Nanofabrication via self-assembly of hybrid materials into well-defined architectures is essential for the next generation of miniaturized devices. This paper describes our group’s achievements towards the development of multifunctional nanostructures via self-assembly of hybrid systems based on the block copolymer PS-b-P4VP and inorganic nanoparticles (NPs) into 0D, 1D, 2D and complex 3D periodic nanostructures. The morphologies of these architectures are adjusted to gain functions via structural control at different dimensions.

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Natural hybrid materials often possess complex, hierarchical architectures at sizes ranging from a few nanometers to several micro- to millimeters. Their collective properties are determined by the combination of both the structure and composition on each length scale. Hierarchical architectures of organic-inorganic hybrid materials are explicitly generated at different scales and with varying degrees of complexity by self-assembly of the soft source materials. Inspired by Nature, this concept can provide a simple, flexible and economical approach to fabricate multifunctional nanostructures for technological applications via self-assembly of functional hybrid materials. However, understanding the fundamental principles of self-assembled soft matter systems and applying this approach to a variety of combinations of organic-inorganic materials is a major challenge in current materials science and engineering.

The ‘bottom-up’ concept has recently gained significant technological importance due the possibility to fabricate nanostructures in a fast, simple, parallel and flexible manner via self-assembly of small building blocks. In this respect, block copolymers are particularly interesting due to their ability to self-assemble into thermodynamically highly stable microphase-separated domains with precisely controlled shapes and domain sizes. By controlling the composition, molecular weight and architectures of the block copolymer macromolecules, a range of 1D, 2D and 3D periodic mesostructures (10-100 nm) can be formed. The idea of combining this sophisticated performance of block copolymers with the functionality of inorganic nanoparticles has commenced as an alternative way to fabricate multifunctional nanostructures of hybrid materials. Previously, the direct incorporation of nanoparticles into the block copolymer matrix was found to disrupt the long-range order of the microphase-separated domains.
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into isotropic structures. Within this framework, a simple approach is developed to fabricate nanostructured hybrid materials with precisely controlled structure of the inorganic components within the polymeric matrix.

The concept is realized by incorporating inorganic nanoparticles selectively within one block of copolymers and directing the self-assembly of the hybrid material into the desired morphology (Fig. 1). These artificial hybrid materials combine not only the properties of their constituents but often have entirely new characteristics depending on the spatial and size distribution of their constituents. Therefore, it is important not only to design and fabricate accurately controlled morphologies, but also to tune the characteristic length-scale of the nanostructures. We will restrict our discussion to one particular diblock copolymer system, polystyrene-b-polyvinyl pyridine (PS-b-P4VP), in combination with different inorganic components including noble metals (Au, Ag, Pt, Pd), semiconductors (CdSe, TiO₂) and magnetic materials (Co, Ni, FeCo and Fe₃O₄). The diblock copolymer serves as a structure-directing agent for the functional (inorganic) component and tuning the self-assembly process enables the fabrication of multifunctional nanostructures at different dimensions and length scales (Fig. 1).

Potential applications of functional hybrid materials

Nanofabrication via self-assembly of block copolymer templated inorganic nanomaterials enables the fabrication of multifunctional nanostructures with significantly enhanced mechanical, optical, electronic and magnetic properties. There is a widespread field of applications for these materials ranging from electronic devices, optics and photonics to biosensors, drug delivery, advanced catalysis and energy conversion/storage. The targeted types of application mainly depend on the properties and functionality of the hybrid materials, which are determined by their chemical composition as well as morphological and structural parameters (Fig. 1). Applications in fields such as catalysis, optics, electronics and hydrogen storage are available, if nanostructures are fabricated via block-copolymer directed self-assembly of metallic nanoparticles, such as Au, Pd, Pt (Fig. 1) in macroscopic ordered domains. These nanoparticles are characterized by extremely large surface/volume ratios leading to a strong enhancement in surface effects such as the unusually high catalytic activity and the hydrogen storage capability. On the other hand, controlling the surface chemistry and shape of the nanoparticles enables their use in optical devices and photo-stable filters. Therefore, optical sensors can be constructed, which detect changes in particle surroundings such as the presence of other chemicals or ligands.

The size of the nanoparticles also allows tuning their electronic and optical properties, which result from the discretisation of the electronic structure (e.g. quantum confinement effect). Therefore, the luminescence band of semiconductor nanoparticles (CdSe, ZnO) can be adjusted as a function of the particle size to fabricate devices such as white LEDs, novel photovoltaic elements and sensors for lab-on-a-chip devices.

