

Synthesis and Characterisation of Nanoparticles in a Microchip

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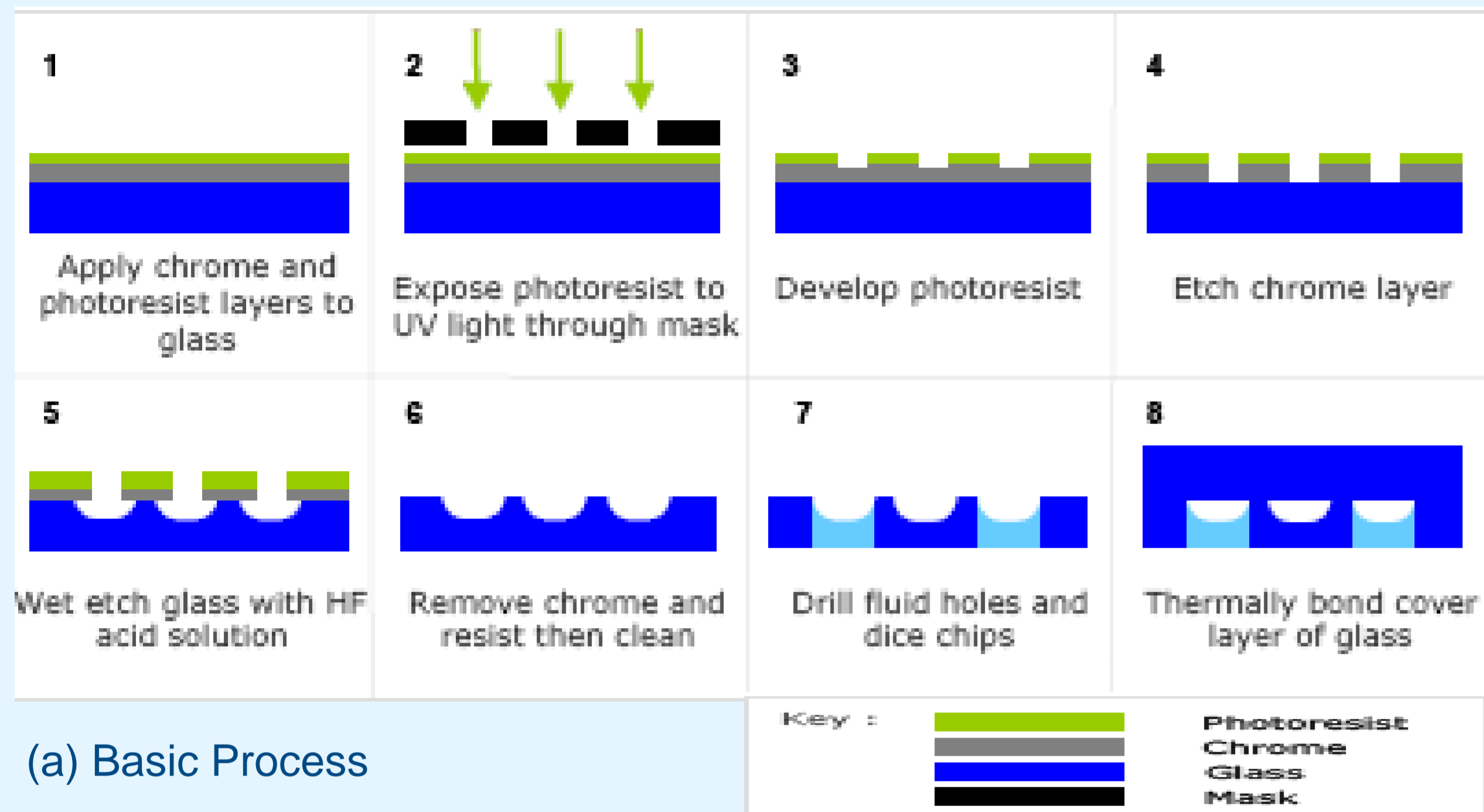
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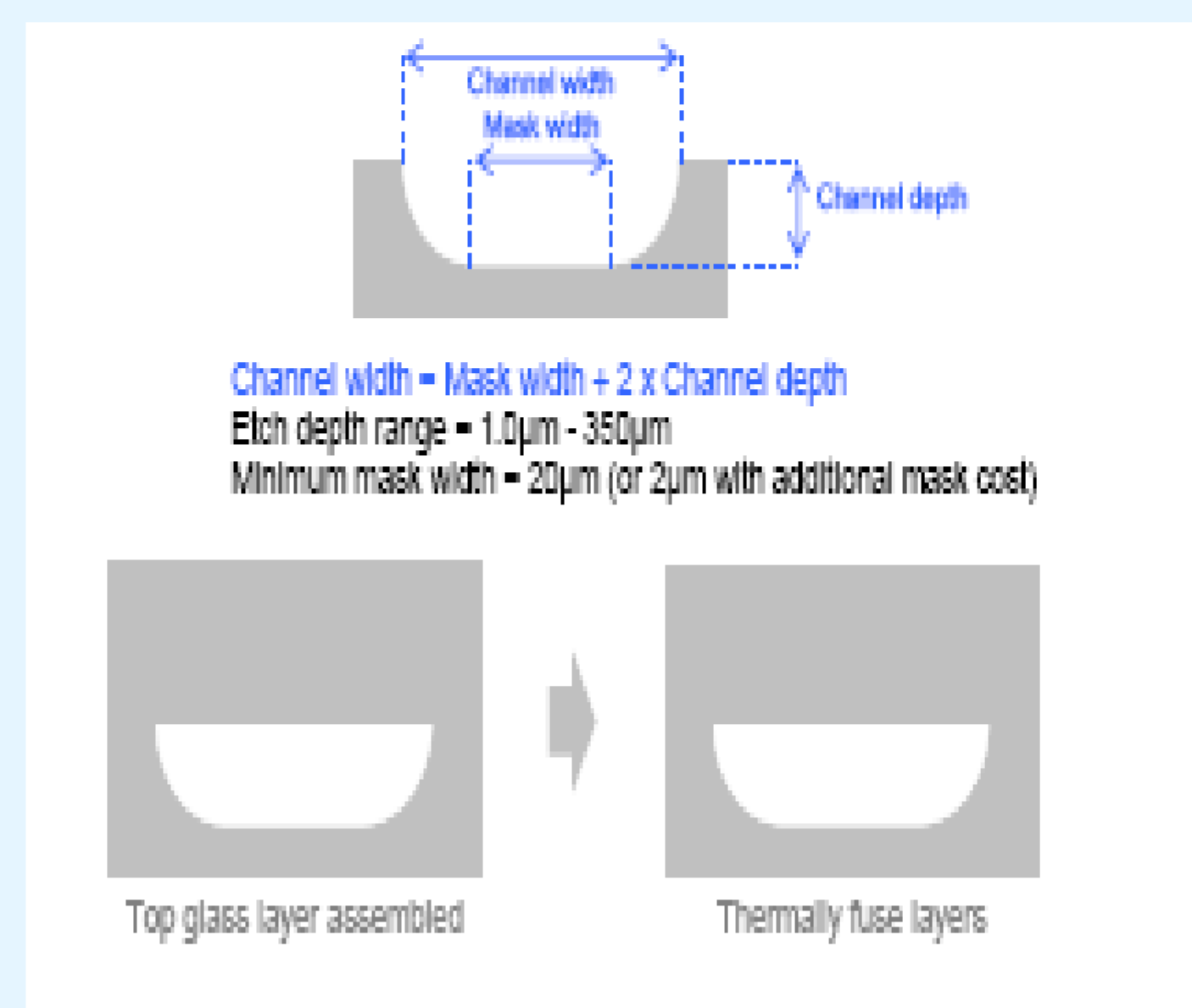
Overview

