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Effects of functional groups and ionization on the structure of alkanethiol-coated gold nanoparticles

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Motivation

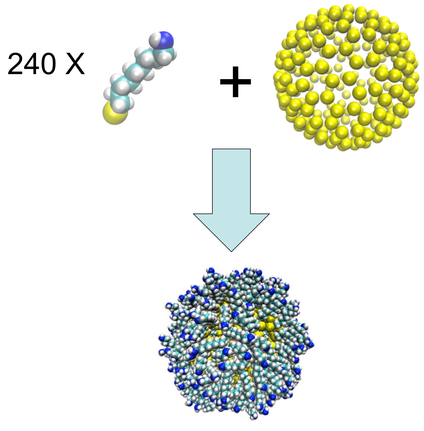
• Self-assembly of nanoparticles is of interest for tailored nanocomposites, high-performance materials, etc.

•Earlier work showed spontaneous asymmetry in nanoparticle coating, even for uniform grafting densities (Lane and Grest, PRL 110, 235501 (2010))

• Coating structure can have a significant effect on NP interactions, solubility and assembly
→ **how is coating structure affected by:**
• **End group**
• **Solvent**
• **Charge/pH**
• **Ccounterion type**
• **Chain length**

Methods

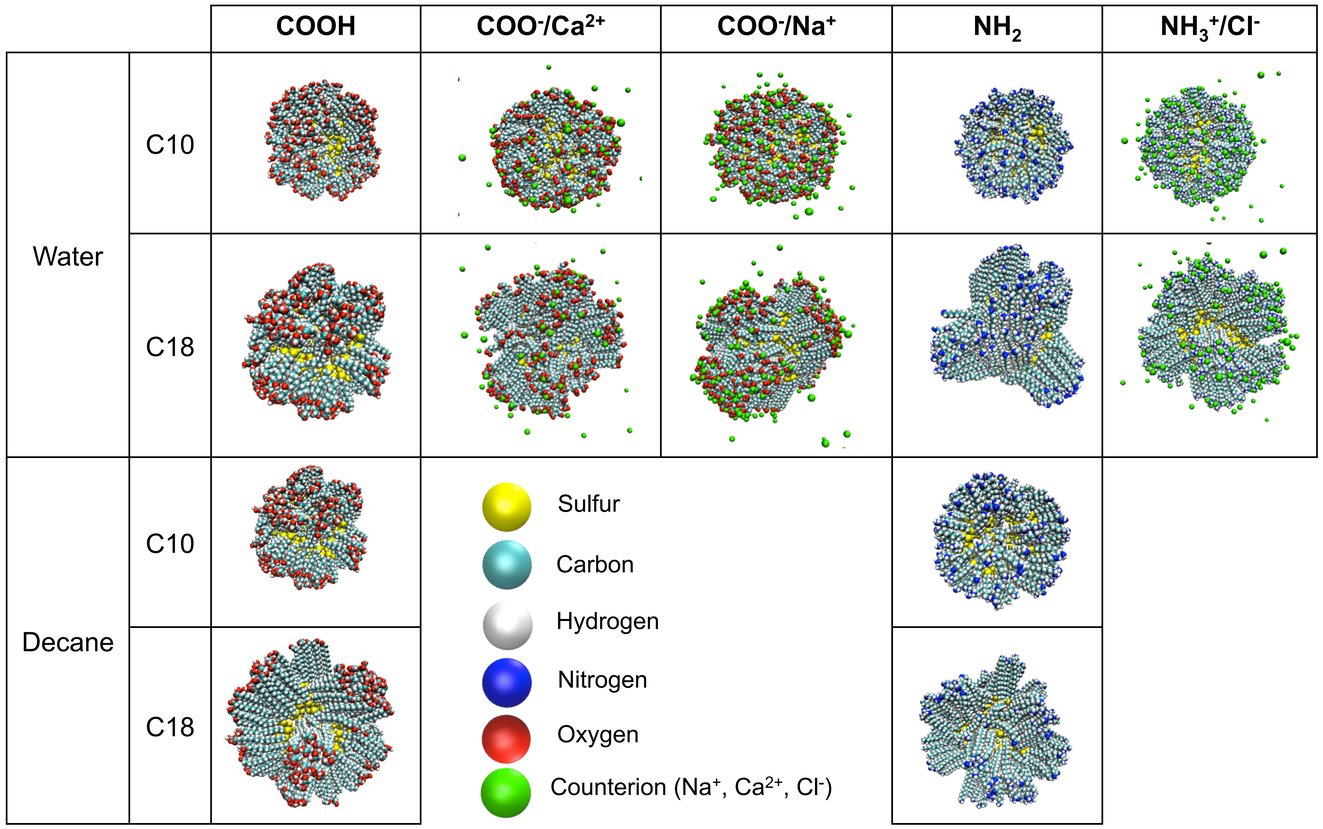
System construction:
- Alkanethiol chains grafted on C-240 fullerene structure
- Sulfur atoms fixed (LAMMPS *fix rigid* command) at C-240 carbon positions, gold atoms omitted
- Large sphere placed at center of NP to keep solvent out
- **Equivalent to 4 nm gold core**



Equilibration:
- For charged systems, counterions added near ionic groups
- All systems equilibrated for 10^6 steps in implicit solvent with appropriate dielectric constant
- Solvated in water (TIP4P) or decane cubic boxes with 160Å side length

→ Total system size ~400,000 atoms

Simulations:
- OPLS/AA force field, LAMMPS MD code
- Short NPT runs followed by NVT production runs
- PPPM dispersion sum used for van der Waals interactions (In 't Veld et al, JCP 127, 144711 (2007)).



Conclusions

- Short chain length (C10) in most cases leads to uniform, symmetric coating
- Long chain length (C18) leads to bundling and nonuniform coating structures
- Ionization tends to stabilize asymmetries in water → higher solubility, less tendency for aggregation
- Ions largely condense on functional groups, facilitate water penetration

Future work

- Vary ionic strength → add additional background salt
- For cases of interest, simulate two or more nanoparticles to study interparticle forces, aggregation in bulk and at surfaces
- Vary nanoparticle core size
- Include gold core with various grafting densities and configurations

Acknowledgements

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Selected density profiles (all water):