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A Facile Method of Producing Femtoliter Metal Cups by Pulsed Laser Ablation

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Cuplike structures of Au, Ag, Cu, Zn, Nb, Cd, Al, In, and Sn in the size range of 300 nm to a few micrometers with an internal volume of a few femtoliters have been produced by the laser ablation of metal targets in a vacuum, by optimizing, in each case, the laser fluence and the substrate temperature. The metal droplets impinging on the substrate seem to undergo a hydraulic jump driven by the surface tension forces before solidifying into cups. The cups are robust and can be functionalized with biomarkers, filled with nanoparticle sols, oxidized to crucibles, or detached from the substrate without causing any deformation. We envisage their potential applications as femtoliter metal containers.

Introduction

The growing interest in single molecule detection and kinetics has given impetus to the technology of making ultrasmall containers. Femto- or picoliter capacity containers are useful when dealing with cellular systems[1] and providing control on diffusion and kinetics.[2] Such small volumes are also economical when handling expensive reagents. Developments in lithography and nanotechnology have offered several tools for producing ultrasmall containers. Conventional photolithography has been used to produce picoliter wells in silicon wafers for the detection of single metal ions and enzyme molecules,[3,4] while soft lithography has been used to fabricate femto- and picoliter containers in an elastomer which has been demonstrated for use in monitoring enzyme action.[5,6] Arrays of wells of zeptoliter (10^{-21} L) capacity have been fabricated on silica[7] as well as titania nanobowls[8] by employing nanosphere lithography and have been used for growing nanoparticles. Such small vials also find applications as inkwells, in the developing technique of dip pen nanolithography for patterning in subnanometer dimensions.[9] Oxide nanopores grown on Si employing focused ion beam lithography have been used for localized functionalization and further immobilization of biomolecules.[10] Recently, there have been numerous developments in using self-assembled biomimetic systems such as phospholipid vesicles, hydrosomes, and liposomes for carrying out single cell reactions.[11,12]

We report, in this article, a simple and straightforward method for producing metal cups of femtoliter capacity employing laser ablation. Pulsed lasers emit nanosecond or femtosecond pulses of sufficiently high fluence (~1 J/cm^2), which can be focused to induce local melting and ejection of any material.[13] Usually, the emanating plume that consists of cluster ions, molten droplets, and particulates from secondary collisions is entrained under controlled conditions to obtain desired nanostructures. Thus, laser ablation has been extensively used for producing clusters,[14] fullerenes,[15] and onion structures of inorganic compounds,[16,17] and various other nanostructures such as nanotubes, nanorods, and nanowires,[18,19] as well as thin films.[20] Without entrainment, the molten droplets present in the plume upon impinging a solid substrate would normally form lumps, although we have noticed stray instances of ring- or cuplike structures in the literature.[21,22] However, these structures have not been commented upon, and there is neither a prescribed method for producing these structures reproducibly nor an understanding of the underlying mechanism. Here, we show how to consistently obtain femtoliter cups from virtually any metal on commonly used substrates by pulsed laser ablation. We have found that the femto-cup formation is a result of a novel hydraulic jump generated by surface tension alone, unlike the conventional gravity-driven jumps.[23−25] The metal femto-cups could be transformed to form inert ceramic cups by external reactions. Furthermore, the cups could be filled with other metals or biomolecules and are available for selective functionalization. We envisage potential applications for the metal cups ranging from nanoscale synthetic chemistry to single cell biology.

A Q-switched frequency-tripled Quanta-Ray (GCR-170) Nd:YAG laser (Spectra-Physics, U.S.A.), $\lambda = 355$ nm, 100 mJ/pulse, repetitive frequency, 10 Hz, was focused on a rotating Ag disc in a vacuum chamber (10^{-7} Torr), and the resultant plume was collected for 20 min on a clean silicon substrate placed at a distance of 4 cm and held 1173 K. Prior to deposition, the Si surface was subjected to standard cleaning procedures involving washing with acetone and deionized water and finally using piranha solution (1:2 H_2O_2:H_2SO_4; *Caution: this mixture reacts violently with organic matter*) followed by deionized water. The cleaned surface was then etched with dilute HF and rinsed with deionized water and mounted in the chamber. Scanning electron microscopy (SEM) using a FEI Nova nanoSEM 600 equipment showed a number of well-

