

Self-assembly of micelles into designed networks

Yong J. Yuan · Alexander T. Pyatenko ·
Masaaki Suzuki

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Abstract The EO₂₀PO₇₀EO₂₀ (molecular weight 5800) amphiphile as a template is to form dispersed micelle structures. Silver nanoparticles, as inorganic precursors synthesized by a laser ablation method in pure water, are able to produce the highly ordered vesicles detected by TEM micrography. The thickness of the outer layer of a micelle, formed by the silver nanoparticles interacting preferentially with the more hydrophilic EO₂₀ block, was around 3.5 nm. The vesicular structure ensembled from micelles is due to proceeding to the mixture of cubic and hexagonal phases.

Keywords Self-assembly · Template · Silver nanoparticles

The fabrication of a designed arrangement of matter at the nano-scale level is a central goal of contemporary engineering endeavors [1]. Well-defined nanostructures at a scale of less than 100 nm were produced due to the size of building blocks and the weak interactions between the building blocks [2]. Amphiphilic block copolymers consist of a hydrophobic polymer that is covalently linked to a hydrophilic polymer. In aqueous solutions, this leads to self-assembly in to

micelle structures and lyotropic phases [3]. Triblock copolymers, such as poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide), offer important materials advantages not associated with conventional low molecular amphiphiles. It was also reported that CdTe crystal growth occurs in a mixture of cubic and hexagonal structures to form tetrapods [4]. These complex fluids can produce designed networks, with use of engineered building blocks. Here, we report novel assemblies consisting triblock copolymers and silver nanoparticles and show how the properties of building blocks and the weak interactions between the ensembles induced by silver nanoparticles.

Nobel metal nanoparticles exhibit unique characteristics that are not observed in bulk metals [5]. It was reported that there are interactions between gold atoms that are similar in strength to hydrogen bonds [6]. Several preparation methods of metal nanoparticles have been developed [7]. Recent advances in strategies for synthesizing silver nanoparticles by a laser-ablation method [8–10], it opened a new avenue to synthesize silver nanoparticles in pure water [11] without purification. The details of synthesis and characterization of silver nanoparticles was presented [11] with very small, spherical at average diameter of 4.2 nm, and their sizes ranging from 2 to 5 nm. Colloidal particles suspended in liquid crystalline media represent a novel composite system that combines the colloidal aspects with the fascinating properties of liquid crystals. The embedded particles create distortion of the liquid-crystalline order around them, giving rise to unusual anisotropic interactions and spatial organization of the particles [12]. Studying such composite self-assembling systems that combine different mechanisms of self-assembly seems a fruitful new direction [13]. Preparations incorporating

Y. J. Yuan (✉)
Industrial Research Limited, Crown Research Institutes,
P.O. Box 31-310, Lower Hutt, New Zealand
e-mail: y.yuan@irl.cri.nz