The advantage of fabricating multifunctional hybrid materials based on self-assembled block copolymers templating inorganic nanoparticles lies not only in the simplicity and flexibility of this approach but also in the precise control over the particle size and their spatial order to build 0D, 1D, 2D or 3D architectures.

Preparation of organic-inorganic hybrid materials

Functional hybrid materials from block copolymer can be synthesized through different strategies including direct polymerization of a monomer that contains metal-organic complexes, assembly of block copolymers with nanoscale metallic species (particles, rods, sheets) or using chemical coordination with organo-metallic compounds. Another simple concept was developed by Cohen et al., who synthesized metallic silver nanoparticles in-situ within amphiphilic diblock copolymers by incorporating inorganic precursors selectively into one block of the block copolymers followed by a chemical reduction step to obtain metallic nanoparticles. Möller and co-workers expanded this concept to the synthesis of size-controlled Au-nanoparticles within PS-b-P2VP diblock micelles. A similar approach is used to incorporate a variety of inorganic components selectively into the vinylpyridine block of the PS-b-P4VP diblock...
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copolymer by simply changing the type of precursor. For example, metallic nanoparticles including noble metal and magnetic nanoparticles are obtained upon chemical reduction of the precursor within the block copolymer matrix. Then, self-assembly of the block copolymers directs the spatial order of the inorganic nanoparticles to fabricate 0D, 1D, 2D and 3D nanomaterials (Fig. 1).

The physical and chemical properties of these nanomaterials are substantially different from those of their bulk equivalent. The reason for such interesting and often useful characteristics, e.g. fluorescence, coulomb-blockade and superparamagnetism, is that the spatial dimensions of nanomaterials are confined to an intermediate state between individual atoms and bulk material. The nanoscale order and spatial arrangement of the inorganic building blocks are important factors, determining the collective properties of the hybrid material. These nanomaterials are classified according to the number of spatial dimensions that are confined to the nanoscale. Based on that, 0D nanostructures can be used as building blocks to construct more complex 1D and 2D architectures. Controlling the structural dimensions and the spatial order of the inorganic components at the nanoscale provides a powerful tool to fabricate multifunctional nanostructures with tailored properties.

**Block copolymer micelles as 0D nanostructures**

The simplest type of nanostructure is a 0D, spherical morphology (e.g. a block copolymer micelle). These micelles form spontaneously in block copolymer solutions under certain conditions, e.g. the presence of a selective solvent and sufficiently high polymer concentration. Both blocks (PS and P4VP) of amphiphilic block copolymers are incompatible with each other and have affinities for two different environments. Hence, in toluene, a good solvent for the PS block, the low solubility of the P4VP block leads to the formation of spherical aggregates, which consist of a P4VP core and a PS corona. Either star-like (Fig. 2a) or crew-cut micelles (Fig. 2b) can be fabricated depending on the relative length of the blocks (NPS and NP4VP) and the nature of the solvent. Both types of block copolymer micelles are excellent candidates to synthesize size-controlled inorganic nanoparticles because they show low polydispersity in molecular weight and are thermodynamically highly stable. The early reports of Möller et al.7-9 showed that inorganic precursors can be incorporated into the micelle’s core followed by chemical reduction to generate metallic nanoparticles. The particle size is determined by the aggregation number and the molar loading coefficient. Förster et al.11 found a simple relationship between the aggregation number Z (number of polymer chains that contribute to one micelle) and the degree of polymerisation of both blocks (NPS and NP4VP):

\[
Z = Z_0 N_{P4VP}^{2} N_{PS}^{0.8}
\]

where \(Z_0\) is a polymer specific parameter, which describes the local packing at the core-corona interface. Based on that, the size of inorganic nanoparticles synthesized in PS-b-P4VP micelles can be controlled through the molecular weight of the block copolymer and its volume fraction. The micrographs of hexagonally ordered micellar films in Fig. 2c-e demonstrate that different micelle diameters are obtained by varying the molecular weight and the relative block length of the PS-b-P4VP block copolymer. The TEM micrographs in Fig. 2f-h show the effect of molecular weight and volume fraction of the P4VP block on the particle size for gold nanoparticles stabilized within PS-b-P4VP micelles.