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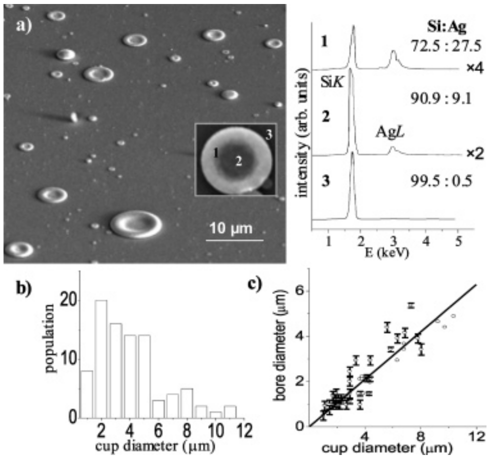

Figure 1. Microscopy on metal cups (a) SEM image of cuplike structures of Ag on a Si substrate obtained by laser ablation (view angle, 60°). Inset shows top view of a 5.8 μm cup. EDX spectra given alongside provide Ag to Si ratios from different locations as marked. (b) A histogram showing the distribution in the cup diameter in the given experiment. (c) A plot of the cup diameter vs bore diameter.

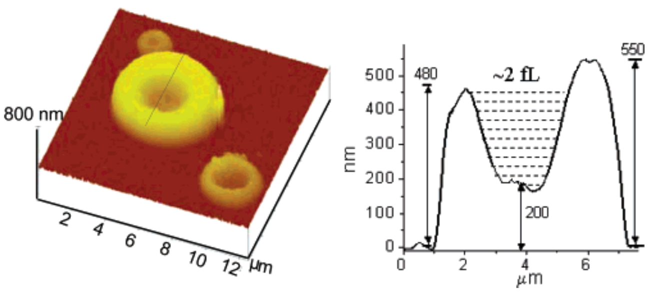

Figure 2. 3D projection of an AFM image showing cups of three different sizes. The height profile of the central cup along the dark line is shown. The hashed region gives an estimate of the inner volume.

formed ringlike structures of Ag of varying outer diameters—from 300 nm to 10 μm (Figure 1a). A closer look at these structures (see inset of Figure 1a) reveals that the central region of the rings is not devoid of the metal. Energy-dispersive X-ray spectra given alongside confirm that a significant amount of silver is present in the bore region (marked 2 in the figure). Hence, these structures are cups rather than rings. From the histogram in Figure 1b, we see that a large percentage of the cups have diameters in the range 2−5 μm. Incidentally, a large percentage of the cups have their outer diameter as twice the bore diameter (see Figure 1c). A 3D view of the atomic force micrograph (Nanocope IV-Multimode, Digital Instruments, Santa Barbara, CA) of cups of three different sizes and the associated height profile analysis of the central cup are shown in Figure 2. The central region is raised from the substrate by a thickness of $\sim$200 $\pm$ 10 nm, and the rims on either side of the profile exhibit heights of $\sim$490 and 550 nm and widths of $\sim$2.0 μm. The internal volume of the cup indicated by the hashed region in the figure is thus $\sim$2 fL. Hence, the rings of different sizes will have a volume varying from 25 aL to 6 fL.

We have attempted to understand the mechanism behind femto-cup formation. The detailed fluid dynamics is discussed in a companion paper,[26] but the mechanism is described here in brief as follows. It is possible that tiny hot metal droplets impinging on the substrate undergo a peculiar flow pattern before freezing into a cuplike structure. The droplet dynamics is such that, rather than make solid blobs on the surface, there is a strong preference, over a range of substrate temperatures, to spread out thinly initially and then display a sudden jump in height at a particular radial location. A sudden increase in fluid height, known as a hydraulic jump, is quite common at large scales.[23−25] Large-scale jumps are always caused by a balance of inertial, gravitational, and viscous forces.[24,25,27,28] In our experiment, however, gravity is irrelevant, since the length scales are small, and besides, the substrate is held vertical. We find that, at small scales, hydraulic jumps can be caused by a balance of inertial, surface tension, and viscous forces. This is because surface tension can offer an adverse pressure due to the azimuthal curvature analogous to the adverse pressure gradient created by gravity. The relative magnitudes of gravity and surface tension may be estimated by the Bond number, given by Bo $= \rho a^2 g/\sigma$; ρ and σ, respectively, are the density and surface tension of the fluid, a is a typical length scale in the problem, and g is the acceleration due to gravity. In the kitchen sink, Bo is on the order of 10, while in our experiment with molten silver, Bo is on the order of 10^{-7} to 10^{-8}. Thus, gravity is the driver in the former flow, and surface tension plays that role in the latter. In ref 26, the shallow water equations upstream of the jump are solved, and it is shown that a hydraulic jump may be expected at a radius corresponding in order of magnitude to the jump radii observed in our experiment. That the shape of the structure is directly related to droplet dynamics is confirmed by varying the substrate orientation with respect to the incoming jet. As the inclination of the substrate away from the normal was increased, the structures were found to be increasingly elliptical. Since laser fluence determines scales and speeds in the incoming jet, the flow dynamics should be affected by the laser energy. Indeed, with a lower laser fluence of 60 mJ/pulse, not only was the population of cups on the substrate considerably reduced, but their shapes were not appreciable. The substrate temperature too affects cup formation. When the substrate is held at 773 K, far below the melting temperature of silver (MP = 1234 K), we observe only a mild tendency to form cups, the droplets not having enough time to flow before solidification. A substrate temperature higher than the melting temperature is also not conducive to the formation of cups. It produced only patchy features. Hence, an optimal pulse energy ($\sim$100 mJ/pulse) and a substrate temperature slightly lower than the melting point of the metal are important in producing these cups. It was also noticed that, at very small sizes (<300 nm), cup formation is primarily inhibited due to limited metal flow.

