

Electron Transfer/Transport in Nanoparticle/Polymer Monolayer Arrays

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Abstract:

Nanoparticle (NP)/Polymer composites exhibiting advantageous optical, electrical and mechanical properties are of interest and in intensive investigations for a variety of applications. A universal, fast and facile method to prepare robust, freestanding and patternable NP/polymer composites by evaporation-induced self-assembly on a fluid interface has been developed. By transferring the NP/polymer films onto discovery platforms with predeposited interdigitating electrodes, electron transfer at the metallic NP/polymer interfaces and electron transport across the composite films have been studied through a combination of electrical and spectroscopic techniques.

Introduction:

We studied the localized electron transfer and electron transport characteristics in a composite polymer consisting of a monolayer of monodisperse gold (Au) nanoparticles and poly-(3-hexylthiophene), or P3HT. The ultra thin films that incorporated the Au NPs were successfully created via an interfacial evaporation induced self-assembly (EISA) process. These films were then successfully transferred to the desired substrate, in this case, a discovery platform, which consisted of a series of interdigitated gold electrodes. The discovery platform was then wire-bonded to a carrier, which allowed for bias voltage to be injected through the device. Raman Spectroscopy was then used to measure variances in scattering intensity as an indirect method of detected charge movement across the device.

Fabrication of Thin Films:

Solutions of P3HT, and Au nanoparticles, in appropriate ratios were dissolved in toluene. One drop of the solution was carefully released over a deionized water surface sitting in a Petri® dish. The solution of P3HT and Au NPs spread out over the surface and a thin film was formed through interfacial evaporation-induced self assembly as shown in Figure 1. The thin film consists of a monolayer of Au NPs spread evenly in a hexagonal close-packed array as shown in Figure 2.

After the toluene evaporated, the thin film was captured on a discovery platform, by submerging the platform under the deionized water and bringing it up through the thin film. The sample was then left to dry undisturbed. Some samples were also thermally annealed to determine if heating would create a better contact between the electrodes and the thin film. It was found that the annealed films showed no significant difference

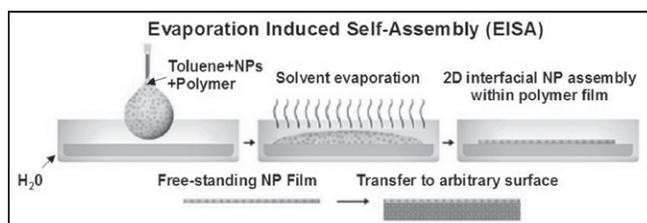


Figure 1: Thin film fabrication via evaporation induced self-assembly.

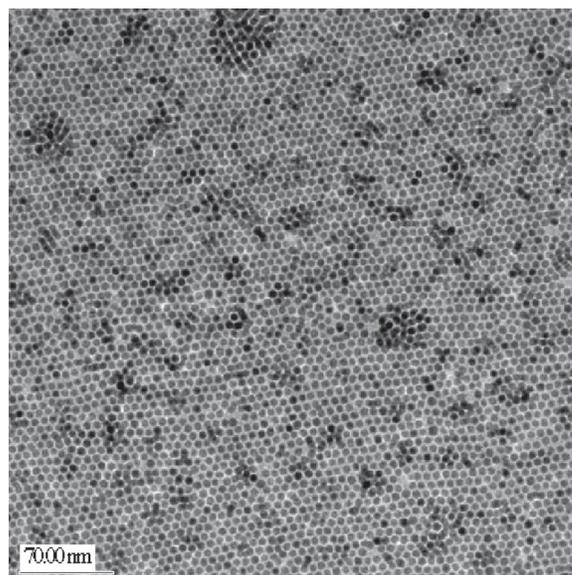


Figure 2: TEM image showing a hexagonal close-packed Au NP/P3HT film.

