

Crosslinking 3D Assemblies of Nanoparticles into Mechanically Strong Aerogels by Surface-Initiated Free Radical Polymerization

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Supporting Information

Simulations of two nanoparticle bending showing that the Young's modulus of an aerogel monolith increases by accumulation of polymer on the skeletal framework

Typical base-catalyzed aerogels consist of 3D assemblies of secondary silica nanoparticles forming pearl-necklace-like structures. In those structures, secondary particles are connected through circular cross-sections, referred to as “necks.” It has been well known that under compression such structures will deform [S1], and the spring rate, a measure of microscopic stiffness of the pearl-necklace-like structure, is defined as the ratio of the applied force to the resulting deflection. Spring rate defined that way is also proportional to the bending stiffness of the macroscopic structure. Consequently, the Young’s modulus, which represents the stiffness of the monolithic aerogel, is proportional to the bending stiffness of the connected secondary nanoparticles. For the calculation of the bending stiffness, we conducted finite element analysis on two identical connected secondary nanoparticles (Figure 1S) using the ABAQUS/Standard software package.

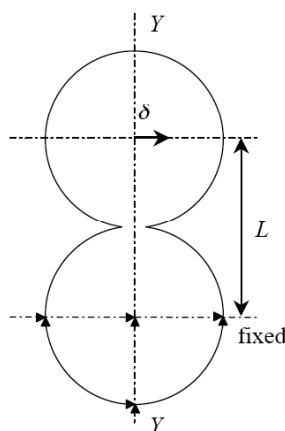


Figure 1S. A two-sphere model for two secondary particles connected to each other. The bottom half of the lower sphere is fixed. A displacement δ is applied at the center of the sphere at the top. “L” represents the center-to-center distance between the two spheres.

For calculation of the bending stiffness, the lower half of the bottom spherical particle was fixed and a small horizontal displacement, $\delta = 0.1 \text{ nm}$ was applied at the center of the top particle as indicated by the horizontal arrow at the center of the sphere at the top. The ratio of the resulting reaction force to the applied displacement gives the spring rate, which is proportional to the bending stiffness. For the native secondary silica nanoparticles (i.e., nanoparticles without a polymer coating) the radius R was set at 35 nm (based on the SEM data shown in the main article). The density of the silica spheres was set at $\rho_s = 1.852 \text{ g cm}^{-3}$ as determined by He pycnometry, and their Young’s modulus was taken as $E_s = 70 \text{ GPa}$. A similar analysis was also conducted with polymer nanoencapsulated silica secondary nanoparticles. For the polymer coating, the Young’s modulus was set at $E_s = 1 \text{ GPa}$ and the density at $\rho_{\text{polymer}} = 1.2 \text{ g cm}^{-3}$.

A parametric study was carried out by varying the neck diameter between the two nanoparticles. (The neck diameter is the diameter of the circular contact area between two identical secondary spherical nanoparticles.) Figure 2S shows an example of the normal stress distribution in the Y direction as a result of the applied displacement (for the specific example $L = 68 \text{ nm}$, and the coating thickness = 10 nm). It is noteworthy that

with the polymer coating applied, the size of the high stress zones, as indicated in Figure 2S(b), becomes smaller than that in the native silica, shown in Figure 2S(a).

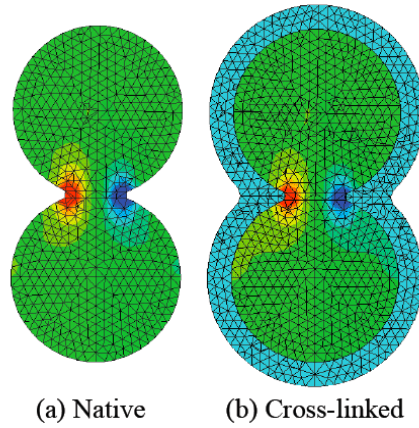


Figure 2S. Contours of the normal stresses in the Y direction (blue: compressive stress; red: tensile stress).

Figure 3S shows the ratio of the bending stiffness of two connected polymer encapsulated secondary nanoparticles to the bending stiffness of two connected native secondary silica nanoparticles, as a function of the dimensionless contact diameter, defined as the contact diameter divided by the secondary nanoparticle diameter. The