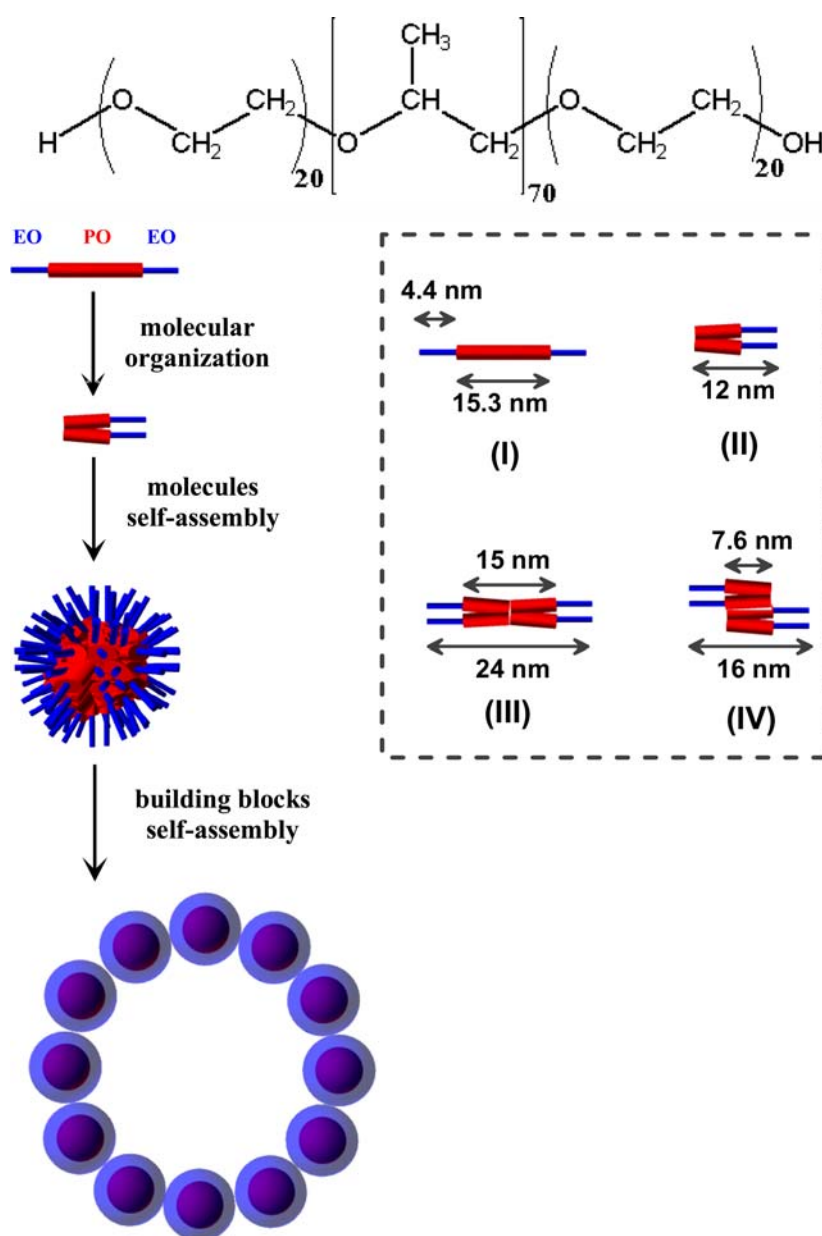
A. T. Pyatenko · M. Suzuki
Nanobiotechnology Group, AIST Institute for Biological
Resources and Functions, 2-17-2-1, Tsukisamu-Higashi,
Toyohira-ku, Sapporo, Japan

inorganic precursors and subsequent induction of self-assembly of ensembles by interaction of silver nanoparticles produce a highly ordered replica of uniform nanostructures.

The most prominent systems have been triblock copolymers of the type poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) ($\text{EO}_m\text{PO}_n\text{EO}_m$) which is commercially available as Pluronics® or Synperonics. It is now well established that block copolymers of the type poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) behave in many ways like normal hydrocarbon surfactants [3] through weak van der Waals interactions. Motivated by the fascinating self-assembly

behaviour of amphiphilic triblock copolymers, it is expected that silver particles induced nanostructures, which are highly desirable for ensuring uniformity, can be fabricated by using amphiphilic triblock copolymers as a template. Here, we focus on the use of the $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (molecular weight 5800) amphiphile as a template to order the assembly of dispersed micelle structures. Based on phase diagrams [3] published for binary mixture (polymer/water), $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ shows a multi phase above 65°C and concentration from 5 (wt)%. It indicated that isotropic phase would proceed to first a cubic phase and then a hexagonal phase, which was separated by a two-phase region.

Scheme 1 Schematic illustration of large-scale nanostructuring-fabrication with a triblock copolymer



As illustrated in Scheme 1, the $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ self-assembly system is envisaged as a series of central-stacked linear units with spherical phase. Under aqueous conditions, the PO_{70} block is expected to display more hydrophobic interaction than the EO_{20} block over range of 35–80°C, [14] thus increasing the tendency for mesoscopic ordering to occur. The hydrophobic PO_{70} domains self-associate into a core to escape contact with water, pushing the hydrophilic EO_{20} domains into a corona surrounding the core. The silver nanoparticles that are added interact preferentially with the laterally disposed and relatively hydrophilic EO_{20} blocks. Typically, our preparations involved the combination of two solutions: 10(wt)% of triblock copolymer dissolved in ethanol (solution I); and silver nanoparticles monodisperse synthesized by laser ablation (solution II). Solution I and II were mixed and left to age for a couple of days at room temperature. This composite solution was cast onto a copper grid, and then subjected to preliminary heating at 60°C under vacuum to quickly remove the ethanol. Heating at 65°C over night carried out further drying.

