

Supporting Information

In-situ insights into the nanoscale deposition of 5, 6-dihydroxyindole-based coatings and the implications on the underwater adhesion mechanism of polydopamine coatings

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Supplementary figures and discussion

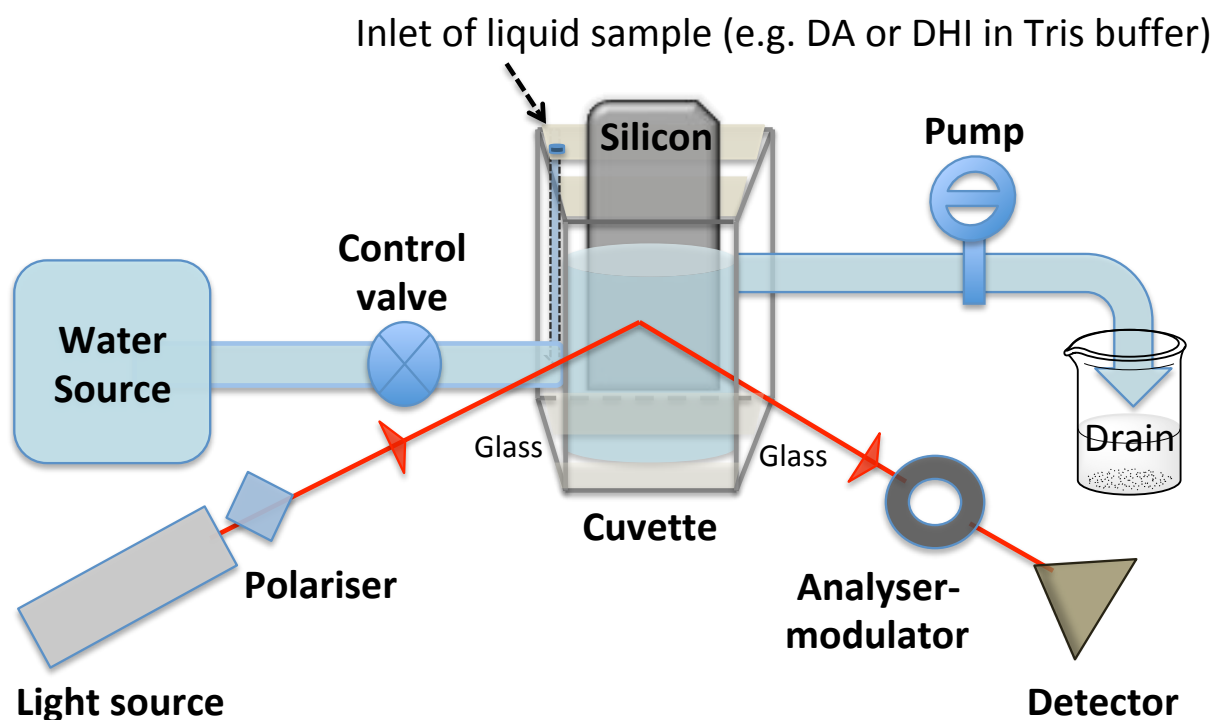


Figure S1. Schematic of the setups of precision ellipsometry system

Figure S1 is adapted from reference 1. For more details of the setup, please refer to reference 1.