Increasing the length of the P4VP block causes the formation of larger particles, while the spacing between the micelles is mainly dependent on the length of the PS block. This simple concept can be applied to synthesize a variety of inorganic nanoparticles in the micelle’s core and simultaneously control the particle diameter. The particle sizes (Dp) are summarized in table 1 for Au nanoparticles synthesized in PS-b-P4VP block copolymers with different molecular weight, volume fraction(\(f_{P4VP}\)) and polydispersity M_w/M_n.
In general the micelle morphology not only stabilizes the nanoparticles in solution but also provides simple ways of tuning their diameter and distance when deposited onto a solid substrate. Therefore, monolayers of particle-loaded micelles are promising candidates for application in catalysis, surface modification and optical coatings.

Fabrication of 1D nano-objects

One-dimensional nanostructures are anisotropic and often possess unique physical properties such as ballistic electron transport and unusual optical characteristics. For instance, metallic nanorods show distinctly different surface plasmon bands compared to spherical nanoparticles, while the band gap of semiconductor nanorods depends not only on their diameter but also on their length\(^1\). Therefore, 1D nanostructures, such as nanowires, nanotubes and nanofibers, are widely regarded as promising candidates for nano-electronics and optoelectronics applications.

Recently, a simple concept was presented to fabricate a variety of 1D metallic nano-objects based on self-assembly of inorganic nanoparticles within PS-b-P4VP micelles\(^12, 13\). As demonstrated above, spherical micelles are formed in selective solvents for the PS block. The addition of a polar co-solvent selectively swells the micelle’s P4VP core, which results in a morphology transition from spherical micelles into a variety of 1D nanostructures (rods and rings). In fact, the morphology of block copolymer aggregates in solution is primarily dependent on three factors: the repulsive interaction among coronal chains, the degree of stretching of the core-forming chains and the interfacial tension at the core-corona interface\(^10, 14\). Precisely tuning the balance

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**Table 1 Characteristics of PS-b-P4VP block copolymers**

<table>
<thead>
<tr>
<th>polymer</th>
<th>PS, g/mol</th>
<th>P4VP, g/mol</th>
<th>(f_{P4VP})</th>
<th>(M_w/M_n)</th>
<th>morphology</th>
<th>(D_P, \text{nm})</th>
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<tr>
<td>PS(<em>{398})P4VP(</em>{18})</td>
<td>41,400</td>
<td>1,900</td>
<td>0.04</td>
<td>1.07</td>
<td>spherical</td>
<td>1.9</td>
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<tr>
<td>PS(<em>{327})P4VP(</em>{28})</td>
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<td>0.08</td>
<td>1.07</td>
<td>spherical</td>
<td>2.3</td>
</tr>
<tr>
<td>PS(<em>{3509})P4VP(</em>{280})</td>
<td>365,000</td>
<td>29,400</td>
<td>0.07</td>
<td>1.23</td>
<td>spherical</td>
<td>6.3</td>
</tr>
<tr>
<td>PS(<em>{3846})P4VP(</em>{364})</td>
<td>400,000</td>
<td>38,200</td>
<td>0.09</td>
<td>1.37</td>
<td>spherical</td>
<td>6.7</td>
</tr>
<tr>
<td>PS(<em>{497})P4VP(</em>{311})</td>
<td>92,700</td>
<td>32,700</td>
<td>0.26</td>
<td>1.13</td>
<td>cylindrical</td>
<td>5.8</td>
</tr>
<tr>
<td>PS(<em>{683})P4VP(</em>{105})</td>
<td>60,632</td>
<td>11,025</td>
<td>0.15</td>
<td>1.1</td>
<td>cylindrical</td>
<td>3.2</td>
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<tr>
<td>PS(<em>{583})P4VP(</em>{185})</td>
<td>60,632</td>
<td>19,425</td>
<td>0.23</td>
<td>1.1</td>
<td>gyroid</td>
<td>3.7</td>
</tr>
<tr>
<td>PS(<em>{206})P4VP(</em>{197})</td>
<td>21,400</td>
<td>20,700</td>
<td>0.49</td>
<td>1.13</td>
<td>lamellar</td>
<td>4.0</td>
</tr>
</tbody>
</table>

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![Fig. 3 Controlling the micelle morphology through the addition of a co-solvent (H\(_2\)O), which selectively swells the micelle’s core (P4VP). The morphology is shifted from spherical micelles to rods and rings as well as vesicles. The TEM micrographs show each of the morphologies separately, where the nanoparticles appear as dark spots in the polymer matrix. The scale bar in the micrographs is 50 nm.](image-url)
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between these factors is critical to control the formation of 1D structures in solution. One possibility is to vary the concentration of polar co-solvent, which is swelling the micelle’s core. The degree of swelling of the metal-loaded P4VP block is adjusted, e.g. through the water content in the solution. As shown in Fig. 3, the morphology changes from spherical micelles to rod- and ring-like structures as well as vesicles as the degree of swelling of the metal-loaded P4VP block increases.

