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Synthesis and Self-Assembly of Titania Nanoplates and Their Encapsulation within a Polystyrene Shell via Photocatalytic Surface-Initiated Polymerization

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Natural composite materials such as nacre have gained significant interest due to their exceptional mechanical properties, including high hardness and toughness.[1] Promising bio-inspired materials are inorganic nanoplates stabilized by a soft layer of organic ligands. These nanoplates can be self-assembled into hierarchically ordered structures, resembling the architecture of tough biocomposites, such as nacre. Here, we explore the synthesis of titania nanoplates (TNPs), their self-assembly into supraparticles via an emulsion-based bottom-up approach, and the subsequent encapsulation within a polymer shell.

Firstly, we introduce new findings regarding the synthesis of oleyl amine-stabilized TNPs using an adapted seeded-growth approach.[2] Parameters allowing the tunability of the edge length and the thickness of the TNPs will be presented. The TNPs can then be assembled into supraparticles via emulsion-induced self-assembly,[3] resulting in the formation of three-dimensional spherical supraparticles with sizes of approximately 100 –400 nm. Subsequent encapsulation within a polymer shell is expected to enhance the mechanical properties of these supraparticles. We developed a novel photocatalytic surface-initiated radical polymerization exploiting the inherent photocatalytic activity of the TNPs. The polymer shell thickness can be tuned by varying the UV light exposure time. An interesting finding is the high degree of order of the individual TNPs within the encapsulated supraparticles, studied via synchrotron small-angle X-ray scattering. This method was also expanded to the assembly and encapsulation of supraparticles from differently shaped titania nanoparticles (rods, dots).

Further, in order to fabricate a hierarchically ordered material with multiple hierarchical levels, we intend to crosslink the supraparticles. To this end, the polystyrene shell of the TNP-based supraparticles was surface-modified using styrene-based functional monomers as a proof of concept. We expect that the encapsulated supraparticles and their higher-level assemblies provide new insights into properties of hierarchically ordered artificial nanocomposites.

[1] M. Eder et al., Science 2018, 362, 543-547.

[2] T. R. Gordon et al., J. Am. Chem. Soc. 2012, 134, 6751-6761.

[3] F. Bai et al., Angew. Chem. Int. Ed. 2007, 46, 6650-6653.

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