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Supporting Information:

Facile Approach to Graphene Oxide and Poly(*N*-vinylcarbazole) Electro-Patterned Films†

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1. Experimental

1.1 Materials

Polystyrene (PS) latex microbeads (0.5 μm in diameter, 2.5% solids (w/v) aqueous suspension, 3.64×10^{11} particles/ml) were purchased from Polysciences, Inc. and were used without any purification. These particles contain a slight anionic charge from sulfate ester. Sodium *n*-dodecyl sulfate (SDS) was used to control the organization of the PS microbeads at the air-liquid interface. Millipore water (18 $\text{M}\Omega\text{cm}$) was used to dilute the PS suspension solution and to control the total concentration of the mixture solution. The acetonitrile (ACN), tetrahydrofuran (THF), sodium *n*-dodecyl sulfate (SDS), and tetrabutylammonium hexafluorophosphate (TBAH) were obtained from Sigma-Aldrich. All solvents were of analytical grade and used without further purification. The nano graphene platelets (NGP) (purity $\geq 99.5\%$) were obtained commercially from XG Sciences. The NGP has a thickness of 5-15 nm and width between 5-25 μm . The tin-doped indium oxide, ITO ($\text{In}_2[\text{Sn}_x]\text{O}_{3-3x}$, one side coated on glass, sheet resistance $\leq 30 \Omega\text{cm}^{-2}$) was purchased from SPI Supplies/Structure Probe, Inc. Prior to use, the ITO substrate was sonicated in Alconox detergent followed by rinsing with ultra pure water. The ITO was then sonicated for 10 min in isopropanol, hexane, and then toluene, respectively, prior to oxygen plasma cleaning for ~ 120 sec. The poly (*N*-vinyl carbazole) (PVK) was purchased from Sigma-Aldrich Chemicals (USA) (ca MW= 25,000-50,000 g/mol).

1.2 Instrumentation

1.2.1 Electrochemistry. Cyclic voltammetry were performed in a conventional three-electrode cell using an Autolab PGSTAT 12 potentiostat (Brinkmann Instruments now MetroOhm USA). The potentiostat was controlled by GPES software (version 4.9). The electrodeposition of the GO/PVK nanocomposite was done using cyclic voltammetric (CV) technique in a standard three electrode measuring cell (fabricated electrochemical cell with a diameter of 1.0 cm and 0.785 cm^3 , Teflon made) with platinum wire as the counter electrode, Ag/AgCl wire as the reference electrode, and the bare or PS coated ITO-substrate as the working electrode.

1.2.2 Atomic Force Microscopy (AFM). The AFM measurements were carried out in a piezo scanner from Agilent Technologies. The scanning rate was between 0.8 to 1.0 lines/s. Commercially available tapping mode tips (TAP300, Silicon AFM Probes, Ted Pella, Inc.) were used on cantilevers with a resonance frequency in the range of 290-410 kHz. The scanning of the electropolymerized film was performed under ambient and dry conditions. All AFM topographic images (AAC tapping mode) were filtered and analyzed by using SPIP software (Scanning Probe Image Processor, Imagemet.com) or Gwyddion 2.19 software.

The current sensing (CS) AFM analyses in contact mode were done on the same set up using Pt-coated Si₃N₄ tip with radius around 20 nm and force constant of 0.5 N/m. The measurements were done under ambient conditions at ~40-50% relative humidity and 20-25 °C temperature. All AFM topographic images (AAC tapping mode) were also filtered and analyzed by using SPIP software (Scanning Probe Image Processor, Imagemet.com) or Gwyddion 2.19 software.

1.2.3 Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR). The ATR FTIR spectra were obtained on a Digilab FTS 7000 equipped with a HgCdTe detector from 4000 to 600 (cm⁻¹) wavenumbers. All spectra were taken with a nominal spectral resolution of 4 cm⁻¹ in absorbance mode. All films were measured under ambient and dry conditions.

1.2.4 Ultraviolet-Visible Spectroscopy (UV-Vis). The UV-Vis spectra were recorded on a HP-8453 UV-Vis spectrometer within the 300-900 nm range. The UV-Vis measurement was done at ambient and dry condition at different areas of the film. The UV-Vis spectra were recorded for an equal concentration of each material.

1.2.5 X-ray Diffraction (XRD). The XRD data was taken using Rigaku Ultima III diffractometer with Cu K α X-ray radiation (λ = 1.54056 Å) from 0.5 - 30° at 0.04°/s.

1.2.5 Thermogravimetric Analysis (TGA). The TGA analysis was performed on a TA Instruments 2950 thermogravimetric analyzer. The experiment was done by heating the sample from 20 to 900 °C at a heating rate of 20 °C/min. All experiments were operated under a N₂ atmosphere at a purge rate of 80-90 mL/min.

1.2.5 X-ray photoelectron spectroscopy (XPS) measurement. A PHI 5700 X-ray photoelectron spectrometer was equipped with a monochromatic Al K α X-ray source ($h\nu$ =1486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated both at high and low resolutions with pass energies of 23.5 eV and 187.85 eV, respectively, a photoelectron take off angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. All spectra were collected at room temperature with a base pressure of 1 x 10⁻⁸ torr. The peaks were analyzed first by background subtraction using the Shirley routine. All the samples were completely dried in argon gas prior to XPS measurements.