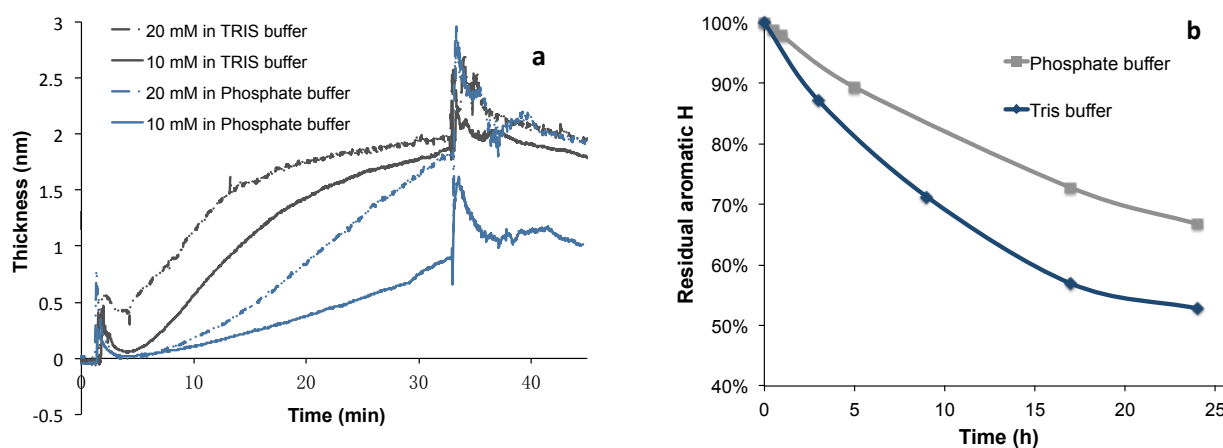


Figure S2. (a) The deposition kinetics of PDA coatings on Si wafers at different concentrations in different buffers; (b) the consumption kinetics of DA in TRIS and phosphate buffer (pH 8.5) based on $^1\text{H-NMR}$ spectra analyses.

It was noted that the use of different buffers significantly influenced the deposition kinetics in the initial stages of the coating process. The use of TRIS buffer led to a faster deposition rate than when phosphate buffer was used (**Figure S2a**). This is possibly due to the fast oxidation and polymerization of DA in TRIS buffer, as verified by an *in-situ* $^1\text{H-NMR}$ study where the consumption of DA occurred

more quickly in TRIS buffer as compared to phosphate buffer (**Figure S2b**). Interestingly, no clear decay in the deposition rate was observed in phosphate buffer within the time frame for which the process was being monitored (30 mins). From the deposition trends, one can predict that the coating thickness in TRIS buffer is self-limiting, while the coating process in phosphate buffer is likely to exhibit continued growth leading to increased thickness. This is consistent with observations from our labs and others that the maximal thickness of coatings achievable under TRIS buffer conditions was *ca.* 40-50nm while the thickness of coatings from equivalent concentrations in phosphate buffer can reach up to 100nm.^[1] Importantly, our ¹H-NMR studies show significant amounts of unreacted DA in both buffers after 24 hrs, indicating that the observed thickness of coating in the presence of TRIS buffer is not due to the DA being exhausted (**Figure S2b**).

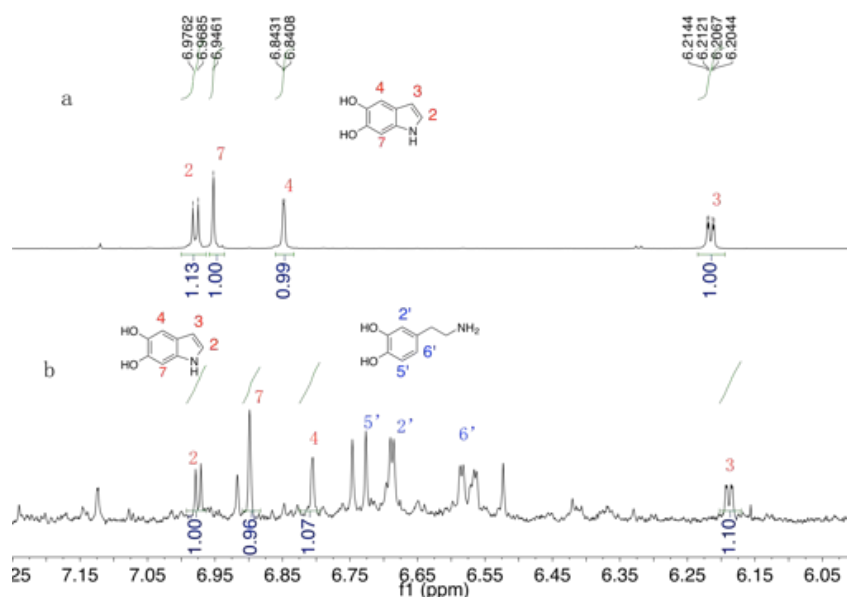


Figure S3. ¹H-NMR spectra of (a) DHI and (b) organic extracts of PDA solution.