A combination of isotropic wet etching and thermal bonding processes were utilised to fabricate a customised glass microchip with multiple reaction chambers. A versatile chip holder was used to interface the microchip to automated micro-syringe pumps which ensured controlled delivery of reagents throughout the microfluidic network, eliminated any leaks and minimised the presence of air-bubbles. Channel surface functionalisation by gold nanoparticles (NP) was attempted by introduction of pre-prepared gold colloids and *in-situ* formation of gold NPs followed by adsorption on the channel wall. The size, and adhesion of gold nanoparticles to the glass surface was compared in the presence of different stabilizers.

Customised Glass Microchip Fabrication



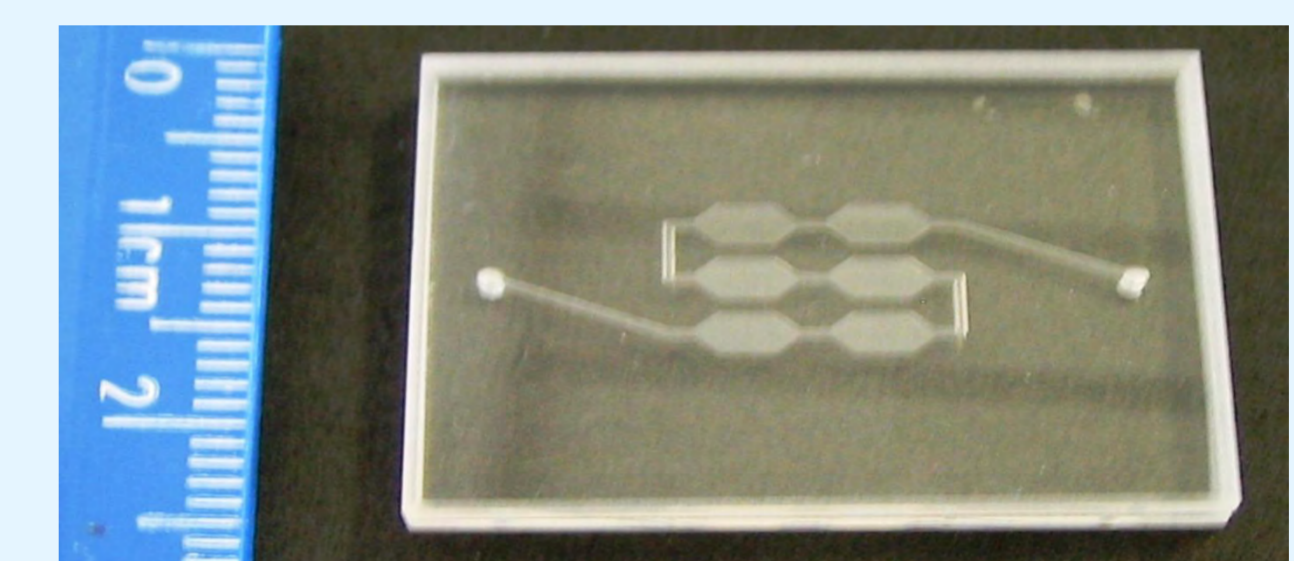
(a) Basic Process



(b) Isotropic wet etching: uniform cross section



(c) Micro-fluidic apparatus

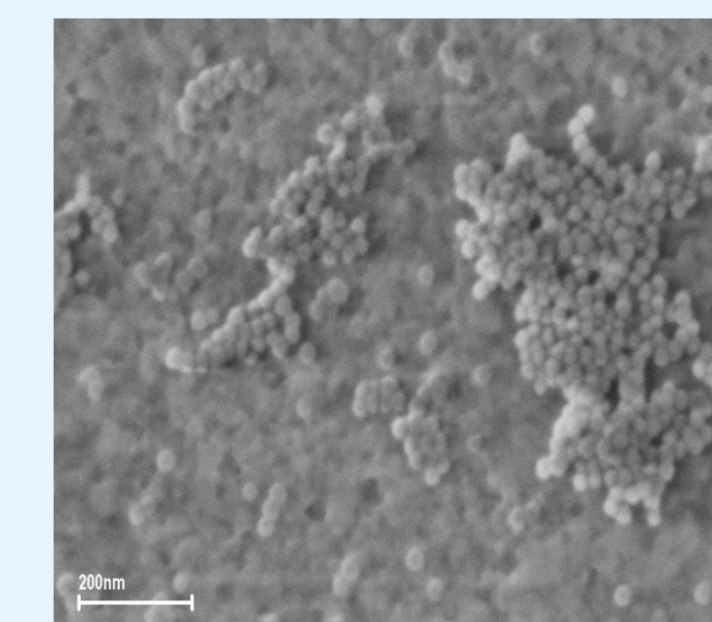


(d) Thermally bonded glass microchip

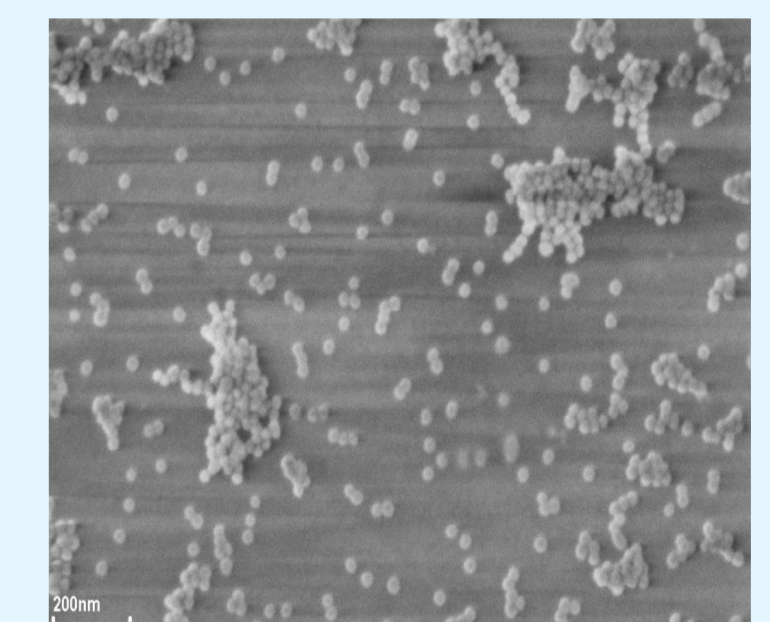
Nanoparticle Synthesis

(A) SAu-citrate, citrate stabilised: HAuCl_4 (0.25 mM) reduced with sodium-citrate (1.7 mM) in aqueous solution at 95°C under reflux for 1 h. Mean Au NP diameter: 18 nm.

Amino functionalization required for adsorption on glass Dense NP aggregation on rough surface of microchannel, more disperse on planar glass surface



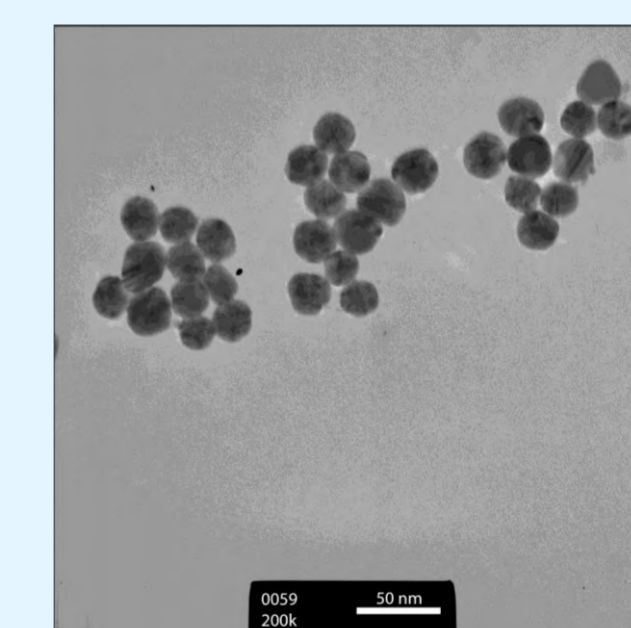
(e) SEM of citrate stabilized Au NP inside glass micro channel