1.3 Preparation of Graphene Oxide and Poly(*N*-vinylcarbazole) Nanocomposite

1.3.1 Preparation of Graphene Oxide

Graphene oxide was synthesized using the improved method reported by Tour and co-workers.^[1] Briefly, graphene nanoplatelet (GNP) (3.0 g) were oxidized by mixing GNP with KMnO₄ (18 g). A 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) was added producing an exothermic reaction that raised the temperature to 35-40°C. The reaction was heated further to 50°C with stirring and maintained for 12 hours, and cooled to room temperature.

The cooled mixture was poured into ice (~400 mL) with 30% H₂O₂ (3 mL). The mixture was sifted through 425 μm and 250 μm US Standard Testing Sieve and then centrifuge at 4000 rpm for 4 hours. The solids were washed with 200 mL of Millipore water while passing it through 425 μm and 250 μm US Standard Testing Sieve and then the mixture was centrifuge at 4000 rpm for 1 hour. The residue was washed with 400 mL of ethanol, then coagulated with 200 mL ether before it was placed in vacuum oven to dry overnight.

1.3.2 Preparation of GO/PVK Nanocomposite Solution

The GO/PVK nanocomposite was prepared using solution mixing process. In a typical synthesis experiment, the weight/volume (mg/mL) (w/v) ratios of PVK and GO were dispersed in *N*-cyclohexyl-2-pyrrolidone (CHP) at 1 mg/mL concentration and ultrasonically agitated for 1 hour. The PVK solution was slowly mixed to a GO solution at 97:3 (% wt.) ratio, respectively followed by sonication for another 30 minutes. The mixture was used to prepare the PVK/GO film. Previously, GO and other polymer composites were also prepared using other methods.^[2]

1.4 Preparation of Graphene Oxide and Poly(*N*-vinylcarbazole) Nanocomposite and Electro-Patterned Film

1.4.1 Polystyrene Layering by Langmuir-Blodgett (LB)-Like Technique

The layering of PS microbeads (or formation of colloidal crystals) was accomplished using a similar procedure described earlier by Grady and co-workers.^[3] The method was called Langmuir-Blodgett (LB)-like technique for it formed a monolayer of PS particles onto flat surfaces without using the conventional LB set-up that employs floating barriers. As shown in Figure 1, the substrate was attached into the dipper motor via Teflon clip and was dipped into an aqueous solution containing PS particles (1 wt. %) and SDS (34.7 mM) as spreading agent. A higher concentration of anionic surfactant (SDS) will result in multiple layers of highly disordered latex spheres while a low concentration will not form a full coverage in hexagonal array. Then the substrate was withdrawn vertically from the solution at a lift-up rate between 0.1 to 0.3 mm/min. Finally, the substrate was dried by suspending it in air for few minutes.

[1] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinititskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, *ACS Nano*, 2010, **4**, 4806.

[2] (a) R. Verdejo, M. M. Bernal, L. J. Romasanta, and M. A. Lopez-Manchado, *J. Mater. Chem.* 2011, **21**, 3301; (b) H. Wang, Q. Hao, X. Yang, L. Lu, and X. Wang, *ACS Appl. Mater. Interfaces* 2010, **2**, 821; (c) Y. Huang, Y. Qin, Y. Zhou, H. Niu, Z.-Z. Yu, and J.-Y. Dong, *Chem. Mater.* 2010, **22**, 4096; (d) G. L. Li, G. Liu, M. Li, D. Wan, K. G. Neoh, and E. T. Kang, *J. Phys. Chem. C* 2010, **114**, 12742. (e) K. W. Putz, O. C. Compton, M. J. Palmeri, S. T. Nguyen, and L. C. Brinson, *Adv. Funct. Mater.* 2010, **20**, 3322. (f) C. Xu, J. Sun, and L. Gao, *J. Mater. Chem.* 2011 Advanced Article.

[3] M. Marquez and B. P. Grady, *Langmuir*, 2004, **20**, 10998.

1.4.2 Electrodeposition of the Graphene Oxide and Poly(N-vinylcarbazole) Nanocomposite

The electrodeposition of the GO/PVK nanocomposite was done using cyclic voltammetric (CV) technique in a standard three electrode measuring cell with platinum wire as the counter electrode, Ag/AgCl wire as the reference electrode, and the bare or PS-coated ITO substrate as the working electrode. The solution for electropolymerization was prepared by mixing 0.1 M TBAH in ACN (4 mL) with GO/PVK (8 μ L) at 3:97 (% wt. ratio) as described above. The potential was scanned between 0 V to 1.5 V at 10 mV/s for 10 CV cycles. After the electrodeposition, the resulting film was washed with ACN thrice, and a monomer free scan was performed by using exactly the same experimental parameters but for 1 CV cycle only. The electrodeposited substrate was dried with nitrogen gas for few minutes.