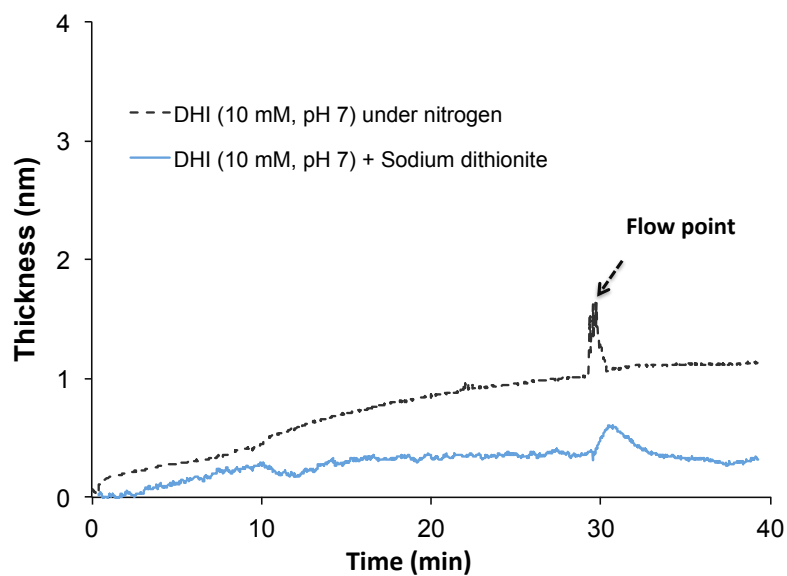


Figure S4. Deposition kinetics of DHI-based coatings with pre-treatment of N_2 and in the presence of reducing agent

