FUNCTIONALIZED PARTICLE IMAGE VELOCIMETRY FOR SIMULTANEOUS MEASUREMENTS IN MICRO/NANOCHANNEL FLOWS

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ABSTRACT
As chemical processes are downscaled and integrated into micro/nano spaces, understanding near-wall ion transport with fluid flows becomes important due to dominant surface effects. This study therefore developed functionalized nanotracer particles for simultaneous measurements of fluid velocity and ion concentration in micro/nanofluidic channels. A method to modify two kinds of fluorescent material on polystyrene bead of 100-1000 nm diameters was established to achieve pH measurement from observed fluorescent color. The method was demonstrated in a mixing of two solutions of different pH by pressure driven flows, and velocity and pH distributions with fluid flow could be successfully obtained.

KEYWORDS: Fluid flow, Particle image velocimetry, pH, Velocity, Nanoparticle

INTRODUCTION
As micro/nanotechnologies developed, integration scale of chemical processes are shifting from microscale to extended nanoscale (10-1000 nm). With downscaling the space size, surface effects become significant due to increased surface-to-volume ratio. Typical surface effect is by electric double layer studied in classical interface science, i.e., an ion screening layer of 1-100 nm thicknesses to cancel the surface charge. The double layer effects generate higher ion conductivity and electroviscous effects. In addition, recently our group has revealed unique liquid properties in extended nanospaces such as higher viscosity, higher proton mobility and concentration, and proton transfer phase with loosely coupled water molecules by hydrogen bond within 50 nm was hypothesized [1]. Therefore, in order to develop micro/nanofluidic applications, understanding ion transport with fluid flow near the interface is important.

Considering the scale of dominant surface effects, a measurement method with the spatial resolution of order of 100 nm, which is smaller than the light wavelengths, is required for experimental studies. Particle image velocimetry (PIV), in which nanoparticles are used as flow tracer, is a powerful tool for measurement of fluid flows in micro/nanofluidic channels [2, 3]. However function of PIV is currently limited to the velocity measurement.

In this study, we proposed a concept of PIV-based simultaneous measurements of flow velocity and ion concentration in micro/nanochannels. A method to add function of the ion concentration measurement to tracer nanoparticles was developed. The simultaneous measurement using functionalized nanotracer was demonstrated in a mixing of two solutions of different pH by pressure driven flows in a microchannel.

FUNCTIONALIZED PARTICLE IMAGE VELOCIMETRY
Figure 1 illustrates the concept of the simultaneous measurement by functionalized particle image velocimetry. Function of the ion concentration measurement is added to nanoparticles for flow tracer. To achieve the ion concentration measurement, particle is modified by two kinds of fluorescent material. The flow velocity can be measured from the particle motion, while the ion concentration can be measured from the fluorescence color.

EXPERIMENTAL
Particle modification method for functionalizing nanoparticles was developed. In order to add function of pH measurement, amino-modified quantum dot of red fluorescence emission (absorption: ~500 nm, emission: 600 nm) and

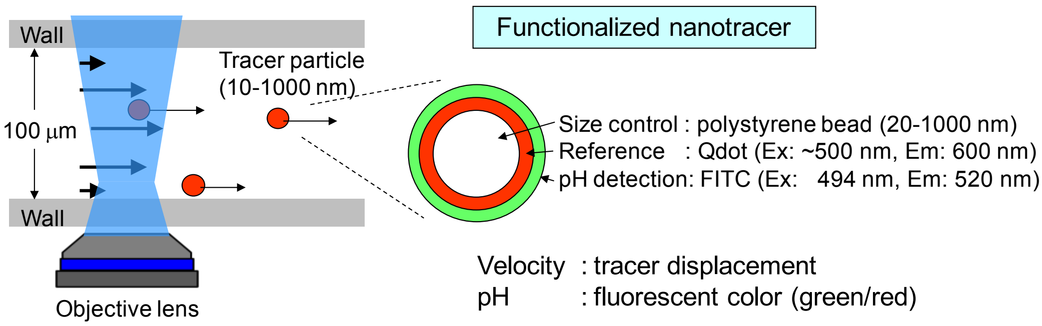

Figure 1. Concept of functionalized particle image velocimetry for simultaneous measurement of flow velocity and pH. Fluorescent materials of different emission wavelengths are modified on particle surface. The velocity is obtained from the particle displacement. pH of liquid is obtained from fluorescent color with a ratio of green and red fluorescent intensities.