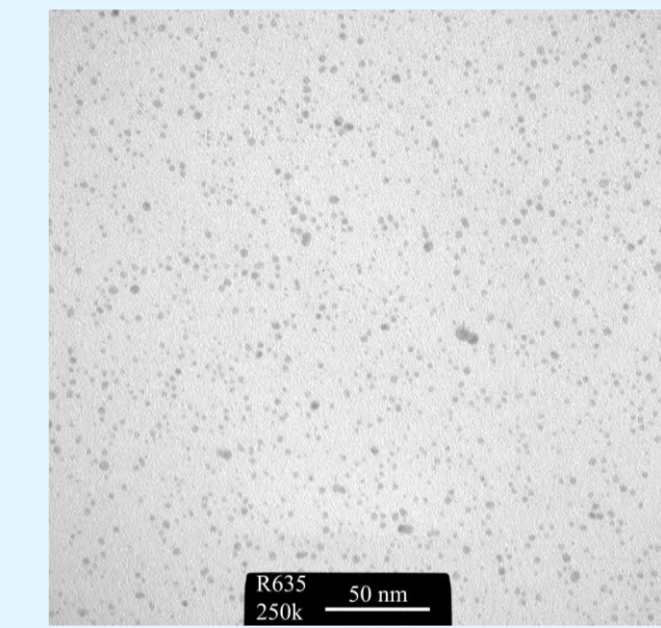
(f) SEM of citrate stabilized Au NP out-with glass microchannel

(B) SAu-PVA, PVA stabilised: HAuCl_4 (0.48 mM) reduced by NaBH_4 (2.42 mM) in aqueous solution in presence of polyvinyl alcohol (64 mg/l) at room temperature. Mean diameter Au NP is 2-3 nm.

PVA stabilised NP adsorbs well on APTS functionalised glass (Gf)



