Supplementary Information

Bio-inspired catechol chemistry: A new way to develop re-modulable and injectable coacervate hydrogel

Yeon Jeong Oh[a], Il Hwan Cho[b], Haeshin Lee[c], Ki-Jung Park[d], Hyukjin Lee[e]* and Sung Young Park[a]*

[a] *Department of Chemical & Biological Engineering Korea National University of Transportation Chungju-Si 380-702, Republic of Korea E-mail: parkchem@ut.ac.kr Fax:+82-(0)43-841-5220; Tel:+82-(0)43-841-5225*

[b] *Central Research Institute Shinpoong Pharm. Co., Ltd. Ansan-Si 434-4, Republic of Korea*

[c] *Department of Chemistry, KAIST, Daejeon 305–70, Republic of Korea*

[d] *Korea Food & Drug Administration Cheongwon-gun 363-700, Republic of Korea*

[e] *College of Pharmacy, Ewha Womans University, Seoul 120-750, Republic of Korea, E-mail: hyukjin@ewha.ac.kr Fax:+82-(0)2-3277-3007; Tel:+82-(0)2-3277-3026*

Table of content

Experimental Section

Materials: Hyaluronic acid (MW 230 kDa) was purchased from LifeCore (Chaska, USA). Dopamine hydrochloride (DN), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), chitosan (MW 5kDa), sodium cyanoborohydride ($NaBH_3CN$), lactose, acetic acid, methanol were purchased from Sigma-Aldrich (Minnesota, USA). N-hydroxysuccinimide (NHS) was purchased from Merck (Germany).

Synthesis of HA-DN and Chitlac: Dopamine conjugated HA (HA) was synthesized according to previous report with slight modification.[1-3] Degrees of substitution (DS) were determined using ^{1}H-NMR spectroscopy (Bruker AVANCE 400). The degree of dopamine substitution for HA-DN was 1.65%, and the synthesis of Chitlac (lactose modified chitosan) was performed according to a procedure reported elsewhere.[4-6]

Complex Coacervate Hydrogels: The complex coacervate formation of binary polymer procedure (3 wt%, chitlac/HA-DN weight ratio of 4:6) was followed by different buffer conditions (Method A: chitlac/HA at pH 8.5, Method B: chitlac/HA-DN at pH 4, Method C: Chitlac/HA-DN at pH 8.5 and pH 7.4, respectively, Method D: chitlac/HA-DN at pH 10, and Method E: chitlac/HA-DN at pH 8.5). The solutions were incubated at 25^{o}C for 12h

Rheological Studies: Rheological properties of various hydrogels were monitored using a rotating rheometer (TA Instruments, AR 1500ex) equipped with a temperature controller. The contribution of a solid-like behavior (storage modulus (G´)) and a liquid-like behavior (loss modulus (G´´)) were recorded with changing temperature using a parallel plate (20 mm). Frequency was optimized to 0.1 Hz as determined using a frequency sweep at 25^{o}C.

