

XPS Characterization of ‘Click’ Surface Chemistry

Author Tim Nunney, Thermo Fisher Scientific, East Grinstead, West Sussex, UK

Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectrometer (XPS) was used to characterize a conductive polymer device. The conducting polymer surface was a precursor in a ‘click’ chemistry process. New data processing methods enabled reductions in acquisition times and improved data quality.

Introduction

The functionalizing of polymer surfaces is an important task in material science. A growth area in this field is the design and manufacture of inexpensive and disposable devices which can be tailored to specific clinical applications. One such application is in cancer immunotherapy, where chemically modified microelectrodes can be used to capture, modify, and analyze white blood cells before reintroducing them to a patient. Conducting polymers, e.g. PEDOT¹, poly(3,4-ethylenedioxythiophene), are attractive as microelectrode material due to low cost, easy processing, and good cell compatibility. The device surfaces are modified by 'click' chemistry; joining smaller units together to generate active surfaces in mild conditions with high selectivity (Figure 1). Here, the necessary 'clickable' handle on the PEDOT material has been created by adding an azide (triple nitrogen) group to the monomer during synthesis.² The chemical shifts identified in XPS analysis can

be used to evaluate the integrity of the starting material, the success of the 'click' process, and the patterning of the device. New XPS data processing algorithms have been refined to allow for reduced acquisition times (which minimize the possibility of damage to the sensitive surface material), while still retaining chemical state information. These methods also allow for improvements in the spatial resolution of an acquired XPS map.

Experimental

Two separate experiments were performed to characterize the surface. The first experiment was to study the changes of PEDOT polymer over time caused by the X-ray exposure. The size of the X-ray spot used was 400 μm . The second experiment was to map the polymer surface using a 30 μm X-ray spot. To produce a map using Thermo Scientific K-Alpha the sample stage is scanned under the X-ray spot. The 128-channel detector in K-Alpha makes it possible to collect spectra using rapid snapshot acquisition mode. This keeps the X-ray exposure to a minimum and enables entire spectral regions to be collected in seconds, but still maintaining the chemical state information. The K-Alpha's turn-key charge compensation system was employed in the analysis. This system enables analysis of insulating samples with the same ease as conductors.



Thermo Scientific K-Alpha XPS

Results

XPS offers many benefits for analysis of these types of samples: quantitative elemental information, chemical state information and surface distribution. The challenges are the small structures and sample damage caused by prolonged X-ray radiation during the analysis. Reducing the acquisition times and maintaining the spatial and chemical state information can be addressed using deconvolution methods which have been integrated to the Thermo Scientific Avantage data system. The theory behind the deconvolution methods has been explained in the Application Data Sheet AN52144.

Figure 2 shows N1s XPS spectra from a large area of the sample. The two peaks on Figure 2a are the result of the different oxidation states of the N atoms in the PEDOT-azide polymer. The peaks due to the N⁺ species and the N⁻ species (Figure 2a insert) are in the expected 1:2 ratio. Under X-ray exposure the azide group starts to degrade resulting in the N₃ species (Figure 2b). By using K-Alpha's rapid snapshot acquisition mode and the deconvolution methods this problem can be overcome and the characterization of the device is possible.

