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LETTER

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Single quantum dot (QD) imaging of fluid flow near surfaces

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Abstract We introduce the use of quantum dot (QD) nanoparticles for near-surface velocimetry and provide preliminary data to demonstrate its feasibility. Evanescent wave illumination is used to image the motion of water-soluble (CdSe)ZnS QDs with a core size of 6 nm within a region of order 100 nm of a surface . Results are presented for the two in-plane components of the velocity field.

With the recent surge of interest in microfluidics and nanofluidics research, various fundamental and practical issues necessitate the interrogation of flow and transport near the surfaces of channels of increasingly smaller size. The most common method for measuring velocities in microchannels is micro-particle image velocimetry, μPIV (Santiago et al. 1998; Meinhart et al. 1999). In μPIV, fluorescent particles with diameters typically in the range 200–300 nm are used to obtain velocity data with an out-of-plane spatial resolution typically of O(1 μm). Near-wall measurements with this method have so far been obtained no closer than 450 nm from the surface. Recently, nano-PIV (nPIV) has been introduced as a technique specifically designed for near-surface interrogation of flow (Zettner and Yoda 2003; Jin et al. 2004; Sadr et al. 2004). This method relies on an evanescent wave illumination generated by the total internal reflection (TIR) of light at the interface between two materials of different refractive indices (Axelrod et al. 1984), e.g., a glass–liquid interface. With this method, the motion of particles within a region of order 100 nm of the surface is measured. In nPIV studies, to date, the size of the seed particles are in the 100–300 nm range; i.e., they are of the same order of, or larger than, the illuminated region. It would be desirable to use much smaller seed particles to reduce some of the complications that can be caused by larger particles such as the modification of evanescent wave field, and particle–fluid interactions that compromise the accuracy of fluid velocity measurement and the ability of particles to move close to the surface. In this paper we introduce the use of quantum dot (QD) nanoparticles for near-surface velocimetry; these particles are an order of magnitude smaller than what has been used to date in nPIV.

Nanocrystal QDs are semiconductor nanoparticles that are chemically synthesized with precisely controlled sizes in the range of 1–10 nm (Murray et al. 1993; Dabboussi et al. 1997; Bruchez et al. 1998; Mattoussi et al. 2000; Murray et al. 2000). Among the most developed QDs for fluorescence imaging, and the type which has been used in this paper are the core-shell dots composed of an optically active nanocrystal core of CdSe surrounded by a protective shell of ZnS. The surface of QD is covered with a ligand shell that can be functionalized for broad chemical flexibility. Several properties of QDs make them extremely attractive for fluid flow studies. By modifying the functional groups in the ligand shell, QDs may be dispersed in specific chemical environments such as polar and nonpolar liquids. Since QDs can be solubilized within the fluid, they are expected to behave more like molecules and some of the near-wall issues of "solid" particles should not manifest themselves to QD tracers (e.g. particle–fluid and particle–wall interactions). The emission wavelength of a QD depends on its size, and can be tuned across the entire visible spectrum by varying the diameter of the particle. The excitation band is very broad, and the emission is independent of the excitation wavelength. Thus, a size series of QDs with different emissions can be excited with the same light source.

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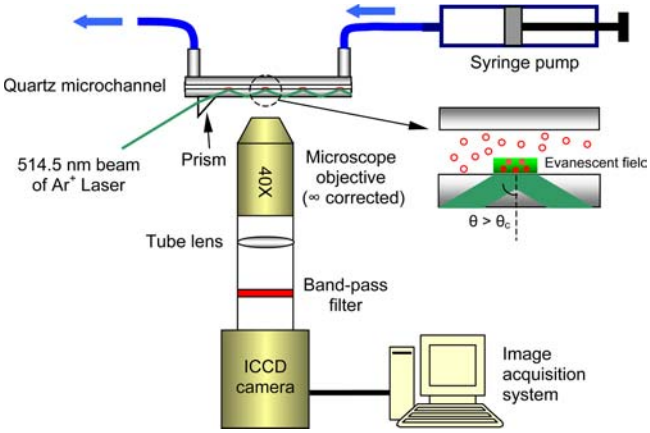

Fig. 1 Schematic of experimental setup

The QDs used in this study were water-soluble (CdSe)ZnS QDs with a core size of 6 nm emitting at $\lambda = 630$ nm with a full-width at half-maximum (FWHM) of ≈ 30 nm. The effective hydrodynamic diameter of the dot was 10.7 nm, as measured by gel filtration. Figure 1 illustrates the general setup of the experiment. A syringe pump was used to flow a dilute aqueous solution of QDs through a quartz microchannel (Starna-Cells, 200 μm channel height) at a flow rate of 0.2 mL/min, resulting in a mean flow speed of about 2 mm/s across the microchannel cross section. The evanescent wave illumination was generated by coupling the beam of an argon ion laser (λ = 514.5 nm) to the wall of the microchannel using a prism. The beam angle θ was greater than the critical angle θ_c to cause the TIR of light at the quartz-water interface. On the basis of the indices of refraction of quartz ($n = 1.46$) and water ($n = 1.33$), the wavelength of excitation, and the incident angle, the thickness of the evanescent wave layer (i.e. its 1/ e point) was estimated to be about 100 nm (see Axelrod et al. 1984). The QDs were imaged onto a 12-bit 1280×1024 pixel ICCD camera (DiCam-Pro), using a Nikon 40× (NA = 0.6) objective along with the appropriate optical filter. The effective magnification was 32× due to the internal optical coupling arrangement within the ICCD camera. Typically, a time series of 400 images were acquired at a rate of 14 frames/s, with an exposure time of 10 ms.