1.4.3 Dissolution of the Polystyrene Template

The PS particles were removed from the surface after CV electrodeposition by dipping the PS-coated substrate in THF twice for 30 minutes. This step is to create the nanocomposite and electro-patterned film array. The THF will remove the PS particles only and not the electrodeposited film of GO and PVK. Then the substrate was allowed to dry naturally under ambient condition.

The composition of GO and PVK in the electrodeposited nanocomposite film was ascertained using high resolution XPS analysis by determining the C/N ratio. For instance, from the obtained atomic concentrations of the high resolution scans (C 1s and N 1s), the C/N ratios of PVK and PVK-GO were calculated. By using the formula $[(C/N)_{PVK/GO} - (C/N)_{PVK}] / (C/N)_{PVK}$, the amount of GO on the surface was estimated to be ~3%, which correlates well with the initial 3 wt% loading of GO in solution.^[4]

[4] C. M. Santos, M. C. R. Tria, R. A. M. V. Vergara, F. Ahmed, R. C. Advincula, and D. F. Rodrigues, *Chem. Commun.* 2011 Advanced Article.

Additional Supporting Data

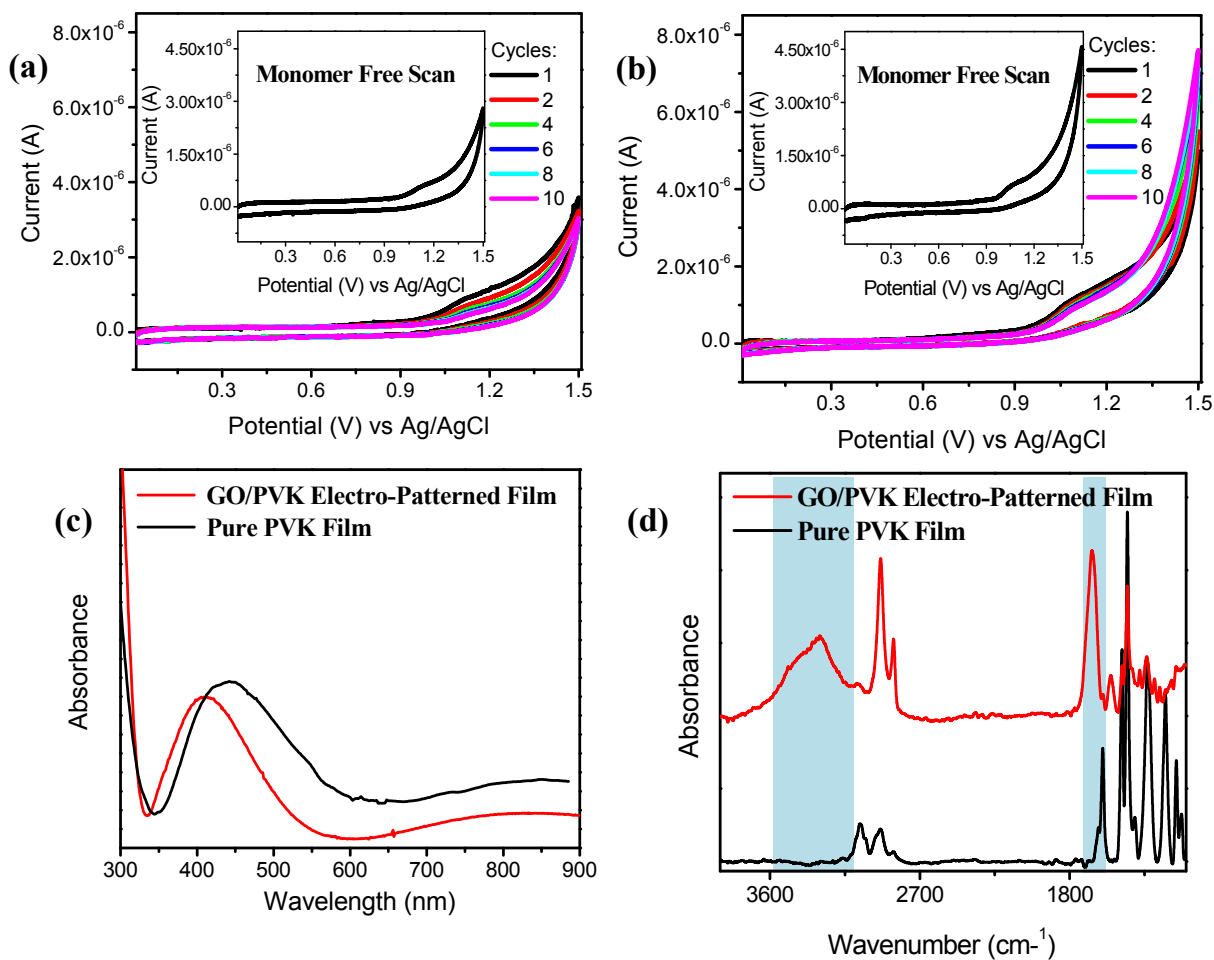


Figure S1. CV diagram (monomer free scan on inset) of the electrodeposition of (a) GO/PVK nanocomposite on PS-coated ITO and (b) pure PVK on bare ITO substrate. (c) UV-Vis and (d) ATR IR spectra of the electro-patterned GO/PVK nanocomposite film and electrodeposited pure PVK film (control) on ITO substrates.

