Abstract

Atomistic molecular dynamics (MD) simulations of bulk aqueous solution of NaCl and functionalized gold nanoparticles (GNPs) in aqueous solution were conducted at 300 K. Bulk NaCl solution systems of different concentration have been studied using various force field parameter sets to investigate aggregation of ions and to choose suitable force field parameters for ions. Gold nanoparticles functionalized with linear and branched hydrocarbon chains with different grafting density (d_f=1, 2/3 and 1/3), chain length ($(CH_2)_l$, l=5, 11, 17 and 23), position of the branching point (4th, 8th and 12th carbon) and terminal groups (CH_3, COO^- and NH_3^+) were modeled to investigate various phenomena at the microscopic level. The solution of a functionalized GNP with ionic terminations was neutralized by excess Na^+ and Cl^- ions. Focus has been given to the penetration depth of water and ions into the diffuse shell of alkanethiols as a function of grafting density, functionalization and chain length. Special focus has been given to the relative accessibility of the gold core by water in dependence of grafting density, chain length and chain shape. The orientation of water molecules inside the hydrocarbon chain environment (from the surface of the gold core to the terminal groups) and near the terminal groups has been studied in detail. Hydrogen bonds between water and polar terminal groups have also been studied. Special attention has been given to the solvent accessible surface area (SASA) of functionalized GNPs, and the coating asymmetry and ways to prevent it.

It is observed that the penetration of water and ions into the hydration shell of alkanethiols increases with decreasing grafting density, irrespective of the terminal group of the hydrocarbon chains. High grafting densities lead to more extended hydrocarbon chains which behave more rigidly. The solvent accessible surface area (SASA) is dependent on the chain length and the terminal group. SASA (per unit chain length) of COO^- group terminated GNPs with chain length (C_l) 5 is the highest among all GNP coated with linear chains. Water molecules orient near the surface of the gold core pointing one hydrogen

towards the center of the gold core irrespective of chain length, terminal group and grafting density. Water molecules cannot access the surface of the gold core of a branched chain GNP as easily as in the linear chain GNP. Branched chains protect the core better than the corresponding linear chains. Among all studied systems, nonpolar group terminated branched chains with chain length 17 and branched at the 4th carbon atom provide the best protection to the nanoparticle core. Coating asymmetry is generally more prominent for longer chains (>11), and the asymmetry can be prevented by introducing branching points.