Understanding how the nanoscale surface roughness contributes to the efficiency of the target-ligand reaction is important for the improvement of biomolecular sensing. Hence, we have examined the contribution of nanoscale convex/concave structures for the DNA reactions on a solid surface. Efficiency of DNA immobilization on convex surfaces has been studied using gold nanoparticles in diameter range from 10 to 50 nm [1]. Contribution of a concave structure on DNA hybridization efficiency was also examined using an inner surface of strictly size-controlled metal hemisphere nanoparticles having a spherical cup shape (nanocups) in diameter range from 140 to 800 nm [2]. In the convex experiments, thiolated DNAs were immobilized on the Au nanoparticle surfaces and the immobilized densities were evaluated with UV-vis spectra measurements (Fig.1a). In the concave experiments, thiolated DNAs were immobilized on only the inner Au layer of the fabricated nanocup, hybridized with complementary DNA-attached 20 nm Au nanocolloids, and the number of the hybridized Au nanocolloids was counted by field emission scanning electron microscopy (Fig.1b). In results, the density of immobilized DNAs on the convex surfaces increased depending on the decrease of gold nanoparticle diameter up to 130 times thicker than that on a flat surface (Fig.2a). The DNA hybridization density on concave surfaces increased gradually as the cup size decreased and reached to 394 μm⁻² on a 140 nm cup, 0.88 times of a flat surface, which indicates about twice increase of the hybridization efficiency in a projection area by the fabrication of small concave structures (Fig.2b). The local density of attached Au nanocolloids within the central 25% at the bottom of the 800 nm nanocups was 444 μm⁻², which was closer to that on a flat surface, and the tendency was common for all diameters of cups, indicating that the size dependency of DNA hybridization efficiency on the concave structures were mostly affected by the lower efficiency of side wall hybridization. These results suggest fabrications of both convex and concave nanostructures with suitable size contribute to the improvement of DNA reaction efficiency on a solid substrate.

References

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Fig. 1: Schematic images of the convex (a) and concave (b) experiments. (a) Thiolated DNAs (SH-DNAs) were immobilized on convex Au nanoparticles, and the densities were estimated by measuring UV-vis spectra of SH-DNAs. (b) Target DNAs were immobilized on inner surfaces of nanocups, and hybridized with complementary Au nanocolloid probes.

Fig. 2: Dependences of DNA reaction efficiencies on convex and concave surfaces. (a) Relationship between maximum number densities of SH-DNA immobilized on gold nanoparticles and diameters of particles. (b) Relationship between nanocup diameter and projection density of Au probes hybridized with target DNAs on nanocups. $D_{FL}$: the density on a flat surface.