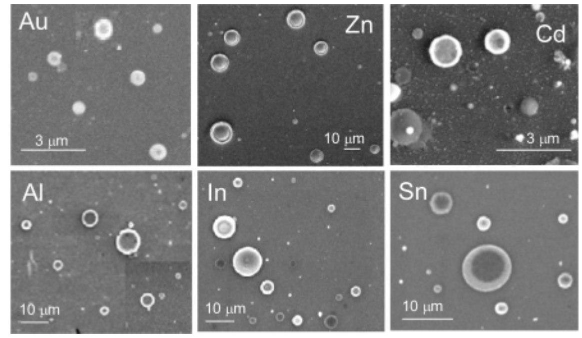

Figure 3. SEM images of femto-cups of various metals. Laser energy: 100 mJ/pulse. Si substrate temperatures: Au, 983 K; Zn, 573 K; Cd, Al, In, and Sn, 300 K.

We have been able to produce femto-cups of various metals (Au, Cu, Zn, Nb, Cd, Al, In, and Sn) and on different substrates: silicon, highly oriented pyrolytic graphite (HOPG), and cover glass. As shown in Figure 3, we observed facile cup formation in all these cases, upon fine-tuning the experimental conditions (see Table 1). The morphology of the cups is essentially similar on the different substrates used in this study. It appears that any nonreactive, flat substrate will do for the

TABLE 1: Experimental Conditions for Femto-Cup Formation

metal (MP, K)	substrate	substrate temperature (K)	laser energy (mJ/pulse)	remarks
Ag	silicon	1093	60	cups and blobs; fewer well-defined cups
(1234.7)	silicon	300, 773, 973, 1093, 1173	100	both cups and blobs; well-defined cups above 500 °C
	HOPG	1073		cups and blobs
	cover glass	773		
Au	silicon	993	100	well-defined cups
(1337)	HOPG	993		well-defined cups
	cover glass	773		cups and blobs
Sn	silicon	300	100	well-defined cups
(504.9)	HOPG			well-defined cups
	cover glass			cups and blobs
Al	silicon	773	100	well-defined cups
(933.3)				
In		300		well-defined cups
(429.6)				
Cu		1073		well-defined cups
(1357.6)				
Zn		573		well-defined cups
(692.5)				
Nb		1273		cups and blobs
(2750)				
Cd		300		cups and blobs
(594.2)				

deposition. We could also make ceramic cups of alumina by oxidizing the Al cups deposited on a Si surface. Figure 4 shows AFM on one such cup. We see that, following the transformation, the overall shape is retained, but the surface had become slightly nonuniform. EDX analysis confirmed the formation of the oxide.

To illustrate the utility of the cups as containers or reaction vessels, we have filled them with nanometals and biomolecules. Figure 5a shows a Sn femto-cup holding a drop of Pt metal from electron beam induced deposition of a volatile organometallic precursor, cyclopentadienyl trimethyl platinum. The subsequent EDX analysis shows the presence of Pt at the center of the cup. Figure 5b shows a confocal fluorescence image of a biomarker adsorbed in an Au cup. To do this, we deposited Au cups on a cover glass with predefined markers and soaked them with Alexa 488 dye and examined under a confocal microscope (Carl Zeiss LSM510). In this experiment, the biomarker seems to be adsorbed all over the cup. Similarly, we were successful in imaging a green fluorescent protein marker (GFP) as well. A more efficient way of filling these cups would be to use a suitable injection pump. Alternatively, we have employed dip-pen nanolithography (DPN) to selectively functionalize the inside of a Ag cup with octanedithiol molecules. In this method, Ag cups were deposited onto a Si substrate with predefined markers, and a silicon nitride tip soaked in octanedithiol was positioned inside the cup and held typically for 15 min.[30] This was followed by DPN with citrate-reduced Au nanoparticles (mean size ∼20 nm). The filled cups were relocated with the help of markers using a fresh tip. Figure 5c shows the AFM image of the Ag cup filled with Au nanoparticles. The height profiles alongside show an increase in the height at the center of the cup by ∼20 nm following deposition of nanoparticles. This opens up new possibilities for local functionalization with biomolecules for specific tethering of enzymes. The cups could be detached by leaching out the substrate. This was possible in the case of Au cups prepared on a cover glass, with the latter removed by dissolving in HF. Figure 6 shows an SEM image of Au cups lifted onto HOPG. We see from the inset that the cup morphology is intact.

