Multilayer Thin film & Microcapsules of Single component via Covalent Bonded Layer-by-Layer Self- Assembly

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Materials:

Melamine formaldehyde (MF) (3.3-3.5 μm, 0.1N HCl soluble) particles were procured from Micro-particles GmbH, Berlin, Germany. Chitosan ($M_W \sim 120000$), Adenine and Glutaraldehyde were obtained from S. D. fine chemicals. All the chemicals were used as received.

Instruments:

The Uv-Visible spectra were recorded with Perkin-Elmer (Lambda 35) spectrometer. FTIR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer, spectrum 1000.

Quartz Crystal Microbalance (QCM):

Gold coated QCM an electrode has modified with MPA by immersing it in MPA-ethanol solution (1 mM) for 24 h. On this modified surface, we have built layer by layer assembly of **CH** & **ACHI**. We have also calculated thickness of each layer of this assembly using following equation;

$$d = -(2.18 \times 10^{-5}) \frac{\Delta F}{\rho}$$

Where d is polymer film thickness (in nm) and ρ is density of polymer film (in g m^{-3}).In literature density of polymer layers has been assumed as $(1.2 \pm 0.1)10^6$ g m^{-3} and using average frequency shift thickness can be measured using above equation.

Scanning Electron Microscopy (SEM):

SEM measurements were carried out at room temperature and at atmospheric pressure using Sirion Scanning electron microscope at 5 kV.

Confocal Laser Scanning Microscopy (CLSM):

CLSM images were collected with Zeiss Confocal microscope using 60 X objective. Samples are dispersed in Milipore water at room temperature the images were collected at 554 nm excitation wave length.

Transmission Electron Microscopy (TEM): Dilute solution of coated MF particles was drop casted on the carbon coated copper grid. The measurements were carried out with Technai F-30 and the instrument was operated at 100 kV.

Experimental Section:

Preparation of Thin film & Microcapsule: Single component multilayer thin film and microcapsules of **CH** and **ACHI** were prepared through glutaraldehyde mediated layer-by-layer covalent bonding as in shown scheme 1. The very first layer is governed by electrostatic interaction between acidified **CH** or **ACHI** and substrate. Then the rest of the assembly is guided by layer-by-layer covalent bonding through imines linkage within primary amine of polymer and aldehyde group of glutaraldehyde. The fresh & clean quartz plate are placed in acidified polymer (**CH / ACHI** (at pH ~ 5)) solution for overnight and incubated in glutaraldehyde solution for known time. These plates were removed from the solution washed gently with water and dried under nitrogen flow. Subsequently these plates were incubated separately in polymer (**CH** (pH of 5) / **ACHI** (pH of 8.5)) solution for further deposition and thus by repeating the process, we have fabricated multilayer thin film of chitosan and its derivative on planner substrate. A very similar experiment has been performed on MF colloidal particles and after deposition of five bilayer of ACHI, we have dissolved the colloidal template (MF particle) at 0.1N HCl to fabricate hollow microcapsule of **ACHI**.

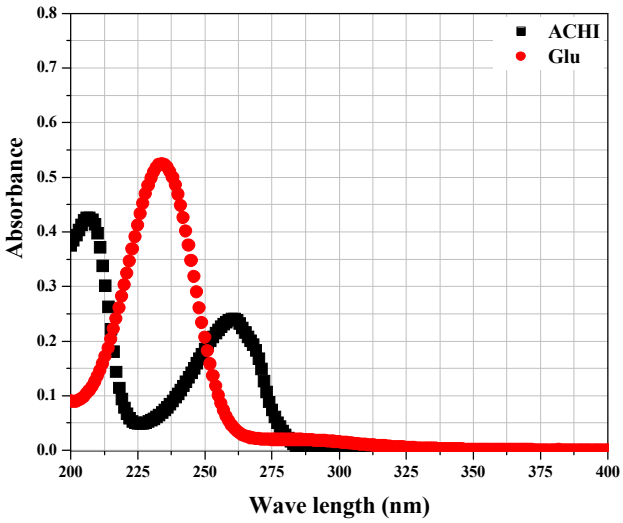

Figure S1: Uv-vis spectra of glutaraldehyde (red colour) & **ACHI** (black colour) in water.

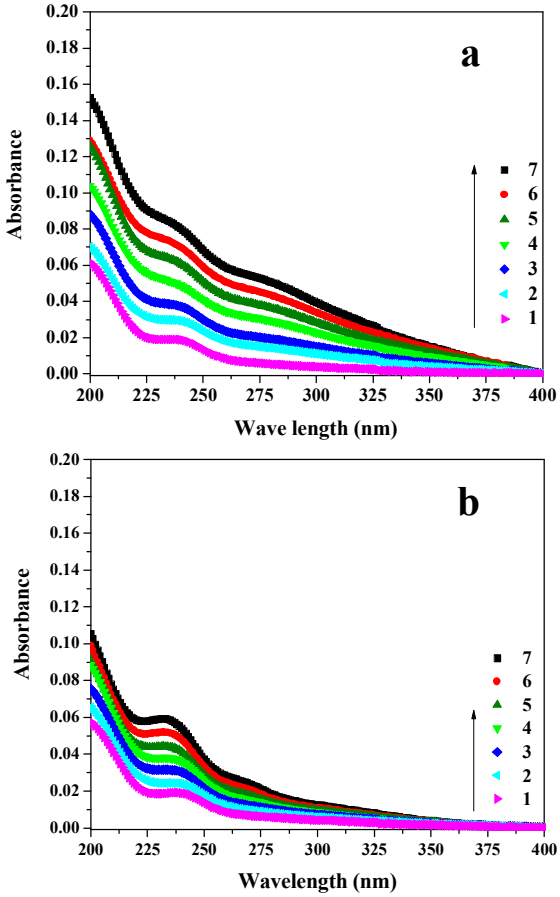

Figure S2: (a) & (b) are Uv-vis signature of glutaraldehyde for multilayer assembly of both ACHI and CH respectively.

