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## ARTICLE

# Turning the chitosan surface from hydrophilic to hydrophobic by layer-by-layer electro-assembly

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By employing an electrostatic generator to enhance or reduce the van der Waals force in a novel layer-by-layer electro-assembly process, this work proven that the chitosan surface can be prepared with turnable wettability, e.g. from the hydrophilic to hydrophobic.

## Introduction

Chitosan, CS, is a natural polymer derived by deacetylation of chitin, and the second most abundant biopolymer in nature after cellulose.<sup>1</sup> Compared with other polysaccharides, CS has several important advantages, including biocompatibility, biodegradability, and nontoxicity.<sup>1</sup> CS is also a natural polyelectrolyte with positive charges and is hydrophilic due to the  $\beta(1\rightarrow4)$  linked D-glucosamine structure.<sup>1</sup>

CS has excellent film-forming property but the hydrophilic property<sup>2-6</sup> limiting its some applications, e.g. food packing.<sup>4</sup> Therefore, some attempts have been made to turn the CS surface from hydrophilic to hydrophobic, e.g. by chemical modification surface. For example, the hydrophobic CS film was prepared by reaction with perfluorinated acid derivatives,<sup>5</sup> or perfluorinated chemicals.<sup>6</sup> As has been known, yet the reported CS surface modifications all using chemical methods.<sup>2-6</sup>

Multilayer nanofilms fabricated by the layer-by-layer self-assembly, LBLSA, method<sup>7,8</sup> can present opposite polyelectrolytes on surface to fit a lot of applications. In the LBLSA process, the van der Waals attraction force, vdW, is the main driving force,<sup>7,8</sup> and using the LBLSA method we have prepared CS/lignosulfonate, LGS, multilayer nanofilms recently.<sup>9</sup>

In this work we reported a case for turning the hydrophilic CS surface to hydrophobic by using a novel layer-by-layer electro-assembly, LBLEA, method. During this process, we employed an electrostatic generator to perform the layer-by-layer electro-assembly in two processes. The one is defined as the van der Waals force, vdW, enhance because the anode electrode linked to the substrate initially coated by the negative LGS solution and the cathode electrode immersed in the positive CS solution, and the another is defined as the vdW reduction because the cathode electrode linked to the LGS-coated substrate and the anode electrode linked to the positive CS solution. To compare with literature reported cases on the use of the LBLEA method,<sup>10-14</sup> this case applied a higher voltage, e.g. 4kV, is greatly than that of all reported cases.

## Experimental

### Materials

A commercial CS powder in microsize obtained from Weifang Kehai Chitosan Co., Ltd, China was used as received as previously.<sup>9</sup> The molecular weight and deacetylation degree of this CS known from the producer are at about  $3\times 10^5$  g/mol and 95%, respectively. The used Ca-LGS is a commercial powder in microsize obtained from Jiangmen Sugar Cane Chemical Factory, Guangdong of China as received as previously.<sup>15</sup> Based on the producer, this LGS has the lignin component  $\geq 55\%$ , deoxidized sugars  $\leq 12\%$ , water insoluble components  $\leq 1.5\%$ , moisture  $\leq 9\%$  and pH of about 5.

A concentrated HAc, a commercial  $H_2SO_4$  and a 30%  $H_2O_2$  as well as other chemicals in analytical grade were purchased from a local chemical store at Shanghai and used as received.<sup>9</sup> A lab-made distilled water was always used in this case.<sup>9</sup>

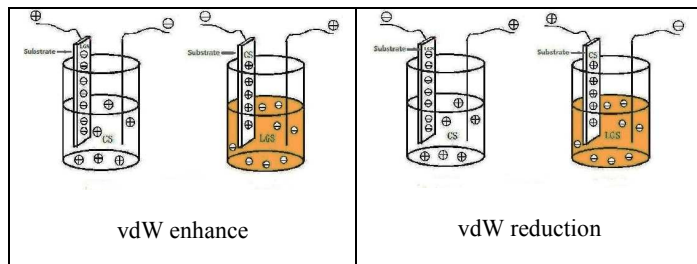
### Layer-by-layer electro-assembly

As the same previously, the CS and LGS solutions were initially prepared by dissolving the CS powder in acetic acid and the LGS powder in water, respectively. On these two solutions, the concentration and pH were kept the same at 2 mg/mL and 4.1, respectively.<sup>9</sup>