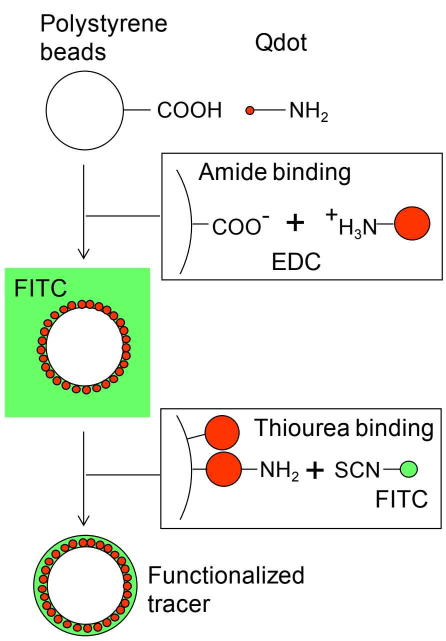

Figure 2. Process of particle modification to construct functionalized nanotracer.

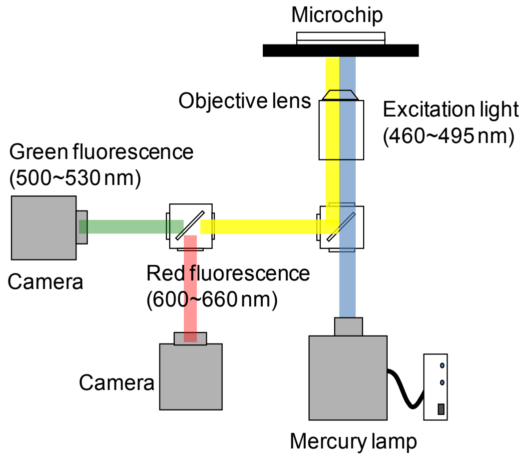

Figure 3. Schematic of measurement system for two-color fluorescence imageing.

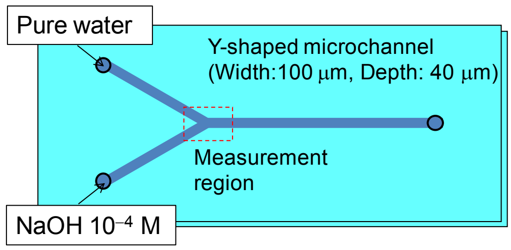

Figure 4. Schematic of Y-shaped microchannel used for simultaneous measurement of pH and fluid velocity.

fluorescein isothiocyanate (FITC) of green fluorescence emission (absorption: 494 nm, emission: 520 nm) were selected as materials for the modification. Since the fluorescence of FITC is strongly dependent on pH, pH can be measured from the fluorescence color by the intensity ratio of green and red fluorescence. Figure 2 shows process of particle modification to achieve pH measurement. Carboxylate-modified polystyrene beads were used to control the tracer size. (1) Amino-modified quantum dots were modified on the polystyrene particles by amino-binding reaction. Then, (2) FITC was modified by thiourea-binding. In order to verify the stability of functinalized nanoparticle, the zeta-potential and diameter of the modified nanoparticles were evaluated.

In order to verify the functionalized nanoparticle for the pH measurement, calibration experiments using buffer solutions of different pH were conducted. Figure 3 shows a schematic of measurement system. Excitation light from a mercury lamp through an optical filter passing wavelengths of 460-495 nm was illuminated to the functionalized nanoparticle of 1000 nm diameter. The fluorescence from the nanoparticle was separated to 500-530 nm wavelengths (green fluorescence) and 600-660 nm wavelengths (red fluorescence), and captured by separate CCD cameras, respectively. Then, a relationship between the pH and observed fluorescence color (intensity ratio of green and red fluorescence) was estimated.

