Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# *Electronic Supplementary Information*

## PEG Functionalization Effect of Silicate-Containing Hydroxyapatite Particles on Effective Collagen Fibrillation with Hydration Layer State Change

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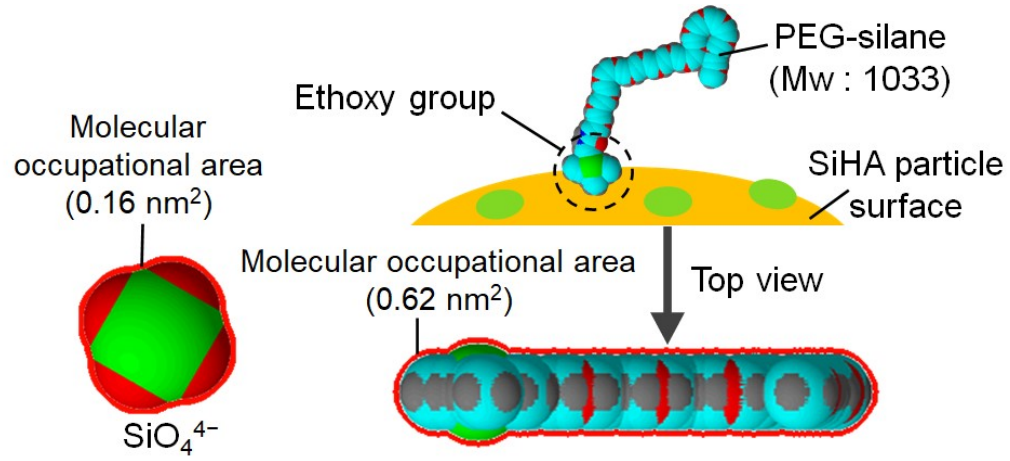
***Scheme S1***




**Scheme S1.** Schematic diagram and molecular occupational area of $SiO_4^{4-}$ and PEG-silane on the particle. The molecular occupational areas were used to calculate the coverage rate (%).

***Figure S1***

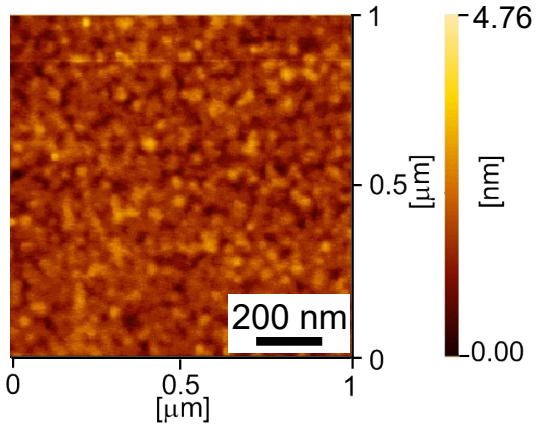



**Figure S1.** AFM topographic image of the Au substrate (i.e., QCM-D Au sensor). The $R_{rms}$ value was 3.8 nm.

***Figure S2***

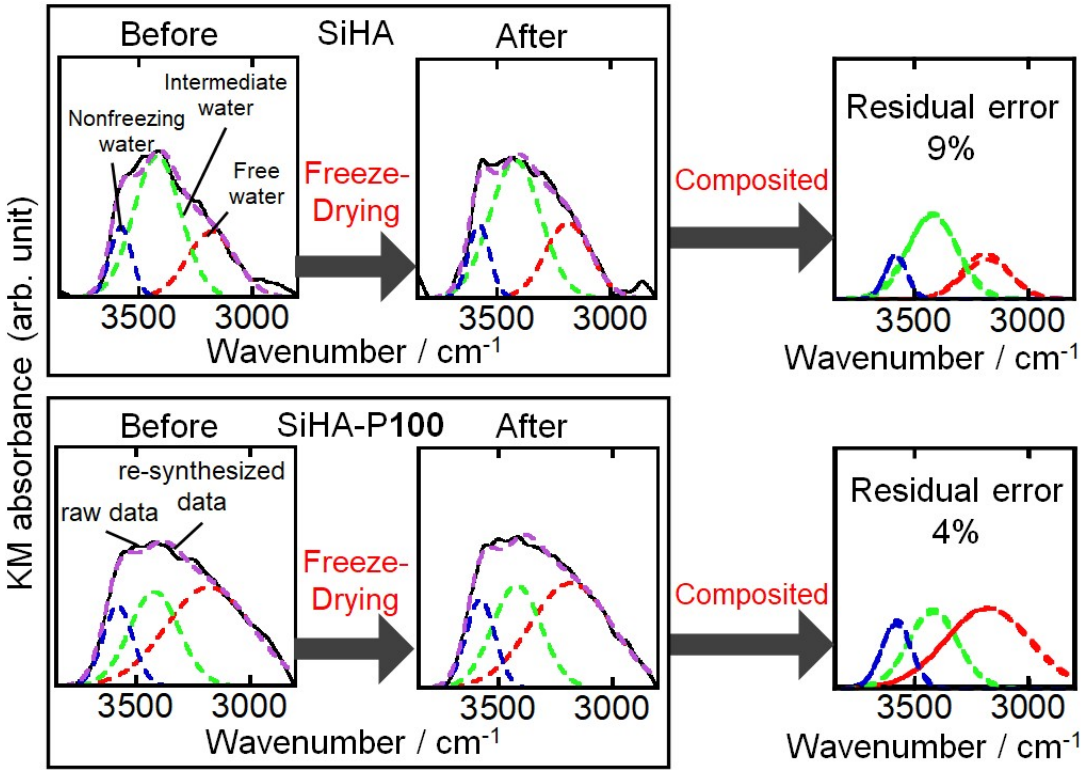
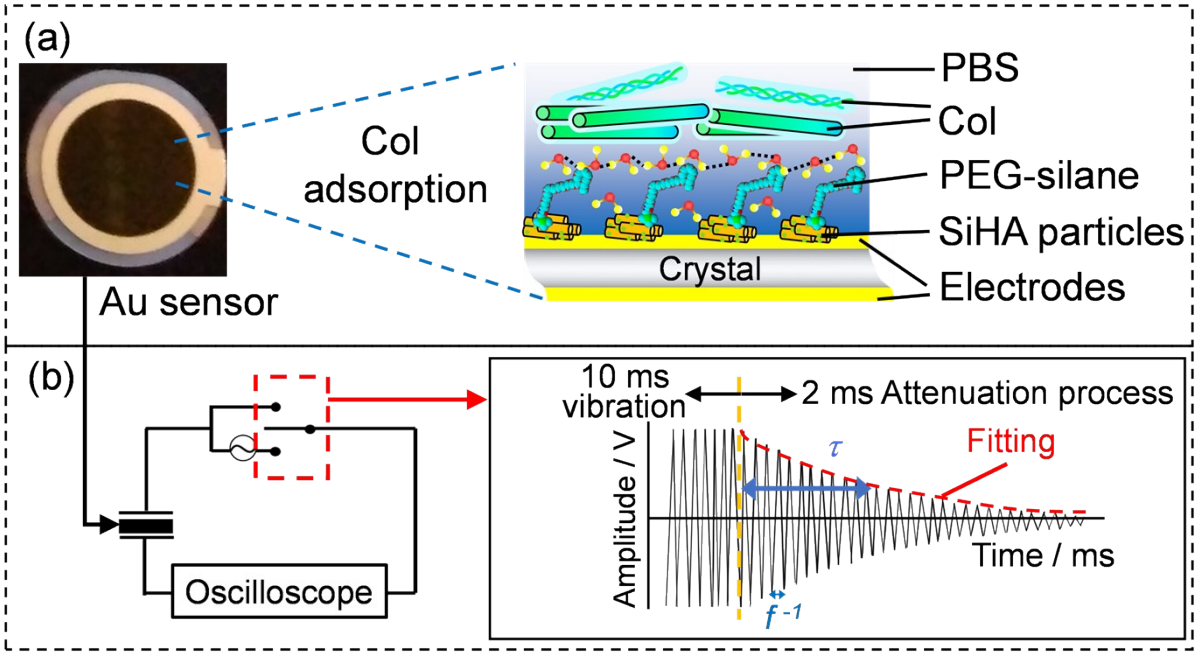


