Interfacial Water Morphology in Hydrated Melanin

Supplementary Information

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Estimation of no. of Water Layers

Assuming a spherical particle of radius 5 nm, yields a volume of:

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(5 \times 10^{-9}\right)^3 = 5.24 \times 10^{-25}\mathrm{m}^3$$

and a density (ρ) of 1.397 g cm^{-3}, the mass of the particle will become

$$m = \rho V = 1397000\ \mathrm{g\ m}^{-3} \times 5.24 \times 10^{-25}\mathrm{m}^3 = 7.31 \times 10^{-19}\mathrm{g}$$

Given a hydration level of 90% relative humidity, or 11.1 × 10^{-3} mol g^{-1} of water adsorbed per gram of melanin (Figure 2), yields 8.78 × 10^{-21} mol, or a mass of water of 1.58 × 10^{-19} g. The data indicates a high density amorphous ice, which at ambient conditions below 120 K has a density of 1.17 g cm^{-3}, it will yield a volume of water:

$$V_w = \frac{m_w}{\rho_w} = \frac{1.58\ \times\ 10^{-19}g}{1.17\ g\ cm^{-3}} = 1.85 \times 10^{-19}\mathrm{cm}^3 = 1.85 \times 10^{-25}\mathrm{m}^3$$

If one now imagines a sphere of melanin coated with water, the total volume of the two substances together will be

$$V_T = V + V_w = 5.24 \times 10^{-25}\text{m}^3 + 1.85 \times 10^{-25}\text{m}^3 = 7.09 \times 10^{-25}\text{m}^3$$

If this hydrated melanin particle is a sphere, the total radius will be

$$r_T = \left(\frac{3V_T}{4\pi}\right)^{1/3} = 5.53 \times 10^{-9}\text{m} = 5.53\ \text{nm}$$

As such, the water layer thickness will be 0.53 nm. Given the density of water we've selected, the average volume one water molecule will occupy is:

$$V_{w,molecule} = \frac{M_w}{N_A\rho_w} = \frac{18.015\ \text{g mol}^{-1}}{6.022 \times 10^{23}\text{mol}^{-1} \times 1.17\ g\ cm^{-3}} = 2.56 \times 10^{-23}cm^3 = 2.56 \times 10^{-29}m^3$$

This implies a spherical radius of 1.83×10^{-10} m or 0.183 nm. Using this value, we divide into the water layer thickness and obtain 2.9 water molecules.

Estimation of no. of Water Layers From Bound Water

If one assumes that the 15%/85% DHI/DHICA ratio obtained from the XPS in reality reflects a 10%/90% ratio with additional water as discussed in the results section of the main manuscript, a useful calculation to determine the upper bound of trapped or bound water on the surface can be useful.

If one utilises the above particle size or mass, and use an average molecular weight for melanin of 151.5 g/mol utilising the ratios for our computational modelling in the methods section, though using a 10%/90% DHI to DHICA ratio, one determines that a particle from above will yield 2.91×10^3 molecules. As indicated in the main manuscript, the water to monomer ratio is about 1:11, yielding 2.64×10^2 molecules. This implies a total volume of the water:

$$V_w = \frac{m_w}{\rho_w} = \frac{7.97 \times 10^{-21}g}{1.17\ g\ cm^{-3}} = 6.81 \times 10^{-21}\text{cm}^3 = 6.81 \times 10^{-27}\text{m}^3$$

Utilising the same calculations as above,

$$V_T = V + V_w = 5.24 \times 10^{-25}\text{m}^3 + 6.81 \times 10^{-27}\text{m}^3 = 5.31 \times 10^{-25}\text{m}^3$$

If this melanin particle is a sphere, the total radius will be

$$r_T = \left(\frac{3V_T}{4\pi}\right)^{1/3} = 5.53 \times 10^{-9}\mathrm{m} = 5.02\ \mathrm{nm}$$

As such, this implies a bound water layer thickness of 0.02 nm. From above, this implies around 2% coverage. It should be noted the above assumes that all the water is on the surface, and none is lodged within the particle, and as such is an upper bound.

