doi:10.2533/chimia.2013.829



Polymer and Colloid Highlights

Division of Polymers, Colloids and Interfaces

A Division of the Swiss Chemical Society

Asymmetrically Functionalized Polymeric Dumbbells

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Keywords: Asymmetric functionalization · Dumbbells · Polymer colloids · Janus nanoparticles

Nanoparticles have been the topic of an enormous number of investigations in the last fifteen years. Their wide variety of properties has spawned numerous applications in material science and engineering, in biomedicine, and other technological fields. At the same time, nanoparticles have also been used in soft matter physics by scientists interested in understanding their properties and behaviour from a more fundamental point of view.

One attractive feature of nanoparticles is the possibility to be used as building blocks for the construction of complex materials. Due to their small size, sometimes comparable to that of proteins, nanoparticles can undergo self-assembly. However, spherical isotropic nanoparticles do not offer a sufficient variety of structures accessible by self-assembly. Therefore, scientists have been working on designing nanoparticles with progressively more complex shape and functionalities, (loosely) imitating molecular and protein systems.^[1]

Asymmetric Janus nanoparticles are the simplest case of anisotropic particles. [2] Different ingenious strategies have been devised to prepare them. Our group has recently summarized the most important methods in a review. [1] Almost all the methods developed so far suffer from excessive complexity and usually lead to the production of small amounts of material. An on-going project in our group is taking advantage of recent developments on the preparation of micrometer-sized non-spherical particles to develop nanosized asymmetrically functionalized polymeric dumbbells. [3]

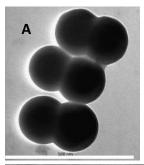
The methodology used starts from uniformly sized polystyrene nanoparticles prepared by means of emulsion polymerization. These particles are then subject to two subsequent swellingpolymerization steps. The first one is performed with styrene and TMPS, a polymerizable silane that renders the surface of the nanoparticles vitrous. Upon a second swelling with monomer and polymerization, the monomer is expelled from the particle and polymerizes into a second lobe, giving rise to a dumbbell. This synthetic procedure presents several advantages. First of all, it can be easily upscaled, since the starting point is simple polystyrene colloids. Second, the particles are naturally asymmetrically functionalized, since only the first lobe (belonging to the seed) is covered by silane groups, which allows one to selectively attach molecules using well-developed silane chemistry. Fig. 1 shows a few examples of dumbbells covering a broad range of sizes, from a few hundred nanometers to less than one hundred nanometers. In order to demonstrate their asymmetric functionalization, one lobe of the particles has been functionalized with a silane bearing a positive charge, thus leading to dipolar particles, since one of the lobes remains negatively charged. By mixing them with negatively charged nanoparticles, one can observe from Fig. 1 how only one hemisphere becomes selectively covered by the small nanoparticles. Our group is currently exploring more advanced functionalization patterns of these dumbbells.

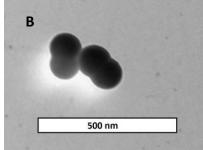
Acknowledgements

This work has been financially supported by the Swiss National Science Foundation (SNF) with grant number PP00P2133597/1.

Received: September 28, 2013

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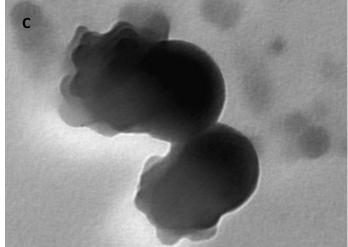


Fig. 1. TEM images of polymeric dumbbells with different sized (a) 400 nm, (b) 100 nm, (c) 400 nm dumbbells with one lobe functionalized with positive charges, while the other lobe bears negative charges. The lobe with positive charges has been coated by negatively charged polystyrene nanolatex particles.

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