A typical instantaneous image of QDs in aqueous solution illuminated by evanescent wave within 100 nm of the surface is shown in Fig. 2 before the flow is turned on. The observation of the image time series clearly shows the random motion of the QDs due to Brownian motion and the appearance/disappearance of QDs in the field of view as a result of the combined effect of the out-of-plane component of Brownian motion and the intermittent blinking phenomenon observed in single dots. The average concentration of QDs within the field of view is affected by the thickness of the depletion layer characterized by the Debye length. For the nearly pure water solution used here, the Debye length is estimated to be about 300 nm; it can be reduced significantly by adding an electrolyte solution. It is worth noting in Fig. 2 that the light from an imaged QD originates from an optically active region 6 nm in size, which is about 1/100 of the excitation wavelength. The apparent image diameter of each dot in this figure is dominated by the diameter of the diffraction-limited point spread function which maps onto about 45 μm or 7 pixels of the detector in our imaging arrangement.

Once the flow was turned on, the velocity of QDs was determined by measuring the displacement of individual QDs in successive frames. The QD dropout out of the evanescent field between successive frames due to out-of-plane Brownian motion is a challenge that needs to be dealt with. This issue, which is discussed in previous nPIV studies (see Sadr et al. 2005), is more significant here because of the much smaller size of QDs, and the correspondingly higher diffusion coefficient. In order to minimize the misidentification of QD image pairs in successive frames, only the QDs that appeared in three or more consecutive frames were considered for processing. This, of course, reduced the total sample size of the available data presented here to about 400 independent velocity measurements. Figure 3, which is a superposition of four consecutive frames, shows an example of two single QDs appearing in three frames.

Fig. 2 Image of 6 nm (CdSe)ZnS quantum dots in aqueous solution within 100 nm of the surface. Field of view is 153 μm×93 μm

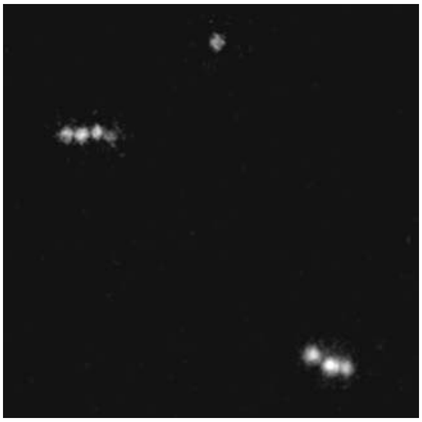

Fig. 3 Superposition of four consecutive frames showing the movement of two single QDs appearing in three frames. Mean flow is from left to right. Field of view is 37 μm×37 μm

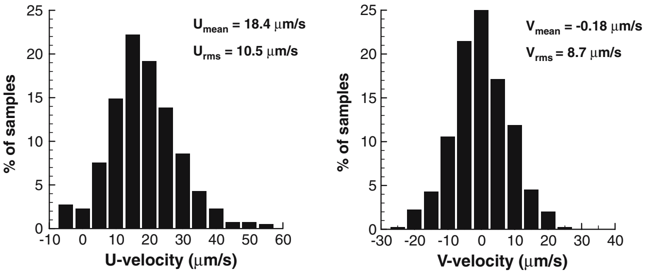

Fig. 4 Histogram of measured streamwise (*U*-component) and cross-stream (*V*-component) velocities in the illuminated plane

This example was specifically selected to show a QD with large enough displacement to be discernible with naked eye. The actual displacements were determined by a direct spatial correlation approach. Results are shown in Fig. 4 in terms of the histograms of the measured streamwise (*U*-component) and cross-stream (*V*-component) velocities in the illuminated plane. The overall mean velocities were measured to be $U_{\mathrm{mean}} = 18.4$ μm/s and $V_{\mathrm{mean}} = -0.18$ μm/s. The small nonzero value of mean cross-stream velocity is consistent with a slight (0.5°) rotational misalignment between the camera and the mean flow direction. We note that both distributions are nearly Gaussian with comparable velocity fluctuation levels (the difference between the fluctuation levels is expected to be mostly due to the relatively small sample size). The high level of velocity fluctuation, 57% of the mean for the streamwise velocity, is expected because of the significant random motion superposed onto the mean flow by Brownian motion of small QDs. Since our method of QD identification for displacement processing necessarily samples only a small portion of all the QDs participating in Brownian motion, the measured fluctuation level is only a lower bound on Brownian fluctuation. Finally, it is noted that even though the position of a QD can be determined with exceptional spatial resolution (typically 1/10 of its apparent image diameter, or 140 nm when projected back onto the flow field), the overall spatial resolution of velocity measurement from a single dot is the distance it moves during the interrogation time. Using the mean *U*-component velocity as a reference, the corresponding mean displacement would suggest a spatial resolution of 1.3 μm.

In summary, we have introduced the use of QD nanoparticles for near-surface velocimetry and provided preliminary data to demonstrate its feasibility. Some of the unique properties of QDs also allow potential solutions to various measurement difficulties. For example, QDs can be designed with much higher prescribed diffusion coefficients by adjusting their hydrodynamic radius through modification of their surface layer. Dots of different diffusion coefficients can be identified by their emission color, as the emission spectrum can be separately controlled through the size of the core. A mixture of different color dots and different hydrodynamic radii (i.e. different diffusivity) can be used to minimize the possibility of misidentification of QD image pairs.

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