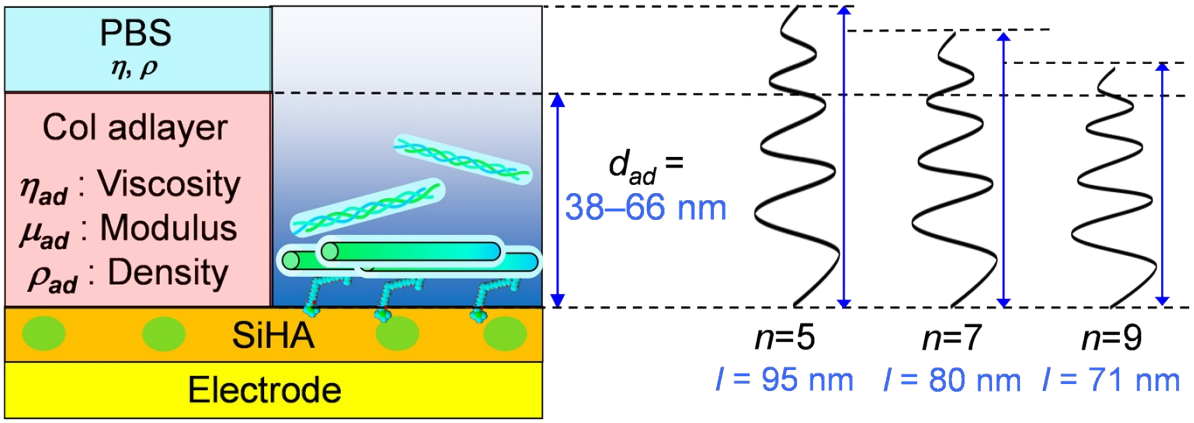

**Figure S2.** FT-IR spectral deconvolution results of three hydration layers formed on the particles of SiHA and SiHA-P**100** before and after freeze-drying. The residual errors with the spectral composition were less than 9 %.

***Scheme S2***




**Scheme S2.** Illustrations of (a) measurement of Col adsorption behavior on the PEG-functionalized SiHA particles using QCM-D sensor, and (b) typical rapid excitation of the QCM-D near resonance, followed by an exponentially damped sinusoidal wave after the rapid disconnection, which can be fitted to calculate the τ.

***Scheme S3***




**Scheme S3.** Scheme of the geometry and parameters used to simulate the hydration layer and Col adlayers on PEG-functionalized SiHA particle film in contact between the QCM-D sensor surface and a semi-infinite Newtonian liquid. The Col adlayer thickness ($d_{ad}$) and detectable height ($l$) of $D$ in the QCM-D system ($n$ = 5, 7, 9) were represented.

