

Nanoplastic glow up: polyethylene pillar arrays for chemical sorption assays

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Chemical sorption to nanoplastic particles is of concern and interest. Nanoplastics can sorb and carry toxic pollutants into cells,¹ while hydrophobic fluorophores can label nanoplastics for detection and sizing². In either scenario, optical microspectroscopy is important for measuring particles and sorbates. Beyond fluorescence, stimulated Raman scattering³ and optical photothermal infrared⁴ (OPTIR) spectroscopy have emerged as methods with submicrometer resolution and high sensitivity to detect and characterize nanoplastics. However, each of these methods has its own limitations, ranging from fluorophore aggregation to limit of detection. Even studies of engineered plastic nanoparticles yield unacceptably high errors⁵. To improve accuracy, we are developing novel standards in the form of nanoplastic arrays.

Previously, we patterned arrays of phenolic-resin nanopillars by electron-beam lithography. Control over pillar size, shape, and position enables microspectroscopy calibrations and study of the dependence of fluorescence intensity on pillar size. Building on this work, at EIPBN 2024, we presented a hot spin-coating process to form nanoscale films of low-density polyethylene (LDPE) for electron-beam lithography and reactive-ion etching. Unlike phenolic-resin resist, LDPE is a common material in consumer goods and packaging, and as a result, a common pollutant. LDPE is also of interest as a fluorophore host material for quantum light sources.

Presently, we advance our nanofabrication process to form arrays of LDPE pillars, and we begin to apply these novel standards to sorption assays of both a popular fluorophore and an optical brightener. The latter is present in laundry detergent to make clothing fluorescent, appearing to glow a clean white, and then pollutes wastewater. To test any effect of our nanofabrication process on LDPE, we compare OPTIR spectra of films before patterning and structures after patterning, finding that the chemical composition is similar (Figure 1a, b). Atomic force micrographs of the pillar array show suitable control of LDPE pillar height, position, and volume (Figure 1c), even as the pattern samples a film with a complex microstructure. We begin to study the interaction of LDPE pillars with rhodamine B (Figure 1c), a common fluorophore, and 4,4'-diamino-2,2'-stilbene disulfonic acid (DSD) (Figure 1d), an optical brightener. Further study of the correlation of fluorescence intensity and pillar volume will elucidate interactions of nanoplastic particles and chemical sorbents of environmental concern and technological interest.