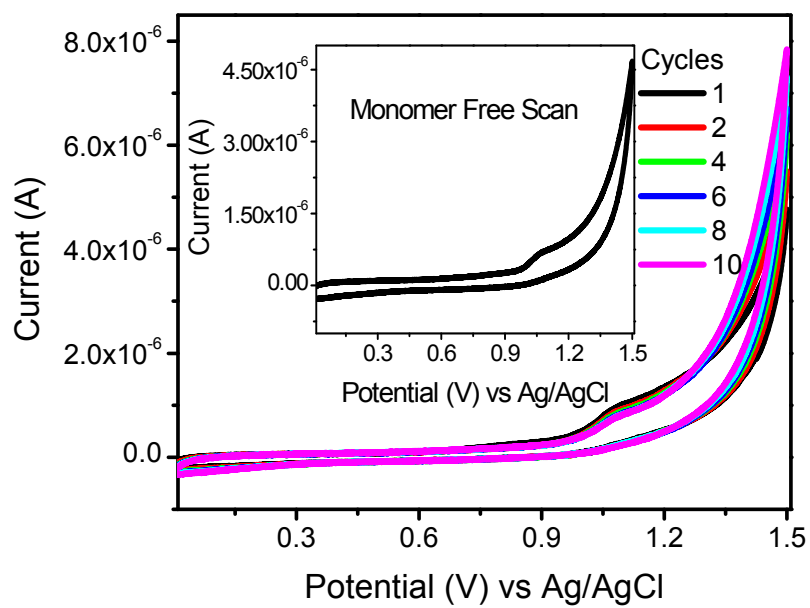


Figure S2. CV diagram of the electrodeposition of GO/PVK on bare ITO substrate with monomer free post polymerization scan (CV 1 cycle in ACN with 0.1 M TBAH) on inset.

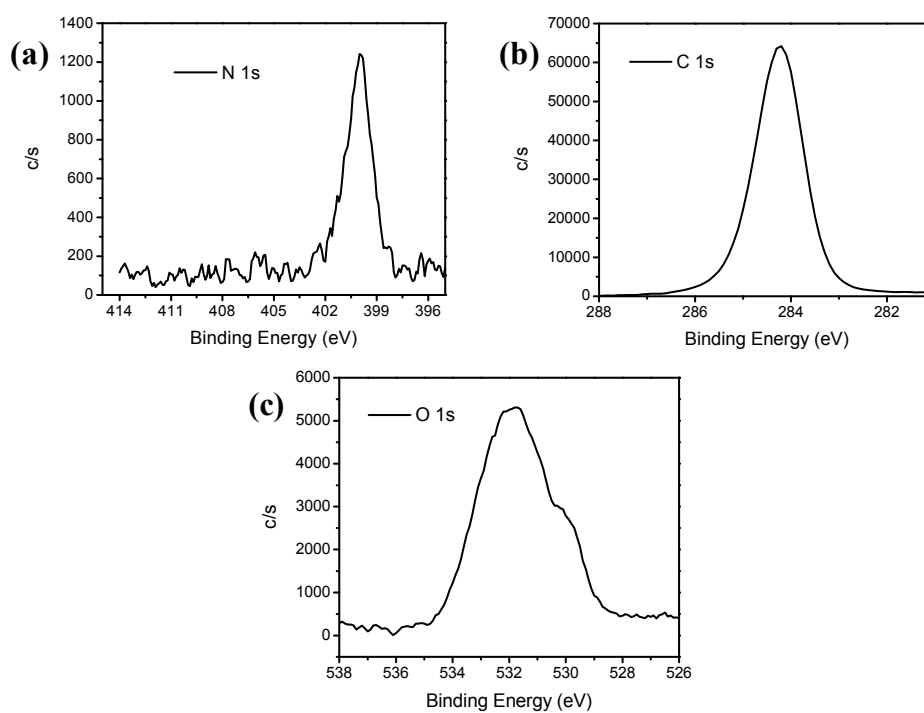


Figure S3. XPS high resolution scans of the GO/PVK nanocomposite and electro-patterned film: (a) N 1s, (b) C 1s, and (c) O 1s.

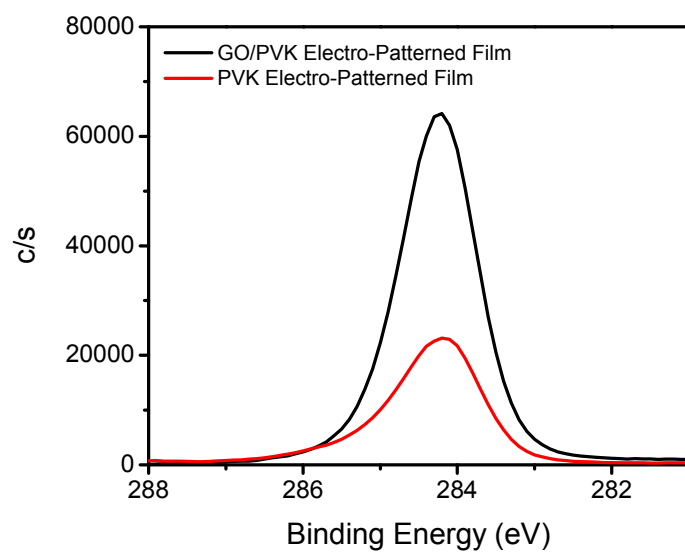


Figure S4. C 1s high resolution scan of the (black curve) GO/PVK nanocomposite and electro-patterned and (red curve) pure PVK electro-patterned film on ITO.