***Figure S3***

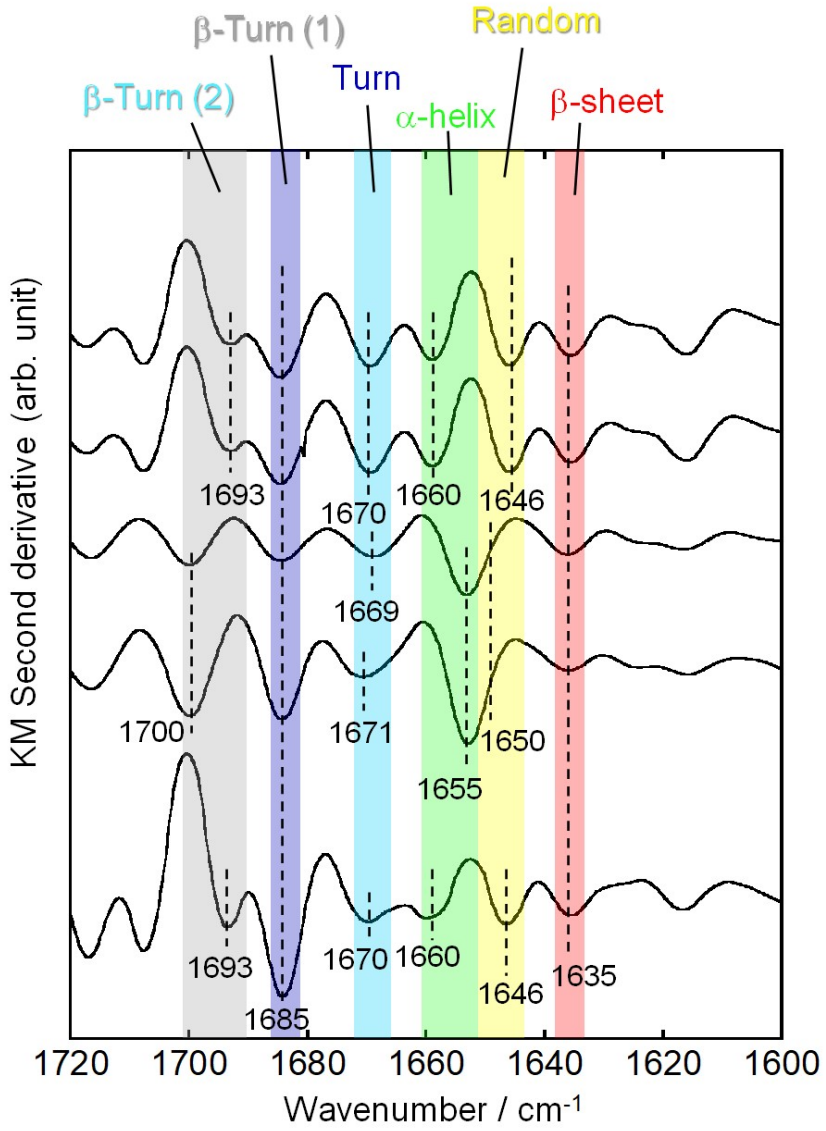



**Figure S3.** The second derivatives of the FT-IR spectra in the Col adlayer of the amide I on the particles.

***Figure S4***

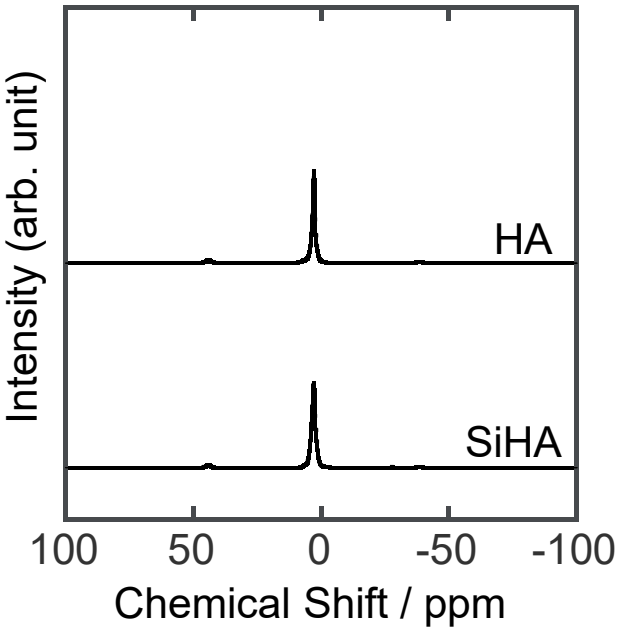



**Figure S4.** Solid-state $^{31}$P–NMR DD/MAS spectra of the HA and SiHA particles.

***Figure S5***

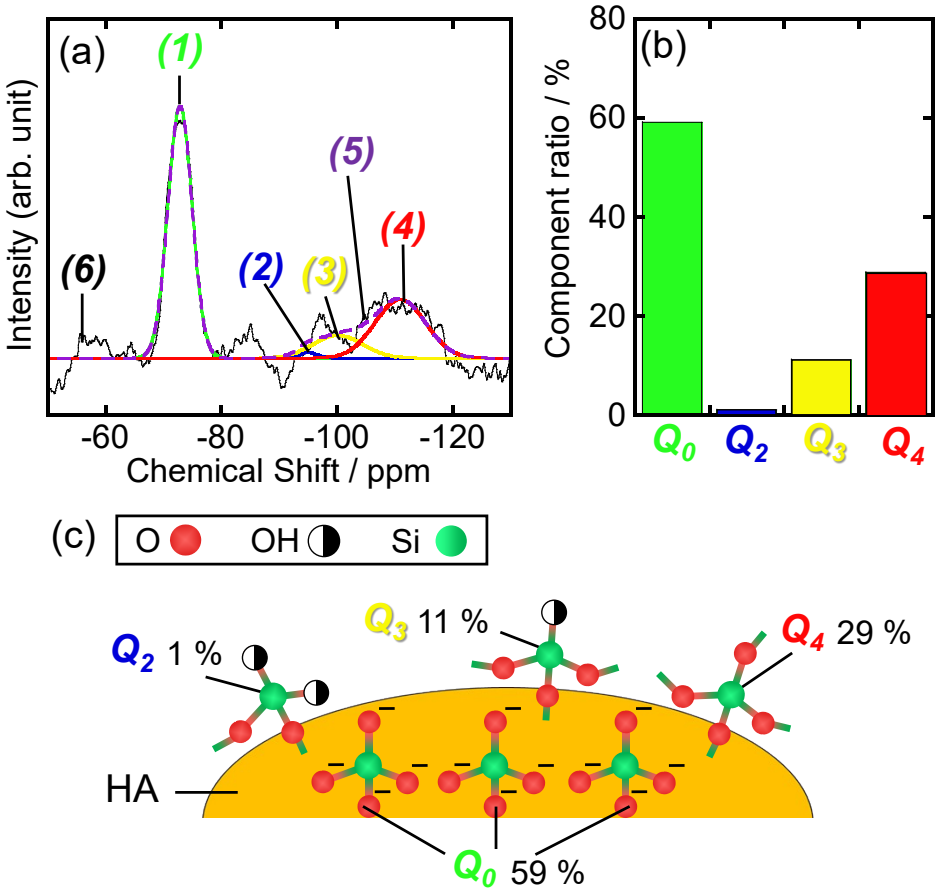
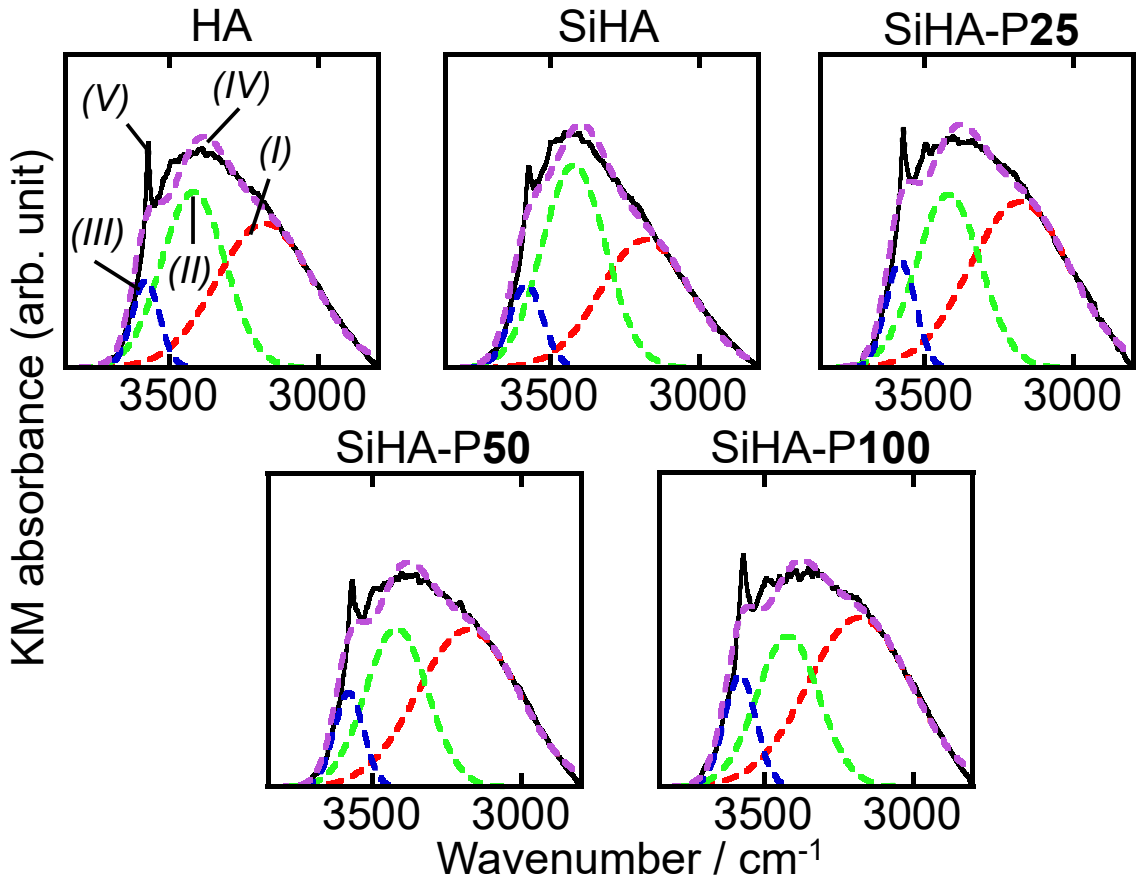



**Figure S5.** (a) Curve-fitting deconvolution result of solid-state $^{29}$Si–NMR spectra of the SiHA particles, indicating the spectral peaks of (1) $Q_0$ (i.e., $SiO_4^{4-}$) at –73 ppm, (2) $Q_2$ (i.e., two Si–O–Si and two Si–OH bonds) at –95 ppm, (3) $Q_3$ (i.e., three Si–O–Si and one Si–OH bonds) at –100 ppm and (4) $Q_4$ (i.e., four Si–O–Si bonds) at –111 ppm, and their (5) re-synthesized and (6) raw spectra. (b) Component ratios of $Q_0$, $Q_2$, $Q_3$ and $Q_4$ based on the curve-fitting deconvolution results. (c) Illustration of the possible state of silicate on the SiHA particles.

***Scheme S6***




**Scheme S6.** FT-IR spectral deconvolution results of three hydration layers formed on the particles. The separated *(I), (II)* and *(III)* peaks are attributed to free, intermediate and nonfreezing water molecular states, respectively, and their *(IV)* re-synthesized and *(V)* raw spectra are represented.