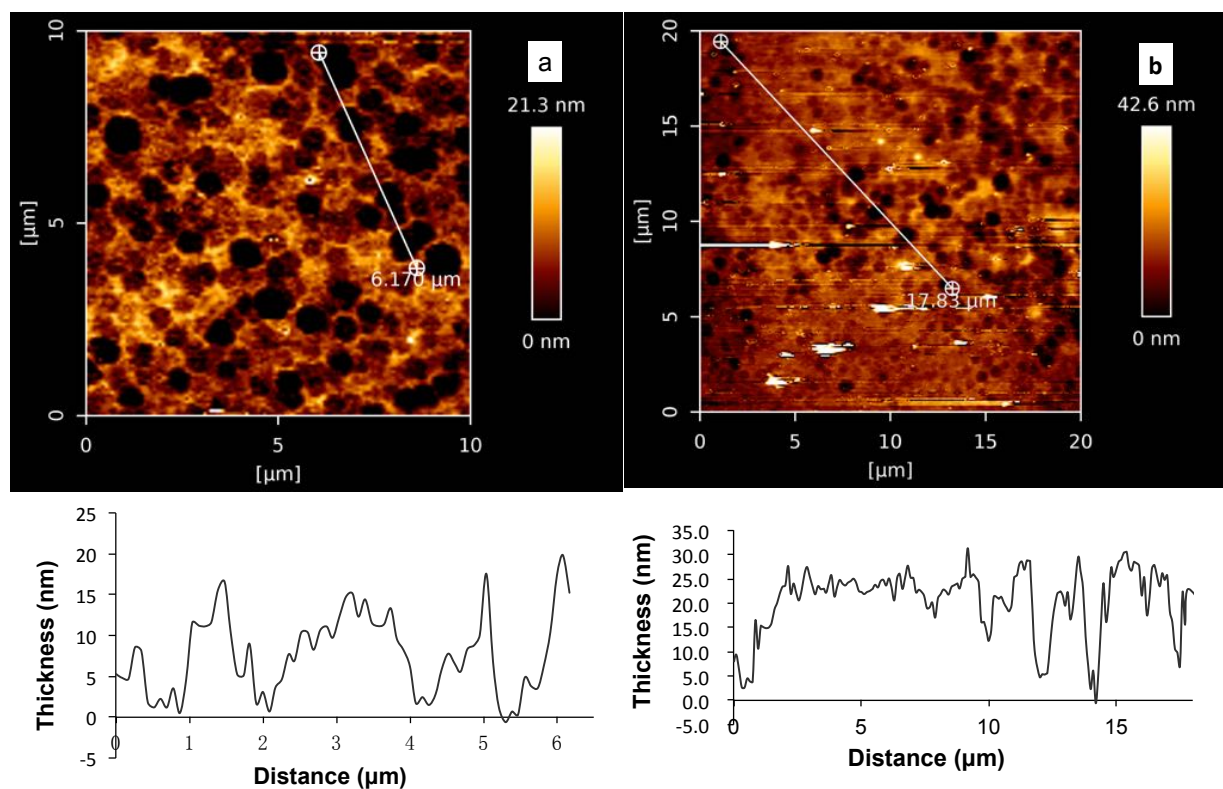


Figure S5. The AFM morphologies of DHI-coatings in TRIS buffer (pH 5) for (a) 30 mins and (b) 6 hrs.

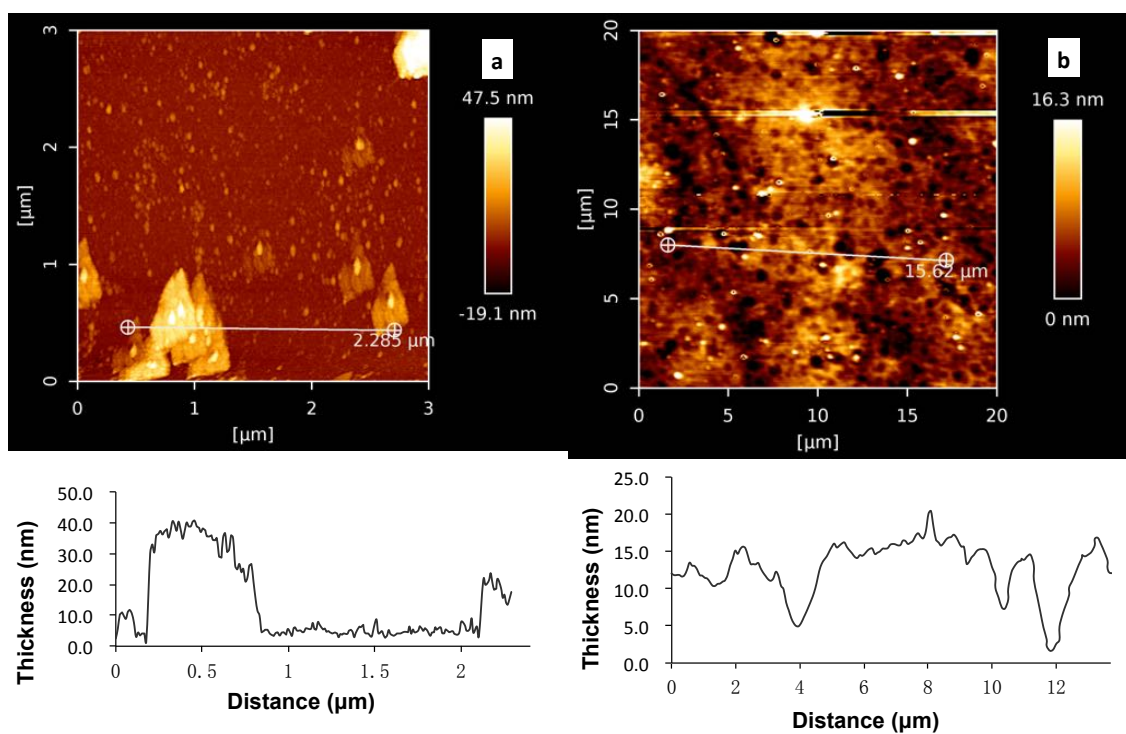


Figure S6. The AFM morphologies of DHI-coatings formed at different TRIS buffers on Silicon wafers:
 (a) pH 8.5, 1 hrs; (b) pH 7, 4 hrs.