A single crystal silicon plate (Zhejiang Crystal-Optech Co. Ltd. China) was used as the substrate. According to the producer, this plate has a smooth surface with a thickness of  $490\pm 10\mu m$ , electric resistance between 10-25  $\Omega$  cm. Before assembly, this plate was cleaned by sonicating 1h in a piranha solution formed by mixing  $H_2SO_4(98\%)$  with  $H_2O_2(30\%)$  at a ratio of 7/3, then immersed in a  $H_2O/H_2O_2/NH_4OH$  (5/1/1%) solution for another 1 h. After these steps, this substrate was dried by hot air as the same as previously.<sup>9</sup>

The vdW controlled LBLEA process was performed as Figure 1 described by employing an electrostatic generator to provide high voltage to form an electro-assembly process. During the electro-assembly process, the substrate was initially treated by immersing it in one solution (CS or LGS) at a concentration of 2 mg/mL and pH 4.1 for 10 min, at 25°C, to build up the first layer then air dried for

reacting with other opposite charged layer under an air stream flow condition.



**Figure 1.** Schematic representation on the layer-by-layer electro-assembly of (CS/LGS)<sub>n</sub> multilayer nanofilms when the van der Waals force in enhance or reduction, respectively.

### Characterization

The surface morphology and section-cross of formed multilayer nanofilms were analyzed by field emission scanning electron microscope, FESEM, (S-4800, HITACHI Co., Ltd.).

The surface topography and roughness of the formed multilayer nanofilms were analyzed by a NanoScope IV (Veeco Co., Ltd) AFM with a tapping mode.

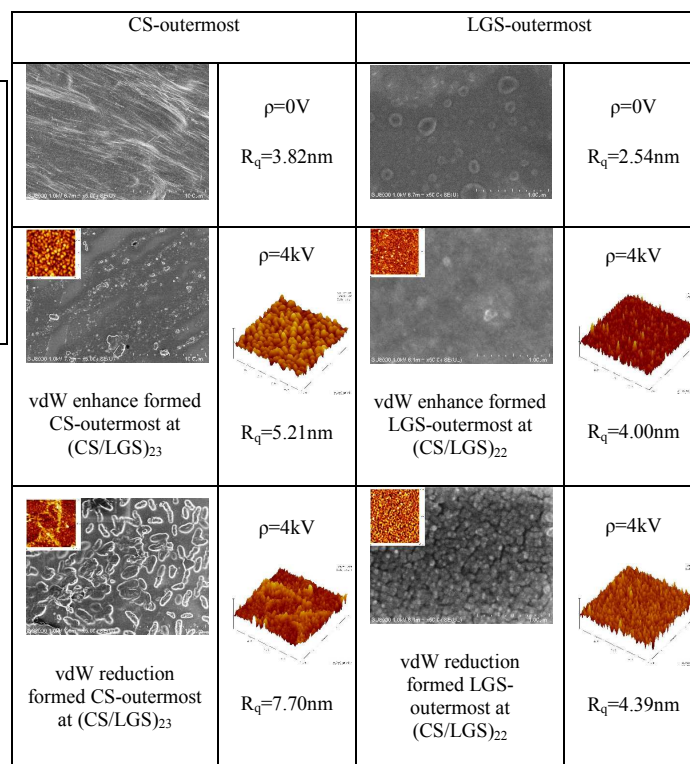
The FTIR spectra were recorded using a NEXUS-670 (Nicolet Co., Ltd) spectrometer in transmission mode by aligning the film on a silicon wafer substrate (1-2 cm<sup>2</sup>) at a Brewster's angle of 75° with respect to the incident beam.

The wetting was performed by means of the sessile drop contact angle measurement using the OCA40 Micro (Dataphysics Co., Ltd). During the measurement, the droplet volume was controlled constantly at about 1 μl for each drop and the temperature was controlled in constant, 25 °C.

### Results and discussion

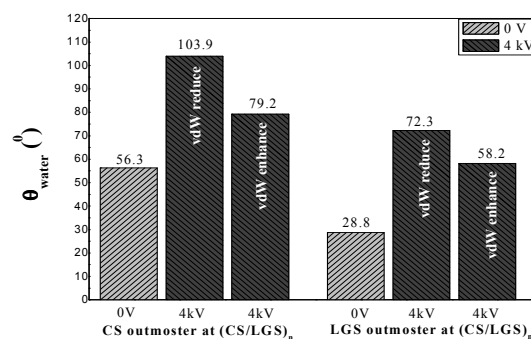
The morphology and surface roughness of those formed (CS/LGS)<sub>n</sub> multilayer nanofilms were showed in **Figure 2**. Of which, the CS-outermost was presented at the **left column** and the LGS-outermost was presented at the **right column**, respectively. In terms of the FESEM images, the normal CS surface has river-like morphology (**Figure 2 top**) and it was changed to rough surface due to formed round particles (**Figure 2 middle**) or rice-like particles (**Figure 2 bottom**) corresponding to the electro-assembly process-induced vdW enhance or reduce, respectively. Similarly, the LGS surface showed different morphologies because its natural surface has few round particles (**Figure 2 top**) and those were increased with the vdW enhance (**Figure 2 middle**) or reduction (**Figure 2 bottom**), respectively. According to the AFM images, the surface roughness was quantitatively known for both CS and LGS surface and the former is obviously roughly than that of the latter, especially after the vdW reduce-based LBLEA process (**Figure 2 bottom**).