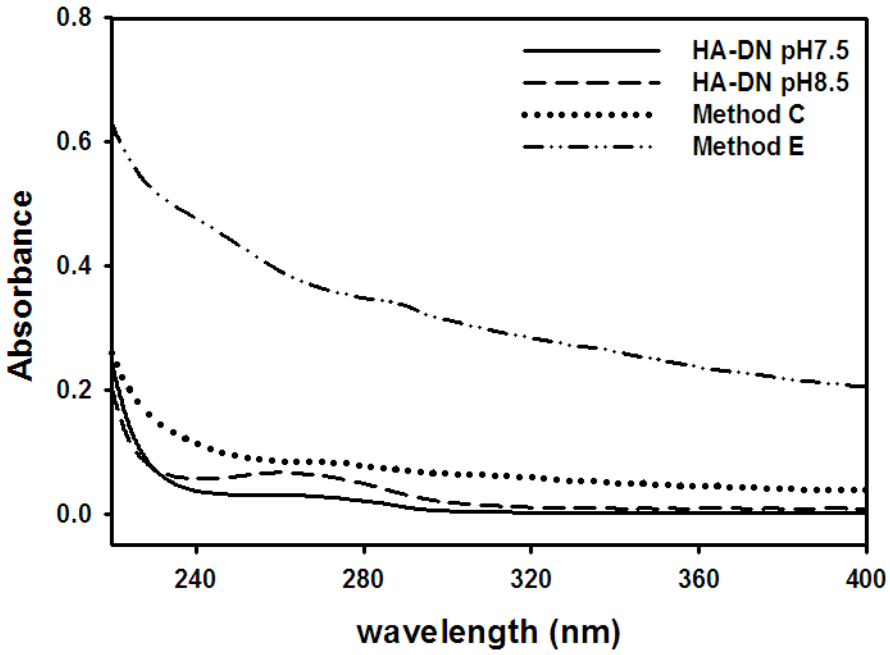

Fig. S1. UV-vis absorbance spectra of HA-DN at pH 7.5 and at pH 8.5, complex coacervate formation following method C and method E. (in all methods, concentration was 0.1 wt% at 25^0C).

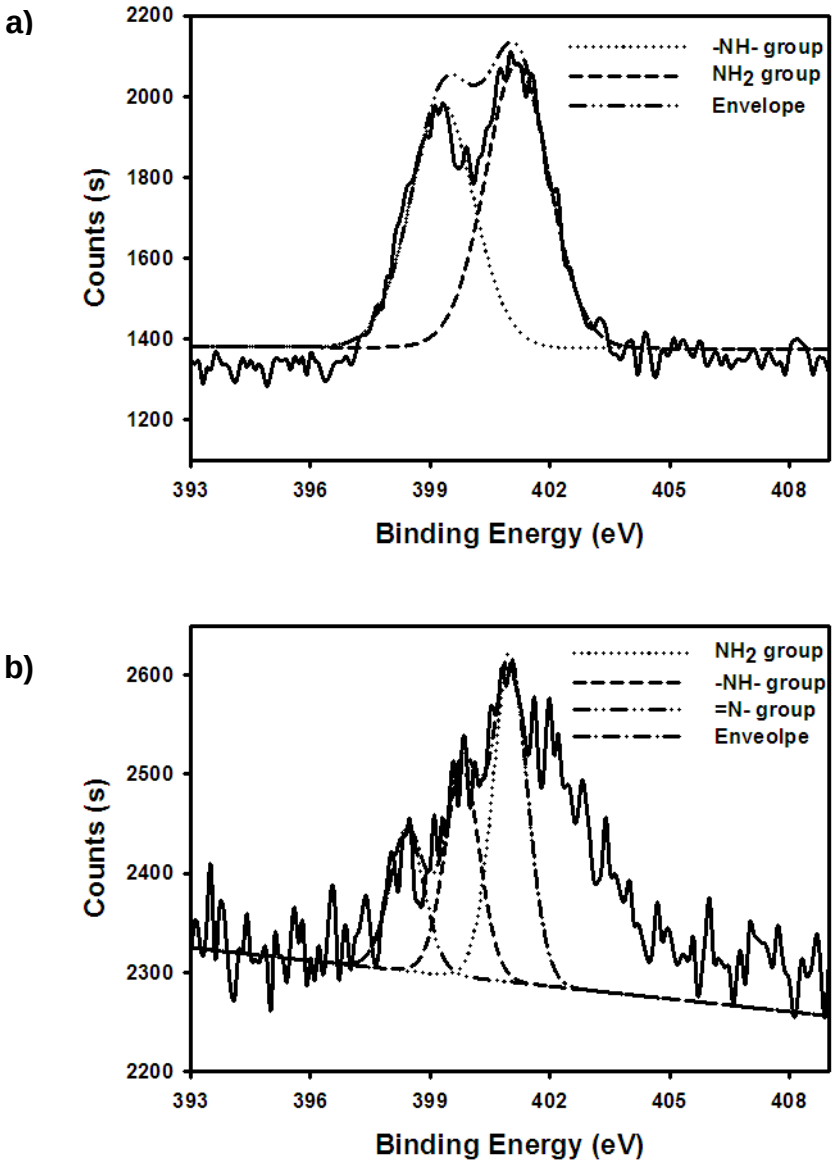

Fig. S2. Elemental analysis by XPS measurement of coacervate hydrogels: a) Chitlac/HA-DN coacervate hydrogels by Method C, b) non-coacervate mixture of Chitlac/HA-DN by Method E.