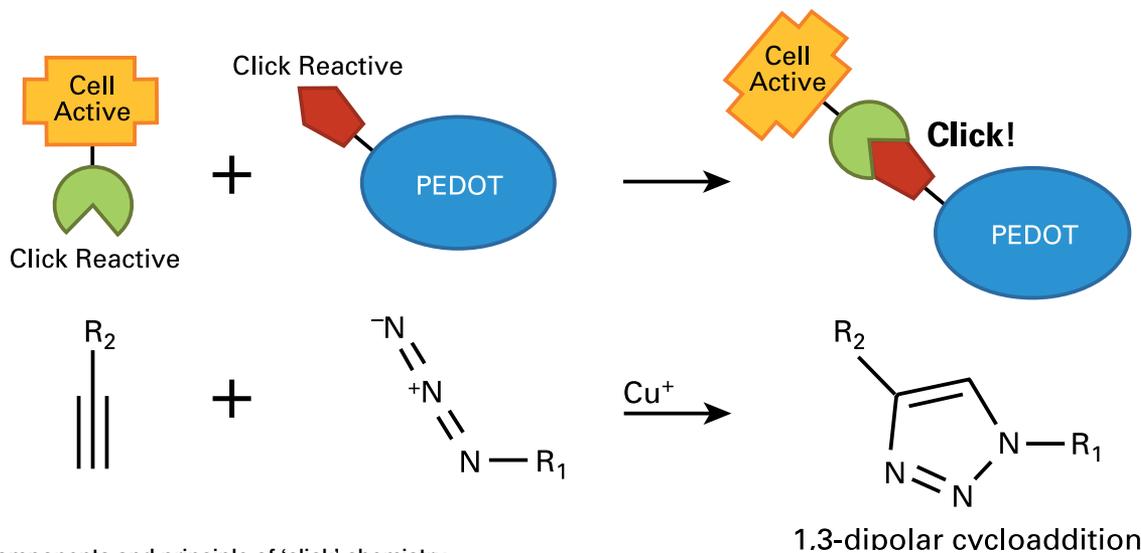


Figure 1: Components and principle of 'click' chemistry

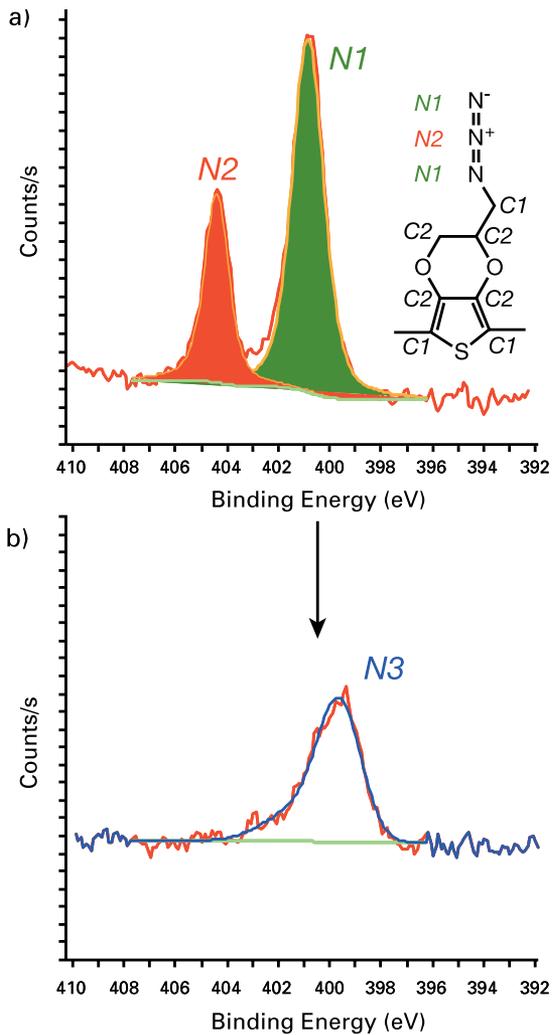


Figure 2: Degradation of PEDOT-azide can be seen in N1s spectra

Figure 3 shows the chemical maps of the micropatterned surface before and after deconvolution of the data. The line scans across the maps show how deconvolution improves the image resolution. The dashed lines are from the map before the deconvolution and the solid lines from the deconvoluted map.

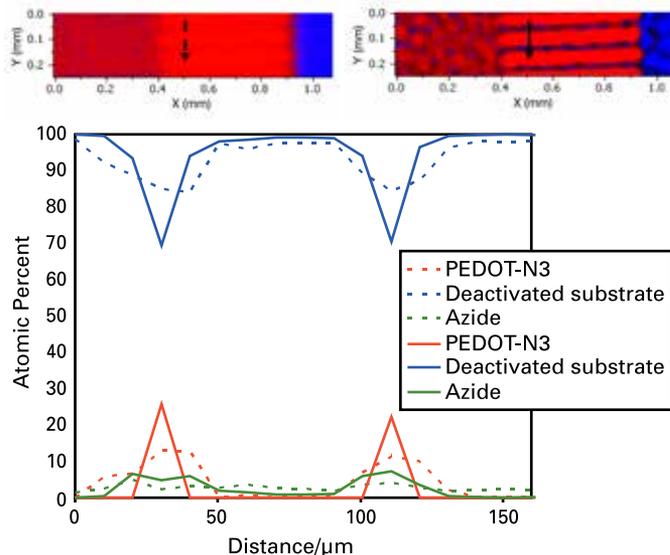


Figure 3: Image deconvolution improves the data acquisition time without compromising the data quality

Summary

The deconvolution routines have substantial benefits for XPS analysis of polymer systems. Reductions in acquisition time are possible by using higher pass energies, resulting in lower exposure of sensitive samples to the X-ray source. Extraction of information from the data can be easier due to improved signal-to-noise ratios and image deconvolution overcomes any limitation due to the size of the X-ray spot, resulting in improved XPS mapping abilities.