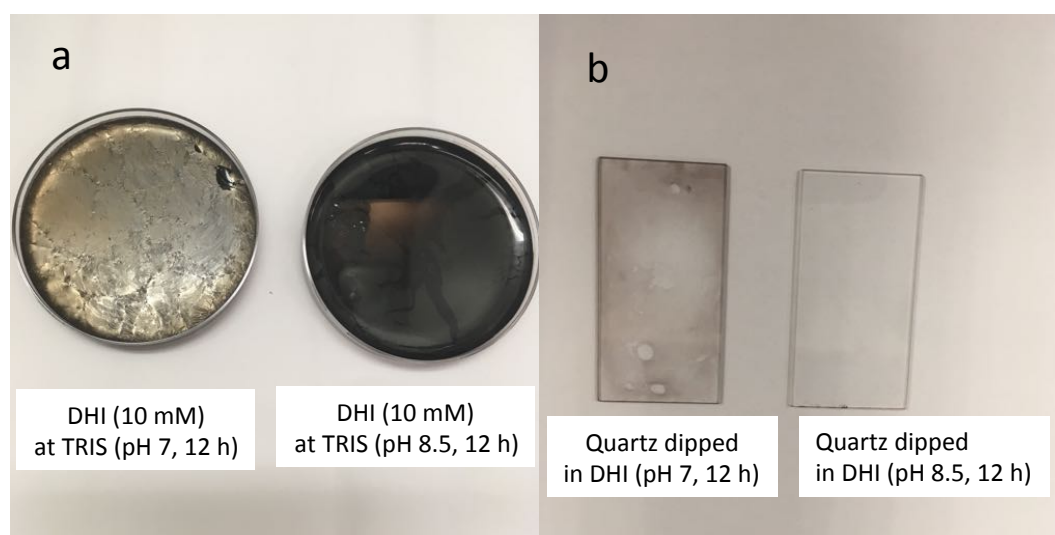
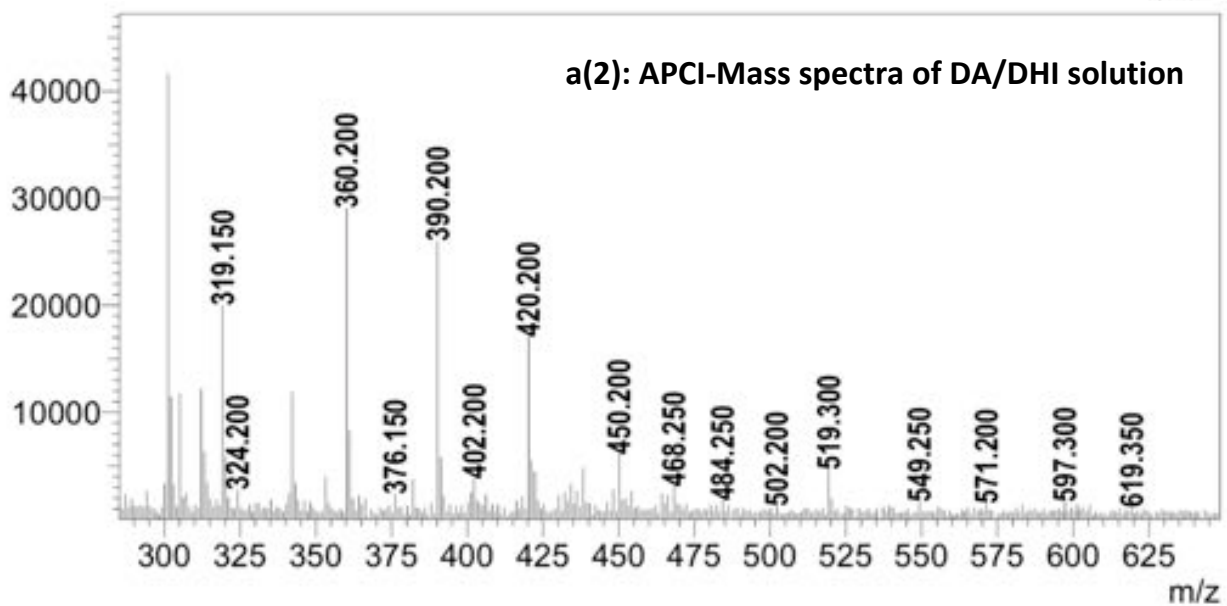
