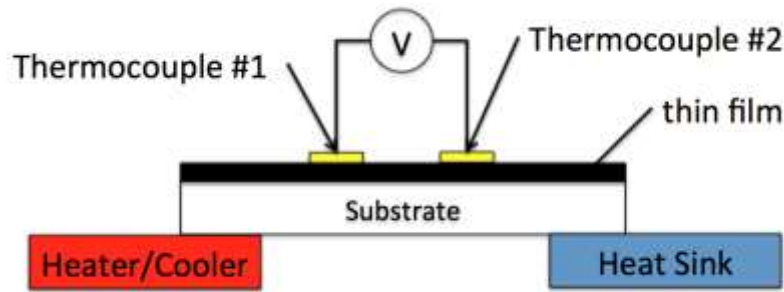


Figure S1: Experimental setup for Seebeck coefficient measurement.

TDTR

The thermal conductivity of the thin PDA and cPDA films was measured using a two-tint implementation of time-domain thermoreflectance (TDTR). The details of the experimental setup have previously been described by Kang (S2), and the multilayer thermal simulation and data reduction have been described by Cahill (S1). The modulation frequency was 12.6 MHz and the pump and probe $1/e^2$ radius were both 25 μm for all measurements. For these measurements a layer of $\sim 80\text{-nm}$ -thick aluminum was deposited on the sample to serve as a thermal transducer. Although the PDA films were quite thin (thicknesses were in a narrow range between 30 - 34nm), they were found to have sufficiently low thermal conductivity to yield good measurement sensitivity. We assume the volumetric heat capacity of the cPDA to be similar to the graphite $C_V = 1.5 \text{ J/cm}^3\text{-K}$, though the measurements were insensitive to the assumed value since the thermal penetration depth at the modulation frequency was more than twice the film thickness.

EXPERIMENTAL RESULTS

TGA

TGA result of PDA powder in N₂ is shown in Figure S2, where a monotonic decrease was observed.

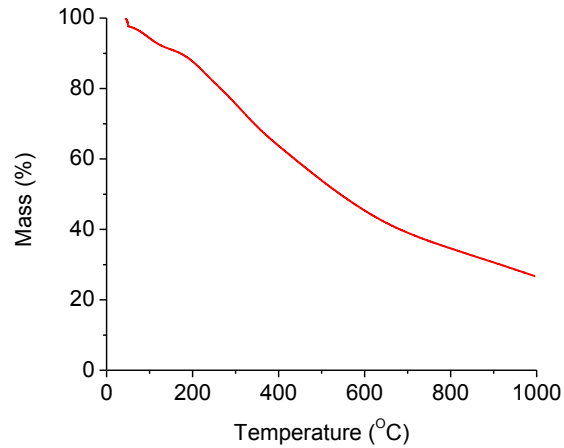


Figure S2. TGA analysis result of PDA in N₂.

AFM

Table S1 shows the AFM roughness data obtained in arithmetic average from 10 μ m x 10 μ m areas on each sample. For all samples, the roughness is less than 1.2 nm. Figure S3 shows three AFM scan on scratches of one sample of different location. Results showed a consistency of thickness throughout the sample and roughness on the high latitude.

Table S1 Thin film roughness obtained from AFM.

| Sample | Ra (nm) |
|----------|---------|
| PDA | 0.448 |
| cPDA-100 | 1.66 |

| | |
|----------|-------|
| cPDA-200 | 1.1 |
| cPDA-300 | 1.12 |
| cPDA-400 | 0.402 |
| cPDA-500 | 0.959 |
| cPDA-600 | 0.665 |
| cPDA-700 | 0.937 |
| cPDA-800 | 1.15 |
| cPDA-900 | 1.19 |

