Synthesis and characterization of immobilized PAMAM dendrons

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Supporting Information

Materials

Silicon Wafers were purchased from Compart technology Ltd, Uk (thickness 525±50µm). .Isopropyl alcohol (99%), Acrylic acid (99%), Polyethyleneimine (50% wt solution in water), Methyl acrylate (HPLC grade), Ethylenediamine (99%) and Copper II) sulphate were all purchased from Sigma Aldrich, Uk.

Sample Preparation and Experimental

1. Silicon Wafer Preparation

Silicon wafers have been prepared for use as substrates for surface modification. Si wafers have been cut into 0.5cm^2 pieces using a diamond cutter before being sonicated for 45 minutes in isopropyl alcohol (99%) Aldrich, UK)). The Sonication solvent was changed at 15 minute intervals. The silicon wafers were stored in fresh isoproponal and blown dry using Nitrogen prior to plasma treatment

2. Plasma polymerisation (PPAA)

Cleaned tweezers that had been sonicated in isopropyl alcohol were used to transport the substrate to the plasma reaction chamber. Acrylic acid (99%) was the selected monomer for plasma polymerisation and was obtained from Sigma Aldrich, UK. The deposition was carried out in a custom built reactor. The RF source (13.56 MHz Coaxial Power Supplies Ltd., Eastbourne, UK) was connected to a matching unit to an externally wound 6- turn copper coil around a 5 litre capacity Pyrex glass cylindrical reactor. Si wafers were placed in the middle of the reaction chamber on a foil wrapped glass slide and evacuated to a pressure below 1 x 10^{-3} mbar. Monomer vapour flowed through the reaction chamber at a rate of 2.5Sccm for 5 minutes before being ignited and the Si wafers being exposed to a 20W, 20 minute plasma treatment. Monomer vapour was allowed to pass through the chamber for a further five minutes after the deposition had finished and before the chamber was vented and the substrates removed. The plasma polymerised acrylic acid (PPAA) thin films formed a platform for subsequent polymer grafting reactions.

3. Physisorption of PEI

Poly-cationic polyethyleneimine (PEI) 50 wt% solution in water (Aldrich, UK) was physisorbed onto the negatively charged acid terminated plasma polymer surface, which was achieved by immersing freshly prepared PPAA thin films into a 3mg/ml PEI solution which had been dissolved in phosphate buffered saline (PBS) (pH7). After the reaction had proceeded to completion the substrates were washed several times rigorously with distilled water to remove any remaining traces of unreacted PEI. Primary amine groups contained within the PEI layer provides reaction sites for subsequent Michael addition and the focal point of dendritic growth.

4. **Dendron Immobilisation**

The amine terminated substrate was subsequently immersed in a (3ml) 1/1 (v/v) Methylacrylate (Aldrich, UK), methanol (HPLC grade, Aldrich, UK) solution for 2hrs, whereby the surface underwent Michael addition to yield an immobilised ester terminated dendron (G0.5). Immersing the ester terminated substrate in a 1/1 (v/v) ethylenediamine (UK), methanol solution for 2hrs rendered an amine terminated dendron (G1) after the amidation reaction had proceeded to completion. Repetition of both Michael addition and amidation steps yielded higher generation dendrons. The substrates were washed several times with methanol after each step to ensure no unreacted reagents remained.

5. Copper Coordination

0.284g Copper (II) sulphate (Aldrich ,Uk) was dissolved in PBS (pH7) to make a 100mM copper sulphate solution. Dendron immobilised silicon wafers were immersed in 1ml copper sulphate solution in a well of a polystyrene 24 well plate overnight at 4˚C. After the reaction had proceeded to completion the silicon wafer substrates were washed thoroughly with distilled water to remove any excess copper.

X-ray photoelectron spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) - XPS was carried out on a Kratos Ultra DLD (Kratos Analytical Ltd, Manchester, UK) photoelectron spectrometer equipped with a monchromated Al Kα source at a power of 150W (300x700 □spot). The pressure in the main UHV chamber was maintained below 5 x 10-8 mbar for all analyses. All data was collected at 90oC relative to the sample plane. Survey scans were performed on each of the samples at pass energies of 160eV and step of 1eV to identify and quantify the elements present. High resolution C1s spectra were also obtained at 20eV and step width of 0.1eV. An electron flood gun was used at all times to charge neutralise the samples. Elemental compositions were determined from the individual peaks using CasaXPS software version 2.3.10 (Casa Software Ltd, Cheshire, UK) using relative sensitivity factors supplied with the instrument. High resolution C 1s spectra were fitted with Gaussian-broadened Lorentzian functions (80% Gaussian) after linear background subtraction. A value of 285 eV for the binding energy of the main C1s component (CHx) was used to correct for charging of specimens under irradiation.