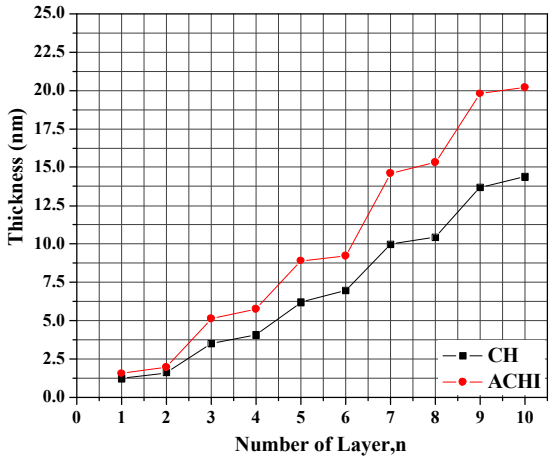

Figure S3: Layer-by-layer growth of both **ACHI** & **CH** multilayer thin film. Even layers (n=2, 4, 6, 8 & 10) are glutaraldehyde layer. Thickness has been measured from QCM study. Incubation time is 30 min for both the cases.

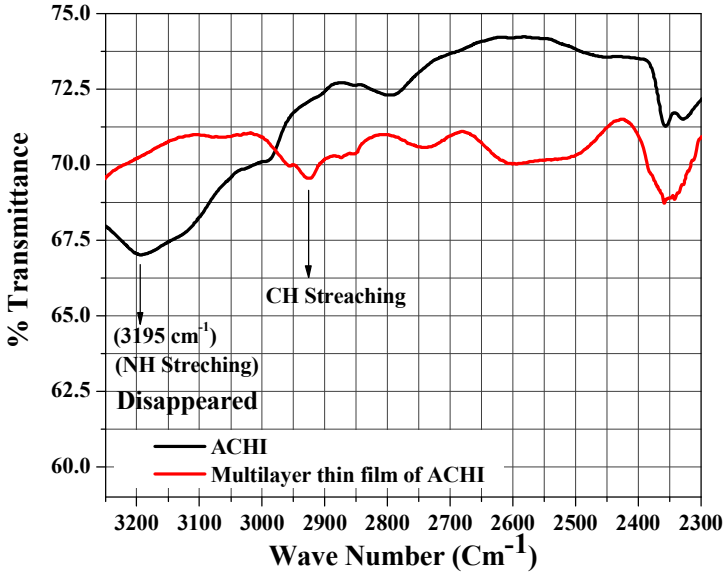

Figure S4: FTIR spectra of **ACHI** polymer alone and its multilayer film**.** N-H stretching of **ACHI** at 3195 cm^{-1} disappeared at multilayer assembly as NH_2 groups are involved in covalent bonding with glutaradehyde molecules and pronounced C-H stretching appeared (due to glutaraldehyde molecules) at 2926 cm^{-1}. This FTIR was collected in transmission mode.

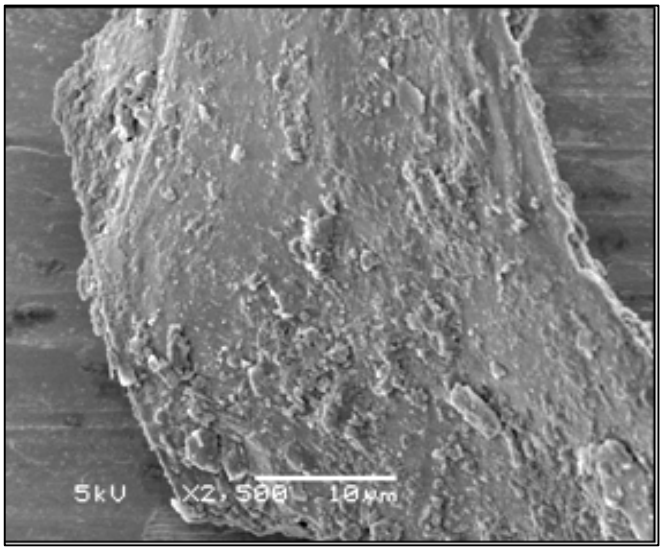

Figure S5: SEM image of scratched multilayer thin film of **ACHI**.

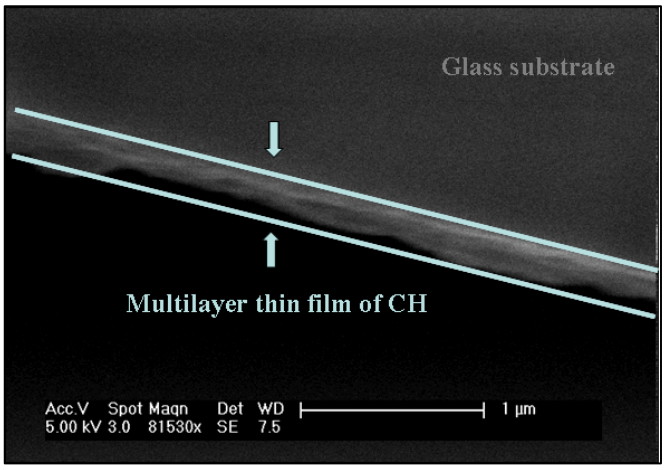

Figure S6: SEM image of cross section of multilayer (15 bilayer) thin film of **CH.**