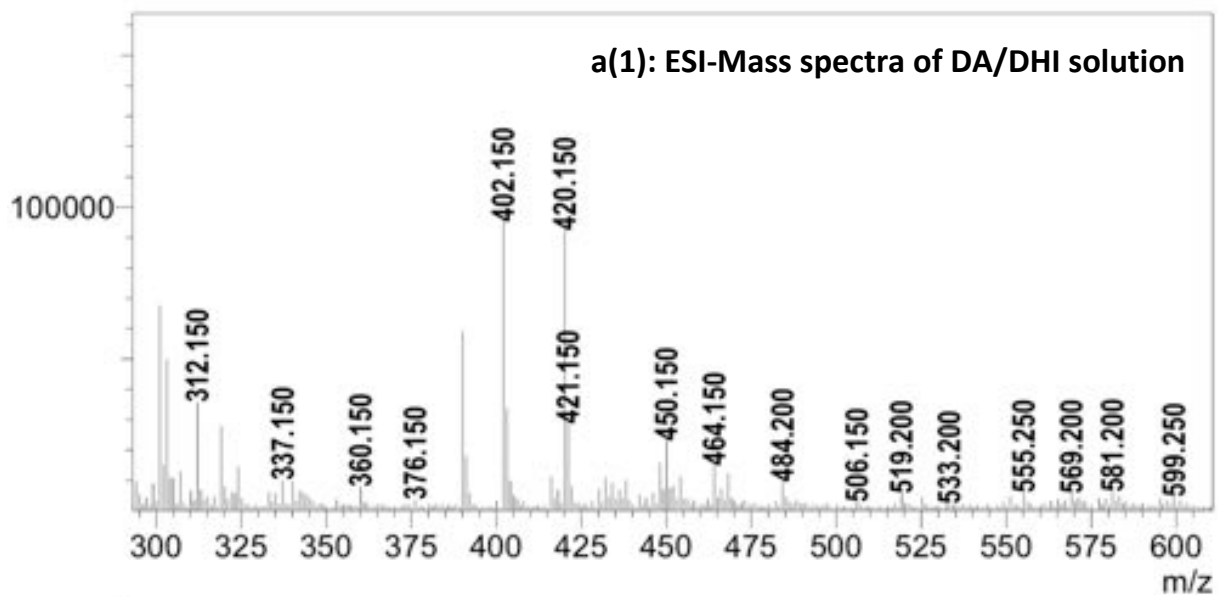
