CONSTRUCTION OF HIERARCHICAL MICROSPHERES WITH NANO-WRINKLED SURFACES AND THEIR APPLICATION

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ABSTRACT

We propose and verify a facile and robust method for generating hierarchically structured microspheres with wrinkled nanopatterns using droplet-based microfluidics. The microspheres show high specific surface area according to the wrinkled nanostructured surface, and fluorescent properties resulting from the introduction of fluorescent nanoparticles. Therefore, they can be applied in many fields, such as coating materials, surface enhanced Raman scattering (SERS), catalysis, separation and biosensing. This process shows advantages of high controllability of materials, precise control over size and uniformity of generated droplets; and the microdroplet production is fast, efficient and in single-step.

KEYWORDS: Hierarchical microsphere, nano-wrinkled surface, droplet microfluidics

INTRODUCTION

Hierarchical structures have attracted intense attentions as novel functional materials due to a variety of applications in catalysis, coating materials, displays, and optical devices [1-4]. Various hierarchical structures have been fabricated through either top-down [5] or bottom-up [3] approaches. However, these methods have some drawbacks in terms of being time-consuming and the need for expensive equipment for the top-down method, and of nanoscale fabrication limitations for the bottom-up method. Droplet-based microfluidics has become a powerful tool to overcome these limitations and fabricate hierarchical microparticles [6] with the advantages of both flexible controllability of structure's components and size, and easy integration of other methods to construct multiple-level hierarchical structures. In this work, the hierarchically three-tier microspheres have been fabricated through the droplet microfluidic technique in combination with photopolymerization in one-step. This proposed hierarchically microsphere shows potential applications for coating material, surface enhanced Raman spectroscopy (SERS) and so on.

EXPERIMENTAL

An aqueous suspension containing different types of polystyrene nanoparticles with N-isopropylacrylamide (NIPAM, as a curable monomer) and N, N-methylene bisacrylamide (MBA, as a cross-linker) was used as the water phase. And the hexadecane with sorbitane monooleate sorbitan oleate (Span80, as the surfactant) and diethoxyacetophenone (DEAP, as a photoinitiator) was used as the oil phase. A flow-focusing microfluidic chip made in polydimethylsiloxane (PDMS) was applied to prepare the monodispersed emulsion droplets. And then the produced droplets were photopolymerized upon UV irradiation (365 nm, 120 mW/cm^2). In addition, thermal evaporation method was used to yield solid microspheres as a controllable approach. By these methods, the composition of hierarchical microcapsules can be precisely and flexibly tuned, showing the advantages of microfluidic technique.

RESULTS AND DISCUSSION

An aqueous suspension of fluorescent and carboxylic acid groups functionalized polystyrene nanoparticles mixed with curable monomer and cross-linker was used to generate uniform droplets as shown in Figure 1. After nanoparticle self-assembly driven by electrostatic repulsion, and UV polymerization, monodispersed microspheres with a nanoscale wrinkled surface were obtained.