The method was demonstrated for a mixing of two solutions of different pH in pressure driven flow. As shown in Figure 4, a Y-shaped microchannel of 100 μm width and 40 μm depth was used for the experiment. Water and NaOH 10^{-4} M seeded with the 1000 nm functionalized nanoparticles were injected from inlets, and the measurement of flow velocity and pH in a junction area was conducted.

RESULTS AND DISCUSSION

In the particle modification process, we optimized the concentration ratio of Qdots and polystyrene beads to 8.0×10^4 to avoid particle aggregation, which was significant problem for modification. By the proposed modification method, functionalized nanoparticles of diameters ranging from 100-1000 nm were successfully produced. The zeta-potential of the 1000 nm functionalized particle was evaluated to be –36 mV, and this indicates the stable dispersion. The diameter of the nanoparticle, which was measured by dynamic scattering, was kept constant with 2% error within one day. Therefore, functionalized nanoparticle with stable dispersion was successfully provided.

Figure 5 shows a relationship between the solution pH and the observed color of fluorescence from the functionalized nanoparticles. The fluorescence dependency on the pH was confirmed in a range from pH 5 to pH 10. From this relationship, a calibration curve for the pH measurement with an error of the pH within 0.09 was obtained.

Figure 6 shows the captured fluorescence image of the junction area in Y-shaped microchannel, and the velocity and pH distribution obtained from the images. Fluorescence color of the particle varies with the mixing of two solutions. The result shows transport of OH^- from the region of higher pH from that of lower pH, which was governed by the convection and diffusion. Therefore, functionalized PIV proposed in this study was successfully demonstrated.

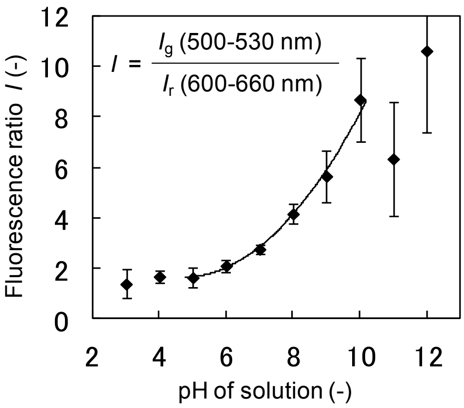

Figure 5. Fluorescence intensity ratio of green and red emitted from 1000 nm functionalized tracers as function of liquid pH.

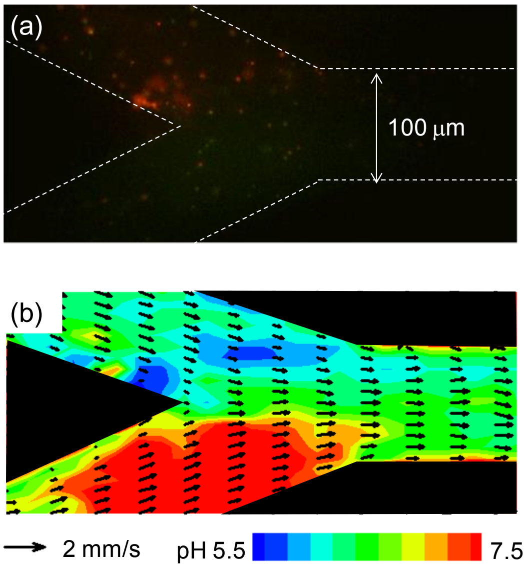

Figure 6. (a) Two-color fluorescence image emitted from functionalized nanotracers flowing through the Y-shaped microchannel. (b) Distribution of pH and fluid velocity obtained from the simultaneous measurement.

CONCLUSION

Functionalized PIV was developed for simultaneous measurements of flow velocity and ion concentration. The method for particle modification by two kinds of fluorescent materials was developed. By selecting optimal fluorescent materials and establishing the modification process, functionalized nanoparticles for the pH measurement in sizes of 100-1000 nm was successfully provided. The simultaneous measurement of flow velocity and pH was successfully demonstrated in the mixing by pressure driven flow in the Y-shaped microchannel. This method will contribute to understanding of interfacial phenomena with ion transport in micro- and nanoscale channels, which is important for applications using dominant surface effects such as separation and chemical reaction.

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