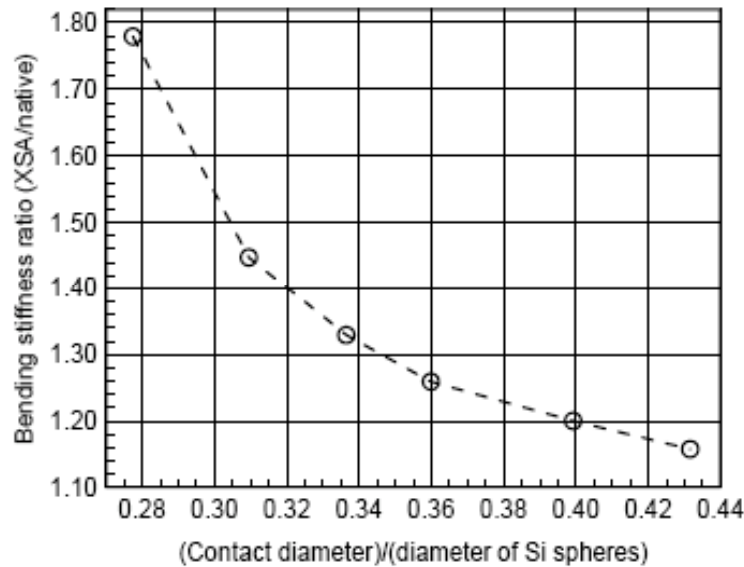


Figure 3S. Bending stiffness ratio of polymer nanoencapsulated secondary silica nanoparticles as a function of the dimensionless contact diameter of the secondary silica nanoparticles.

results show that for all contact diameters, the bending stiffness increases when the secondary nanoparticles are coated with a conformal polymer layer. When the contact

diameter is small, the bending stiffness of the two-spheres is small, so that the width increase of the necks due to the polymer nanoencapsulation will contribute to a large increase in bending stiffness. When the contact diameter of the native spheres is large, the bending stiffness of the two secondary silica nanoparticles is also relatively high. But yet, the polymer nanoencapsulation will still contribute to a large increase in the bending stiffness.

Finally, for a fixed contact diameter, the polymer layer thickness was varied to determine its effect on the bending stiffness and Young's modulus. It is emphasized that the Young's modulus increase is proportional to the increase of bending stiffness of crosslinked aerogels with slender necks. Figure 4S plots the bending stiffness ratio of the polymer encapsulated to native silica two-sphere model as a function of the density due to the increase of nanoencapsulated polymer thickness. The dimensionless contact diameters were fixed at 0.2774, 0.3364, and 0.3992, respectively, while the polymer thickness varies from 2 nm to 22 nm. At an initial dimensionless contact diameter of 0.2774, the bending stiffness (and also the Young's modulus) is anticipated to improve from 26% to 138%. At a dimensionless contact diameter of 0.3992, the stiffness increases from 3% to 35% when the polymer encapsulation thickness varies from 2 nm to 22 nm. A larger increase in stiffness is anticipated when the initial contact diameter of the native nanoparticles is small. This seems to be the case for our actual polymer crosslinked aerogel samples: the modulus of the native aerogels is relatively low, therefore the contact diameter should be relatively small; after polymer nanoencapsulation we observe a large increase in the Young's modulus implying that the contact diameter increases dramatically.

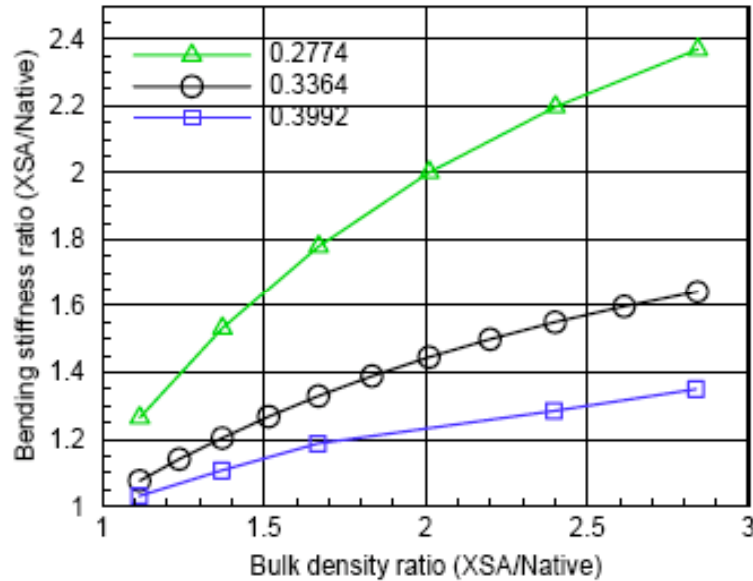


Figure 4S. Bending stiffness ratio of polymer encapsulated secondary silica nanoparticles to the neat silica nanoparticles for dimensionless contact diameters of 0.2774, 0.3364, and 0.3992, as a function of the increase in densities of cross-linked samples due to polymer nanoencapsulation.

Reference

- S1. Juvinall, R. C.; Marshek, K.M., *Fundamentals of Machine Component Design*, 3rd Edition, John Wiley & Sons, Inc., **2000**.