

High Efficiency Amine Functionalization of Cyclo Olefin Polymer Surfaces for Biodiagnostics.

Supplementary information

S1. Experimental

S1.1 PECVD system

The experiment was carried out in an aluminium vacuum chamber, connected to a 13.56 MHz RF power source with an automated match-box. In the PECVD process, the input radio frequency (RF) current/ voltage is supplied to the powered electrode with respect to the grounded chamber for creating the plasma, Fig S1. Charged species (free electrons and ions) present in the chamber are accelerated by the electric field and collide with molecules of the source gases. In this way, the source gas molecules are excited to higher energy states, primarily by inelastic collisions with the energetic electrons, and dissociate into a variety of radicals, ions, atoms and more electrons. Since the energy required for excitation and dissociation is lower than that of ionization, the plasma will produce a large supply of excited and dissociated molecules and thus reactive radicals, even for a modest fraction of ionization. Radicals and atoms, generated in the plasma, travel to the growing film surface through a gas phase diffusion process. They are then adsorbed onto the surface and form chemical bonds at favourable sites to form an amorphous network.

The computer controlled CD 300 plasma system used for the deposition is schemed in figure 1 and consists of 1) vacuum chamber, 2) rotary and mechanical booster pump, 3) electrodes, RF generator and automatic matching unit, 4) liquid precursor container, 5) mass flow controllers (MFC) and manifold.

The vacuum chamber is an aluminium based container. The pressure in the chamber was measured using a Granville-Phillips gauge. Edwards EH mechanical booster pump backed by an Edwards E1M40 rotary pump was used to pump down the chamber. The rotary pump was connected through a port at the bottom of the chamber.

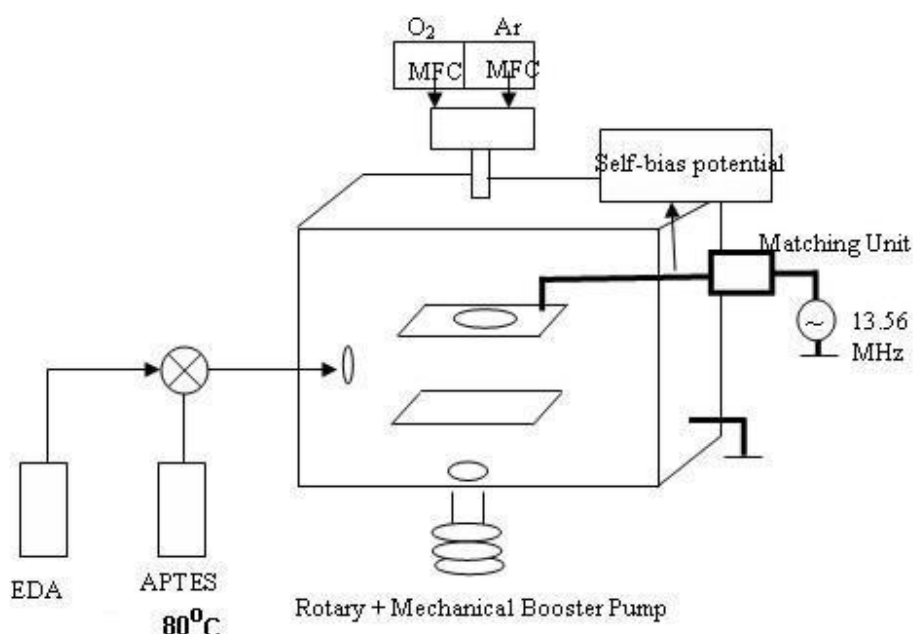


Figure S1. Schematic diagram of 13.56 MHz RF PECVD reactor

The powered electrode, 24cm X 21cm plate with a 6cm diameter with a hole in the middle, was placed slightly below the top of the chamber and the chamber wall was grounded. The powered electrode is cooled with running water. Also a 24cm X 21cm X 1.2cm electrically isolated, water cooled hollow metallic setup placed 10 cm away from the powered electrode is used as the substrate holder. The powered electrode (PE) is separated from the ground chamber by ceramic spacers and a floating potential (FP) electrode is placed under the powered electrode. During the process, electric potential from the RF generator is applied to the powered electrode, which in turn excited the gases present in the chamber to a plasma state. The RF generator was connected to the chamber through an automated matching box. The mass flow controllers (MFC) were used to control the flow of gases. Before each MFC, a shut off valve was installed to avoid leakage of any gas that was not used during the process.

