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Arrays of nitrogen-doped multiwall carbon nanotubes (MWCNTs) have been vertically grown on silicon substrates using an aerosol-assistant catalytic chemical vapour deposition (CCVD) method. To check the possibility controlling the chemical state of nitrogen in MWCNTs we changed the composition of the reaction mixture. Acetonitrile or benzylamine was taken as a nitrogen source, while ferrocene served as a catalyst source. We also replaced a portion of nitrogen-containing solvent by toluene which preserving the other CCVD parameters (temperature, ferrocene concentration, synthesis duration, gas flow) are constant. Electronic structure of the N-MWCNTs was studied using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The first spectroscopy is surface-sensitive, and the second one probes the depth of nanotubes. We find that at low concentration of nitrogen-containing precursor in the reaction mixture the benzylamine promotes formation of graphitic-like nitrogen (direct substitution for carbon atom in nanotube walls), while both graphitic nitrogen and pyridinic-like (location of nitrogen at vacancy) nitrogen atoms are formed with the use of acetonitrile. From comparison of the XPS spectra measured with different excitation energy and NEXAFS data acquired at Auger and total-yield electrons we also discuss the distribution different forms of nitrogen (graphitic, pyridinic, and molecular) from the nanotube surface to the nanotube cavity depending on the aerosol composition.