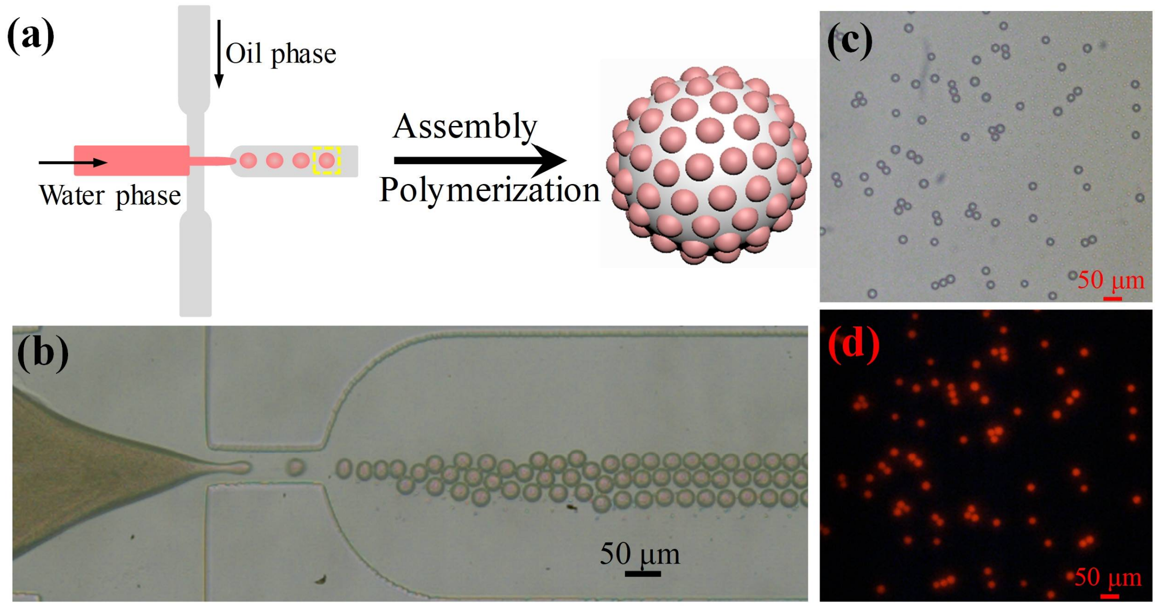

Figure 1: (a) Schematic of the fabrication of microspheres with wrinkled surfaces using microfluidic chip. (b) Optical image of the droplet generation in the flow-focus microfluidic device. Optical images of the generated droplets under (c) the bright field, and (d) fluorescent field.