In conclusion, we have established, by employing pulsed laser ablation, a simple and straightforward method to produce femtocup structures of various metals (Ag, Au, Cu, Sn, Cd, Zn, Nb, In, Al) on flat substrates such as Si, HOPG, and glass. The method is, in principle, extendable to other materials. The

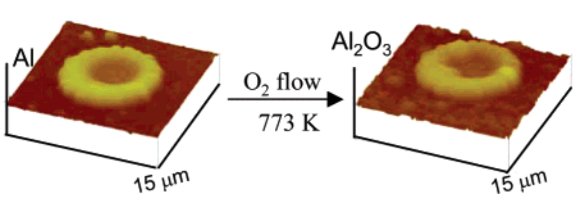

Figure 4. AFM images of an Al cup on a Si surface (left) and after oxidation to form an alumina cup (right). The feature of interest was monitored with the aid of predefined markers on the substrate.[29]

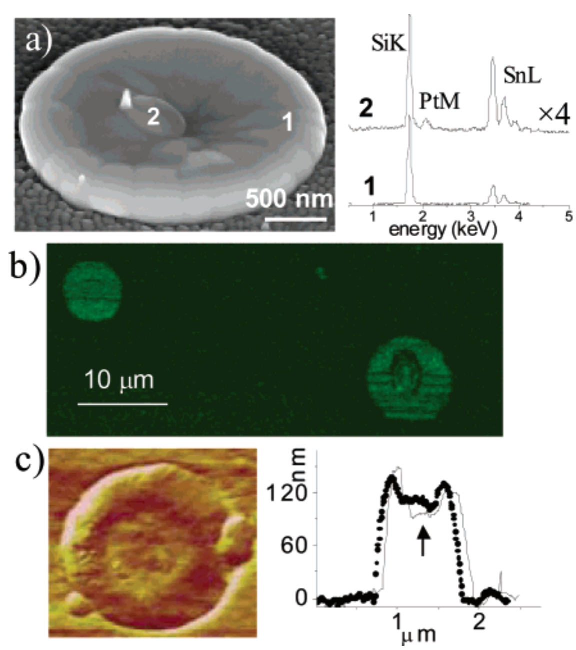

Figure 5. Filling up the femtocups. (a) A Sn cup filled with Pt metal by e-beam assisted metal deposition along with the EDX spectra. (b) Fluorescence image of Au cups adsorbed with Alexa 488 dye molecules. (c) AFM image of an Ag cup selectively functionalized with octanedithiol in the bore region by dip pen lithography, followed by Au nanoparticle adsorption. The height profile after DPN (dotted line) is raised in the center than before DPN (solid line), showing pickup of nanoparticles in the cup (see arrow).

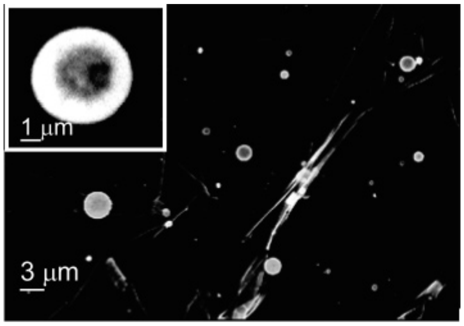

Figure 6. SEM image of Au cups lifted on to HOPG after leaching out the substrate, a microscopy cover glass, by dissolving in HF. Inset shows a closer view of a cup.

formation of these cups is attributed to the dynamics of the molten metal droplets, with the right combination of size and velocity, which translate to experimental conditions of laser pulse energy and substrate temperature. Optimal conditions for the formation of cups are thus moderate laser energies (100 mJ/pulse) and substrate temperatures close to but below the melting point of the metal under study. A hydraulic jump solely driven by surface tension is found to be the underlying mechanism in shaping these nanostructures. However, the laser ablation process provides little control over their size distribution. With a proper metal injection system designed to deliver uniform droplets, it should be possible to produce patterned cup structures with well-defined sizes. The novelty of the metal cups is that they could be chemically transformed while retaining their shape. The utility of the cups as femtoliter containers is demonstrated by filling them with fluorescent biomarkers and metal nanoparticles.

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