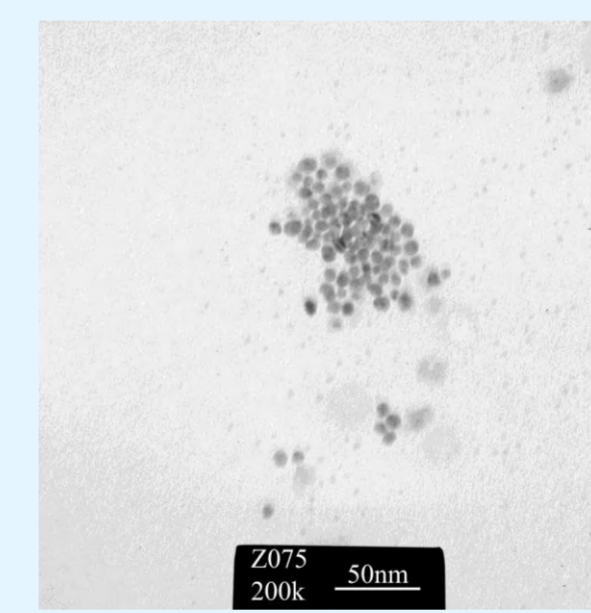
(g) TEM of citrate stabilized Au NP



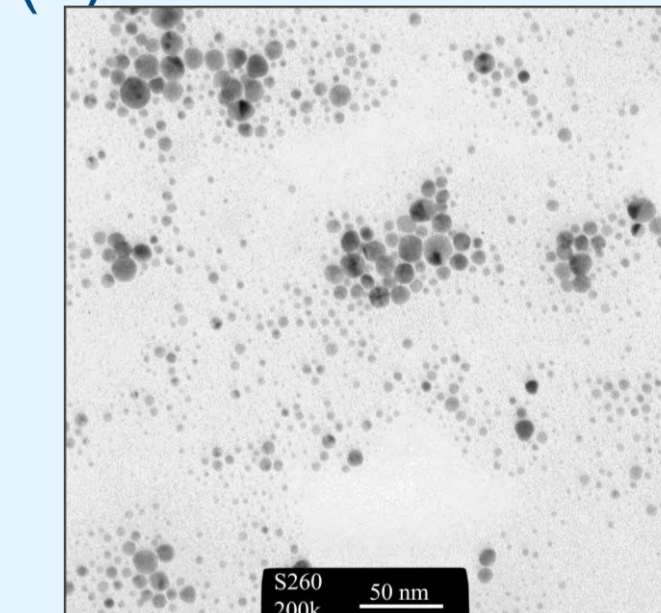
(h) TEM of PVA stabilized Au NP

(C) SAu-Triton, Triton X-100 stabilised: Aqueous 0.05 mM HAuCl_4 ; 0.8 mM Triton X-100 UV irradiated for 30 min at room temperature. Mean Au NP diameter 6-7 nm.

Triton stabilized NP adsorb poorly on amino functionalized surface and not on glass