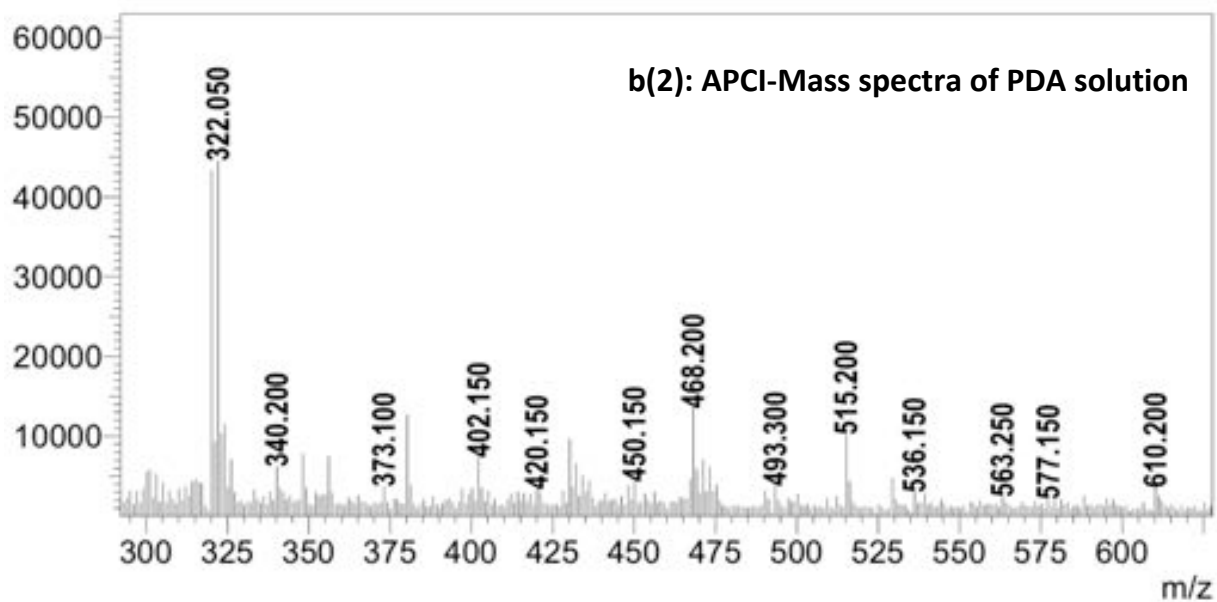
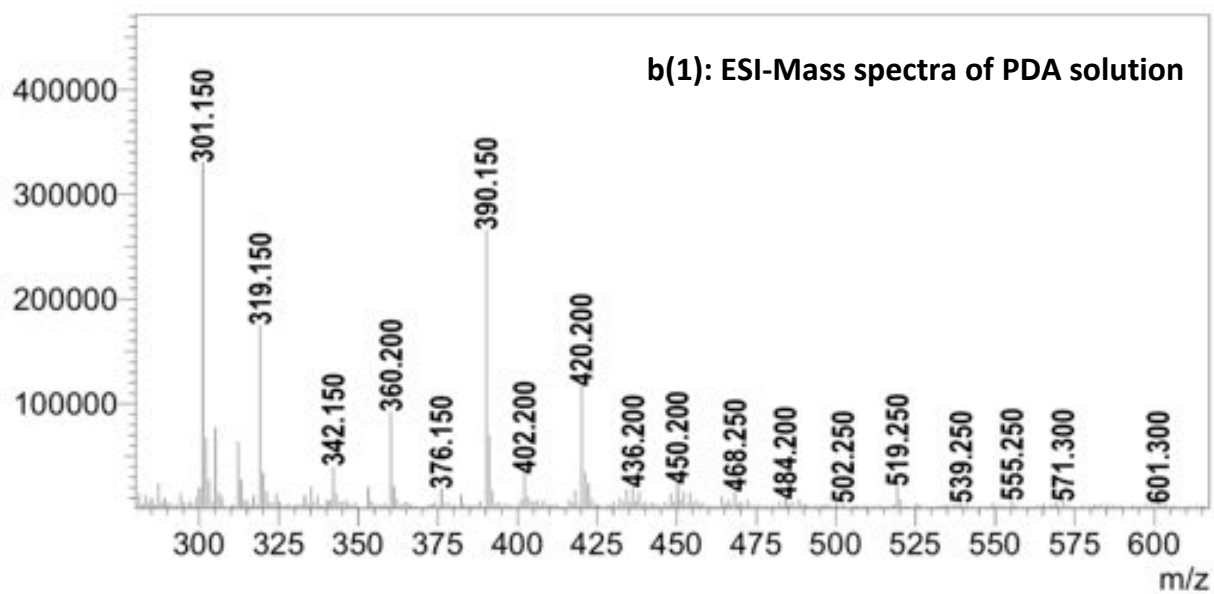


