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Patchy Polymer Micelles and Hybrids: Self-Assembly, Characterization and Utilization in Catalysis

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Block copolymer self-assembly in solution opens the way to well-defined compartmentalized nanostructures with emerging applications in drug delivery, optoelectronic devices or as template for metal nanoparticles (NPs). Recently, semi-crystalline block copolymers gained increasing attention, since crystallization-driven self-assembly (CDSA) gives access to well-defined worm-like crystalline-core micelle (wCCMs) with narrow length distributions and high aspect ratios. We have shown that CDSA of polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) (SEM) triblock terpolymers yields in well-defined wCCMs with a nanometre-sized patchy corona, consisting of polystyrene (PS) and poly(methyl methacrylate) (PMMA) patches. Here, transmission electron microscopy (TEM) on selectively stained wCCMs is the key method to prove the patchy structure of the corona.[1]

Functional wCCMs with tailor-made, functional corona patches were prepared by an efficient post-polymerization modification of the PMMA block via amidation with different *N*,*N*-dialkylethylene-diamines and further on employed as templates for the incorporation of metal and metal oxide NPs.[2] Different strategies, like ligand exchange or co-precipitation of polymer stabilised NPs with one surface patch, were developed that allow the incorporation of NPs in specific regions of the patchy wCCM corona. Moreover, the regio-selective loading of only one corona patch with nanometer-sized NPs can be harnessed as a facile method to selectively stain corona patches for TEM studies.

In this hybrids the NPs are well-separated and arranged in defined distances as controlled by the patchy structure of the corona, opening interesting applications in heterogeneous catalysis.[3,4] To meet the demands of an efficient heterogeneous catalyst, i.e., effective prevention of NP agglomeration and high reusability, we combined coaxial electrospinning (top-down) with CDSA (bottom-up) to prepare patchy nonwovens with functional, nanometer-sized patches at the nonwoven´s surface. Loading of these patchy nonwovens with gold NPs leads to an efficient and recyclable catalyst for the mild alcoholysis of dimethylphenylsilane. These patchy nonwovens are broadly applicable templates, as the chemistry and size of the patches can be tailored to meet the requirements for the incorporation of a specific NP type.

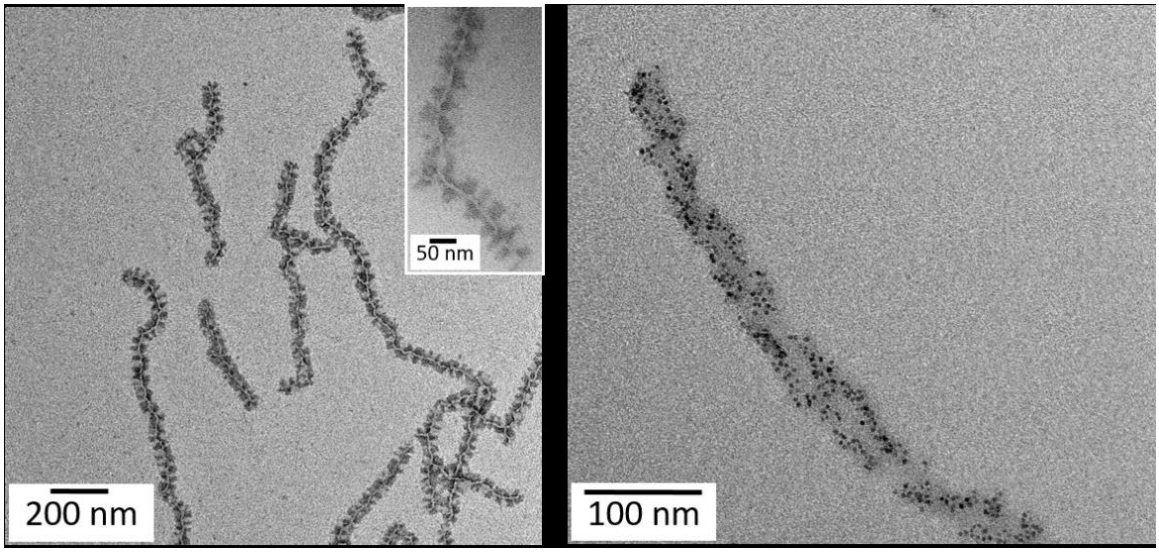

Figure 1. Left: Patchy functional wCCMs, Right: Patchy wCCMs/ZnO NP hybrid

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