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Short communication

Concentrating nanoparticles in environmental monitoring

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ABSTRACT

There are significant challenges in assessing the toxicity of nanoparticles in the environment in which effective methods for detection are crucial. An inexpensive method that uses superhydrophobic well with an evaporating droplet followed by a simple squeeze flow is described here and found to provide practical high nanoparticle collection from samples for detection. The process could be hastened by placing a radiant heater close to the droplet if temperature rises in the sample can be tolerated.

1. Introduction

The expanding use of nanotechnology in recent years is strongly attributed to the possibility of nanostructured materials to be tailored to attain different physicochemical properties, such as mechanical, chemical, magnetic, optical or electric properties compared with bulk materials (Wise et al., 2010). Nevertheless, the exact novel properties of nano-size materials in the sub-100 nm size range also portend toxic effects. Thus far, studies have demonstrated that nanoparticles introduce toxic effects at the cellular, subcellular and biomolecular levels, such as genes and proteins (Lewinski et al., 2008; Esmaeillou et al., 2013; Tang et al., 2015). There are significant challenges in assessing the fate and exposure of nanoparticles in the environment owing to the relative lack of information on their use, potential pathways and sinks in the aquatic environment (Gottschalk and Nowack, 2011; Yu et al., 2013). A major challenge is to devise methods for nanoparticle collection and its subsequent detection in environmental matrices. Detection methods can include the use of microscopy-related techniques such as environmental scanning electron microscopy (ESEM) (Muscariello et al., 2005) and atomic force microscopy (AFM) (Pyrgiotakis et al., 2014), or chromatography-related techniques are coupled to other techniques such as inductively coupled-plasma mass spectrometry (ICP-MS) (Böhme et al., 2014). Recent advances in portable and lensless light microscopy offer the capacity to image nanoparticles without the aid of fluorescence, which then facilitates on-site monitoring (Greenbaum et al., 2013).

If a liquid meniscus can be made to form between the nanoparticle and a surface, an attractive force, the capillary force, can develop to the extent that it dominates over other surface forces (Butt & Kappl, 2009). It has been recently found that when a droplet of nanoparticles in suspension was sandwiched using a circular coverslip, the resultant squeeze flow resulted in particles concentrated at the coverslip rim (Cheong et al., 2013, 2014). While this approach benefited from the squeeze flow concentration effect, it may be necessary to obtain a means to achieve imaging and detection modalities for samples that harbor extremely low concentrations of nanoparticles.

Evaporation has been used as a classical means of concentrating particles with negligible sample loss. Nevertheless, it has continued to be harnessed to accomplish various novel scientific applications to date (Kraus et al., 2007; Ghasemi et al., 2014). When a droplet containing particles in suspension is evaporated from a surface, it produces a coffee stain deposit (Deegan et al., 1997). This is due primarily to the capillary flow of particles toward the edge of the drop, which remains relatively pinned, and where the rate of evaporation is more heightened. Since the coffee stain effect can essentially concentrate particles, heightened collection there to about the same extent as the squeeze flow approach is possible, although the process will be slower. If the droplet pinning effect can be eliminated, it is conceivable that a significant increase in the nanoparticle concentration is possible.

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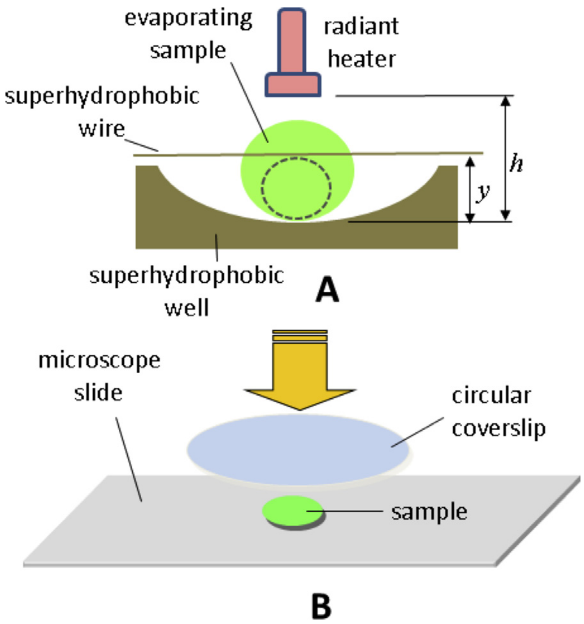

Fig. 1. Schematic description of the method to concentrate nanoparticles for sensing in which (A) a sample drop is placed in a superhydrophobic well such that evaporation, assisted by a radiant heater, will reduce its height over time to break the electrical continuity between the well and suspended superhydrophobic thin wire. This gives indication of the right volume drop needed to be transferred to (B) a microscope slide from which a circular coverslip placed on will create a squeeze flow to bring the nanoparticles to the edge of the coverslip for microscope examination.

