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Feature article

Encapsulation of inorganic nanoparticles into block copolymer micellar aggregates: Strategies and precise localization of nanoparticles☆

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ABSTRACT

Precise assembly and localization of preformed inorganic nanoparticles (NPs) in block copolymer (BCP) assemblies are of great importance in realizing the formation of nano-hybrids with high performance. Properties of the nanocomposites depend not only on those of individual building blocks but also on their spatial organization at different length scales, demonstrating unique optical, electrical, and magnetic properties. With the aid of the BCPs, NPs can form a broader range of structures in the nanoscopically confined geometry. Thus, many studies have focused on the selective localization of NPs in BCP aggregates. In this paper, we will outline recent advances in the preparation strategies for precise localization of inorganic NPs into BCP micelles, including co-precipitation, supramolecular assembly, interfacial instabilities of emulsion droplets, heating–cooling, electrostatic interaction, and others. Manipulating the balance between enthalpic and entropic contributions provides one of the opportunities to precisely control the spatial distribution of NPs in BCPs assemblies. We will focus on the principles of precise control of dispersion and localization of the NPs in BCP micelles. Potential applications of the hybrid micelles will finally be discussed, followed by the summary and outlook of this emerging area.

1. Introduction

Nanoparticles (NPs) exhibit unique properties associated with optical, electrical, and magnetic behavior, which are different from the properties in their bulk materials [1]. Ensembles of NPs may exhibit properties different from those of the individual building blocks due to coupling and exchange phenomena. Collective properties of nanostructured arrays of NPs can be accessed by tailoring the spatial arrangement of the NPs over multiple length scales [2]. Recent development in NPs synthesis provides a plethora of inorganic NPs, building the foundation for constructing hybrid nanocomposites with unlimited possibilities.

Amphiphilic block copolymers (BCPs) can self-assemble into various nanostructures such as spherical/cylindrical micelles, lamella phases, or vesicle membranes depending on block ratio of the BCPs, solubility of the blocks in the solvents, solvent composition/concentration, immiscibility of the solvents, and temperature/pH of the solutions [3–8]. These predictable BCP aggregates have attracted considerable interest not only for academic reasons, but also because of potential applications in the fields of medicine, biology, electronics, and catalysis. Particularly, the self-assembled nanostructures can be utilized as nanotemplates to synthesize semiconductor or metal NPs with controlled size and morphology or to direct metal NPs deposition and further control the spatial distributions of NPs at one to three dimensions [9–16].

Recently, many studies have focused on the encapsulation of NPs into BCP aggregates since these hybrid aggregates can combine the properties from the parent constituents and generate new properties to meet the requirements in applications such as labeled materials, photonic nanodevices, or chemical sensors [17]. Encapsulation of NPs in BCP micellar aggregates can serve many purposes: (1) *Improving stability*: The stability of NP suspension is often critically dependent on the structure of ligands that are bound to NP surface. Several methods have been developed to

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stabilize NPs and to maintain their properties in water, including surface functionalization by small molecules, polymers, or biomolecule ligands [18]. However, over long period of time, these ligands can dissociate. Even a strong thiol ligand could dissociate from Au surface under the environment of high temperature, competing biological thiols, and chemical cleaving agents, not to mention ligands bond by weak interactions [19–22]. Encapsulation of NPs in the BCP micelles provides a suitable environment for further stabilizing the NPs. After cross-linking, the hybrid micelles will be substantially more stable to heat and pH, allowing them to be more useful in biological or biotechnological protocols requiring harsh conditions [23]. (2) *Reducing toxicity* [24]: As-synthesized NPs are normally coated with bilayer of surfactant molecules, for example, cetyl trimethylammonium bromide (CTAB), on gold NPs. Yet, clinical applications of these photothermally active NPs are currently limited by the cytotoxicity of CTAB, and also the nonspecific uptake of CTAB-coated NPs [25]. Several approaches have been developed to replace the original CTAB coating with a new enclosure formed by other materials, including the commonly-used conjugation of NPs with poly(ethylene oxide) (PEO) thiols. Yet again, this method does not normally produce dense PEO brushes, and incomplete coverage of gold NPs with PEO has been shown to result in insufficient stability of the NPs against aggregation and under physiological conditions [26]. Encapsulation of NPs in the core of the micelles can reduce the potential toxicity of NPs. (3) *Easy to be multi-functionalized*: An alternative approach used to fabricate multifunctional NPs is to simultaneously incorporate different NPs within a nanoscale micellar carrier [27]. In this case, each component can be prepared in monodisperse form prior to encapsulation, and size/composition of the products can be closely controlled, the general self-assembly method can provide multiple-core NPs with predictable physical properties. (4) *Improving collective properties*: Controlled clustering of magnetic NPs inside BCP aggregates results in high particle loading and a considerable increase in detection sensitivity in magnetic resonance imaging (MRI) [28–30]. Moreover, the aggregates loaded with magnetic NPs and drugs can be directed on the targeting locations by magnetic fields [29]. Drug release can be controlled through an oscillating magnetic field producing local hyperthermia in the magnetic particle loaded portion of the aggregates, which requires the precise localization of NPs in the corresponding parts of the aggregates (e.g., micelle core or vesicle walls) [28]. (5) *Serving as template for functional cavity formation*: The encapsulated NPs can serve as a sacrificial nanotemplate for hollow polymer capsules formation by cross-linking of the resultant polymer shell, followed by removal of the template of NPs [31–33].