Purely 1D nano-objects, e.g. rod- and ring-like structures, are obtained at water contents of \(5 \leq \frac{n_{H_2O}}{n_{4VP}} \leq 30\), with respect to the number of pyridine units \((n_{4VP})\). At lower water contents, only spherical aggregates are formed, while vesicles are obtained at very high concentrations of water \(\left(\frac{n_{H_2O}}{n_{4VP}} > 100\right)\).

This simple concept is generic since it can be applied to fabricate 1D nano-objects loaded with different types of nanoparticles. Therefore, our approach provides a highly flexible and versatile tool to fabricate a variety of functional nanostructures with properties specifically designed for targeted use in catalysis, optics, electronics or hydrogen storage.

2D nanostructures via self-assembly in thin film

2D nanostructures have been prepared for decades in the form of thin metallic films. Recently it became apparent that laterally nanostructured thin films can greatly enhance the surface properties of a given material. Common examples include self-cleaning glass, anti-reflective coatings, biocompatible layers and scratch resistant paints among many others.

A key challenge in nanotechnology is to tune the surface properties of thin films by controlling the lateral nanostructure of the functional hybrid materials. Recently we reported on a straightforward method to fabricate well-defined honeycomb patterns with characteristic dimensions between 50 nm and 5 \(\mu m\) by simply spin-coating solutions of the PS-b-P4VP hybrid material onto solid substrates.

As demonstrated in the previous section, a variety of 1D structures are fabricated by controlling the self-assembly of the block copolymer in solution e.g. by adding co-solvent. The same concept is applied to fabricate block copolymer vesicles loaded with inorganic nanoparticles and using them as building blocks to fabricate 2D nanostructures in thin film. As shown in Fig. 4a, the vesicles are spin-coated onto solid substrates to form porous structures in thin film, where the pore size is defined by the vesicle diameter. Subsequently, the block copolymer matrix is extracted via oxygen plasma etching leaving behind purely inorganic nanostructures, which replicate the original film morphology.

Well ordered thin films with regular honeycomb structures can be fabricated only when vesicles with similar diameters are deposited onto the substrates. As shown in Fig. 4b-c, the lateral length scale of these patterns can be controlled in the range from less than 100 nm to several \(\mu m\). These honeycomb films significantly affect the surface properties, e.g. the wetting behavior of the coated substrate. While the original substrate (SiO\(_2\)) is moderately hydrophilic (water contact angle WCA = 38°), the honeycomb films show strongly hydrophobic surface properties with contact angles up to 115°. After plasma etching, slightly lower...
contact angles were measured (WCA = 89°) indicating a less hydrophobic surface [Fig. 4d]. The surface properties further depend on the size of the honeycomb structures and the film thickness\(^{16}\), which can be adjusted through the vesicle diameter and the etching time. Besides the wetting properties of the surface, additional functionality is provided by the inorganic nanostructures, which exhibit specific catalytic, optical, electronic or magnetic properties depending on the type of the inorganic material.

### 3D periodic nanostructures in bulk

The need for 3D nanostructured hybrid materials relies on the outstanding properties that these materials can exhibit when the nanostructures (1-100 nm) exhibit alignments at a macroscopic level (1-100 mm). For example, when hybrid nanostructures interact with light, energy can be captured due to the excitation of different electron states. When this energy can be collected based on a macroscopic organization of these nanostructures, the potential to achieve highly efficient solar cells becomes a reality\(^{17}\). Lithographic techniques are successful at nanostructuring materials typically within 100 nm to several micrometers\(^{18}\). However, for applications with scales smaller than 50 nm, lithographic methods fail to deliver results in a timely scale or within a reasonable cost-benefit relationship.