S2. Characterization

S2.1 XPS

The XPS data were collected on a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyser. Spectra were excited using monochromatic Al K α X-rays (1486.69 eV) with the X-ray source operating at 100W. This instrument illuminates a large area on the surface and then using hybrid magnetic and electrostatic lenses collects photoelectrons from a desired location on the surface. In this case the analysis area was a 220 by 220 micron spot. The measurements were carried out in a normal emission geometry. A charge neutralisation system was used to alleviate sample charge buildup, resulting in a shift of approximately 3eV to lower binding energy. Survey scans were collected with a 160eV pass energy, whilst core level scans were collected with a pass energy of 20eV. The analysis chamber was at pressures in the 10⁻⁹ torr range throughout the data collection.

Data analysis was performed using CasaXPS (www.casaXPS.com). Shirley backgrounds were used in the peak fitting. Quantification of survey scans utilised relative sensitivity factors supplied with the instrument. Core level data were fitted using Gaussian-Lorentzian peaks (30% Lorentzian). The binding energy scale was corrected for the neutraliser shift by using the C 1s signal from saturated hydrocarbon at 285.0 eV as an internal standard. The elements present in the coating C, N, O, Si were detected using the XPS survey scan, Fig S2. High resolution scans of individual core levels show the various bonding states.

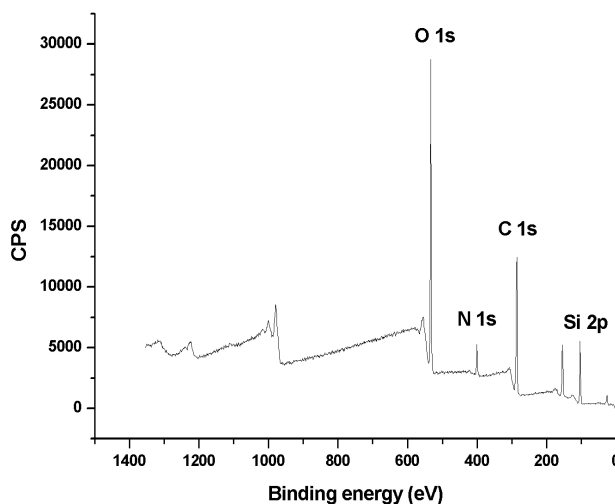


Figure S2. XPS survey scan collected with 160 eV pass energy.

S2.2 Quantification of amine groups using SulfoSDTB

A freshly prepared solution of sulfosuccinimidyl-4-[2-(4,4-dimethoxytrityl)]butyrate (sSDTB) (0.1 mM at pH = 8.0) was taken and the samples are immersed for 30 minutes at room temperature. After incubation, all substrates

were thoroughly rinsed with water and then treated with a 37.5 % perchloric acid to allow the formation of 4,4'-dimethoxytrityl cation from the substrates. Since the reaction between the amines and the sSDTB proceeds with 1:1 stoichiometric ratio, the concentration of the released cation measured by UV/vis spectrophotometer at 498 nm was used to quantify the amine group density (Fig. S3).

