

**Supporting Information to**  
**Controlled Amino-functionalization by Electrochemical**  
**Reduction of Bromo and Nitro Azo Benzene Layers Bound to**  
**Si(111) Surfaces**

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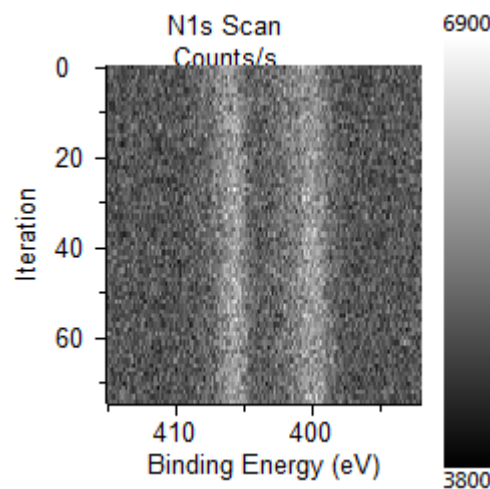
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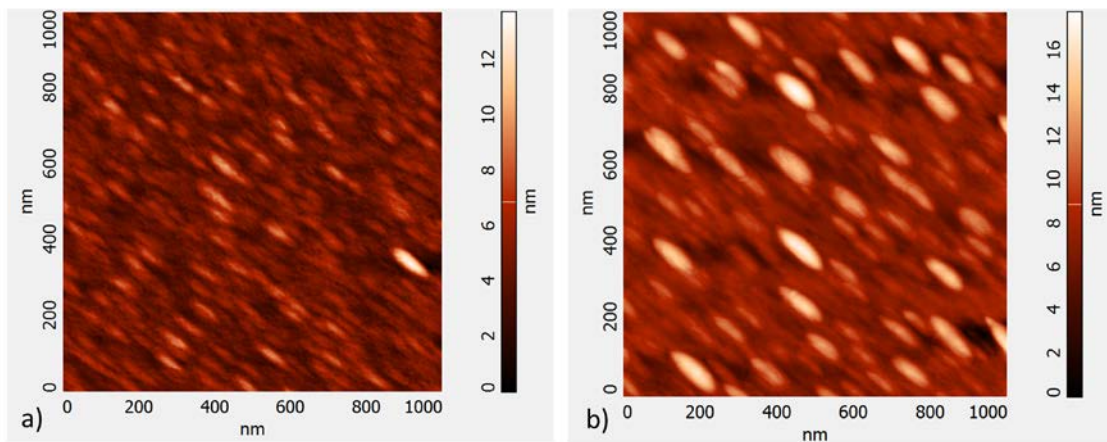
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### Constant N<sub>1s</sub> signal upon XPS illumination



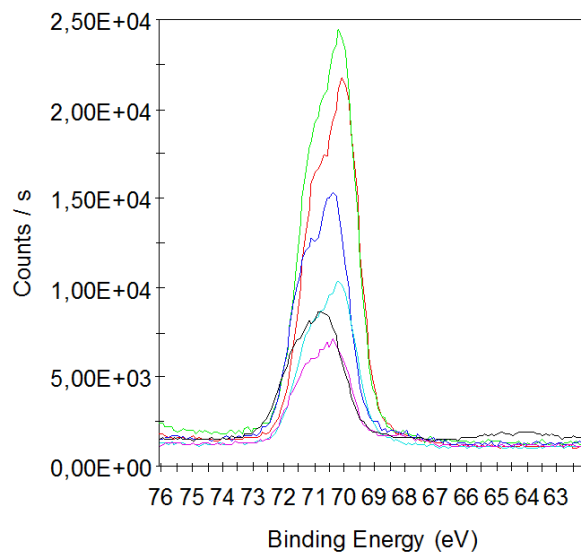
**Figure A1.** XPS N<sub>1s</sub> spectra taken during 15 min (75 iterations) upon illuminating a sample of 4-nitrobenzenediazonium electrografted on Si with a pass energy of 50 eV. No significant changes were observed in the peak intensities with X-ray exposure time.

### RMS roughness of the samples in AFM



**Figure A2.** AFM topography scans of the samples before (a) and after (b) the electroreduction of 4-bromobenzediazonium on Si. Upon electroreduction the rms roughness value increased from 1.1 nm to 1.5 nm for a  $1 \times 1 \mu\text{m}^2$  scan.

### Electroreduction of 4-BBD-modified Si (Azo-bond cleavage)



**Figure A3.** XPS Br<sub>3d</sub> spectra of bromobenzene electrografted on Si (3 upper graphs), and bromobenzene after the reduction of azobenzene on Si (3 lower graphs). On average the reduction is 43%.