Electronic Supplementary Information for:

Understanding the curvature effect of silica nanoparticles on lysozyme adsorption orientation and conformation: a mesoscopic coarse-grained simulation study

Gaobo Yu, Jian Zhou*

School of Chemistry and Chemical Engineering, Guangdong Provincial Key Lab for Green

Chemical Product Technology, South China University of Technology, Guangzhou, 510640,
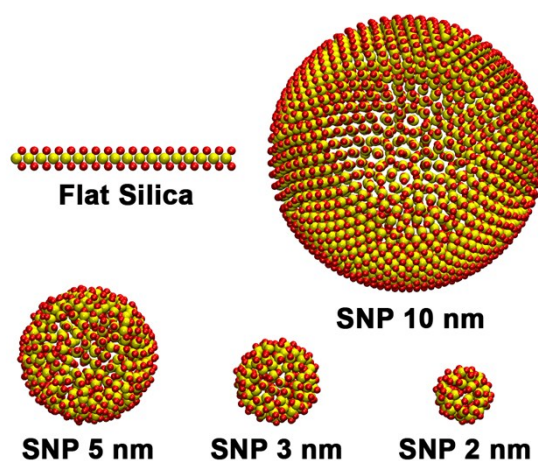
China. E-mail: jianzhou@scut.edu.cn

Fig. S1 Five different SNP (mica-like) surfaces in this work, which are all made up of silanol groups.

In order to investigate the effect of surface charge density (σ), we simulated the lysozyme adsorption on three σ (-0.021, -0.0105 and -0.0021 e/Å^2) of five mica-like SNPs, and analyzed the corresponding adsorption energies (U_{ele} and U_{vdW}) and orientation distribution of lysozyme adsorbed on different-sized SNPs, as shown in Figure S2 and Figure S3, respectively.
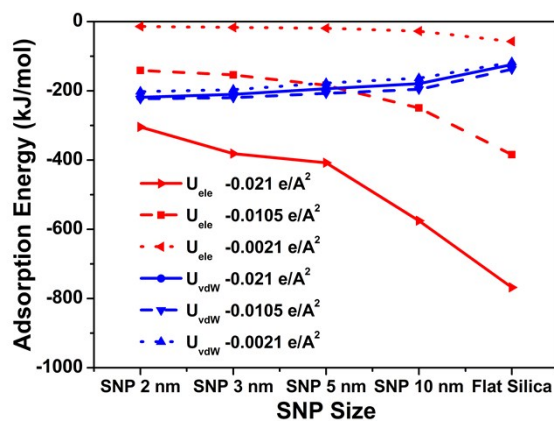

Fig. S2 Adsorption energies of lysozyme on different-sized SNPs (i.e., flat silica, SNP 10 nm, SNP 5 nm, SNP 3 nm and SNP 2 nm) at -0.021 e/Å^2 (solid), -0.0105Å^2 (dash) and -0.0021 e/Å^2 (dot). The red and blue lines are for properties of electrostatic interactions (U_{ele}) and van der Waals (vdW) interactions (U_{vdW}), respectively.

From Figure S2, we can see that the electrostatic interactions (U_{ele}) and vdW interactions (U_{vdW}) can be influenced by surface charge densities (-0.021, -0.0105 and -0.0021 e/Å^2) and SNP diameters (flat silica, SNP 10 nm, SNP 5 nm, SNP 3 nm and SNP 2 nm). As the surface charge density decreases, the U_{ele} between the adsorbed lysozyme and SNPs becomes weaker and increases slower, while the corresponding U_{vdW} do not have an obvious change and the values are maintained at around -200 kJ/mol. As we know, the lysozyme adsorption on silica surfaces is driven by electrostatic attractions,[14, 21, 47] however, it should be noted that hydrophobic interactions in the BMW-MARTINI force field are still overestimated in contrast to the experimental observations.[36] Because of this, we can explain that the lysozyme adsorption process is driven by electrostatic interactions at a stronger σ (-0.021 e/Å^2) and the vdW interactions dominate lysozyme adsorption at a lower σ (-0.0021 e/Å^2), as displayed in Figure S2. While for the intermediate σ (-0.0105 e/Å^2), U_{ele} can dominate the lysozyme to adsorb onto a larger SNP (i.e., a smaller curvature), but it is driven by U_{vdW} at a smaller SNP (about SNP