(i) TEM of Triton stabilized Au NP

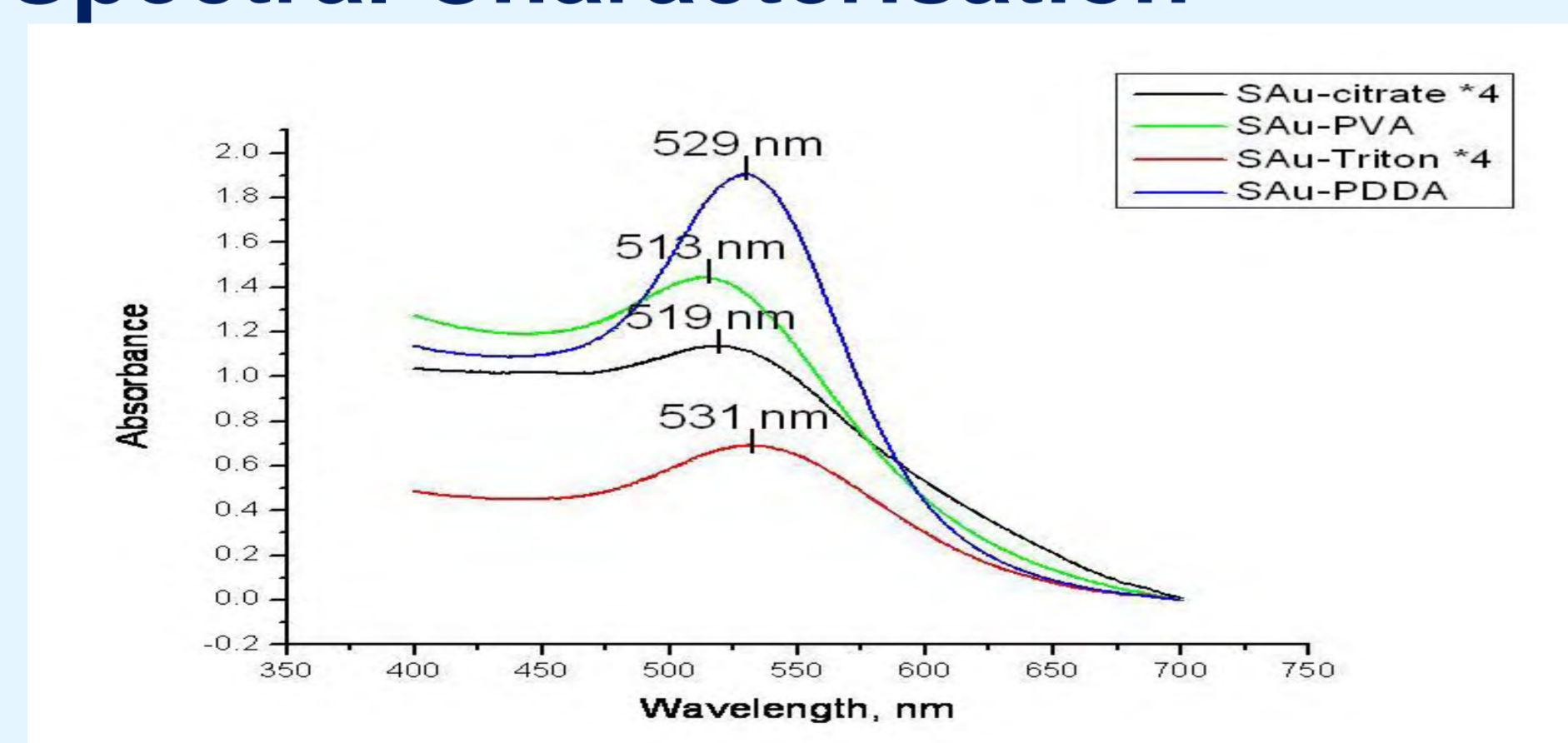


(j) TEM of PDDA stabilized Au NP

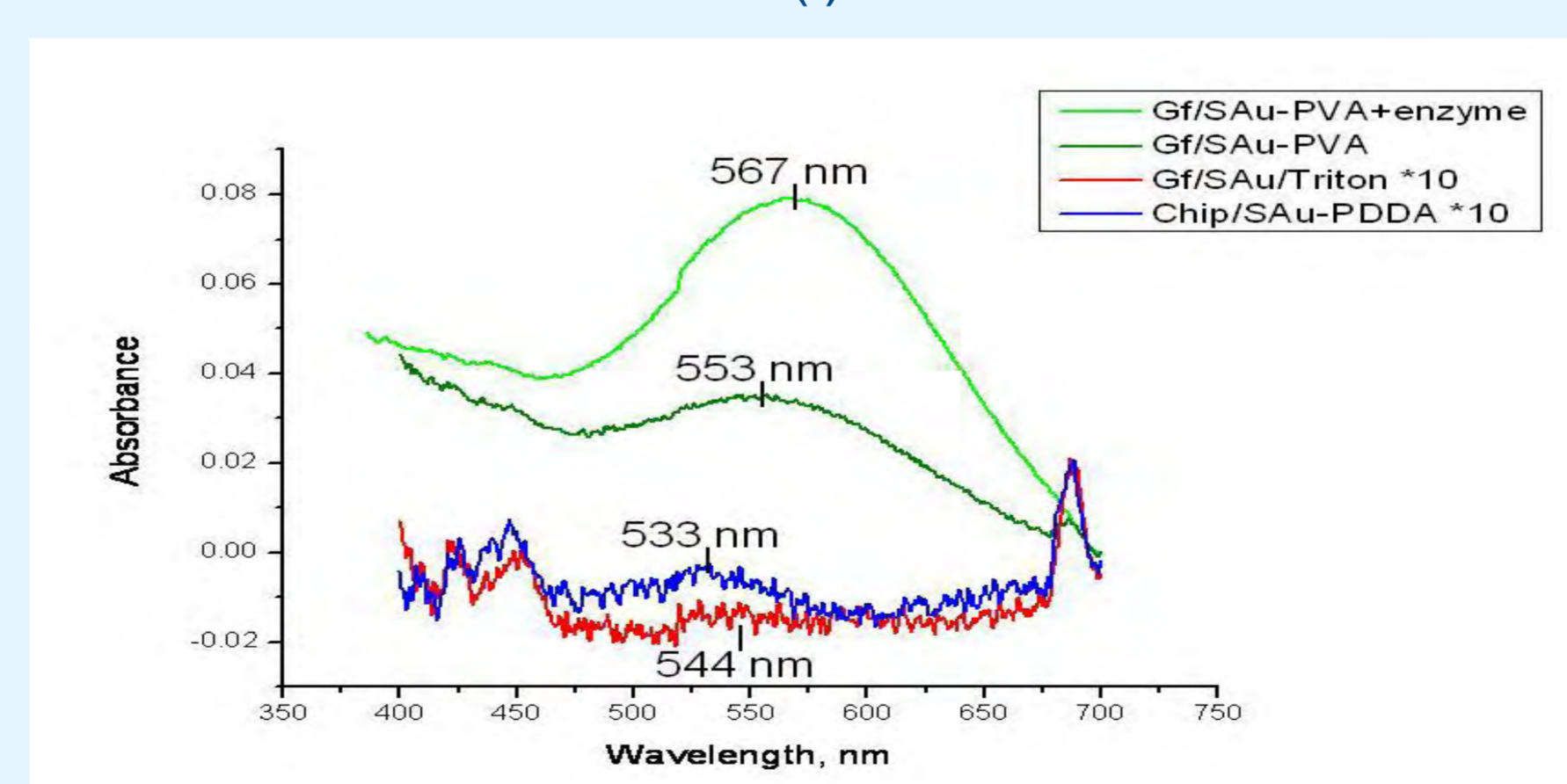
(D) SAu-PDDA, Polydiallyldimethyl ammoniumchloride (PDDA) stabilised: HAuCl_4 (0.46 mM) reduced by NaBH_4 (2.31 mM) in presence of PDDA (118 mg/l) at room temperature. Mean diameter of Au NP 2-3 nm.