***Figure S7***

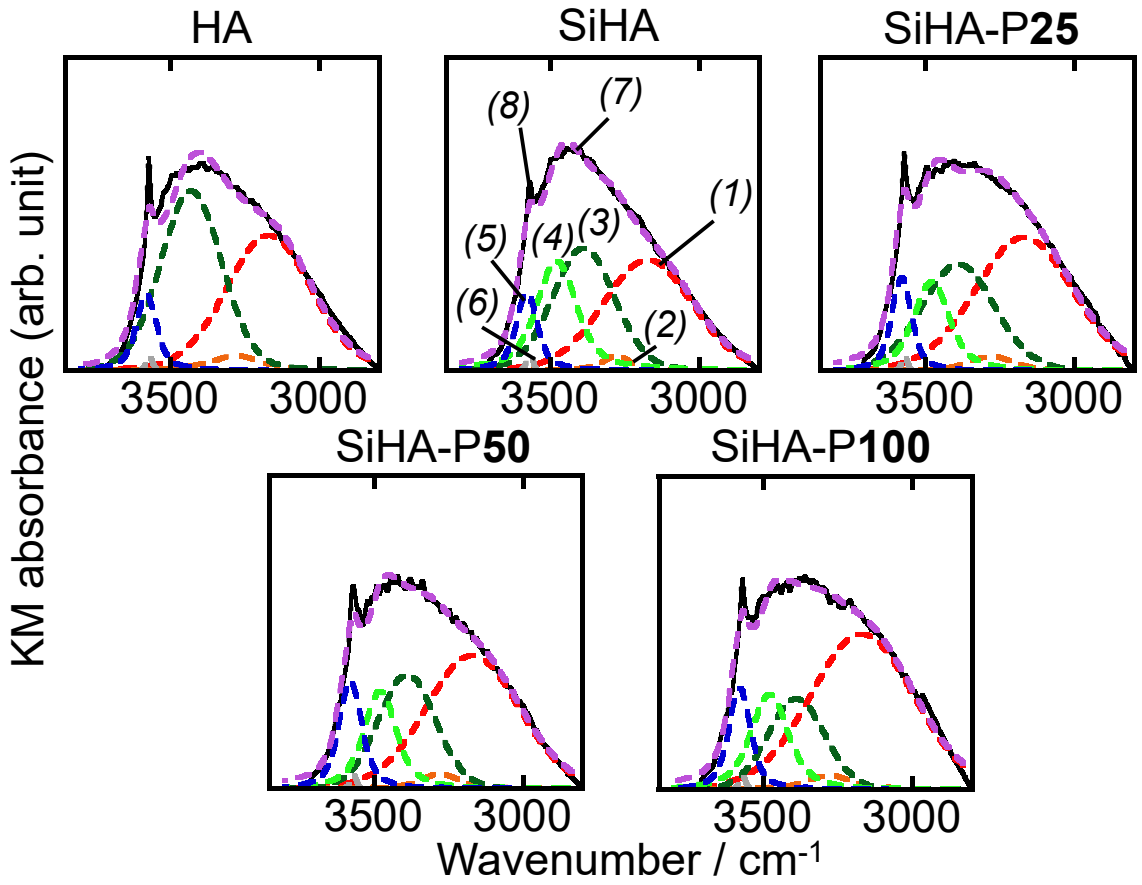



**Figure S7.** FT-IR spectral deconvolution results of six water-interactive states formed on the particles, indicating the separated spectra of *(1)* asymmetric O–H stretching vibration between water molecules, *(2*) O–H bending vibration of water molecules, *(3)* symmetric O–H stretching vibration of water molecules, *(4*) non-stretching O–H vibration of water on Si–OH, *(5*) hydrogen-bonded stretching O–H vibration of water molecules and stretching O–H vibration of water on Si–OH, and *(6*) non-stretching O–H vibration of structural O–H in HA, respectively, and *(7)* their re-synthesized and *(8)* raw spectra.

***Figure S8***

(a)

| | | |
|---|---|---|
| (*1*) Asymmetric O–H stretching vibration between water molecules | | **Free water** |
| (*2*) O–H bending vibration of water molecules | | |
| (*3*) Symmetric O–H stretching vibration of water molecules | | **Intermediate water** |
| (*4*) Non-stretching O–H vibration of water on Si–OH | | |
| (*5*) | Hydrogen-bonded stretching O–H vibration of water molecules<br>Stretching O–H vibration of water on Si–OH | **Nonfreezing water** |
| (*6*) Non-stretching O–H vibration of structural O–H in HA | | – |

(b)

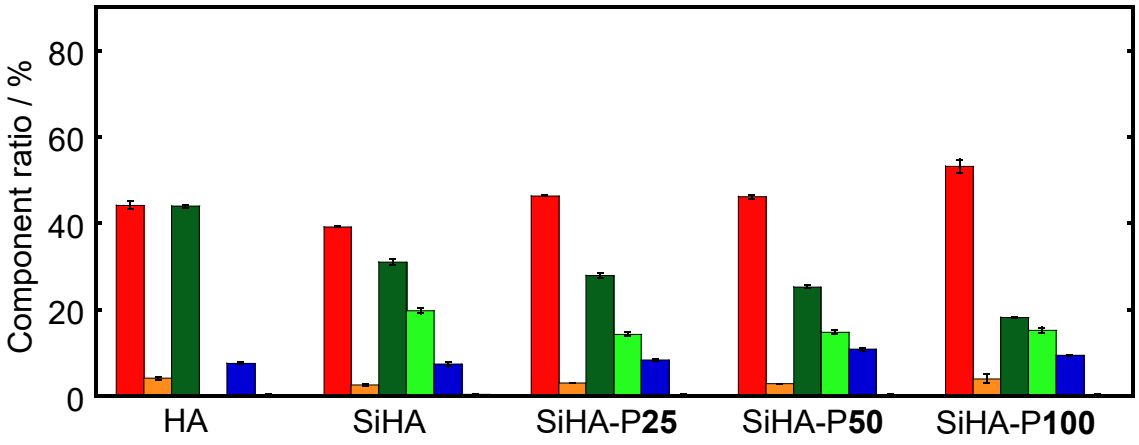



**Figure S8.** (a) Assignments of the six water-interactive states formed on the particles for **Figure S7** and (b) resultant six component ratios.