Since the surface structure of these (CS/LGS)<sub>n</sub> multilayer nanofilms was formed by aggregation of both the CS and LGS molecules,<sup>9</sup> **Figure 2** showed surface behaviours indicated that the LBLEA method has advantages in control the vdW enhance or reduce to influence the opposite charged polyelectrolyte aggregation in positive or negative surface. In fact, to compare with literature reported low voltage-based assembly processes<sup>16</sup> can lead a conclusion that the use of a higher voltage-based LBLEA process can greatly change the surface morphology for films.



**Figure 2.** FESEM and AFM images of the film outermost on CS- (left column) or LGS- (right column) for (CS/LGS)<sub>n</sub> multilayer nanofilms in relation to the wetting results and the van der Waals attraction force enhance or reduction, respectively.

Wetting results showed that the water contact angle,  $\theta_w$ , on the pure CS and LGS surface was at 56.3° and 28.8° (**Figure 3**), respectively, both in hydrophilic and especially the LGS. **Figure 3** indicated that the LBLEA process indeed increased the  $\theta_w$  for both CS and LGS surface, especially the vdW reduce, because this turned the CS surface from hydrophilic to hydrophobic. These wetting results are interested and well agreed with literature.<sup>17-19</sup>



**Figure 3.** Wettability of CS and LGS surface formed by LBLEA method at 0V or 4kV in relation to the van der Waals attraction force enhance or reduce, respectively.

The thickness of those (CS/LGS)<sub>n</sub> multilayer films was estimated according to the FESEM images of the cross-section of (CS/LGS)<sub>42</sub> in relation to both the vdW enhance or reduce as showed in Figure 4. Observe that the average layer thickness was at 8.10 or 11.90nm corresponding to the vdW enhance or reduce, respectively, and greater than that of the electricity-free samples.<sup>9</sup> Nevertheless, these differences significantly indicated that the structure of opposite charges-based nanofilm would be loosely by the LBLEA method than that of the LBLSA method formed structure.

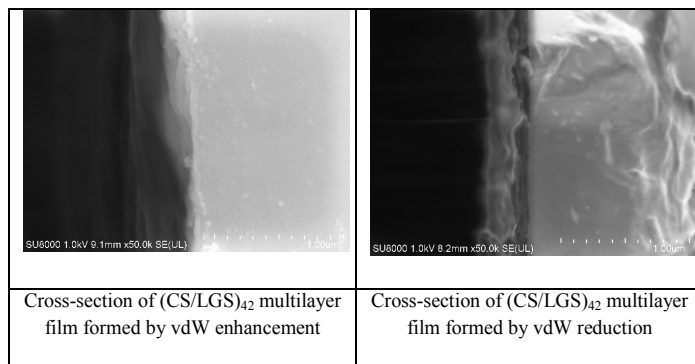


Figure 4. FESEM images of the cross-section of the (CS/LGS)<sub>42</sub> multilayer nanofilms formed by van der Waals attraction force enhancement (left) or reduction (right), respectively.

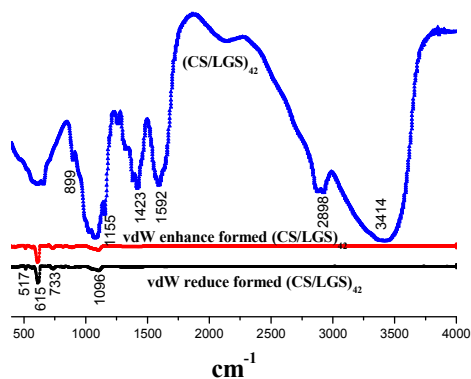


Figure 5. FTIR spectra of (CS/LGS)<sub>42</sub> multilayer nanofilms formed by LBLSA and LBLEA methods in relation to the van der Waals attraction force enhancement or reduction, respectively.

