Tensions at Liquid Interfaces: A General Filter for the Separation of Micro-/Nanoparticles

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In this letter, we put forward a new strategy for the separation of micro-/nanoparticles with different sizes and densities by using the tensions at liquid interfaces. The interactions between particles and a liquid—liquid interface have been analyzed. Furthermore, we applied our strategy to the separation of two size-distributed Cu$_2$O particles by using the water and n-pentanol interface, which demonstrates the feasibility of the proposed separation method.

Introduction

Properties of micro-/nanoparticles may depend on their size and shape. Therefore, rigorous control of the size and the shape of micro-/nanocrystallities enables us to obtain novel materials with specific functionality. In recent years, great effort has been devoted to the control of the size and shapes of micro-/nanoparticles. For example, on the basis of the concept of size-devoted to the control of the size and shapes of micro-/nanoparticles fractions in micro-/nanoscales regions. Therefore, rigorous control of the size and the shape of the original broadly size distributed samples. In this approach, another important technique to achieve a uniform size distribution relies on the separation of a uniform fraction of the original broad size distributed samples. In this approach, a filter strategy by using some porous membranes, known as a classical separation technique, could be adopted to separate certain high-resolution chromatography, high-gradient magnetic separation, sedimentation technique, size exclusion chromatography, and electrostatic size-selection technique employing a low-pressure differential mobility analyzer, have also been reported to separate or fractionate nanomaterials in various systems. In addition, by applying size-selective precipitation, small nanoparticles can be kept in solution as colloids whereas larger nanoparticles aggregate and precipitate because of the greater van der Waals or dipolar interactions upon introducing a poor solvent into a colloidal nanoparticle solution to reduce the solvation power. Owing to the fact that most of these separation and purification techniques were developed for either specific types or specific sizes of nanoparticles, there exists a significant challenge in developing rapid, inexpensive, efficient, and versatile methods for the fractionation and purification of micro-/nanoparticles. In this letter, a general filter using the tensions at liquid interfaces is reported for the separation of small particles on the submicrometer scale, which can be a versatile filter for kinds of materials.

Experiment

Two size-distributed Cu$_2$O particles with diameters of 2 μm and 400 nm were used for the separation. First, the particles were dispersed in 300 μL of n-pentanol or a mixture of n-pentanol (300 μL) and ethanol (75 μL). Then solution with suspended particles was added to a centrifugal tube in which 2.5 mL of deionized water was added first. After this system was centrifuged (4000 rpm) for about 5 min, the particles supported on the interface and on the bottom of the centrifugal tube were collected, respectively. Then the collected products were washed with ethanol three times to remove the n-pentanol. X-ray diffraction was performed on a PANalytical X-Pert diffractometer using Cu Ka radiation. The morphologies of the products were observed with the LEO1530 scanning electron microscope.

Results and Discussion

In daily life, one may find that fine iron powder can float on water surfaces but iron pieces sink. Also, an aluminum coin can float horizontally on a water surface but not vertically. These phenomena are in fact the effect of the surface tension of the liquid and imply that surface tension can be logically applied for the separation of particles of different sizes and morphologies by rational technical design. Our strategy combines the surface phenomena at an interface between two liquid phases and the centripetal force as shown in the schematic diagram in Figure 1, where the density of phase I is smaller than that of phase II. A raw product of nonuniform small particles may first be well dispersed in liquid phase I; this dispersion is carefully transferred

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to the top of liquid phase II (Figure 1a). This sample is centrifuged, during which heavier particles will pass through the interface and lighter ones will float on the interface (Figure 1b). Thus, the raw product can be separated into two parts: one part is retained on the interface and the other is on the bottom of phase II as in Figure 1c.

Although the interactions between a particle and a liquid—liquid interface are complicated, we may simplify it as follows. Figure 2 shows a diagram of various force vectors on a spherical particle (as an adapted model for simplicity) located on the liquid/liquid interface during centrifugation in our experiments. As the particle is supported on the interface (Figure 2), its movement must be affected by the forces of gravity, buoyancy, and interfacial tension. When the proper centrifugal force is applied to this system, the total external force experienced by a particle in the interface can be expressed as \( F_{\text{total}} = F_C + G + F_T + F_B \), where \( F_C \) is centrifugal force, \( G \) is gravity, \( F_B \) is the buoyancy force (under the centrifugal force and the gravity force field), and \( F_T \) is the composite tensile force of various tensions on the interface that interact on the particle. Under our experimental conditions, the angular velocity is 4000 rpm, and the radius of centrifugation is about 10 cm. The centrifugal acceleration is calculated to be more than 1 order of magnitude of the gravitational acceleration (10 m/s²). Furthermore, the direction of the gravitational acceleration is almost vertical to the centrifugal acceleration during centrifugation as shown in Figure 2. Therefore, gravity \( G \) can be ignored, and the total external force simplifies to \( F_{\text{total}} = F_C + F_T + F_B \). When the total external force vector points to phase II, the particle will break the liquid/liquid interface and pass through; otherwise, the particle will float on the interface. For a specific particle, the critical value of the tensile force interacting with the particle at the moment of passing can be adjusted by the choice of liquids. Furthermore, the centrifugal force can be adjusted by the velocity of centrifugation. Therefore, the passage of a particle can be controlled to either pass through or stay on the interface by the centrifugation speed and choice of liquid. Because the centrifugal force is proportional to its velocity, \( F_{\text{total}} \) must be much more favorable to point to phase II when a particle is larger by increasing the centrifugation speed (Supporting Information).