***Figure S9***

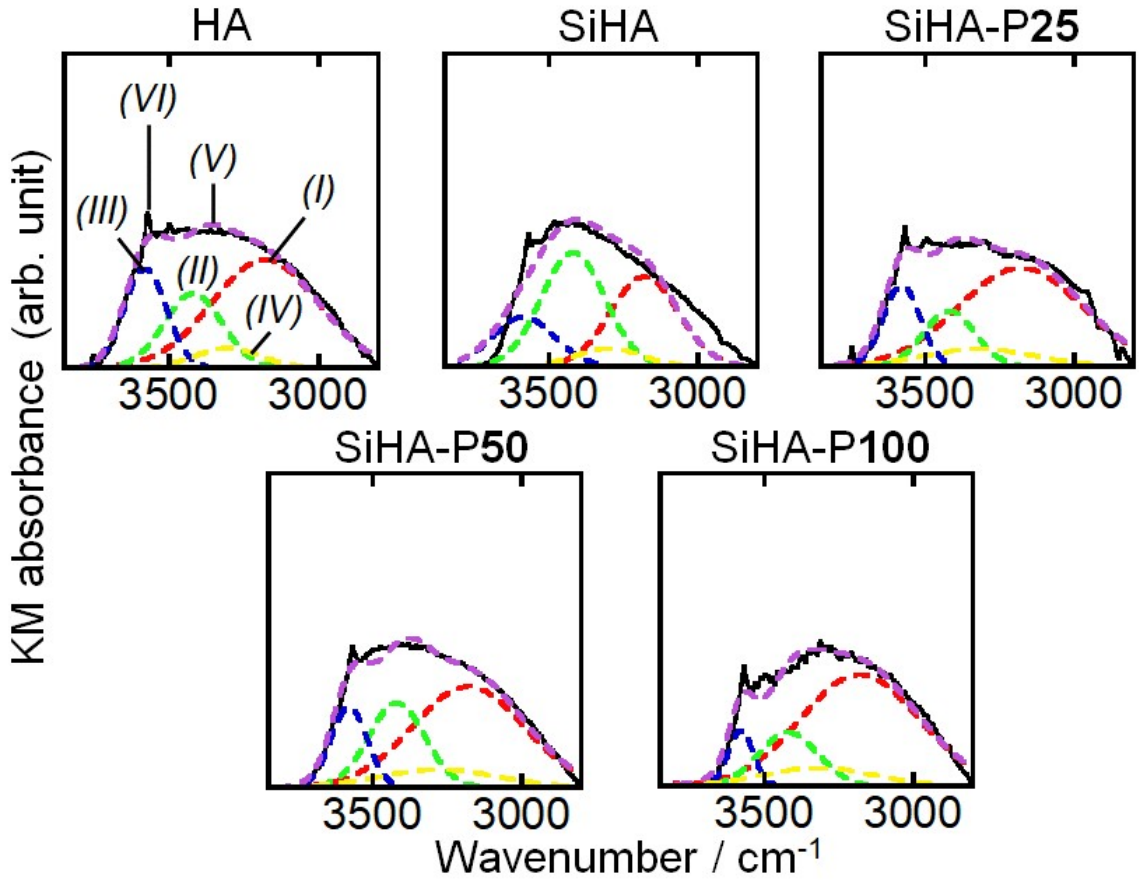



**Figure S9.** FT-IR spectral deconvolution results of three hydration layers formed on the Col-adsorbed particles. The separated *(I), (II)* and *(III)* and *(IV)* peaks are attributed to free, intermediate, nonfreezing water molecular states and N–H stretching vibration of Col, and their *(V)* re-synthesized and *(VI)* raw spectra are represented.