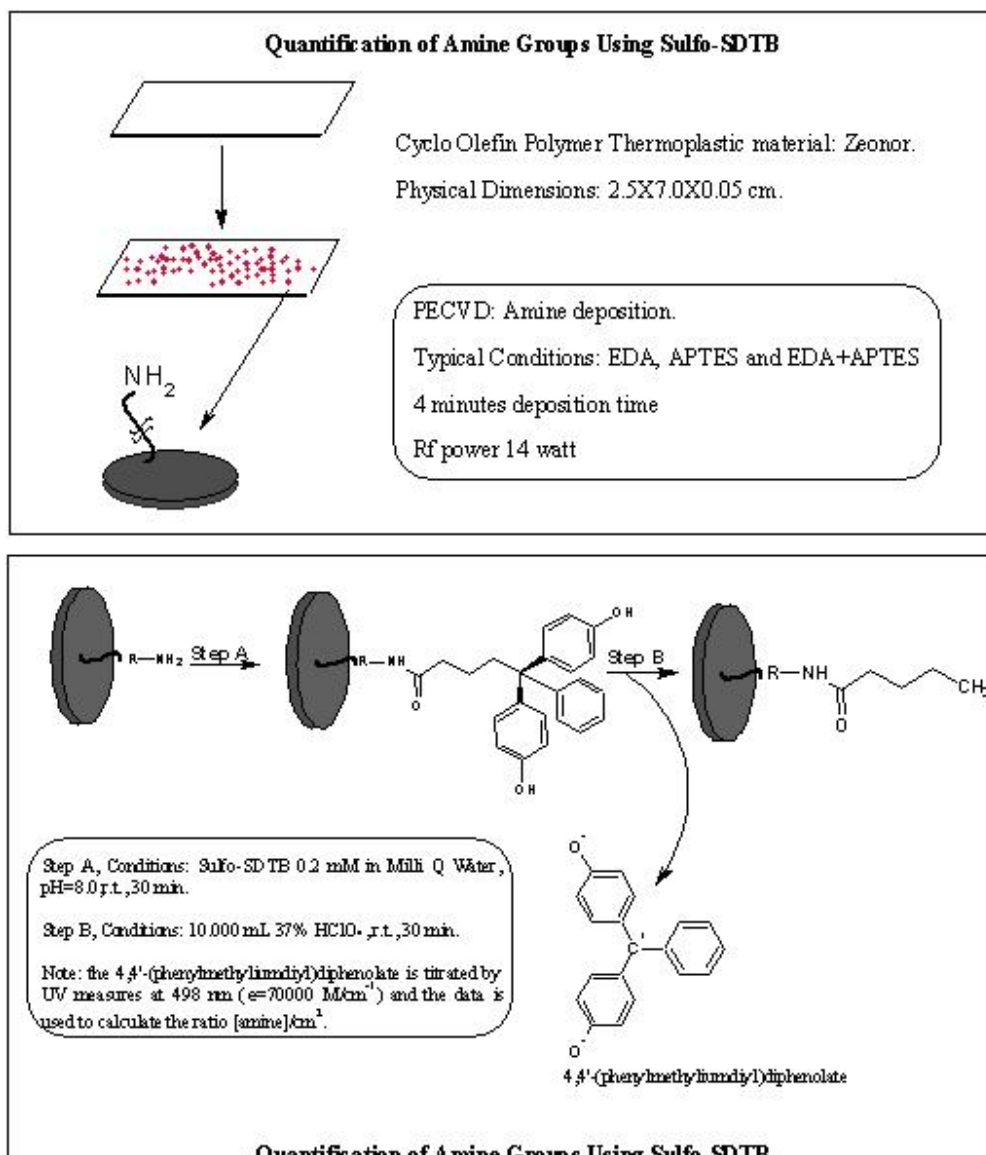


Figure S3. The schematic showing the sSDTB reaction mechanism used for quantification of amine functional groups

