Polythiophene-Gold Nanoparticle Hybrid Systems: Langmuir-Blodgett Assembly of Nanostructured Films

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Supporting Information

Experiment details:

Materials

Regio-regular poly (3-(2-methoxyethoxy) ethoxymethylthiophene-2, 5-diyl (PMEEMT), regio-regular poly (3-dodecylthiophene-2, 5-diyl) (PDDT) and octadecyltrichlorosilane (OTS) (Sigma-Aldrich) were used as received. Chloroform and toluene (HPLC grade) were purchased from Merck and Tedia respectively, and were used as received. Silicon wafers from Engage Electronics Pte Ltd., Singapore were 0.6 mm thick, p-doped, polished on one side and with a natural oxide layer.

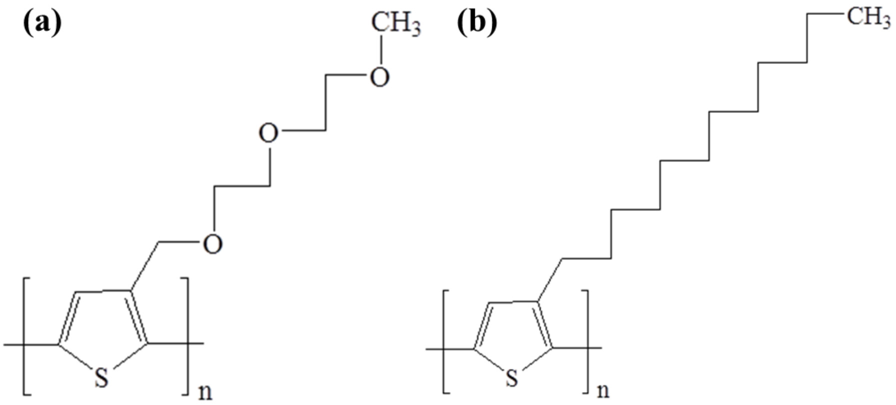

Fig. S1 Molecular structures of (a) PMEEMT and (b) PDDT.

Substrate preparation

The silicon wafers and glass slides were treated with a 7/3 (v/v) mixture of concentrated sulphuric acid and 30% hydrogen peroxide at 70 ^{o}C for 45 min. *Caution: piranha solution is highly oxidative, wear proper personal protective equipment (PPE) when handling it.* The substrates were then rinsed with deionized water and methanol, and then finally blown dry with nitrogen. Subsequently, the substrates were rendered hydrophobic by immersing them in a 3 mM solution of OTS in toluene at room temperature for 2 h. The substrates were then rinsed in copious amount of toluene, followed by sonication for 10 min and rinsing again successively in toluene and methanol, and finally blown dry with nitrogen.

Langmuir-Blodgett film deposition

The investigation of surface pressure–area isotherms and deposition of the Langmuir-Blodgett films was carried out at room temperature on an alternate layer Langmuir–Blodgett trough (NIMA Technology, model 622) equipped with two symmetrically arranged barriers. A Wilhelmy-type film balance was used to measure the surface pressure. Deionized water of 18.2 MΩ.cm resistivity was used as the sub-phase. 200 µL of the 0.43 mg/ml of PMEEMT in chloroform solution was spread slowly on the water surface by a micro syringe. After the solvent fully evaporated, the surface area was gradually decreased by computer controlled compression barriers. The isotherms were measured by compressing the films with a barrier speed of 50 cm^{2}/min. The molecular area was calculated based on the molecular mass of the monomeric repeating unit of polythiophene chains. The monolayer deposition was carried out at a surface pressure of 25 mN/m and the polythiophene was transferred by vertical deposition at a speed of 5 mm/min. A holding time of 480 s was imposed between each dipping cycle to dry the films. The deposition of mixed PMEEMT and PDDT films on solid substrates was carried out by a similar procedure. Finally, the films were blown dry in nitrogen and stored in a desiccator.

Synthesis and deposition of gold nanoparticles

Gold nanoparticles (AuNP) were prepared by standard method reported in the literature [29]. Specifically, 1 mM of gold (III) chloride trihydrate was prepared in 30 ml of deionized water, and the solution was refluxed at 100 °C with stirring at 600 rpm for 10 min. 3 ml of 38.8 mM sodium citrate in deionized water was added to the refluxing solution. Stirring was continued for 45 min. The color of the mixture evolved gradually from gray to purple and finally to wine red, indicating the formation of AuNP. The AuNPs were deposited by ex-situ method i.e. the nanoparticles were incorporated into the PMEEMT LB films by immersing the film-laden substrate into the AuNPs solution for 30 min while the solution was stirred at 600 rpm. The substrates were washed with deionized water to retain only the bound AuNPs and blown dry with nitrogen.

Characterization

UV-Visible absorption spectra were recorded on a Shimadzu UV-1601 PC scanning spectrophotometer operating at a resolution of 1 nm. A bare quartz slide was used as the background. Surface morphologies were investigated using a Nanoscope III atomic force microscope (AFM). All images were collected in air using the tapping mode and a monolithic silicon tip. The drive frequency was 330±50 kHz, and the voltage was between 3.0 and 4.0 V. The drive amplitude was about 300 mV and the scan rate was 0.5-1.0 Hz. Thickness characterization was performed by ellipsometry (WVASE 32, J.A.Woollam Co. Inc.,). Scanning spectra were acquired over the wavelength range of 600-1000 nm at three different incidence angles, 65^o, 70^o and 75^o. The modelling for the thin film measurement used silicon (Si.MAT) as the base layer with 0.6 mm thickness, the silicon dioxide (SiO_2.MAT) as the next layer with a thickness of 2.5 to 3 nm and the Cauchy package (CAUCHY.MAT) for the polymer films. The thicknesses were averaged over multiple readings. Contact angle of the surface modified LB films was obtained from a KSV CAM 200 contact angle and surface tension analyzer using a 5 µl water droplet. A cleaned silicon wafer was used as the reference. The gold nanoparticles were imaged by transmission electron microscopy (JEM-2010, JEOL USA Inc.). The electron beam accelerating voltage of the microscope was set at 200 kV. The sample was prepared by depositing a drop of gold nanoparticle solution on to a copper grid coated with carbon film. The surface morphology of the polythiophene films and the distribution of nanoparticles on the polythiophene films were studied by field emission scanning electron microscopy (JSM6700F, JEOL USA Inc.). Current-voltage (I-V) characteristics were measured by an HP4156 semiconductor parameter analyzer.

Current density-voltage (J-V) analysis

Fig. S2 Schematic representation of metal-insulator-semiconductor (MIS) device structure.

Aluminium electrodes of 0.3 mm dia. were thermally evaporated on the films through a mask. A potential sweep of -4 V to 4 V was applied across the source electrode and the corresponding current was measured at the drain electrode.