

Use of electrografted aryldiazonium salts to control the surface conductivity and reactivity of ZnO

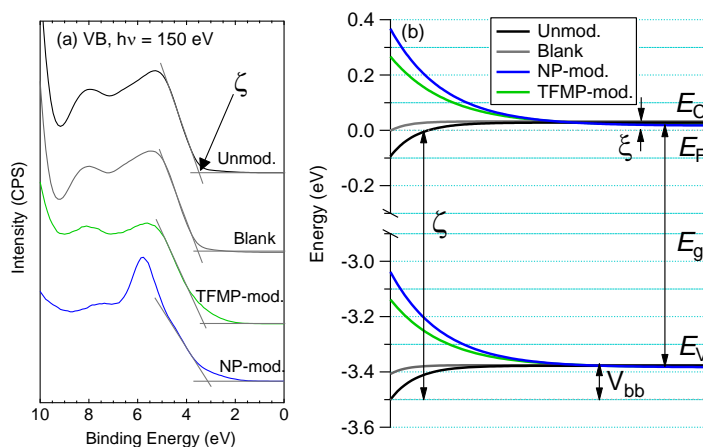
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Zinc oxide (ZnO) is a transparent, earth-abundant, wide band-gap semiconductor with high surface sensitivity and reactivity that must be controlled for use in electronic applications, in particular transparent thin film transistors and UV photodetectors. In ambient conditions, the ZnO surface is terminated by hydroxyl groups that cause the conduction and valence bands to bend downwards, creating an electron accumulation layer that renders the surface highly susceptible to unwanted atmospheric adsorbates [1]. The surface hydroxyl termination can be deliberately replaced with covalently bonded organic functional groups. In doing so, the surface band bending and surface conductivity can be directly manipulated. In this work, nitro- and trifluoromethyl-phenyl multilayered films have been attached to ZnO by electrografting from aryldiazonium salt solutions. Synchrotron X-ray photoemission spectroscopy confirms that both surface modifiers remove the native downward band bending, with the nitro-phenyl termination producing a large upwards band bending consistent with an electron-depleted surface. It was also observed that X-ray-induced reduction of the nitro-terminated film serves to further increase the upward band bending, which is an unexpected and as yet unexplained phenomenon. Diazonium salt chemistry has been rarely used to modify ZnO, yet this work indicates that it is a highly promising surface modification strategy for controlling the surface conductivity and reactivity of this technologically-important transparent semiconductor.



[1] R. Heinhold et al., Phys. Rev. B **88**, 23 (2013)

Figure 1. (a) Synchrotron XPS valence band spectra and (b) energy-level diagram showing band bending for unmodified ZnO, as well as trifluoromethylphenyl- (TFMP-) and nitrophenyl- (NP-) modified ZnO. Blank-treated sample is also shown.

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Supplementary Page

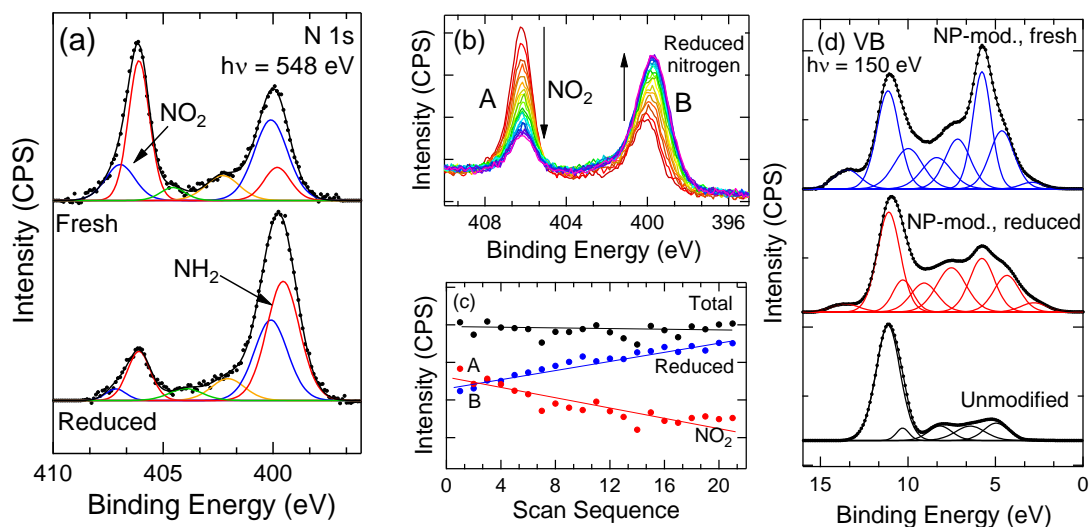


Figure 2. (a) XPS N 1s spectra for NP-modified ZnO showing the reduction of the NO₂ group (binding energy ~406 eV) to amine (binding energy ~399.5 eV) after prolonged X-ray irradiation. Spectra were gathered using a photon slit size of 9 μm . (b) XPS N 1s spectra for NP-modified ZnO during continuous single-scans for 540 s ($h\nu = 548$ eV, slit size = 20 μm). (c) NO₂ (blue), reduced NO₂ plus azo (red), and total N (black) N 1s peak areas during the irradiation shown in (b). Lines are to guide the eye. (d) XPS valence band spectra ($h\nu = 150$ eV) for fresh and reduced NP-modified ZnO, and unmodified ZnO.