The FTIR spectra of (CS/LGS)<sub>n</sub> multilayer films formed by both LBLSA and LBLEA were presented in Figure 5. Observe that the electricity-free (CS/LGS)<sub>n</sub> multilayer nanofilm presented visible CS and LGS peaks at 3414 cm<sup>-1</sup> due to the O-H or N-H vibration of CS, at 2898 cm<sup>-1</sup> due to the C-H stretching of CS, at 1592 cm<sup>-1</sup> due to the carbonyl asymmetric stretching vibration of CS<sup>3</sup> and the C=C stretching of phenyl in LGS,<sup>15</sup> at 1423 cm<sup>-1</sup> corresponding to the amide II of CS and the antisymmetric stretching of the methyl and methylene of LGS,<sup>15</sup> at 1155 cm<sup>-1</sup> due to the C-O vibration of CS,<sup>3</sup> and S=O stretching of LGS.<sup>15</sup> The electricity-free (CS/LGS)<sub>n</sub> multilayer nanofilm also showed a new peak at 899 cm<sup>-1</sup> assigned to the ring stretching considerable due to the interpenetration of CS and LGS molecules.<sup>9</sup> To compare this electricity-free sample, two LBLEA-based (CS/LGS)<sub>n</sub> multilayer nanofilms showed obviously differences because some intense peaks disappeared indicating the

electro-assembly induced interactions between CS and LGS leading some structure changed on formed films, e.g. the peaks located at 3414, 2898, 1592, 1423, 1155 and 899 cm<sup>-1</sup> removed in two electro-assembled samples (Figure 5). It is also found that these two electro-assembled samples both showed a new peak at about 733 cm<sup>-1</sup>, to suggest that the applied voltage would change the film structure.

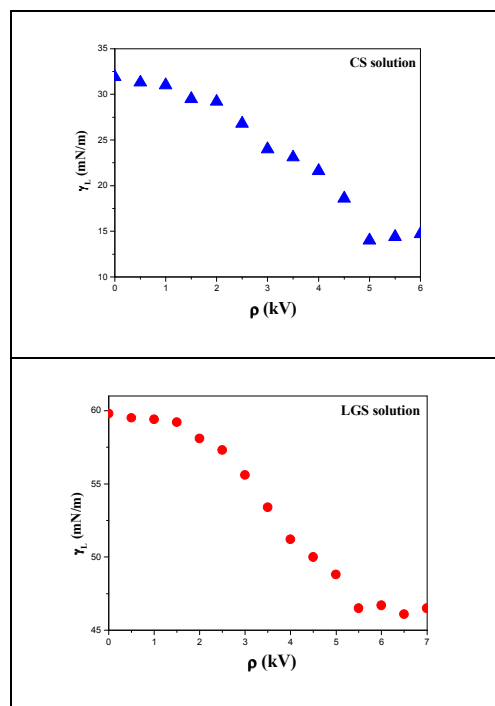


Figure 6. Effect of applied voltages on the surface tension of CS and LGS solution, respectively.

Since the difference between the LBLSA and LBLEA is obviously in the use or not use the electricity, to investigate the effect of applied electric voltage on the surface tension of both CS and LGS solution is required and necessary. Figure 6 showed that the surface tension of either the CS or the LGS solution both was reduced with the voltage increase, and each presented a critical surface tension, e.g. the former at about 15 and the latter at about 46 mN/m each corresponding to a critical voltage at about 5 and 5.5 kV, respectively. This surface tension behaviour importantly implied that the structure and properties of the LBLEA formed film is mainly caused by the low surface tension solution. Moreover, the electro-assembly provided two vdW control possibilities, e.g. in enhancement or reduction (Figure 1), for forming these films than that of the normal LBLSA.

In terms of Figure 6, the surface tension of CS solution was lower than that of the LGS solution due to the latter formed by water. This behaviour is important because this indeed influenced the LBLEA process and formed films.

On the basis of above discussions, a related mechanism on forming the turnable CS surface is primarily known as that the presence of an extra electric field would reduce the surface tension of polymer solution to influence the film formation and related structure. During this electro-assembly process, the vdW enhancement or reduction would cause the film surface roughness increase, especially the latter.

## Conclusions

In summary, this work proven that the CS surface can be formed in hydrophobic by using the vdW controlled LBLEA method. The reason on such method can form hydrophobic CS surface is found due to the presence of an electric field induced reduction of the surface tension of those solutions, the film surface roughness increase and the structure changes.

## Notes and references

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