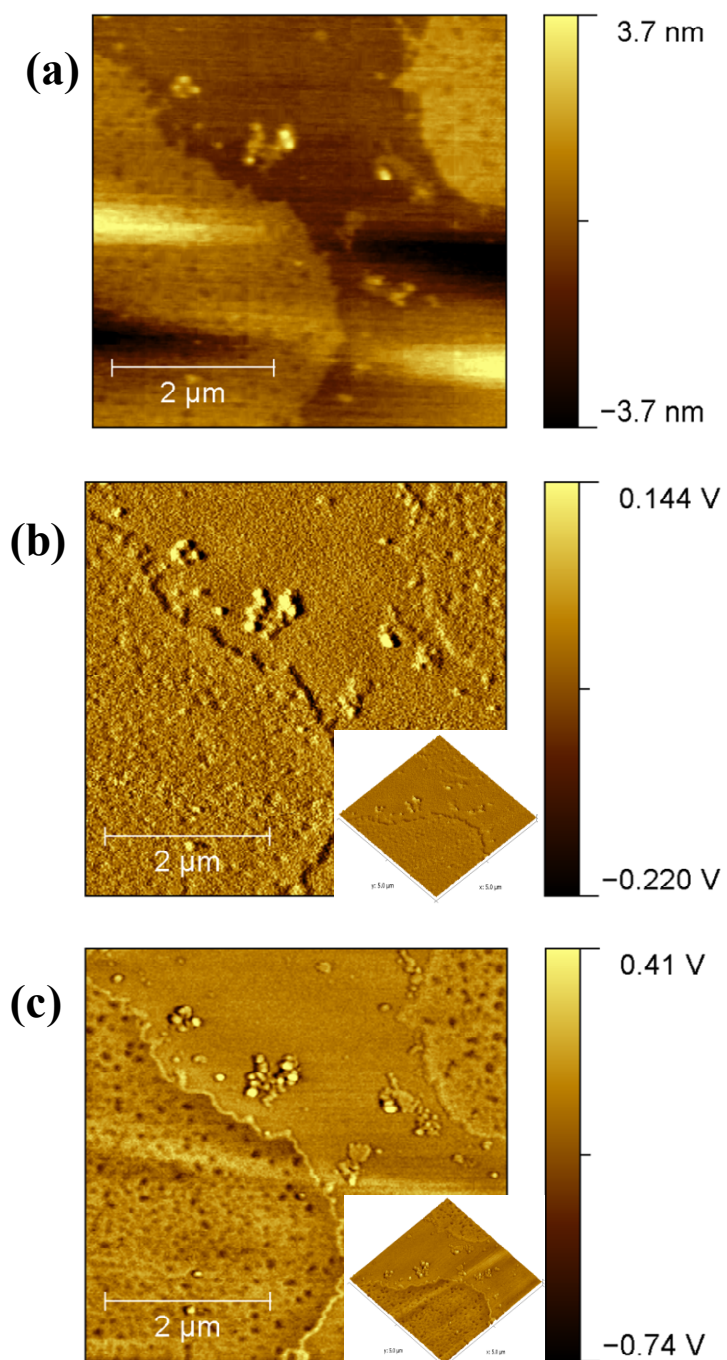


Figure S5. AFM topography 2D images (3D on inset) of the spin coated GO on mica: (a) Topography, (b) Amplitude, (c) Phase.