Low intensity UV spectra of PDDA stabilised NP determined in sealed glass microchip

Spectral Characterisation



Different Au NP solutions show surface plasmon bands of gold at different wavelengths (*4 magnify spectra x 4 for better visibility)



The plasmon bands shift if Au adsorbed on the APTS functionalised glass and a further shift occurs when enzyme is attached (*10 magnify spectra x 10 for better visibility)

Spectra of functionalised glass and Gold PVA NP solutions (Gf/SAu PVA) have lower absorbance than similar solutions in the presence of enzyme

XPS Spectral Analysis

Samples	Atomic concentration (%) determined by XPS				
	Au	N	C	Si	O
G _u Unmodified Glass	-	-	11.8	25.9	62.3
G _f Functionalised Glass	-	9.3	57.3	8.8	24.6
G _f /SAu-citrate_ unsat.	1.04	1.3	24.1	21.7	51.9
G _f /SAu-citrate	0.05	-	25.5	21.9	51.6
G _f /SAu-citrate	2.5	2.9	47.8	15.2	31.6
G _f /SAu-PVA	2.9	1.1	25.9	20.5	49.6
G _f /SAu-Triton	0.6	1.4	21.6	22.2	54.2
G _f /SAu-Triton_ UV in situ	0.7	2.3	34.8	17.8	44.4

Au coverage (in line with Au conc.) highest for G_f/SAu-citrate and G_f/SAu-PVA.

Triton stabilized Au NPs do not adsorb well.

Au NPs are predominantly bonded to amino functions, N conc. decreases by Au deposition.

Future Application

Reproducible attachment of gold nanoparticles to free, clean microchip-surface will be advantageous to provide a matrix for immobilisation of enzymes and other biomolecules for future applications. This was confirmed by attachment of glucose oxidase to citrate stabilized gold nanoparticles. Enzyme activity studies also verify that enzyme can bind to gold or APTS functionalised glass, therefore the enzyme may be used as a label for future *in-situ* assay within the microchip.

Acknowledgements

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