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Determination of counterion distribution around DNA coated nanoparticles (DNA-AuNP) by small angle X-ray scattering $(SAXS)^1$ SUMIT KEWALRAMANI, CHEUKYUI LEUNG, JOS ZWANIKKEN, ROBERT MACFARLANE, MONICA OLVERA DE LA CRUZ, CHAD MIRKIN, MICHAEL BEDZYK, Northwestern University — The interactions between DNA-Au nanoparticles (AuNP) and the surrounding cationic counterion layer critically determine the melting behavior of DNA duplexes on isolated DNA-AuNP and in crystalline assemblies of DNA-AuNPs. Also, the counterion layer is speculated to cause the enhanced stability of DNA-AuNPs against nuclease degradation, as compared to isolated DNAs. This makes DNA-AuNPs attractive for bio-diagnostic and therapeutic applications. To probe the ion cloud around DNA-AuNPs, we apply the isomorphous heavy ion replacement SAXS approach. Specifically, the SAXS measurements are carried out on DNA-AuNPS dispersed in a series of solutions that contain different monovalent ions (Na⁺, K⁺, Rb⁺ or Cs⁺). The combined analysis of all four intensity profiles makes it possible to extract, in a model-independent manner, the cation profile contribution $I_{cat}(q)$ from the SAXS intensity that is averaged over the polydispersity of AuNPs. The $I_{cat}(q)$ is found to be consistent with the cation dependent SAXS intensities that are derived on the basis of classical DFT calculations for the counterion distribution around DNA-AuNPs.

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