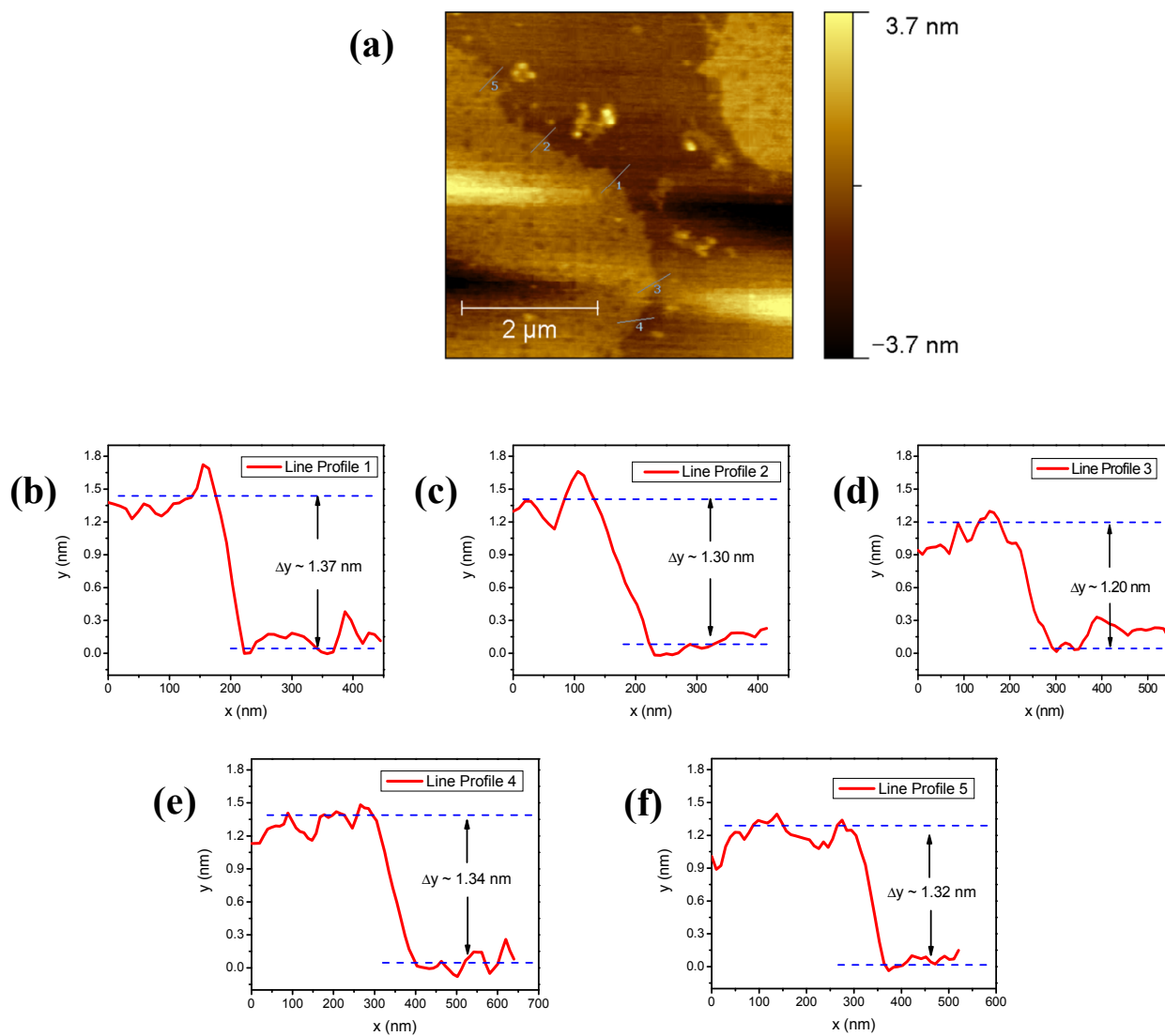


Figure S6. (a) AFM topography 2D image with (b-f) line profile of the spin coated GO on mica.