Supplementary Figures

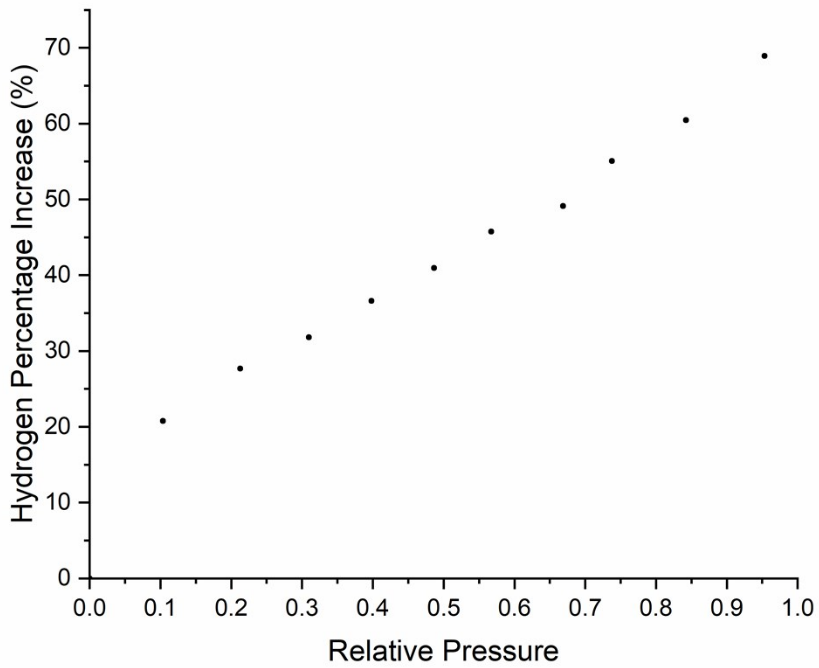

Figure S1. The adsorption isotherm of Figure 2 transformed into percentage change of hydrogen gained relative to the hydrogen content of the dry sample. In order to achieve the transformation, a molecular mass of melanin was assumed to 153.99 g mol^{-1}, consistent with 75% quinone, 20% quinone methide and 5% catechol with 15% monomers containing COOH moieties. This is consistent with the XPS elemental analysis and our computational modelling as explained in the main text. The total number of hydrogens per monomer was assumed to be 5.1, in line with the above ratios.

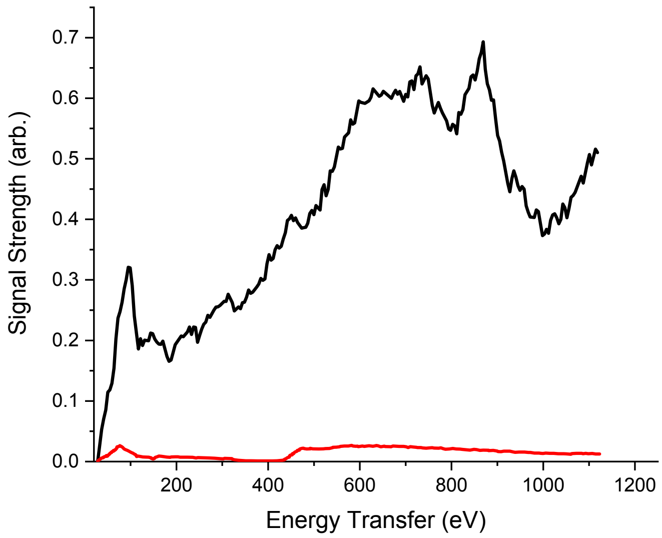

Figure S2. The melanin dry spectra is plotted alongside the spectra for high density amorphous (HDA) ice[1], which we use as a model spectrum for potentially trapped water. The calculation was performed as follows, the average oxygen content per monomer moiety was estimated from the 15%/85% ratio of DHI to DHICA, which comes to around 2.3 oxygens per monomer. If one redoes the calculation for 10%/90%, one obtains 2.2 oxygens per monomer. If, for arguments sake one assumes that the difference, 0.1 oxygens per monomer, is due to trapped water per our discussion in the main manuscript, this would equate to 1 water molecule to 9 DHI plus 1 DHICA. With these values in place, one can calculate the average amount of hydrogen per monomer for a 10%/90% ratio (using the various oxidative weights in the main manuscript), which comes to 5.1 hydrogens per monomer. If one then accounts for the water content, this would results in 5.3 hydrogen per monomer. This hydrogen difference from the water is equal to ~3.8%. Hence the total INS signal of the dry spectra from trapped water could be up to 3.8% total. Ideally, one would want the total spectra for the dry melanin and the HAD ice to integrate across, however, the reported HDA spectrum is quite limited as depicted above. As such, we restricted ourselves to the window, which leads to an artificial inflation of the model water spectrum. We integrated the INS dry spectrum, and then from it determined 3.8% of the area, and obtained the HDA ice spectrum commensurate with that value. As can be seen, the model trapped water signal is negligible compared to the dry INS melanin spectrum.

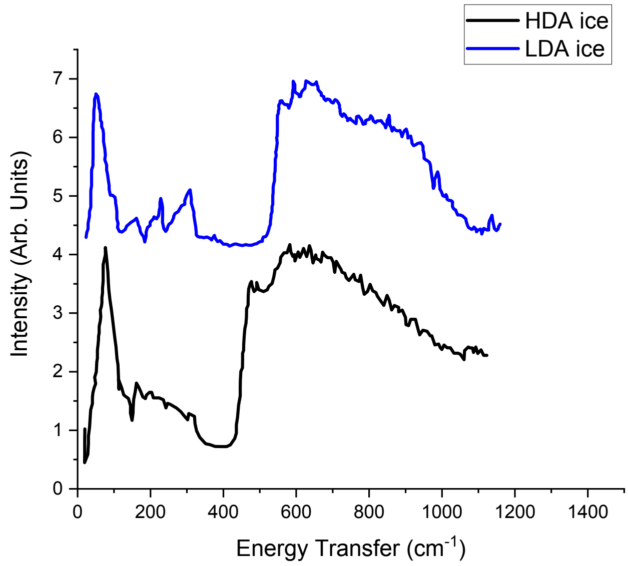

Figure S3. Depicted is data extracted from the literature for high density amorphous ice (HDA ice)[1] and low density amorphous ice (LDA ice)[2].

References

1. Kolesnikov, A. I.; Li, J.; Parker, S. F.; Eccleston, R. S.; Loong, C. K., Vibrational dynamics of amorphous ice. *Physical Review B* **1999,** *59* (5), 3569-3578.
2. Li, J., Inelastic neutron scattering studies of hydrogen bonding in ices. *The Journal of Chemical Physics* **1996,** *105* (16), 6733-6755.