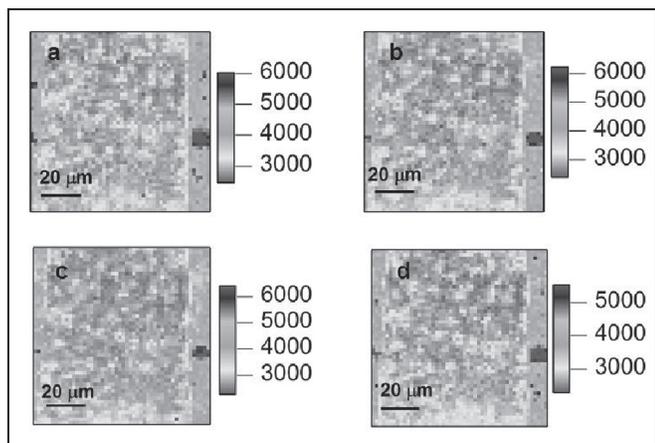


Figure 3: $C = C$ mode of P3HT/Au monolayer on discovery platform: a) 0 V; b) 50 V; c) 100 V; d) 150 V.

from the other samples. Thin films without Au NPs were also made as a control and comparison.

Detecting Charge Mobility Across Thin Films:

Four voltages—0 V, 50 V, 100 V and 150 V—were used on the device sample by a function generator and amplifier. A laser of 488 nm generated by an Ar-Kr ion laser head was used to excite the sample. $390 \mu\text{W}$ Raman scattering light was then collected by a sensitive EMCCD. For a single Raman spectrum, acquisition time was ~ 500 ms.

Figure 3 shows the Raman intensity images of the dominant peak, $C = C$ stretching mode of P3HT on the discovery platform sample under different voltages with excitation 488 nm to understand charge transport. The scan range was set to be $100 \mu\text{m}$ and we selected the region purposely to cross two of the Au electrodes. The intensity drop of these images shown may be due to a photodegradation issue, since the same region exposed to high power intensity laser $\sim 10^4 \text{ W/cm}^2$ and air. The features here clearly show two electrodes surrounding a nearby region. Lower intensity regions are indicated as red color and assigned to Au electrode because of the less P3HT in these regions; high intensity region are denoted as blue color and assumed to be between electrodes due to thicker composite layer.

Figure 4 shows the difference images of $C = C$ mode, which indicate the voltage effect on Raman intensity. The electrode and nanoparticle features are still distinguishable in these difference images. Au electrode regions show positive differences (about 0.2); however, for materials around an

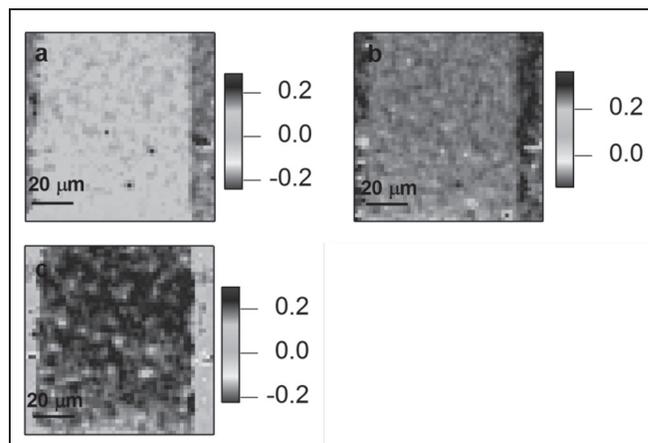


Figure 4: Difference image of $C = C$ mode: a) 0-50 V; b) 0-100 V; c) 0-150 V.

electrode, they turn to negative and close zero (-0.2-0.1) values at 150 V.

Results and Future Work:

We were able to successfully view changes in intensity of the $C = C$ mode of the film indicating that there is some sort of charge movement on the localized level. Although we only had a cursory data set, it seemed that we could conclude that bias-induced chemical changes occurred at the molecule-electrode interface, possibly from charge injection. Also there was no significant charge transfer character that existed in hybrid films as oppose to pure polymer films.

Future things we hope to accomplish are to develop a method to measure current and voltage simultaneously while measuring the Raman scattering effect, determine how size of NPs affects the detection of charge mobility in the composite film, measure the effects on electron mobility when the discovery platform is treated as a FET, and test Raman Scattering at different excitation wavelengths.

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