ABSTRACT
This paper presents the plasmonic microcapsules with well-ordered nanoparticles embedded in polymer network fabricated by using a microfluidic device. The well-ordered nanoparticle arrays on the microcapsule form high-density uniform “hot-spots” with a deposited metal film, on which the localized surface plasmon resonance effect is obtained. These plasmonic microcapsules can be engineered and modified by nanoparticle size and the metal film thickness. Repeatable Surface-Enhanced Raman Scattering (SERS) effect has been obtained with the highest analytical enhancement factor of $10^7$ being achieved.

KEYWORDS: Microcapsule, Microfluidic, SERS, Surface Plasmonics

INTRODUCTION
Surface plasmon resonance, typically SERS technology has been intensively developed as a label-free sensing and detection technology for chemical and biological applications. These substrates can either be fabricated by patterning nanostructures on solid surfaces via top-down method[1-3] or nanoparticle assembles by bottom-up method[4]. Generally, nanopatterning process can be well-controlled; however, the process is slow and expensive. Nanoparticles self-assembly approach can fabricate the nanoparticle-based SERS substrates quickly; however, the uniformity and reproducibility is not guaranteed. In this report, we use microfluidic technology to engineer the microdroplets and self-assembly of nanoparticles with precisely controlled liquid volume and nanoparticle concentration. By depositing a thin layer of metal film on microcapsule surface, the high-density SERS “hot-spots” are formed between nanoparticles.

Figure 1 shows the process of creating monodisperse microcapsules with well-ordered nanoparticles on the surface. Figures 3 shows the reflection spectra and SERS spectra of the microcapsules varying with Au film thickness and encapsulated nanoparticle size. When 378 nm nanoparticles are used, the optimal SERS signal is obtained at the Au film thickness of 198 nm according to the “coupling effect” of the hot spot and laser source. The highest SERS analytical enhancement factor of $4.3 \times 10^7$ is obtained for 4-MBT molecules. Via this technology, high sensitive plasmonic microcapsules can be produced quickly with high yield and reproducibility.

RESULTS AND DISCUSSION

![Image of microcapsules and nanoparticles]
Figure 1. (A) Snapshot of the droplet generation in a flow-focusing microfluidic generator. (B) Optical microscope image of the monodisperse microcapsules. The average diameter is 16.6 μm with the coefficient of variation (CV, %) of 1.38. The scale bar is 50 μm. (C) and (D) SEM images of microcapsules with well-ordered SiO2 nanoarrays.

Figure 2. SERS spectra of the plasmonic microcapsules at different Au film thickness with nanoparticle diameter of 378 nm (A) and encapsulated nanoparticle size with Au film thickness of 198 nm (B).

CONCLUSION
Homogeneous microcapsules with nanoparticle arrays are successfully fabricated by microfluidic technology. These microcapsules show dramatic SERS effect, for which the SERS enhancement factor can be tuned by nanoparticle size or metal film thickness.

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