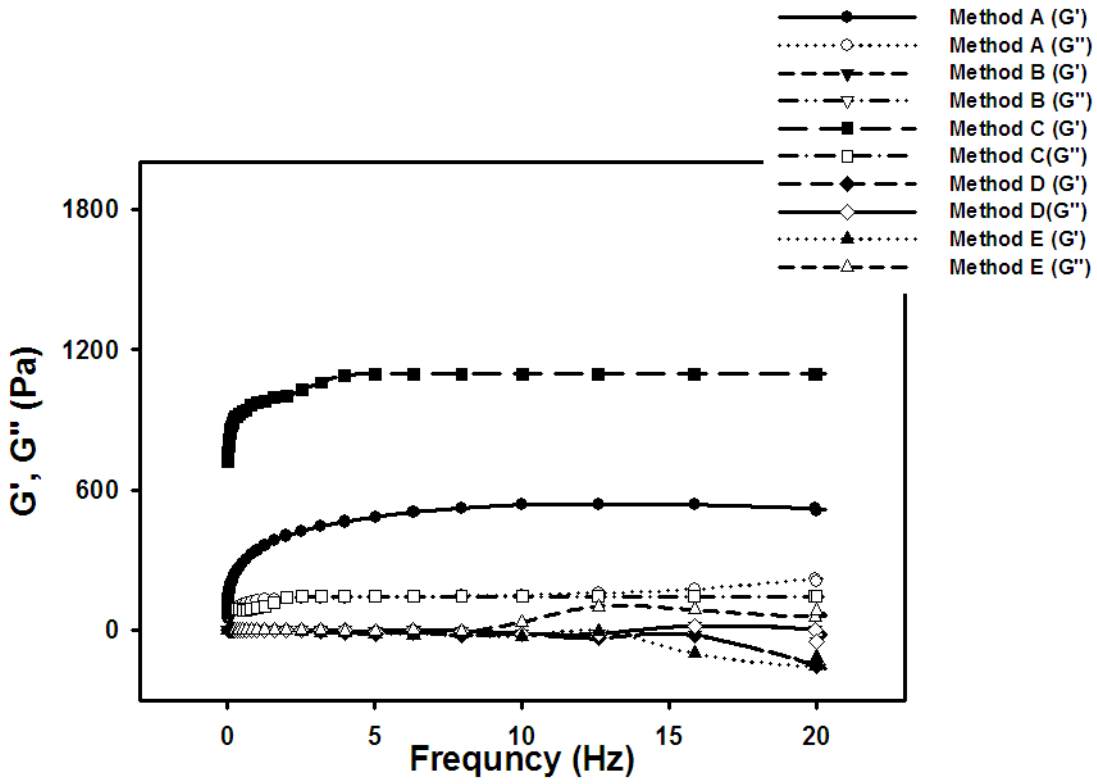

Fig. S3. Rheological characterization of bio-inspired coacervate hydrogels comparison of G' (storage modulus) vs. G" (loss modulus) at different Frequency sweep between 0.1 to 20 Hz condition method A, B, C, D and E.

References

1. Y. Lee, H. J. Chung, S. Yeo, C-H Ahn, H. Lee, P. B. Messersmith and T. G. Park, *Soft Matter* 2010**, 6,** 977.

2. Y. Lee, H. Lee, Y. B. Kim, J. Kim, T. Hyeon, H. W. Park, P. B. Messersmith and T. G. Park, *Adv. Mater.* 2008, **20**, 4154.

3. T. G. Kim, Y. Lee and T. G. Park, *Int. J. Pharm.* 2010, **384**, 181.

4. I. Donatia, S. Stredanskaa, G. Silvestrinib, A. Veterea, P. Marcona, E. Marsicha, P. Mozetica, A. Gaminia, S. Paolettia and F. Vittura, *Biomaterials* 2005, **26**, 987.

5. I. Donati, M. Borgogna, E. Turello, A. Cesaro and S. Paoletti, *Biomacromolecules* 2007, **8**, 1471.

6. M. Yalani and L. D. Hall, *Macromolecules* 1984, **17**, 272.