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Microflow-assisted assembling of multi-scale polymer particles by controlling surface properties and interactions

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ABSTRACT

Microscale hydrogel particles are particularly attractive in a wide range of optical and sensing applications. Furthermore, controlled surface interactions of nanoscale particles play a pivotal role for the construction of nanoassembly architectures. Considering these both advantages, different types of multi-scale polymer assembly particles have been prepared by using modified microfluidic platforms. It is shown that microreactors allow simultaneous size and color tuning of the microparticles in a single step process. Moreover, patterned assembly particles can be produced via flow-assisted encapsulation of fluorescent polymer nanoparticles in microparticles interior. In further progress, three different reaction strategies were employed for the formation of controlled nanoscale polymer assembly particles by controlling particles surface properties and electrostatic interactions. On one hand, assembling can be realized because of the interaction between oppositely charged particles. But, adsorbing nanoparticles can be arranged on the host nanoparticle by maintaining certain distance between each other due to inter-particles repulsive force, on the other hand. Finally, a layer-by-layer charge-switching approach has been implemented for the construction of different levels of nanoassembly particles.

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1. Introduction

Hydrogel particles are of great interest for a wide range of biotechnological and therapeutic applications because of their hydrophilic, biocompatible and highly tunable nature [1–4]. In addition, these particles provide an essential cross-linking network for the use in sensing applications [5]. Fundamental properties and applications demand for an appropriate material selection. Major aspects, on the other side, such as size distribution, surface functionalities, degradability, and stability against different surroundings are equally influential. Swellable microparticles with incorporated metal nanoparticles are attractive for miniaturized diagnostics, labeling, sensing and catalysis [6–8]. Likewise, doping of the active materials, particularly functional polymer nanoparticles and different fluorophores in the hydrogel particles can create reliable systems for the delivery of multiple cargos at targeted sites. For example, significant concentration of insulin can be delivered (self-regulated release of actives) within a short time to the diabetic patient upon glucose responsive polymeric delivery systems [9].

Secondly, some progresses in order to mimicking the modular principles of biomolecular and cellular construction by nano-technical architectures were realized in case of thin films and surface technology. But, there is a significant inconsis-

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tency for bringing this method for continuing the bottom-up principle into the mid-nanometer and higher-nanometer range. Electrical charging, polarization, and chemical interactions are mainly responsible for the formation of complex structures in molecular nanotechnology [10]. Interactions of the nanoparticles are in a key position for bridging the technological gap between molecular dimension and high-precision mechanical manufacturing. Interestingly, electrical forces are also able to control the interactions of nanoparticles [11,12] and the stability of colloidal solutions [13,14]. Nucleation, growth, and assembling steps of the nanoparticles demand for a strict control of local reaction and transport conditions for well-defined in-situ interfacial interactions. Recently, the formation of colloidal clusters on the basis of assembling the small particles have emerged significantly [15–19]. These clusters mimic the structures and then properties of simple chemical molecules such as H₂O and CO₂. On the other side, single-step routes for producing complex and shape-controlled polymer nanoparticles *via in-situ* nanoassembling were performed [13,20,21]. Smaller nanoparticles are unstable in the solution due to high surface energy. Charged ligands can be applied on the surface which sustain the stability of nanoparticles in solution by inter-particles repulsive force [20], and can also be useful for tuning the surface morphology and introduce additional functionality [22,23]. Key demand for a strong assembly is the availability of high charge density at surface. Poly-ionic electrolytes fulfill such requirement by compensating the charge of inner surface and providing a high charge density at outer surface. Layer-by-layer modification is well-known for planar surface [24], and a reversibly switching surface by external stimuli can open the opportunity for interfacial engineering [25]. Here, it is shown that desired layers of oppositely charged polyelectrolytes can be used on the polymer nanoparticles for controlled electrostatic nanoassembly formation. Assemblies of two or more different domains can combine physical, chemical and physicochemical properties of the materials for various applications. To maintain the inter-particles distance between assembling particles is another key challenge for screening the properties of particulate assembly. Appropriate concentrations, very homogeneous reaction environment and charge management, therefore, become essential components for architecting uniform nanoassemblies. Microreaction technology, where nanoliter and picoliter volumes can be manipulated in a microscale channel, is a promising strategy in order to provide such platforms [26–28]. Efficient reactant mixing, fast phase transfer, low volume and high surface areas for reactions are the advantages of this technique [29]. Moreover, nucleation and growth processes of forming nanoparticles can be realized in an extremely uniform environment and produce distinct nanoparticles as well as nanoparticle assemblies of high homogeneity. This technology can also be efficiently useful for preparing morphology controlled particles [30,31]. Therefore, in the present work it is described how these principles can also be used for a controlled *ex-situ*, *in-situ* and flow assembling of nanoscale polymer particles. Moreover, the formation strategies and synthesis approaches of nanometer up to micrometer scale polymer particles and multi-scale tunable assembly particles are given. In case of hydrogel microparticles; nanoparticles loading capacity, controlled mixing of different fluorophores, and combined fluorescence effect are described. In nanoscale assembly; assembling strength between oppositely charged nanoparticles on the basis of their size and charge density, combined fluorescence effect during *ex-situ* assembling, nanoparticles size growth during *in-situ* assembling, and nanoparticles assembling precision by maintaining specific distance in microflow arrangement are presented.

2. Experimental section

2.1. Microreactor design

A complete microreactor framework was lithographically fabricated as described in our previous report [32]. Photolithographic procedures using an optical mask aligner and dry etching processes for the micro-patterning of the mask layer were applied for the fabrication of the silicon (Si) chip. The silicon microchip (Fig. S1, Supporting Information) has been placed inside a micro-channel, where it was embedded into two fluidic chamber walls. The width of the capillary slit was adjusted to about 0.2 mm. The Si-membrane (0.7 × 0.7 mm²) with a single hole or hole array was placed into a rectangular-shaped chamber with sloped side walls inside the Si-chip with an outer size of 0.9 × 0.9 mm².

2.2. Synthesis of polyacrylamide fluorescent hydrogel microparticles

By using a modified Si membrane-based microflow arrangement, size and color tuned polyacrylamide hydrogel particles were produced *via* photopolymerization. The continuous phase has been made up of different concentrations of picosurf (from 0.002% up to 0.2%) in Novec 7500. The dispersed phase is a solution of 0.6 g acrylamide:bis-acrylamide (19:1) in 2 mL of deionized water. For initiating the polymerization reaction, 16 μL 2-hydroxy-2-methylpropiophenone (HMPP photoinitiator mixed with 24 μL of ethylene glycol) was added to the monomer solution. For monochromatic hydrogel particles, 1 mg Titan yellow dye has been dissolved in 2 mL of dispersed monomer phase solution. Both solutions (continuous and dispersed phase) were filled up in the glass syringes and linked up to the microreactor for actuation and forming the droplets. The flow of the generated droplets has been led through the UV irradiation zone where photopolymerization took place and droplets became solidified (residence time of about 0.5 s). For tuning the size of the droplets and therefore of the particles, the flow rate ratios and the picosurf concentration has been varied continuously. Once, the particles were formed the carrier solution has been decanted from the collection tube and the particles were repeatedly washed with deionized water.

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