As evidenced by TEM in Fig. 1, a corona-surrounded domain of the templated micelle was incorporated by silver, due to the hydrophilic interactions between silver and ethylene oxide. The diameter of the micelle varies over the range of 12–20 nm due to

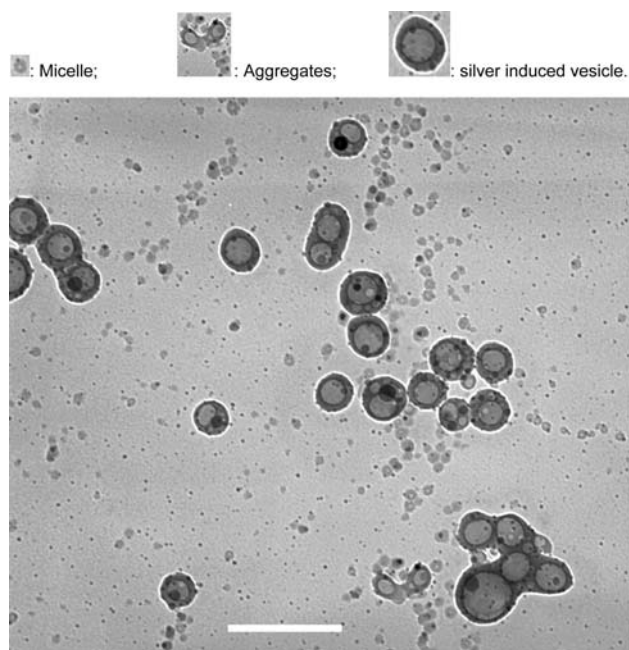
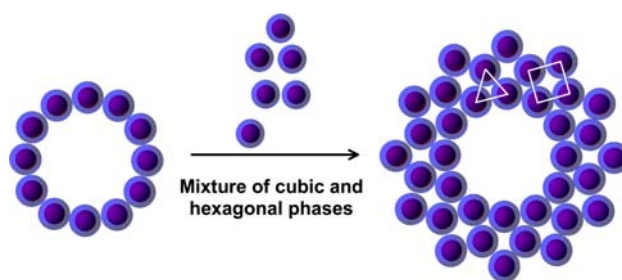


Fig. 1 Formation of nanostructured micelles, aggregates and vesicles in the mixture of cubic and hexagonal phases of $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ induced by silver nanoparticles. TEM micrograph of vesicles and their ensembles was taken at 200 kV (accelerating voltage). Scale bar: 200 nm



Scheme 2 A vesicle ensembled from micelles due to the interaction of a cubic phase and then a hexagonal phase. Cubic and hexagonal phases are highlighted as a square and a triangle, respectively

variably self-associated PO_{70} core diameter from 16 to 24 nm as estimated in Scheme 1-III and 1-IV. The thickness of the outer layer of a micelle, formed by the silver nanoparticles interacting preferentially with the more hydrophilic EO_{20} block, around 3.5 nm corresponding to 4.4 nm as illustrated in Scheme 1-I. The silver-silver interaction ensembles micelles into aggregates, which further reorganize into vesicles. The vesicular structure ensembled from micelles was illustrated in Scheme 2, due to proceeding to the mixture of cubic and hexagonal phases. It is that binary mixture [3] which arises the re-organization of micelles into vesicles induced by silver nanoparticles. From the fluid state, in which micelles move randomly and ceaselessly, to the ordered vesicle is a long journey, and one of the most remarkable reactions in all of chemistry.

It was also observed that rearrangement of silver nanoparticles was due to yield the new structure under electron bombardment. The change in morphology as shown in Fig. 2 results from the transformation by electron beam activation energies. As indicated, there are silver particle ensembles and “pin-holes” at

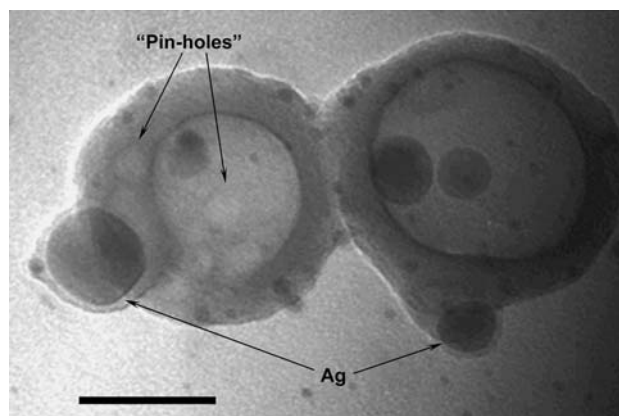


Fig. 2 TEM micrograph of vesicles after electron-beam bombardment. Accelerating voltage: 200 kV. Scale bar: 40 nm

approximate 15 nm, due to silver particles' relocation. In this case, transformation rate are high and the process can be accomplished in the solid state. The silver particles re-organize to give the new structures and the transformation can proceed without disrupting the ensemble units—vesicles.

In conclusion, the concepts of template fabrication have become increasingly important, with isotropic, anisotropic, or hierarchical structures being obtained, [1] depending on the type of template self-organization mechanism employed. The use of template structures with metal nanoparticles to organize ensembles opens up the huge potential for structures over all length scales, leading to the development of novel nano-devices and sensors.

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