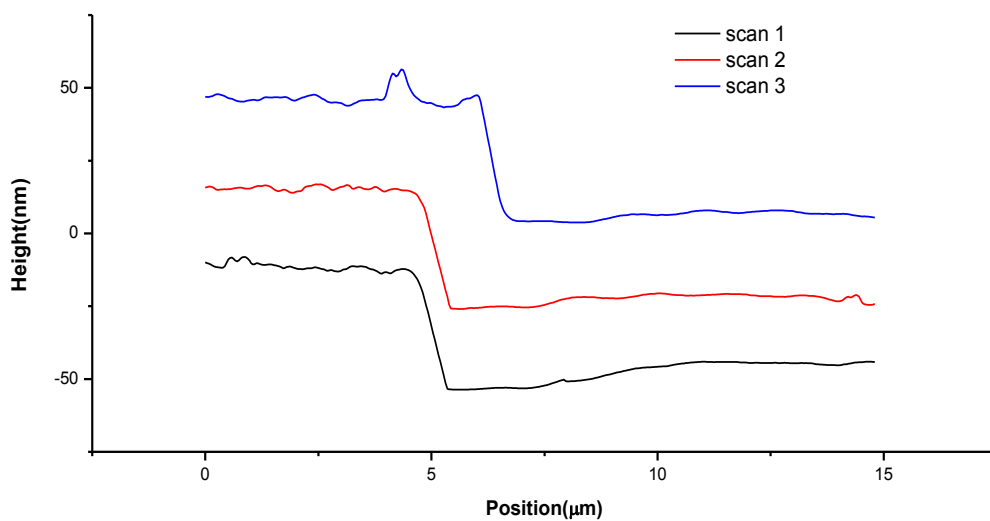


Figure S3. Example of AFM cross-section scans showing the thickness of a PDA film at three different locations.

EDS

EDS on powder samples showed the elemental composition of the PDA and cPDA after different heat treatment temperature.

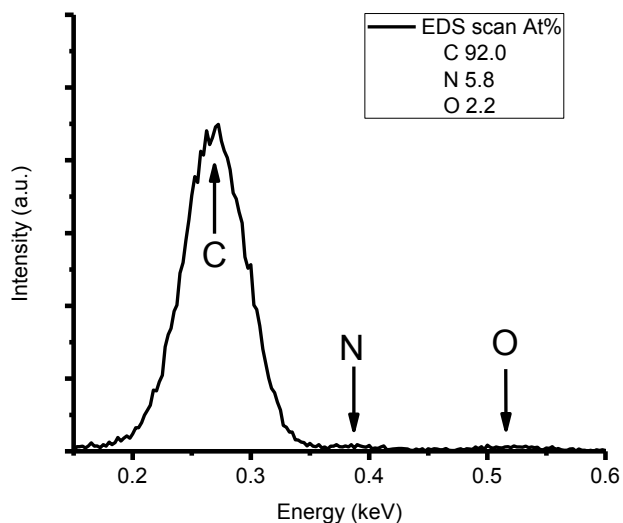


Figure S4. EDS result obtained on cPDA sample after heat treated at 800°C showing the chemical composition. The atomic percentage of the individual elements, i.e. C, N, and O, is listed at the top-right corner.

XRD Results

XRD profiles of all PDA and cPDA thin film samples prepared on fused silica substrates are shown in Figure S3, which appeared similar with a broad peak around 21°. Scans were also performed on blank substrates to obtain the background. Figure S5 compares the XRD profiles of the PDA sample and the 500°C heat-treated and 900°C heat-treated cPDA samples after background was subtracted, where similar profiles were observed.

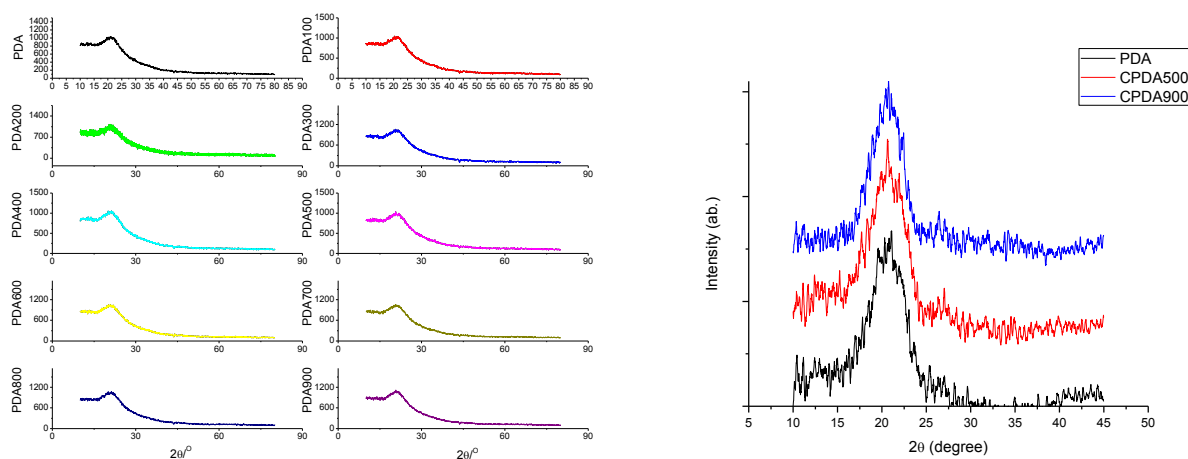


Figure S5. (a) XRD profiles of PDA and cPDA thin film samples. (b) Comparison of XRD profiles of PDA and cPDA (heat treated at 500°C and 900°C) samples after subtracting the background.

REFERENCE

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