To experimentally demonstrate the above proposed strategy, two size-distributed particles of pure Cu₂O were found to be an ideal model of a raw sample. The X-ray diffraction (XRD) pattern shows that the sample is a pure cubic Cu₂O phase only (Figure 3a), and its SEM image shows that the sample contains particles with diameters of 2 µm and 400 nm, respectively (Figure 3b). It should be noted that we cannot separate the 2 µm particles from the 400 nm ones by gravity or simple centrifugation because both kinds of particles are too large to form colloids or to be suspended in solution for a long time. To separate these particles, the following procedure was applied. First, the raw sample was ultrasonically dispersed in 0.3 mL of n-pentanol. The dispersion was next carefully added to a centrifugal tube containing a water phase (about 2.5 mL) as shown in Figure 4a. Because of the immiscibility between n-pentanol and water, an interface was formed. This tube was centrifuged at 4000 rpm for about 5 min to afford Figure 4b where all of the Cu₂O particles were found to float on the n-pentanol/water interface. This fact implies that the tensile forces interaction on Cu₂O particles is too large. To separate the particles, the tensile forces were carefully adjusted by adding ethanol to n-pentanol. When a mixture of ethanol and n-pentanol (1:4 by volume) was adopted as phase I, the sample was separated into two parts by centrifuging at 4000 rpm for about 5 min, in which one part of the Cu₂O particles appeared on the interface and the other appeared at the bottom of the tube (Figure 4c). The SEM image (Figure 3c) shows the particles collected from the liquid interface, which contains no particle of ~2 µm. Figure 3d shows the particles collected from the bottom of the tube that contain primarily larger particles (about 2 µm in size) together with a small number of 400 nm particles. The appearance of the latter ones on the bottom of the tube could be due to the fact that preloaded small particles on the interface collided with the water phase when the larger particles were passing through the interface.

It should be noted that our proposed strategy can also be applied to the separation of nanomaterials with different densities. We have tried to apply our proposed method to the separation of some raw products. The raw products that we tried to separate contained silver@carbon nanocables, silver nanowires, and some small particles. After separation by the proposed method, the fractions collected from the bottom of the centrifugation tube consisted of almost silver nanowires, whereas other fractions have been filtered on the interface (Supporting Information).

Although more systematic experiments should be carried out for the fine separation of small particles, the above experiments have demonstrated unambiguously that the tension at liquid interfaces is a general filter for the separation of small particles on the micro- and very likely the nanoscale with different sizes. To a certain extent, our strategy is similar to the well-known separation method by the buoyancy of materials in the liquid, by which materials with a larger specific density than the liquid density should sink. However, by applying the separation method of buoyancy, we cannot separate materials with the same specific density. Furthermore, it is difficult to find a liquid with a very high specific density. Obviously, our strategy has overcome these disadvantages.

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The key factor for a small particle to float on an interface is that the particle should be hydrophobic to phase II so that the particle has a large contact angle to float on phase II. It seems strange that our strategy has been successfully applied to the separation of metal oxide (Cu$_2$O) particles, which should be hydrophilic with water (phase II). Hydrophobic properties of Cu$_2$O particles at the interface could be generated by the adsorption of $n$-pentanol molecules on the particle surface when they were dispersed in $n$-pentanol. Therefore, the original hydrophobic property of the particles for the separation becomes less important.

In conclusion, the tension at liquid interfaces has been applied to the separation of small particles on the micro- and very likely the nanoscale with different sizes or densities. This method is versatile for the separation of all kinds of materials.

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**Supporting Information Available:** Theoretical estimation of interfacial tensile forces on a particle preloaded in the liquid/liquid interface and SEM images of the separation of raw products containing silver@carbon nanocables, silver nanowires, and some nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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