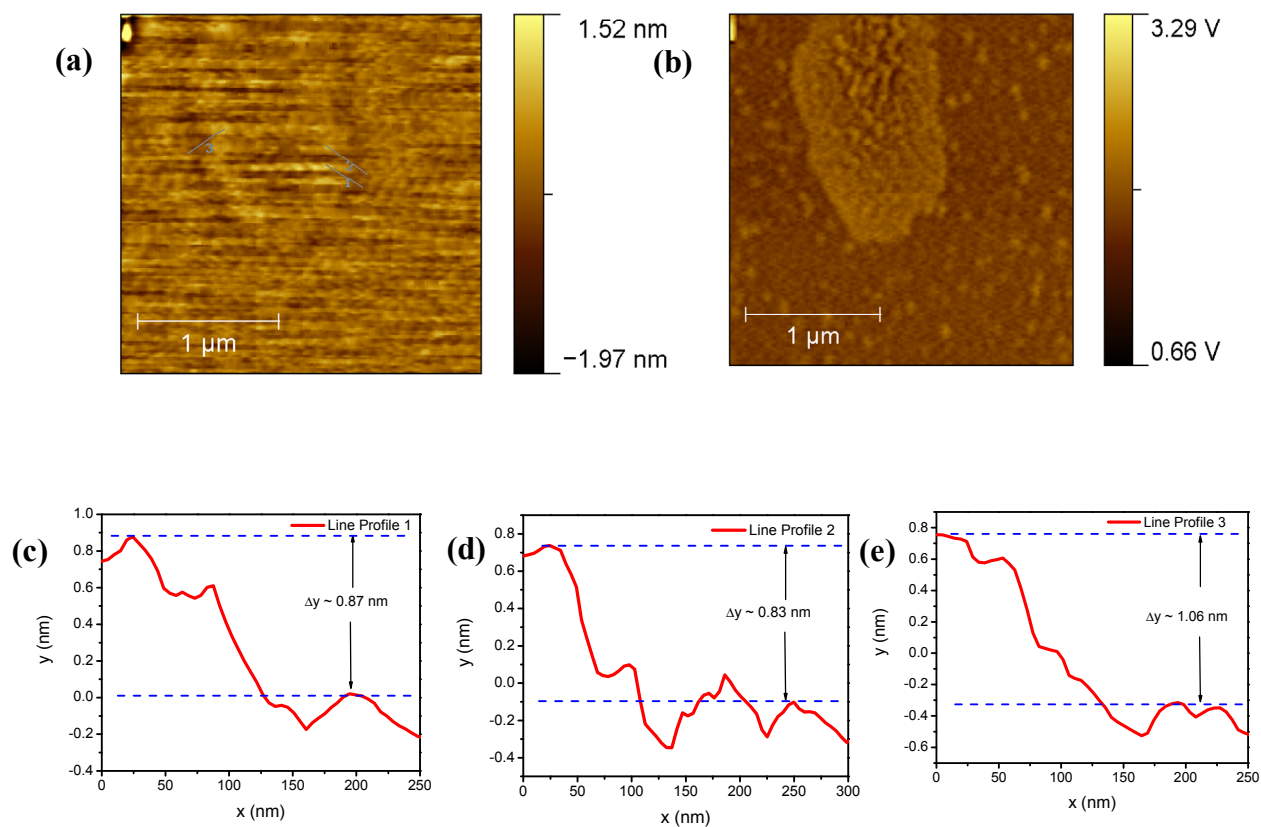


Figure S7. AFM (a) topography and (b) phase 2D images with (c-e) line profile analysis of the reduced graphene oxide (RGO).

