Abstract

We investigated the interaction of TiO_2 and CeO_2 nanoparticles with various charged species in suspension, using a combination of experimental, computational, and theoretical approaches.

Initially, we focused on the effect of stereochemistry and the size of the hydrophobic group in the repeating unit of poly(α-alkyl carboxylic acids) on the properties of nanoparticle suspensions. Zeta potential measurements and dynamic light scattering (DLS) showed that the addition of polyacids decreases the zeta potential in the pH range where the acids are partially or fully deprotonated. We used poly(methacrylic acid) in atactic (aPMA) and isotactic (iPMA) forms and compared their influence on nanoparticle aggregation and zeta potential. Differences between the two forms were small, with iPMA causing a slightly larger shift of the isoelectric point (ΔpH_{IEP}) for both TiO_2 and CeO_2.

To examine the effect of hydrophobicity, we used poly(acrylic acid) (PAA), PMA, and poly(ethacrylic acid) (PEA). The addition of PAA caused the largest shift in the pH_{IEP} of TiO_2 nanoparticles ($\Delta pH_{IEP} \approx 3.5$), followed by PMA ($\Delta pH_{IEP} \approx 2.8$), and PEA ($\Delta pH_{IEP} \approx 1$). DLS measurements confirmed increased aggregation close to the pH_{IEP}, indicating reduced suspension stability. Similar trends were observed for interactions between polyacids and CeO_2.

Molecular dynamics (MD) and Monte Carlo simulations revealed how polymers bind to nanoparticle surfaces depending on surface charge and acid ionization degree. Umbrella sampling simulations enabled estimation of free energies of adsorption of polyacids on TiO_2. More hydrophobic polyacids have higher pK_a values, are less charged at a given pH, and form fewer hydrogen bonds with the surface, resulting in weaker adsorption and a smaller impact on suspension properties.

We also studied interactions of divalent cations with TiO_2 and CeO_2 nanoparticles. Nanoparticles with various geometries (nanospheres, nanoplates, nanowires) were synthesized and characterized using transmission/scanning electron microscopy (TEM, SEM), powder X-ray diffraction (XRD), and the Brunauer–Emmett–Teller (BET) method. TEM measurements and MD simulations showed that cations preferentially bind to the edges of TiO_2 nanoplates, likely due to a higher concentration of surface defects at the edges. Smaller spherical nanoparticles exhibited higher adsorption capacity than larger spherical nanoparticles, due to their larger specific surface area.

Heavy metal adsorption on TiO_2 nanoplates was analyzed using Pb^{2+} as model ions. Despite both the nanoparticles and ions carrying a positive charge at pH 3–5, adsorption still occurred. A particularly interesting observation was the formation of PbO nanoclusters under the electron beam in TEM, which grew and migrated onto the microscope's carbon grid with prolonged irradiation.

Due to the limited solubility of multivalent heavy metal ions over a wide pH range, we further investigated the interaction of nanoparticles with alkaline earth metal cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}). TEM, X-ray photoelectron spectroscopy (XPS), zeta potential measurements, and simulations (MD, *ab initio* MD (AIMD)) showed that cations with higher molar mass adsorb more favorably onto TiO_2 nanoparticles and more strongly affect their zeta potential. The presence of monovalent ions reduced the adsorption of divalent cations, as confirmed by XPS and MD simulations. AIMD simulations were also used to examine the interaction of alkaline earth cations with CeO_2 nanoparticles, showing that more strongly hydrated and smaller cations bind farther away from the surface and are coordinated by fewer surface oxygen atoms. We also developed a theoretical model to describe the nanoparticle surface in contact with an ionic solution based on density functional theory.