Different strategies have been proposed to template arrays of inorganic nanowires in-situ by using BCP-systems. However, so far those strategies have not provided a robust control of particle size, particle distribution or regularity in the resulting morphologies\(^{19}\). Common problems include low nanoparticle densities with respect to domain sizes\(^{20, \, 21}\) and affected periodicity of the resulting morphologies\(^{17}\). These problems arise since the coordination and reduction of the inorganic precursors take place in a solvent that can swell/dissolve one or both of the blocks of the polymer. Thus the polymer chains can rearrange conformations around the nanoparticles in the mobile concentrated solution, disrupting the inherent periodicities of the block copolymer.

One of the successful approaches to incorporate inorganic materials in bulk was explored by Wiesner and co-workers\(^{23}\). In their approach\(^{23}\),
an inorganic aluminosilicate ceramic material preferentially swells the PEO block of a PS-b-PEO diblock copolymer system. Varying the content of ceramic component, the volume fraction can be changed so that it is possible to shift to different morphologies starting from a single BCP system.

The approach in bulk takes advantage of a coordination process that starts in solution. The generation of the nanoparticles is promoted by a selective coordination of an inorganic precursor (a metallic salt - M) to a specific functional block (B) of a diblock copolymer (A-b-B) in solution. Through evaporation of the solvent, the BCP undergoes a process of self-assembly, where the functional block carries the precursor to its own nanodomains, separated from the non-functionalized domains (the A-block). After solvent evaporation, there is no mobility in the system and the microphase separated morphology is fixed. Subsequently, the inorganic precursor (for instance Au-precursor) is reduced to its elemental state in the form of nanoparticles, where the nanoparticles grow while being confined to the functional block (for example P4VP) of the block-copolymer (PS-b-P4VP). This block acts as a nanoreactor that controls the Au-nanoparticle growth in terms of size and size distribution (Fig. 5). Depending on the selected precursor, the inorganic component may exhibit conductive, semiconductive or magnetic properties.

With their attractive property of self-assembly, block copolymers can control the spatial arrangement of the inorganic components into 3D periodical patterns. Varying the volume fraction of one of the blocks, the material can adopt different morphologies such as body centered 3D periodical patterns. Varying the volume fraction of one of the blocks, the material can adopt different morphologies such as body centered cubic spheres (Fig. 5a), hexagonally-packed cylinders (Fig. 5b), gyroids structure (Fig. 5c) and lamellae (Fig. 5d). Having characteristic domain spacings between 10 nm and 100 nm, BCP morphologies can be tuned accurately by changing molecular weight or the volume fraction.

The newly generated gold nanoparticles mimic the morphology of a PS-b-P4VP diblock copolymer. Subsequently, macroscopic order can be induced through large amplitude oscillating shear (LAOS) or other external field. In typical LAOS experiments, the material is placed between parallel plates; mechanical shear is applied by oscillations of the lower plate, where parameters including frequency, strain and temperature are commanded by the user. Initially, 3D order is confined to polydomains with different orientations that make the bulk material in average isotropic. Under appropriate conditions of shearing, local order can be extended to macroscopic dimensions, aiming for a single-domain anisotropic material. Preliminary results proved successful in producing macroscopically aligned hybrid block copolymers with lamellar and hexagonal-cylinders morphologies. The isotropic characteristic determines the special properties intended for the material in bulk, i.e., photonic band gap materials (spherical morphology), electronic multi-contact devices, high-surface area catalysts, nano-wires (hexagonally packed cylinders), nano-capacitors (lamellar structure) and solar cells (gyroids).

Conclusions

We have demonstrated a simple, flexible and highly versatile approach to fabricate multifunctional nanostructures by tuning the self-assembly of block copolymer-based hybrid materials. The concept is applied to generate nanostructures at all dimensions from 0D nano-objects to complex 3D periodic nanostructures in bulk. Hybrid materials based on polystyrene-b-poly(4-vinylpyridine) in combination with inorganic nanoparticles were synthesized in-situ by incorporating functional elements, such as metallic or semiconductor nanoparticles, selectively into the P4VP block of the copolymer. The PS-b-P4VP block copolymer then directs the self-assembly of the nanoparticles and controls their spatial arrangement to fabricate multifunctional nanostructures. Hence, tuning the self-assembly of the block copolymer, e.g. by changing the molecular weight, volume fraction or solution conditions, provides a powerful tool to fabricate well-defined nanostructured hybrid materials for application in a wide range of technologies.

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