Superhydrophobic (SH) surfaces, which occur in nature through examples like lotus leaves, can now be fabricated using various means on metallic and non-metallic substrates (Wu et al., 2014; Lau et al., 2014). As the liquid predominantly rests on the tops of the surface asperities, or commonly referred to as assuming the Cassie wetting state, it will prevent pinning at the contact line. However, this same effect has the capacity to engender movement of the droplet on the surface even with the slightest amount of tilt. The use of SH wells has been found to offer a ready solution to the undesired movement problem (Vuong et al., 2015). We adapt a low cost and practical technique for enhanced collection of nanoparticles by coupling SH evaporation to the squeeze flow approach. Since evaporation is a relatively slower process (compared to a squeeze flow) there is a need to develop an alerting capability when sample reduction to the right volume is attained.

2. Methods and materials

With the approach, a SH well created on an electrically conducting substrate holds the liquid sample in the form of a droplet as it is evaporated (see Fig. 1A). A radiant heater is placed above the droplet to help increase the evaporation rate without agitating the droplet. As the liquid volume is reduced with evaporation, the concentration of nanoparticles in the suspension will increase. A thin SH wire, suspended above the SH well, will exhibit electrical continuity with the well when the liquid engulfs the wire. By setting the wire to a height y from the base of the well to correspond to the liquid volume V using

$$V = \frac{\pi y^3}{6} \qquad (1)$$

it is possible to use the loss of electrical conductivity when the droplet loses contact with the thin wire to indicate when the required volume has been reached from evaporation. An electrical circuit devised to provide an audible alarm through a buzzer when this happens is provided as supplementary material. When the appropriate droplet volume is reached, it can be easily transferred using a light puff of air (Vuong et al., 2015) from the well to a microscope slide (Fig. 1B) where the approach previously reported (Cheong et al., 2013) is used to bring the concentrated nanoparticles to the edge of the circular coverslip for microscopic imaging.

A mechanical press was used to depress a steel bearing onto a copper plate surface to create the semi-spherical wells through indentation. To render the copper well and wire superhydrophobic,

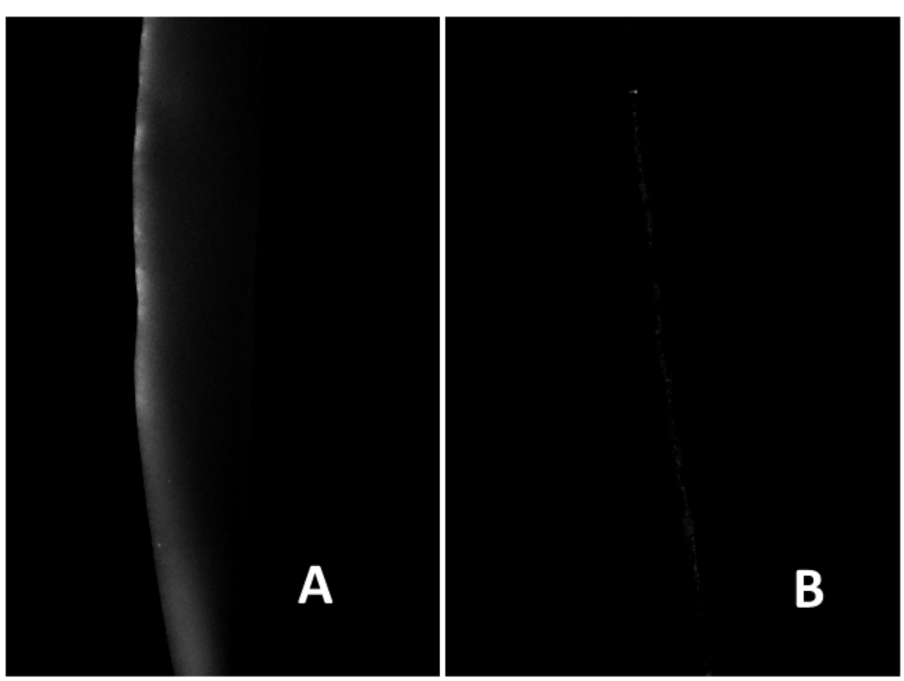

Fig. 2. Fluorescence microscopy images recorded using squeeze flow with (A) and without (B) the evaporation concentration step using the same exposure settings on the microscope. It can be seen that incorporating the evaporation approach significantly increased the collection of nanoparticles.