

**University of Puerto Rico  
Mayagüez Campus  
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**by**

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**DEVELOPMENT OF ALTERNATIVE TECHNIQUES:  
MATERIALS PROCESSING BY LASER ABLATION MICRO/NANOTEXTURING AND  
CYCLIC VOLTAMMETRY MONITORING OF TNT DEGRADATION BY FUNGI**

**ABSTRACT**

Laser ablation of substrates is an alternative to more costly and complex lithographic and chemical etching routes in the preparation of micro and nanoscale structures. Pulsed lasers operating in the femtosecond time regime have presented excellent micro/nanotexturing efficiency. However, their general use has been hampered by its high cost of implementation for large area texturing, an ideal property for materials fabrication, in general, and for fabrication of surface-enhanced Raman scattering (SERS) based substrates for biophysical studies and for explosives detection. In contrast, nanosecond pulsed lasers are better suited to this purpose but tend to introduce melting to the surfaces as a result of longer pulse durations. This work focuses on investigating the parameters of fluence/energy density ( $J/cm^2$ ) and number of third harmonic pulses of a flash-pumped, Nd:YAG nanosecond laser operating in Q-switch mode and at 10 Hz for the optimum micro/nanotexturing of Si in air. Silicon wafers were exposed to fluence between  $0.15 J/cm^2$  and  $3.0 J/cm^2$  at 50-2000 laser pulses. Columnar shaped structures having dimensions in both micro and nano scales were evident for low fluence and low number of pulses. These structures lined the perimeter of the ablated regions more uniformly and had average separations close to the wavelength, reaching heights in the hundreds of nanometers to slightly greater than  $1 \mu m$  above the surface.

Another important theme covered in our investigations was the application of cyclic voltammetry (CV) to the study and testing of fungi as prospective biodegraders of the explosive, 2,4,6-trinitrotoluene (TNT), an important environmental pollutant commonly found in soils and aquifers of past or current military sites. Since conventional modes of remediation for this pollutant has proven costly and environmentally unfriendly, researchers have turned to the use of microorganisms, an eco-friendly and much more cost-effective alternative because the breakdown action towards explosives could be exploited from their natural metabolic machinery. Within the scope of these live

machines, fungi are of particular interest because they have not been as widely studied for this task, in contrast to bacteria. A technique that can assess the degradation ability for TNT by fungi in aqueous media is therefore highly desirable. Here, we demonstrate an electrochemical technique based on cyclic voltammetry that can be implemented to monitor TNT degradation in aqueous media after contact with fungi. The fungus used in this study was an isolate belonging to the *Aspergillus* genus. The means of monitoring the degradation activity of fungi for TNT was by exploiting the easily reducible three nitro groups of TNT, measuring changes in current at their characteristic peak potential and relating them to concentration of this analyte. During the first 21 days of exposure to a 68 ppm TNT stock aqueous solution, the TNT concentration decreased by 44% to 38 ppm before plateauing through the 58<sup>th</sup> day of the study.