Polymer and Colloid Highlights

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Formulation of Multifunctional Material Dispersions

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Inorganic nanoparticles of lamellar structure have been in the focus of investigations by numerous research groups due to their growing applications, *e.g.* as ion exchangers, molecular sieves, drug carriers, selective catalysts or building blocks in novel materials. In addition, many of them are potential sources of unilamellar nanosheets which can be obtained by liquid exfoliation from the layered forms. In several applications, these nanomaterials are used in dispersions where aggregation of the particles is an important issue. For instance in catalysis, stable dispersions are required during the catalytic run, however, the catalysts can be removed by aggregation and subsequent sedimentation after the reaction terminated.

Despite the substantial importance of the aggregation in dispersions, there is a lack of comprehensive studies dealing with stability of layered inorganic materials in aqueous medium. Therefore, we have recently focused on preparation and dispersion characteristics of lamellar structures such as layered double hydroxides,[1] titanates[2] and graphite oxide.[3] They are multifunctional materials with applications ranging from the preparation of solar cells through sensor development to catalysis. One of the most promising ways to tune the aggregation processes in aqueous dispersions of these charged nanomaterials is to add oppositely charged polyelectrolytes to the samples.[4] As an example, surface charge properties and aggregation processes were probed in aqueous dispersion of titanate nanowires (TiONWs) by electrophoretic mobility (EPM) and dynamic light scattering (DLS).

The TiONWs possess net negative charge at alkaline pH as revealed by EPM measurements (Fig. 1). Positively charged poly(diallyldimethyl ammonium) chloride (PDADMAC) molecules adsorb on the oppositely charged TiONW surfaces leading to charge neutralization and subsequent charge reversal at higher polyelectrolyte doses until the electrophoretic mobility values reach a plateau which corresponds to the maximum amount of adsorbed PDADMAC on the surface. Further added polyelectrolyte remains dissolved in the bulk.

Time-resolved DLS has been proven as a powerful tool to follow aggregation in dispersions.[5] Our results showed that the TiONW samples are unstable, *i.e.* the nanowires aggregate rapidly close to the charge neutralization point (Fig. 1) indicated by stability ratio values close to unity. The overall charge of the
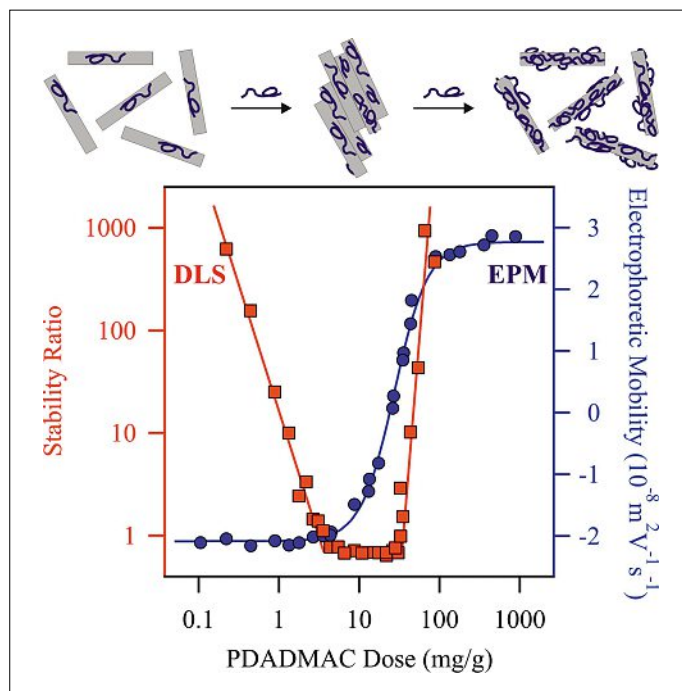

Fig. 1. Top: schematic representation of stable and aggregating TiONWs in the presence of PDADMAC. Bottom: stability ratios (squares, DLS) and electrophoretic mobilities (spheres, EPM) of TiONWs as a function of the dose (mg polyelectrolyte normalized to 1 g TiONW) of PDADMAC at pH 9.0 and 1.0 mM ionic strength adjusted by KCl.

particles is zero at this dose, therefore, the aggregation is driven by attractive, mainly van der Waals interactions. The stability ratios increase below and above this polyelectrolyte dose, since the TiONWs form stable dispersions at low and high PDADMAC doses where the particles possess charge due to the repulsion between the electrostatic double layers around the nanowires. This behaviour is in good qualitative agreement with the classical theory developed by Derjaguin, Landau, Verwey and Overbeek.

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