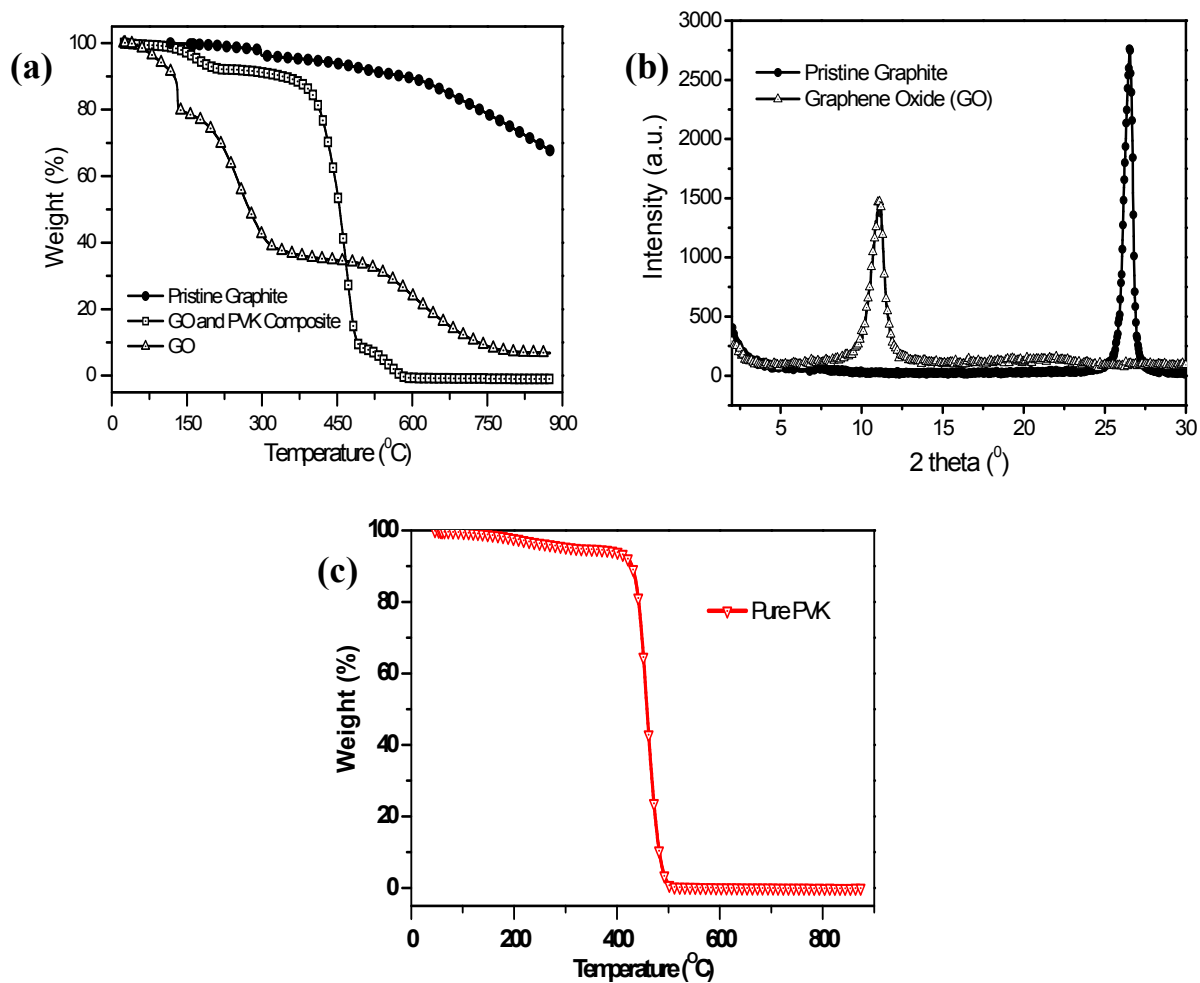


Figure S8. (a) TGA thermogram and (b) XRD data of GO/PVK nanocomposite as compared to pristine GO or graphite. (c) TGA thermogram of pure PVK as control. The TGA data shows the formation of the nanocomposite pattern. First, the TGA data for graphene oxide is consistent with the published literature^[1] with weight loss between 150 to 300° C corresponding to CO, CO₂, and steam release^[5] from the most labile functional groups. The weight loss from 450 to 900 °C can be attributed to the removal of more stable oxygen functionalities.^[6] The TGA data for the PVK-GO nanocomposites indicated a three-step decomposition process. The first 2 steps are consistent with the thermal degradation of the PVK, corresponding to the degradation of the side chains and polymer backbone, while the observed third decomposition step corresponds to the oxidation and decomposition of GO. The XRD data shows the typical peak for graphene oxide^[1] with a diffraction band at $2\theta = 11.1^\circ$, corresponding to a d spacing of 0.8 nm. The peak at $2\theta \sim 25^\circ$, which is known peak for graphite, has disappeared in the XRD curve for the graphene oxide.

[5] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. B. T. Nguyen, and R. S. Ruoff, *Carbon* 2007, **45**, 1558.

[6] J. Shen, Y. Hu, M. Shi, X. Lu, C. Qin, C. Li, and M. Ye, *Chem. Mater.* 2009, **21**, 3514.

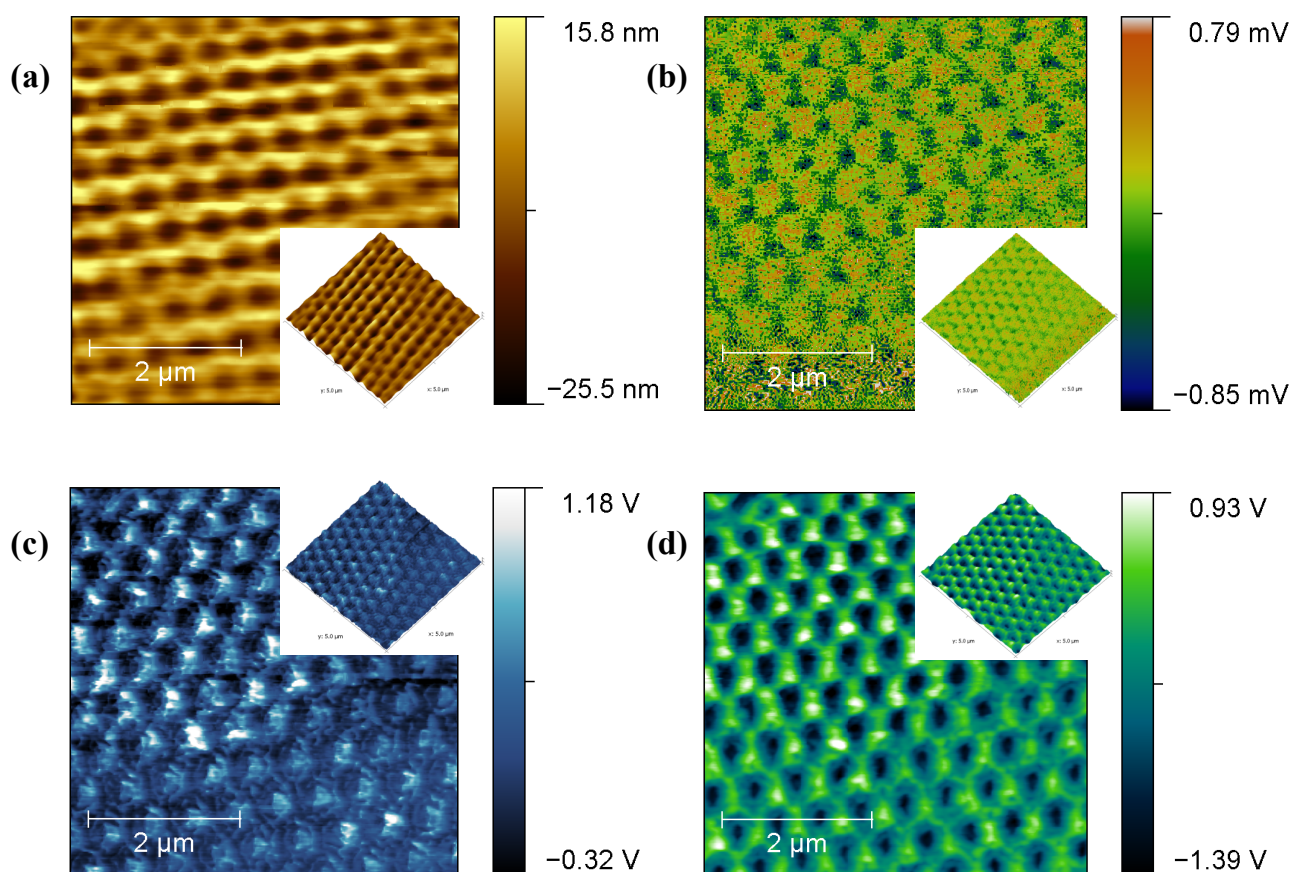


Figure S9. (a) Contact topography and (b-d) current sensing (CS) - AFM 2D images (3D images on inset) of the GO/PVK nanocomposite and electro-patterned films.