Figure S7 a: DHI solutions at pH 7 and pH 8.5 after 12 h; **b:** Quartz substrates dipped in DHI solution at pH 7 and pH 8.5 for 12 h.





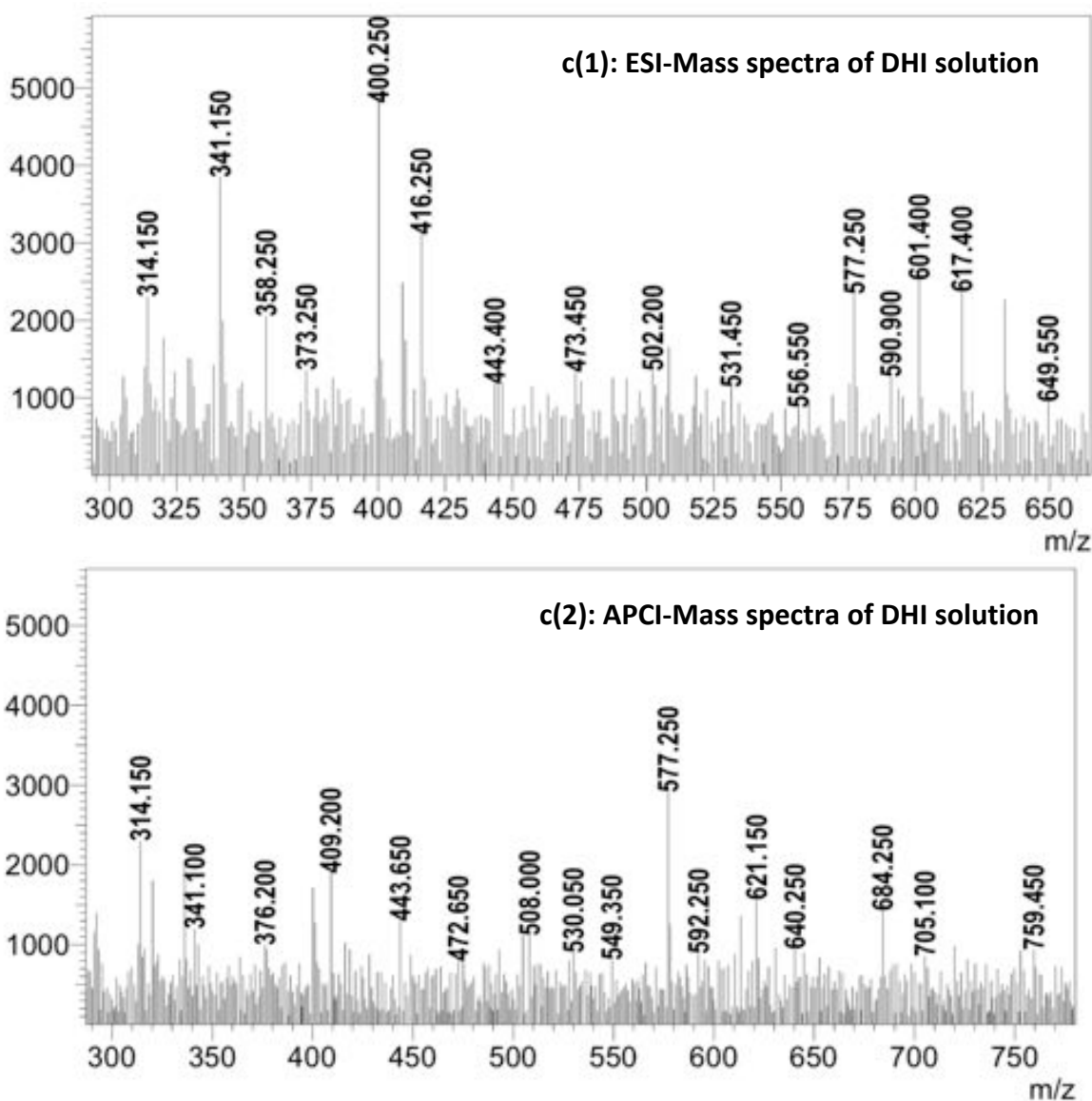


Figure S8. Mass spectra analyses (positive mode) on the main components in (a) DA/DHI solution (30 mins), (b) PDA solution (4hrs) and (c) DHI solution (30 mins).

References

- [1] H. H. Lau, R. Murney, N. L. Yakovlev, M. V. Novoselova, S. H. Lim, N. Roy, H. Singh, G. B. Sukhorukov, B. Haigh, M. V. Kiryukhin, *J. Colloid Interface Sci.*, 2017, **505**, 332-340.
- [2] a) F. Bernsmann, V. Ball, F. Addiego, A. Ponche, M. Michel, J. J. d. A. Gracio, V. Toniazzo, D. Ruch, *Langmuir* **2011**, 27, 2819-2825; b) N. F. Della Vecchia, A. Luchini, A. Napolitano, G. D'Errico, G. Vitiello, N. Szekely, M. d'Ischia, L. Paduano, *Langmuir* 2014, **30**, 9811-9818.