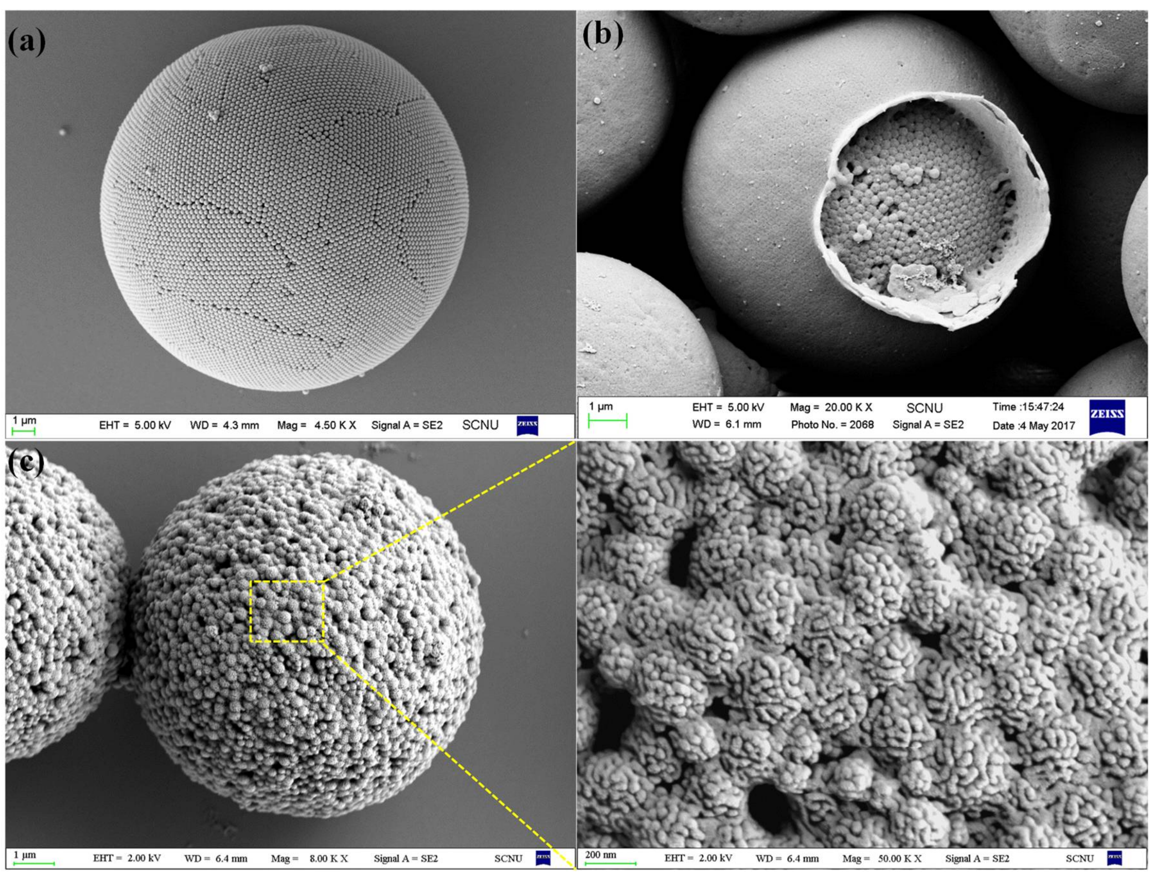

Figure 2: Scanning electronic microscope (SEM) images of the hierarchical microspheres with different surface textures. (a) Microspheres with pure polystyrene nanoparticles patterned hexagonally. (b) Microspheres with hexagonal nanopatterns of adhesive polystyrene nanoparticles. (c) Microspheres with polystyrene nanoparticles covered with nano-wrinkles.

As shown in Figure 2(*a*), when only the polystyrene nanoparticle suspension without any monomer and cross-linker was used to generate the microparticles and dried by thermal evaporation at 60 °C overnight, the nanoparticles are close-packed without chemical reactions occurred on the surface. As a control experiment, a normal polystyrene nanoparticle (without further carboxylic group treatment) suspension with a monomer and cross-linker was used as the water phase to generate microspheres using the same method. In this case, we found that monomers and cross-linkers, infiltrated in the gaps among the nanoparticles and polymerized into a thin film, but did not change the surface morphology obviously, as shown in Figure 2 (*b*). Figure 2 (*c*) shows the structures of the produced wrinkled microspheres. The nano-wrinkled surface is expected to be raised from the interfacial instability of the interface layer confined in the nanoparticle's surface through the hydrogen bonding [7] between the –NH group from the prepolymer (PNIPAM) and the –COOH group from the polystyrene nanoparticle's surface during the gradient photopolymerization process.

In this way, we have proposed a simple and fast method to construct microspheres with nano-wrinkled surface with large specific surface area. Figure 3 illustrates the applications of the produced microspheres as a coating material to prepare superhydrophobic surface and a SERS-active substrate for detecting Rhodamine 6G molecules.

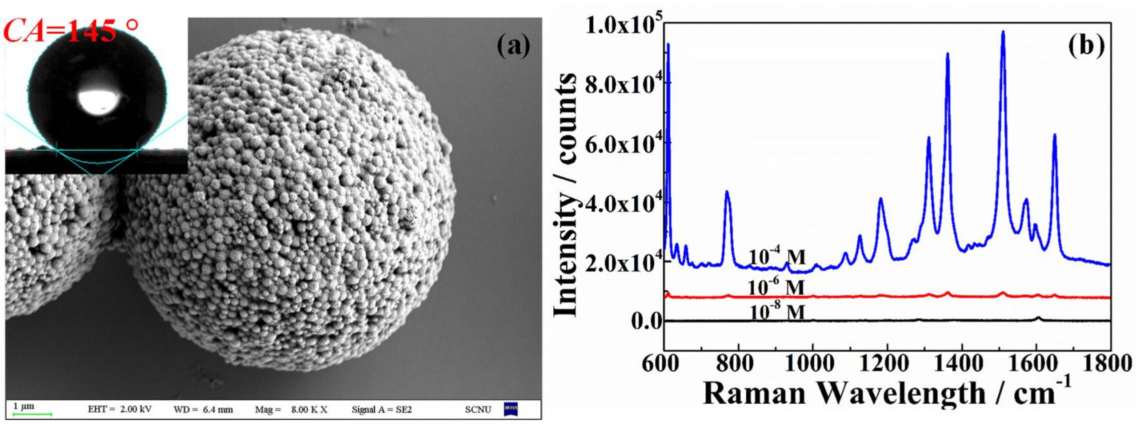

Figure 3: (a) Illustration of the superhydrophobic properties on produced wrinkled microspheres. (b) Raman spectrum of R6G with different concentrations, with the microsphere surface coated with 60 nm Ag film.

CONCLUSION

Microspheres with nano-wrinkled surface are constructed by a one-step using the microfluidic technique, including self-assembly and UV polymerization. The fabricated microspheres show multi-level hierarchical structures of high spatial frequency and have potential applications in surface coating and chemical sensing.

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