S2.3 Functionalised Nanoparticle synthesis

Preparation of silica NPs

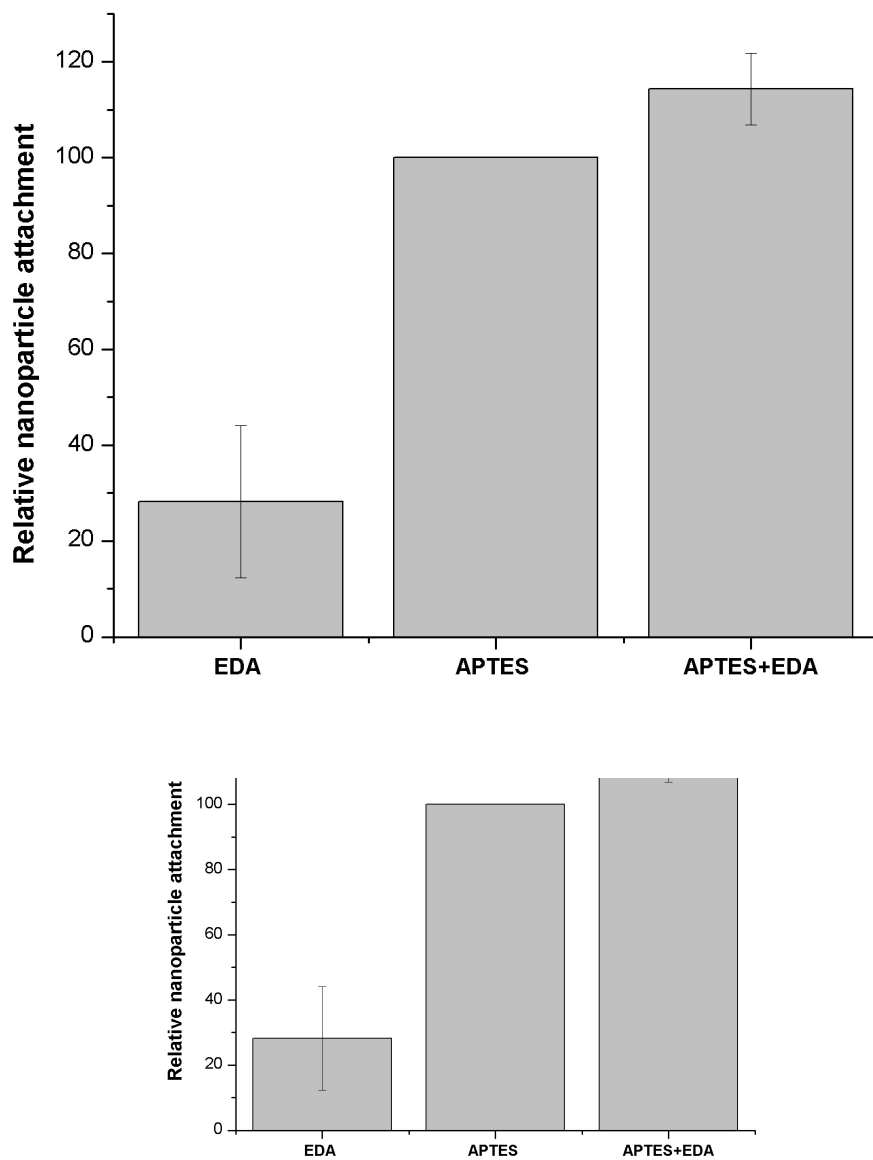


Figure S4. Relative nanoparticle attachment data on a set of triplicate of EDA, APTES and APTES+EDA coatings.

S2.4 Demonstration on microfluidic platform

Biosensor devices made of COP substrates (G1.0) were injection molded to form micropillar structure by Åmic AB (Sweden) and used as received. [Jönsson et al., Lab on a Chip 2008, 8, 1191–1197]. The height of the micropillars was 65–70 μm , top diameter was ca 50 μm , bottom diameter was ca 70 μm , the distance between the centres of the pillars in a row was 85 μm and the distance between the centres of the pillars in a column was 185 μm . The fluorescence intensity of the plasma modified microfluidic chips attached with NIR dye doped nanoparticles were then studied in a fluorescent scanner. The fluorescent intensity along the microfluidic channel is shown in Fig. S6.

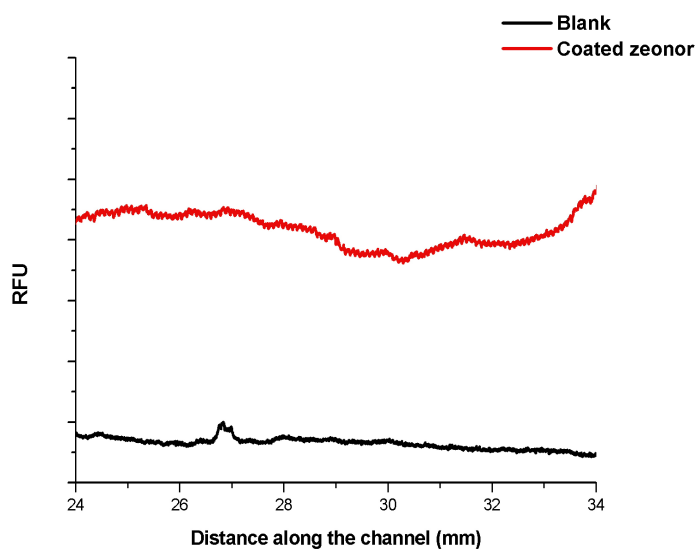


Figure S5. Fluorescence intensity of the dye doped nanoparticles attached to APTES+EDA coated microfluidic chip.