403c Microfluidic Synthesis and Surface-Engineering of Colloidal Nanoparticles

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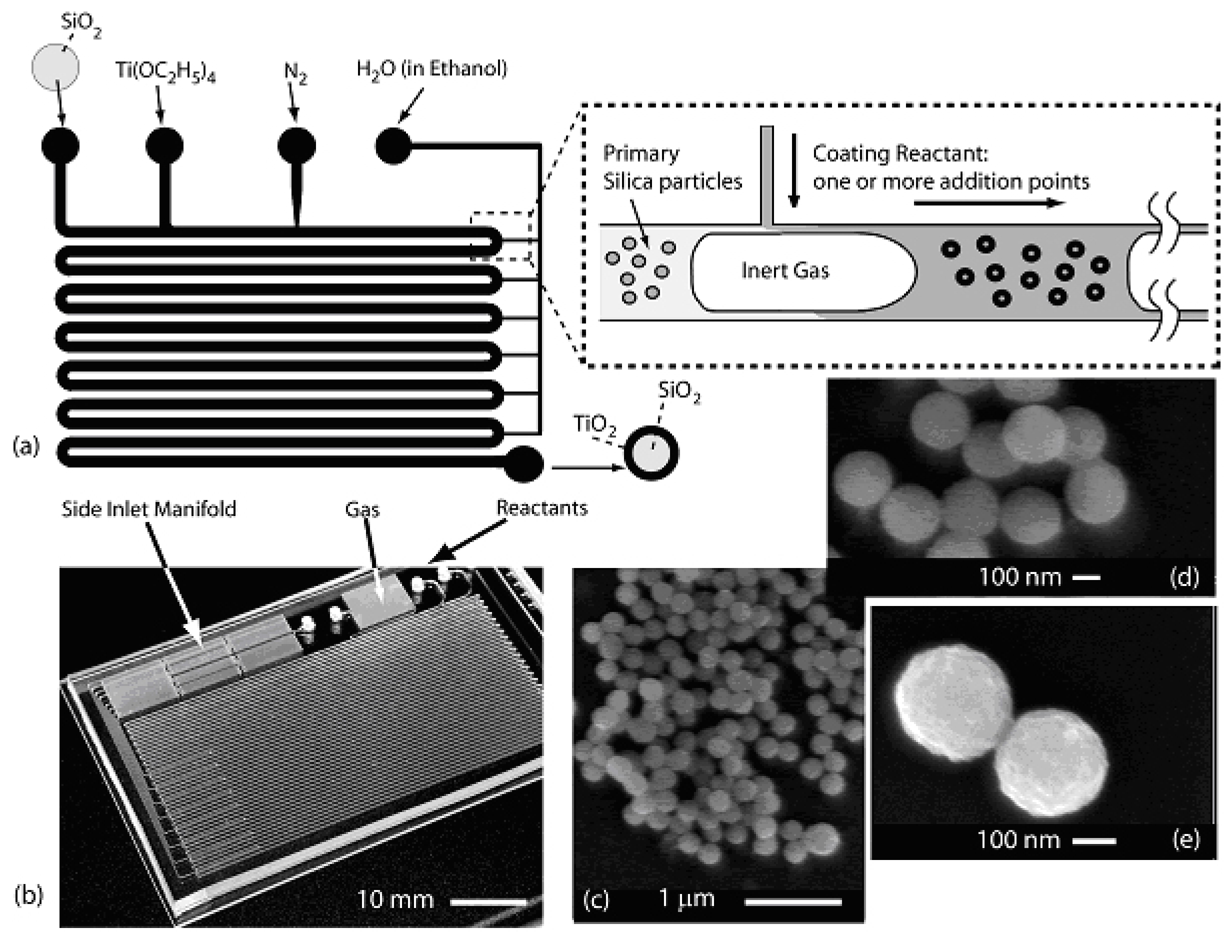
There is considerable interest in fabricating core-shell materials with tailored optical, chemical and surface properties. Core-shell particles such as titania (TiO2)-coated silica (SiO2) are potentially useful in a broad range of applications [1]. New methods of engineering such materials with controlled precision are required to overcome the difficulties associated with conventional synthesis techniques limited to multi-step batch processes. We have previously demonstrated continuous synthesis of monodisperse colloidal silica in a segmented flow microreactor [2]. Here we report the design, fabrication and operation of a simple microfluidic reactor that allows continuous addition of small amounts of secondary reactant at fixed intervals along the main reaction channel. This enables controlled surface-coating reactions to be performed on colloidal silica nanoparticles.

The rate of reactant addition and mixing are important parameters in inorganic colloidal coating reactions. The state of aggregation of the colloidal particles to be coated, and the occurrence of secondary nucleation strongly depend on these parameters. Figure 1(a) illustrates the principle of our technique. Primary silica particles obtained by the Stöber sol-gel process are rapidly mixed with a titanium alkoxide precursor in a segmented flow. Hydrolysis of the titanium alkoxide and subsequent coating of the silica particles is accomplished by the introduction of small amounts of water (dissolved in ethanol) at several points along the main reactor microchannel. The concentration of the added alkoxide and water, as well as the number of points of secondary addition is such that homogeneous nucleation of a second solid phase of titania nanoparticles does not occur, and only heterogeneous growth of titania occurs on the silica surface. The segmentation of the flow ensures rapid mixing of the added reactant with the suspended particles, and also narrows particle size distributions [2].

Figure 1(b) is photograph of a segmented flow microreactor for the over-coating of silica particles. Figures 1(c) and (d) are SEM micrograph of 210 nm silica cores coated with a 5 nm later of titania using the microfluidic technique, and illustrate that the particles are relatively unagglomerated. Figure 1 (e) is a high resolution SEM micrograph of 280 nm silica cores coated with a 25 nm thick titania layer. The grainy nature of the particle surface in Figure 1(e) is due to the mechanism of titania coating, which involves heterocoagulation of unstable titania nuclei on the silica surface [1]. Extension of this technique to multiple layers enables synthesis of particles with engineered optical properties. Moreover, the microfluidic approach provides for organic surface modifications which when combined with unique optical responses open new sensor opportunities.

1. Caruso, F., Advanced Materials 2000, 13, pp. 11-16.

2. Khan, S. A., Günther, A., Schmidt, M.A., and Jensen, K.F. Langmuir 2004, 20, pp.8604-8611.


SiO2
Ti(OC2H5)4
N2
H2O (in Ethanol)
Primary
Silica particles
Coating Reactant:
one or more addition points
Inert Gas
(a)
TiO2
SiO2
Side Inlet Manifold
Gas
Reactants
(b)
10 mm
(c)
1 μm
100 nm
(d)
100 nm
(e)