When NPs have been encapsulated into the BCP micellar aggregates, many factors, including the content, distribution, orientation, and localization of NPs in the polymer matrix should be considered, which play significant roles in determining the properties and performances of the polymer nanocomposites. Each micelle contains three different kinds of regions, including core, interface, and corona, among which NPs can be localized selectively in different regions by using the suitable methods [34]. Precise control of NPs location within BCP aggregates demonstrates many advantages [11]: (1) *Locating NPs in the micellar core*: Encapsulation of quantum dots (QDs) in the core of the polymer micelles can not only improve the stability of the NP and reduce toxicity to animal body, but also could preserve the unique optical performance of QDs [24]. Incorporation of NPs in the center of micelles might be useful in the area of labeling or catalytic applications, where the particles need to be protected on all sides by the hydrophobic wall-forming materials. For example, a thin polymer layer (~10 nm), which is easily penetrated by small organic molecules, but with much more difficulty by inorganic ions, acting as a barrier to inorganic ions, which might poison the catalyst, at only a slight cost in overall speed of the reaction. In addition, the central localization can provide equal protection for all the NPs, rather than having some more exposed to the potentially toxic environment than others if the NPs are randomly located within the wall [35]. (2) *Locating NPs in the core and corona*: Separated electron–donor and electron–acceptor in different domains with tailored spacing will be beneficial for the optoelectronic applications. The micellar scaffold that contains specific domains can be used to partition different species in micelles. For example, when QDs were located in the corona and conducting polymer (e.g., poly(3-hexylthiophenes) (P3HT)) was encapsulated into the core of the micelles, the excited-state photoluminescence quenching of the QDs occurred in this case, induced by the P3HT, enabling electronic energy transfer between the QDs and the P3HT [36]. On the other hand, when fluorophores or QDs are in close proximity to metal NPs, QD–metal interaction can result in either enhancement or quenching of photoluminescence (PL) emission. Very short distance (<5 nm) between QDs and metal NPs gives rise to PL quenching [37], whereas longer separation (~10–20 nm) leads to distant-dependent PL enhancement [38]. BCP assemblies offer precise location control of embedded NPs, necessary for varying their optical properties by tuning the exciton–plasmon coupling between QDs and metallic NPs. Recently, Farinha et al. [39] encapsulated QDs in the core of the micelles and incorporated Au NPs in the coronas with a precise distance between QDs and Au NP of ~20 nm. The precise spacing between QDs and Au NPs prevents any quenching of QDs PL by the metal NP and leads to an apparent enhancement of QD PL emission (~8 times) relative to QD emission from micelles without Au NPs [39].

Until now, there are two main methods to incorporate NPs into BCP micelles, one is *in situ* method (NPs can be formed *in situ* inside the BCP micelles by using chemical reaction [9]), while the other is *ex situ* method (co-assembly of the preformed NPs and BCPs [40]). By comparison, the latter approach offers an effective means to precisely control size and position of NPs in BCP micelles. In this feature article, we will first discuss the preparation strategies for precise localization of preformed inorganic NPs into BCP micelles. Then, we will review various factors affecting precise localization of the NPs in the micelles and the possible mechanisms of this area. Finally, we will end with possible applications of the hybrid micelles in biomedical area, catalysis, sensors, etc., followed by a brief outlook on the future trends in this emerging area. Considering the topic, studies on encapsulation of preformed NPs into polymer bulk or thin films and the *in situ* methods are not included in this paper, detailed reviews covering the above aspects have been published elsewhere [41–46].

2. Strategies for encapsulation of preformed NPs into BCP micelles

2.1. Co-precipitation method

Encapsulation of preformed inorganic NPs into BCP micelles can be performed through co-precipitation method—co-assembly of NPs and amphiphilic BCPs in selective solvent. In 2005, by using the co-precipitation approach, Taton group prepared hybrid micelles based on amphiphilic BCPs polystyrene–poly(acrylic acid) (PS–PAA) and gold NPs (Fig. 1) [47]. Typically, homogeneous solution was first prepared by dissolving PS–PAA and citrate-capped Au NPs in a good solvent such as N, N-dimethyl-formamide (DMF). Selective solvent (e.g., water) simultaneously desolvated the NPs and the hydrophobic polymer block (PS), leading to the aggregation of the NPs with the hydrophobic block, forming hydrophobic parts of the