diameter < 5 nm). That is to say, as the surface curvature of SNPs increases, the domination interaction can be turned from U_{ele} to U_{vdW}.
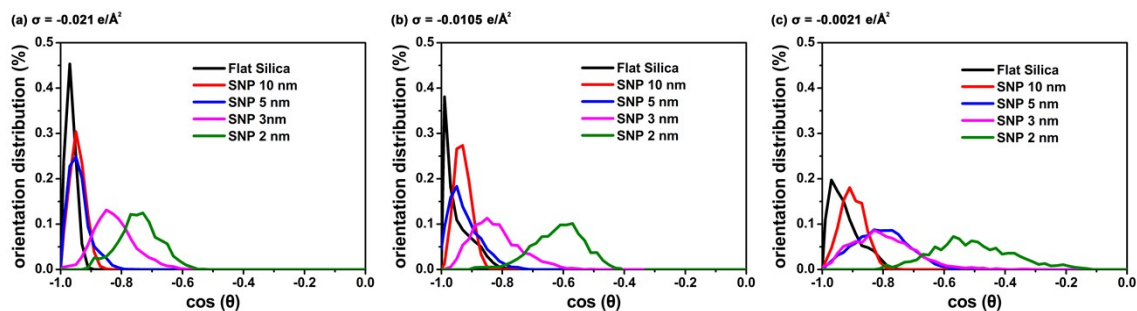

Fig. S3 Orientation distribution of lysozyme adsorbed on different-sized SNPs (i.e., flat silica, SNP 10 nm, SNP 5 nm, SNP 3 nm and SNP 2 nm) at -0.021 e/Å^2 (a), -0.0105Å^2 (b) and -0.0021 e/Å^2 (c). The black, red, blue, magenta and green lines are for properties of flat silica, SNP-10, SNP-5, SNP-3 and SNP-2 systems, respectively.

Figure S3 shows the effect of surface charge densities (-0.021, -0.0105 and -0.0021 e/Å^2) on the orientation distribution of lysozyme adsorbed on different-sized SNPs (i.e., flat silica, SNP 10 nm, SNP 5 nm, SNP 3 nm and SNP 2 nm). From Figure S3, at each σ, it can be found that lysozyme tends to adsorb with a "bottom end-on" orientation (cos θ < −0.60)[30-31, 48] and reach a narrower orientation distribution on a larger SNP (i.e., a lower curvature surface) which is consistent with the discussion in the main text. However, as the σ decreases, we can figure out a clear tendency that all orientation distributions of lysozyme adsorbed on different-sized SNPs become obviously wider, meanwhile, the preferred orientation of adsorbed lysozyme upon SNPs turns from the "bottom end-on" orientation to the "side-on" orientation (cos θ < −0.60), as shown in Figure S3. Therefore, at a stronger σ, the adsorbed lysozyme upon SNPs can be stable with a concentrated orientation distribution. As a conclusion, a lower surface charge density can result in a wider orientation distribution of lysozyme upon SNPs, and it is unfavorable to get the controlled protein adsorption.
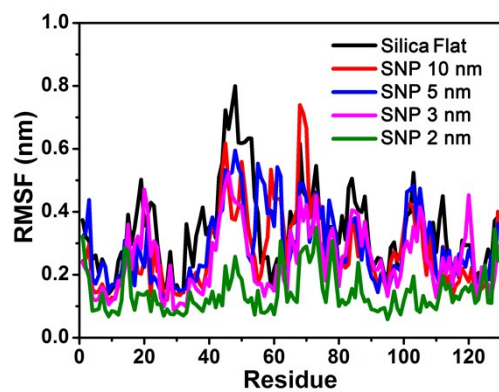
Fig. S4 The RMSF of lysozyme adsorbed on different-sized SNPs (i.e., flat silica, SNP 10 nm, SNP 5 nm, SNP 3 nm, and SNP 2 nm) at 0.01 M.