Janus Dumbbells: A flexible template for colloidal chemistry

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Abstract

The recent development of nanotechnology led to an increased amount of scientist working on nanoparticles worldwide. However, most of the studies are focusing on spherical isotropic nanoparticles, which are the easier to prepare. We used a described procedure [1,2] to prepare shape-anisotropic, asymmetrically-functionalized dumbbells nanoparticles covering a good range of size and aspect ratio. We then used the presence of silane groups on one hemisphere of the dumbbells only to selectively functionalize the nanoparticles [1], creating different types of hybrids.

The hydrolysis and condensation of a silane precursor covered one bulb with a thin layer of silica. Upon removal of the polymeric template, we prepared silica nanobowls bearing a well-defined opening in their shell. Calcination of the template at 550 °C led to purely hydrophilic silica nanobowls, while the dissolution of the template in THF gave birth to Janus nanobowls having a thin polymer layer on their inner side. We proved the different reactivity of the inside and outside surfaces by selectively binding oppositely-charged silica nanoparticles. They selectively adhered outside the Janus nanobowls, while they were present both inside and outside the nanobowls prepared by calcination [2].

Magnetic anisotropic nanoparticles were prepared either by attaching negatively charged Superparamagnetic Iron Oxide Nanoparticles (SPIONS) on dipolar dumbbells, or by preparing dumbbells with commercially available magnetic beads as seed nanoparticles. In both cases, we obtained asymmetric dumbbells with magnetic nanoparticles only on one side. We then studied the impact of shape-anisotropy on the directed self-assembly of these nanoparticles in the presence of an external magnetic field. We showed that it is possible to change the types of chain-like structures obtained by tuning the aspect ratio of the dumbbells.

Using the same dipolar dumbbells, we prepared Janus nanomotors by selectively attaching citrate-coated platinum nanocrystals on one hemisphere. The resulting nanoparticles can undergo self-propulsion when place in a solution containing hydrogen peroxide fuel. The catalytic decomposition of the fuel is only taking place on one side of the dumbbells, generating a gradient which leads to effective propulsion.

Finally, we made the dumbbells temperature-responsive by growing some poly-N-isopropylacrylamide brushes on one hemisphere. We first attached an initiator to the dumbbells by silane chemistry, and then used a surface initiated atom transfer radical polymerization (ATRP) to grow the PNIPAM chains. This renders the dumbbells hydrophilic below 32 °C (PNIPAM LCST), and amphiphilic above. We showed that it is possible to induce aggregation between the dumbbells by hydrophobic interactions above LCST. These stimuli-responsive nanoparticles have also been used to prepare multiple Pickering emulsions.

References

[1] F. Guignard, M. Lattuada, Chimia (Polymer and Colloid Highlights), 67, 829 (2013)

[2] F. Guignard, M. Lattuada, Langmuir, 2015, 31 (16), 4635–4643