References

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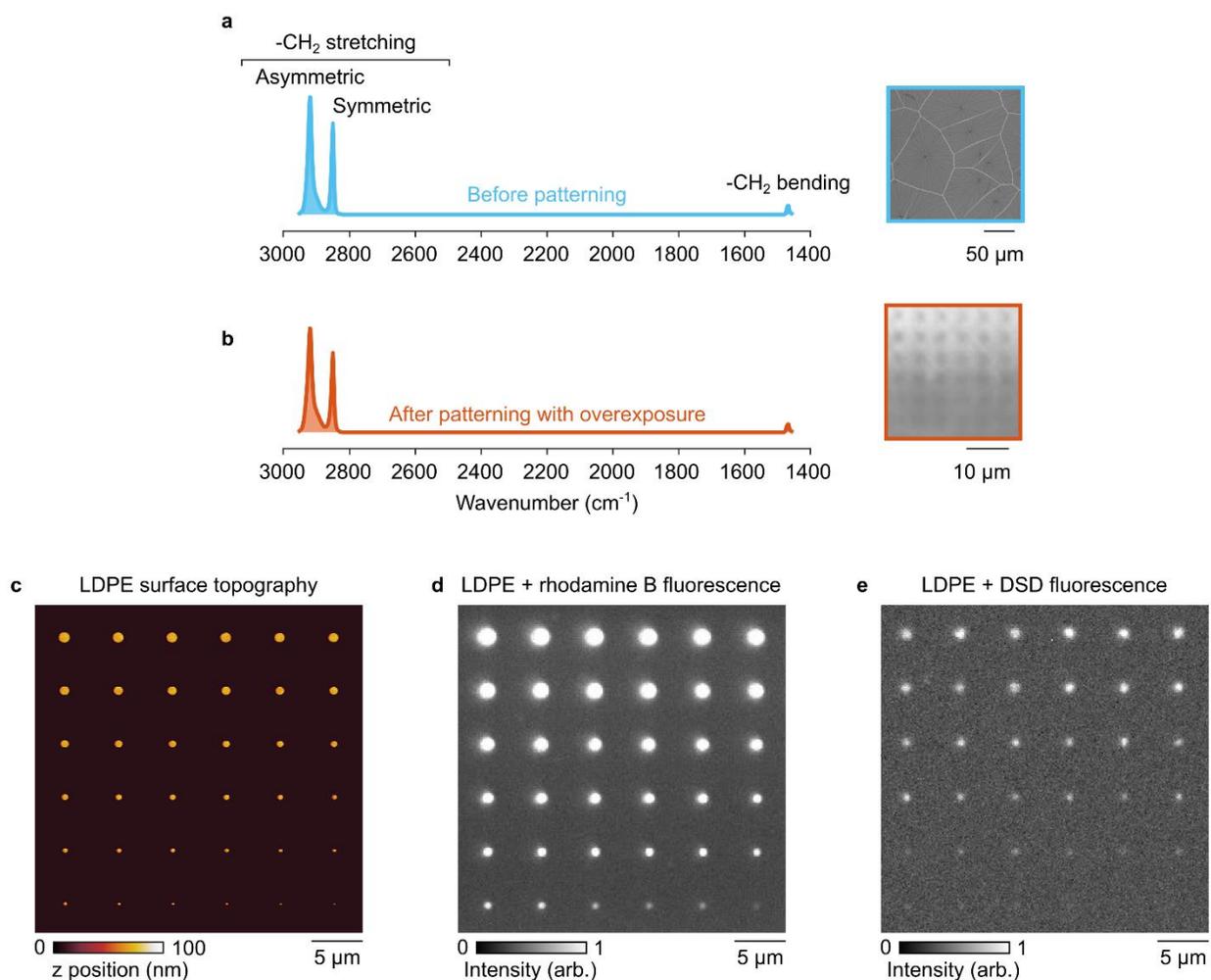


Figure 1. Spectra and micrographs of LDPE films and pillars. (a-b) Optical photothermal infrared (OPTIR) spectra showing chemical composition of plastic nanostructures before and after nanofabrication, which consists of electron-beam lithography and reactive-ion etching. The three main absorption peaks of polyethylene in the IR region are the -CH₂ asymmetric stretch peak at 2919 cm⁻¹, the -CH₂ symmetric stretch peak at 2850 cm⁻¹, and the -CH₂ bending peak at 1456 cm⁻¹. (a) (Left) OPTIR spectrum showing three absorption peaks consistent with LDPE. (Right) Optical micrograph showing an LDPE film before nanofabrication. The nucleation sites and spherulite boundaries form as the LDPE solidifies during hot spin-coating (b) (Left) OPTIR spectrum showing similar absorption peaks for LDPE as in panel (a), indicating that even after overexposure with the electron beam, the LDPE composition remains the same. (Right) Optical micrograph showing features after patterning by electron-beam lithography. (c-d) Micrographs of several types showing dimensional and optical properties of LDPE pillars. (c) Atomic force micrograph showing pillars of similar height of approximately 76 nm and diameters varying from approximately 1000 nm down to approximately 100 nm, before chemical sorption. (d) Fluorescence micrograph of LDPE pillars after soaking in an aqueous solution of rhodamine B. (e) Fluorescence micrograph of LDPE pillars after soaking in an aqueous solution of DSD. For both (c) and (d), the peak wavelength of fluorescence excitation is approximately 550 nm, and fluorescence emission is collected through a long-pass filter above 590 nm.

Acknowledgements. We gratefully acknowledge funding support by the National Institute of Standards and Technology (NIST) in support of the Circular Economy (CE) Program.