Characterization of Chitosan during Its Electro-deposition on Gold Electrode by In-situ Electrochemical-FTIR (EC-FTIR)

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Different biological components are recently being studied to perform a particular function, that is, to facilitate fabrication in a widely range applications, at the micro- and nano-scales. Well-recognized information within the structure of biological materials enables them to self-assemble without the need of externally applied stimuli. In particular interest, chitosan with its unique structure of amine at C-2 position of glucosamine was recently exploited for bio-fabrication in food, medical, and textile applications. The charge state and properties of amine at C-2 position itself substantially depends on pH, as can be shown in the Fig. 1. At low pH (pH < 6), the primary amines are protonated and positively charged, giving polycationic behavior of water-soluble chitosan. However, when the pH approaches or exceeds its pK_a (≈ 6.3), chitosan's amines are deprotonated (less charged), insoluble and reactive, due to the formation of network junction that was created from the lowering of its electrostatic repulsion.

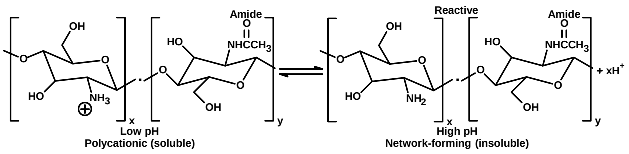

Fig. 1: The schematic illustration of chitosan's versatility for bio-fabrication.

With slightly modification from commonly a used electromical method, we report here that insoluble chitosan can be successfully deposited on the gold electrode surface in a response to locally applied constant current. The mechanism for electro-deposition of chitosan on gold electrode itself is shown in the Fig. 2. If a negative current is constantly applied, then a working electrode is treated as a cathode. This cathode is able to generate constantly electrons for consuming protons and further building a high localized pH on the cathode surface, thus, the deposition of insoluble chitosan can start occurs. Moreover, we are also able to monitor and characterize the chitosan during its electro-deposition of on gold electrode for the first time with the use of in-situ EC-FTIR technique due to its surface sensitivity.

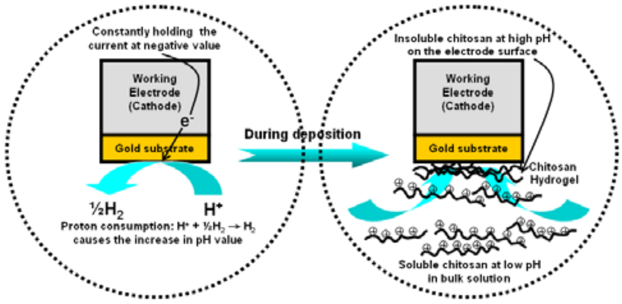

Fig. 2: The mechanism for the electro-deposition of chitosan on gold electrode in response to applied current.

As can be seen in the Fig. 3, the feature of amide and —NH_2 out plane bending are easily observed in the region 1640 - 1560 cm^{-1} and 900 - 650 cm^{-1}, respectively. Assigned feature of —C—O—C— vibration appears at 1150 - 1070 cm^{-1}. The —OH group apperars at wavenumber of 3500 - 3700 cm^{-1}. The dissolved CO_2 form can be confirmed from its constant features during the depostion. The combination of these observed features confirms the formation of insoluble chitosan from the locally higher pH on the gold electrode surface. Interestingly, the feature at 3000 cm^{-1} assigned to primary amine (—NH_3^+) of soluble chitosan is also observed. These findings indicate the formation of two main layers on gold surface take places, the insoluble chitosan layer and followed by the soluble chitosan layer, as predicted from the pH gradient in the Fig. 2. Moreover, this bilayer chitosan with its hydrophilic behavior is substantially novel result and can be widely used in many incorporated bio-material applications.

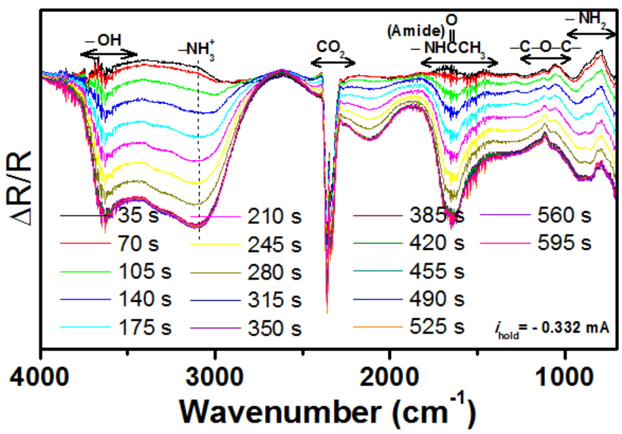

Fig. 3: The in-situ EC-FTIR spectrum of chitosan during its electro-deposition on gold electrode. The resolution and scan speed are 4 cm^{-1} and 35 sec./scan, respectively