***Figure S10***

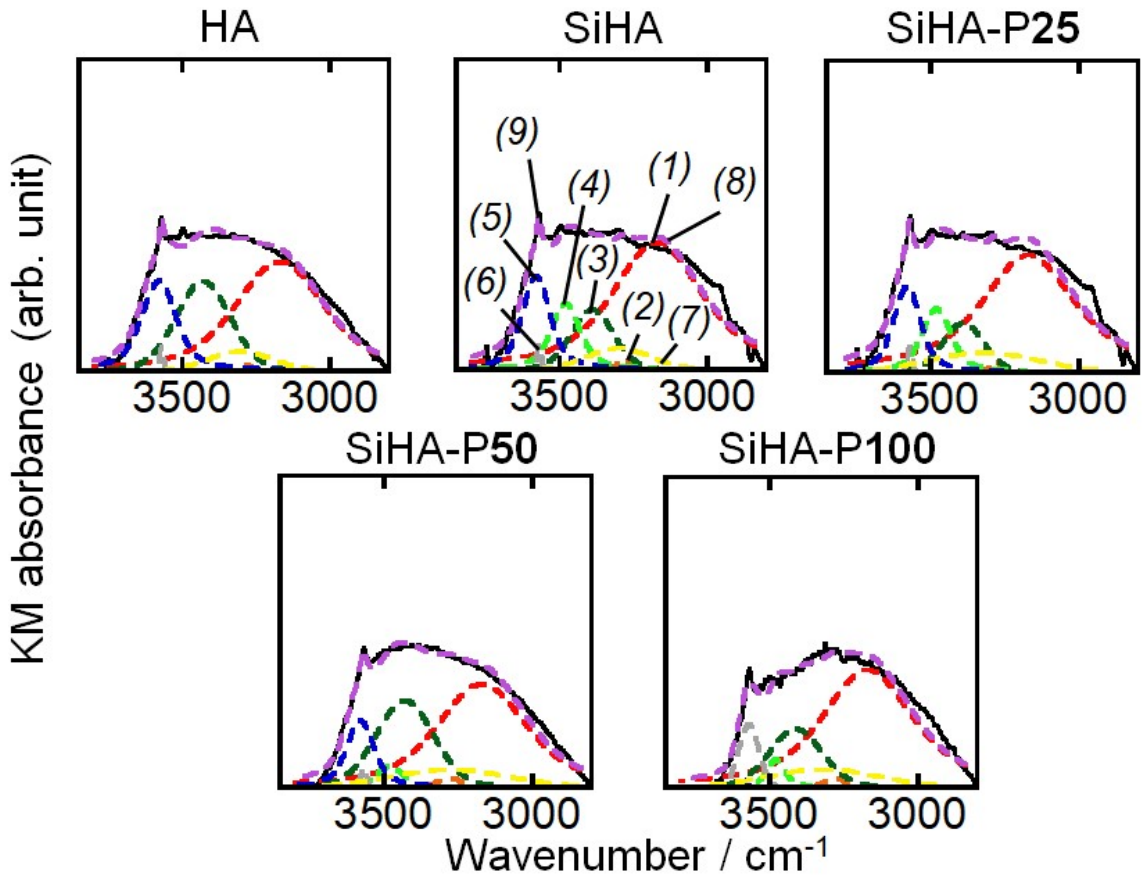



**Figure S10.** FT-IR spectral deconvolution results of six water-interactive states formed on the Col-adsorbed particles, indicating the separated spectra of *(1)* asymmetric O–H stretching vibration between water molecules, *(2*) O–H bending vibration of water molecules, *(3)* symmetric O–H stretching vibration of water molecules, *(4*) non-stretching O–H vibration of water on Si–OH, *(5*) hydrogen-bonded stretching O–H vibration and stretching O–H vibration of water on Si–OH, *(6*) non-stretching O–H vibration of structural O–H in HA and *(7*) N–H stretching vibration of Col, respectively, and *(8)* their re-synthesized and *(9)* raw spectra.

***Figure S11***

(a)

| | | |
|---|---|---|
| (*1*) | Asymmetric O–H stretching vibration between water molecules | Free water |
| (*2*) | O–H bending vibration of water molecules | |
| (*3*) | Symmetric O–H stretching vibration of water molecules | Intermediate water |
| (*4*) | Stretching and bending O–H vibration of water on Si–OH | |
| (*5*) | Hydrogen-bonded stretching O–H vibration of water molecules<br>Stretching O–H vibration of water on Si–OH | Nonfreezing water |
| (*6*) | Non-stretching O–H vibration of structural O–H in HA | – |
| (*7*) | N–H stretching vibration of Col | – |

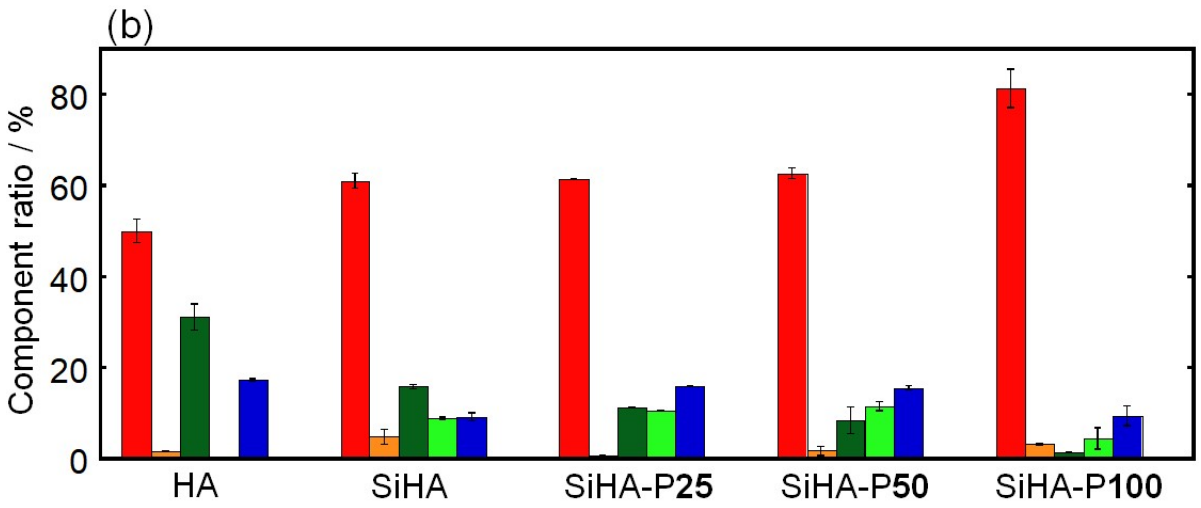



**Figure S11.** (a) Assignments of the six water-interactive states and N–H stretching vibration of Col formed on the particles for **Figure S10** and (b) resultant six components and N–H stretching vibration of Col ratios.

