Enhanced water-responsive energy density of regenerated silk fibroin via hydrophilic modification

Maheen K. Khan,[ab] Vignesh Athiyarath,[b] Darjan Podbevšek,[b] Yeojin Jung,[ab] Yuchen Zhang,[ab] and Xi Chen*[abc]

a. Advanced Science Research Center (ASRC) at the Graduate Center, City University of New York, 85 St Nicholas Terrace, New York, NY 10031, USA

b. Department of Chemical Engineering, The City College of New York, 160 Convent Avenue, New York, NY, 10031, USA

c. PhD Programs in Chemistry and Physics, The Graduate Center of the City University of New York, 365 Fifth Avenue, New York, NY, 10016, USA

Bombyx mori regenerated silk fibroin expands and contracts in response to changes in environmental relative humidity and could be used to develop high-performance actuators. We found that the water-responsive actuation energy density of regenerated silk fibroin is more than doubled by enhancing its hydrophilicity, through tyrosine residue modification, increasing from 1.6 MJ m^{-3} to 3.5 MJ m^{-3}. Diazonium coupling chemistry was used to functionalize silk fibroin's tyrosine residues with a charged sulfonate group. At higher degrees of modification, the material's bulk hydrophilicity increased, lowering its water contact angle, and raising its maximum water uptake. Fourier transform infrared spectroscopy revealed that while the secondary structure of regenerated silk fibroin remained largely unchanged, the structure of the adsorbed water shifted toward a higher proportion of mobile versus bound water. These findings suggest that water-responsive performance of regenerated silk fibroin depends on the properties of its confined water, and that enhanced hydrophilicity via tyrosine residue modification provides a promising strategy for developing high performance silk-based water-responsive actuators.