Supporting information for: Local Charge Injection and Extraction on Surface-Modified Al_2O_3 Nanoparticles in LDPE

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Experimental

The thin films were produced by adding 23 mg of extruded LDPE/Al₂O₃ (cable grade LDPE from Borealis, Al₂O₃; Nanodur, CAS number 1344-428-1) to 5 ml p-xylene (CAS number: 106-42-3, \geq 99%, Sigma Aldrich) in a ball reactor, with a water-connected reflux-condenser. The surface modification of the Al₂O₃-nanoparticles and the extrusion of the nanocomposites have been reported by Liu *et al.*^{S1} The mixture was heated to 130 °C in an oil bath and kept for 3 hours with constant stirring to ensure complete dissolving of the polyethylene. Au films, 50 nm thick, were deposited by thermal e-gun evaporation in a home built UHV deposition system (Eurovac/Thermionics) over a 3 nm sticking layer of Ti, on a silicon wafer (Polished Wafer, MEMC Electronic Materials). Before deposition of the p-xylene suspension the Aucoated wafer was cleaned in acetone (\geq 99.5%, Fischer Scientific), 2-propanol (\geq 98%, VWR) and then milliQ water (18.2 mOhm.cm at 25 °C) for 10 minutes in ultrasonication bath (DTH 2510, Branson) respectively, in accordance with the cleaning method of Mellbring *et al.*^{S2}

To ensure that the LDPE did not crystallize too quickly, a heating gun (30-9323, Co/Tech Tools) was coupled to regulate the temperature of the spin-coater (KW-4A, Chmat Technology). After complete wetting the wafer was spun for 60 seconds at 2500 rpm to form a thin, continuous film. The wafer was annealed by gradual reduction of the temperature from 130 °C to 30 °C over 4 hours in a lab furnace (UT6120, Heraeus) to evaporate any residual p-xylene and to re-crystallize the polyethylene film. A Hitachi S-4800 field emission scanning electron microscope (FE-SEM) was used to verify that a homogeneous film was formed and that Al_2O_3 -nanoparticles were distributed over the film. The thickness of the film was determined using a KLA-Tenor P15 Surface Profiler.

The ImEFM^{S3} scans were performed on a Dimension Icon AFM (Bruker) equipped with a Multifrequency Lockin Amplifier and dedicated control and analysis software (Intermodulation Products AB). The probe used was a platinum coated tapping mode cantilever HQ:NSC15/Pt (MikroMasch). During the scans, the sample was grounded through the bottom Au electrode, while an AC voltage of 6 V was applied to the probe to perform the surface potential measurement. Were applicable, an additional DC voltage bias was applied to the probe. The cantilever was mechanically excited at its resonance frequency with an amplitude of 40 nm peak-to-peak, and the surface was tracked by maintaining an amplitude set-point of 75%. All the acquired images have 256x256 pixel resolution, with 2 ms pixel time. The resulting imaging time is approximately four and a half minutes.

SEM Images



Figure S1: Scanning Electron Microscope (SEM) images of a representative area of the sample. Al_2O_3 nanoparticles are clearly visible embedded in the different crystalline phases of the low density polyethylene. (b) shows a zoom over the area marked by the red box in (a). The scale bar in both images is 1 μ m.

ImEFM time sequence



Figure S2: Consecutive ImEFM scans of the Al_2O_3 nanoparticles embedded in LDPE. The images show the surface potential V_{SP} under condition of none (a-b), positive (c-d), and negative (e-g) DC bias. As in Figure 2 of the main article, an offset is applied to all color scales so that they are centered on the average value of the surface potential over the LDPE matrix. The black scale bar in all images is 100 nm. Each scan takes approximately 4.5 minutes. At 0 V (a-b) and +2 V (c-d) DC bias, the images don't show significant change when the scan is repeated. On the contrary, at +2 V DC bias (e-g) the features on the image undergo a gradual change util the contrast is lost.

Charge diffusion

In the energy band explanation given in the main manuscript, we presented the occupation of hole trap states in a static manner, being either occupied or unoccupied, depending on the DC bias. In actual fact a dynamic equilibrium between the tip and the surface is reached. There is also in principle some diffusion of the injected charge away from the scanned area via hopping conductivity.^{S4} This conductivity in the insulating matrix is however very small, so that any charge that could leak away is easily replenished from the tip which is continuously scanning over the surface.

We have observed this slow charge diffusion in experiments where the tip is held at high bias (6 V) while contacting the surface for an extended time (5 s). Subsequent scans (Figure S3) image the non-uniform potential due to the charge that was locally injected in to the PE matrix, which very slowly recovers to a uniform potential over the scan area (> 1 h).



Figure S3: Consecutive ImEFM scans over an LDPE sample. Charge was injected at a single point by biasing the AFM tip to 6 V and keeping the contact for 5 s. The images show a gradual diffusion of the injected charge over an extended period of time, with each scan requiring about 4.5 min. The white scale-bar is 200 nm, and the colorbar ranges between 0.9 V (red) and -0.2 V (blue) for all images.

References

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