***Figure S12***

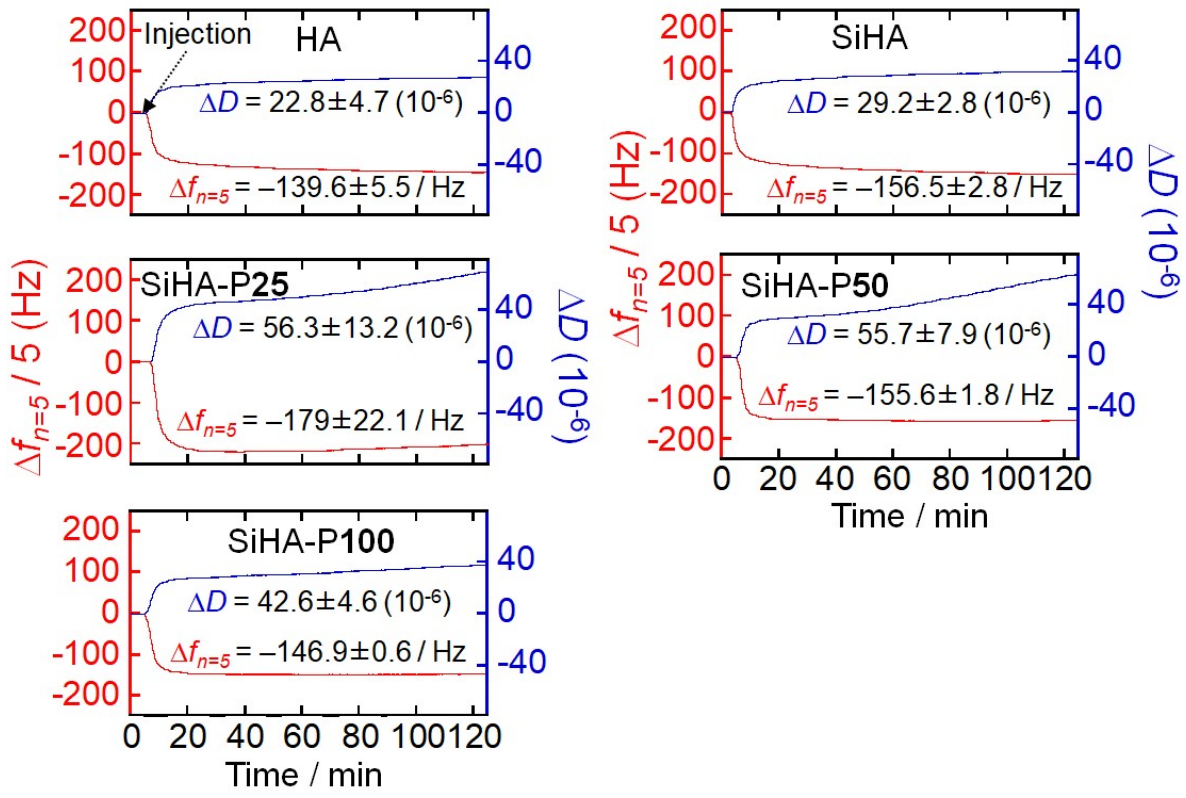



**Figure S12.** $\Delta D$ and $\Delta f$ curves with the CoI adsorption process on the particle films.

***Figure S13***

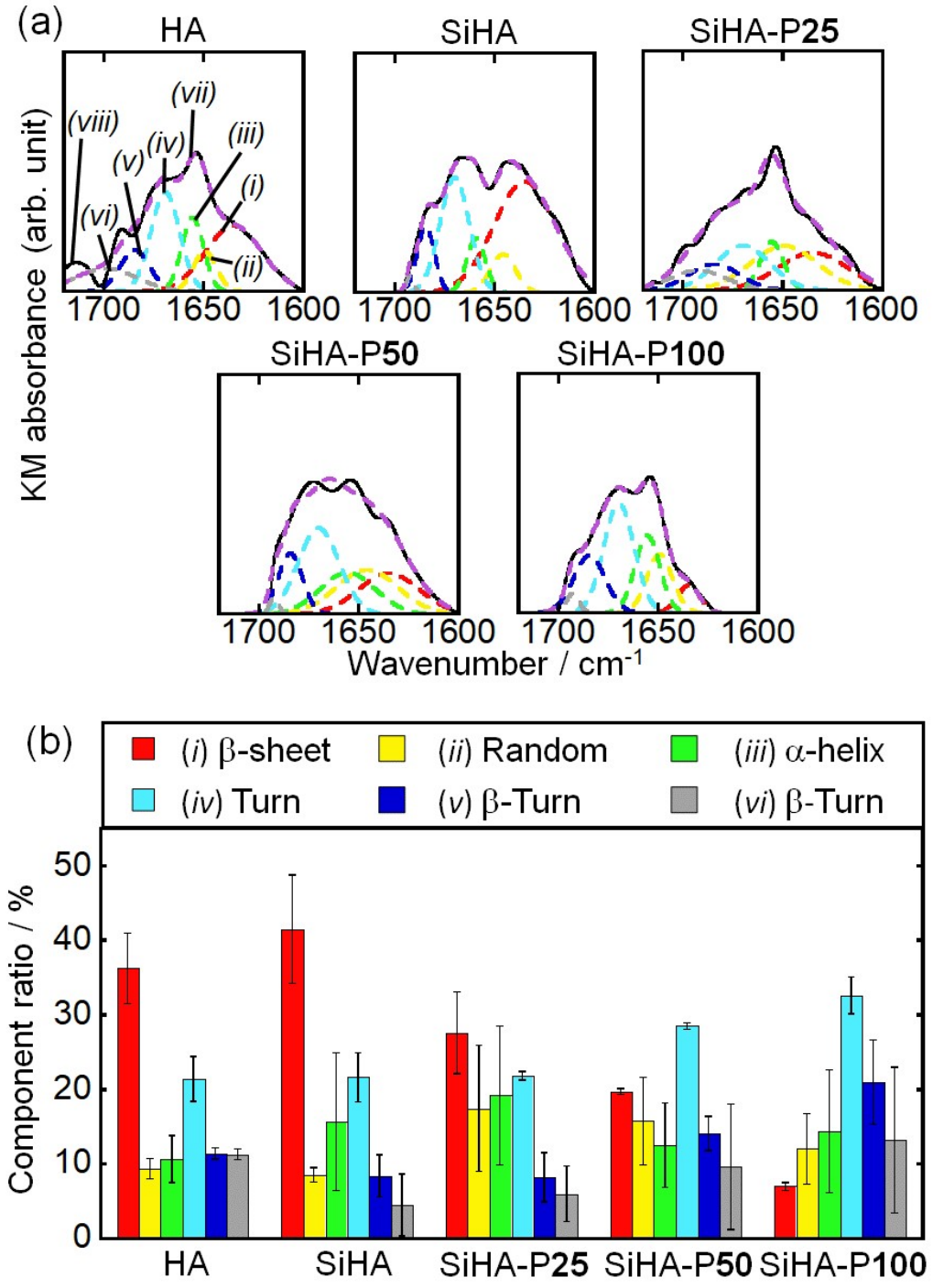



**Figure S13.** (a) FT-IR spectral deconvolution results of the amide I bands of the adsorbed Col on the particles to provide the secondary structural components ((*i*) β-sheet, (*ii*) random, (*iii*) α-helix, (*iv*)(*v*) β-turn, (*vi*) turn), and their (*vii*) re-synthesized and (*viii*) raw spectra. (b) Component ratios on the secondary structures of the amide I bands in the adsorbed Col on the particles.