Formation of Metal Oxides Based Surface Hollow Nanolenses and Their Optical Properties

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Threshold Impact

Introduction

- Surface nanodroplets are of significant interest because of their novel fundamental properties (Figure 1). [1]
- Recent works reported a preparation of optical-active surface nanolenses based on the polymerization of nanodroplets. [2]
- In this work, we develop an approach to prepare surface hollow nanolenses comprising a layer of metal oxides that serves as a shell.
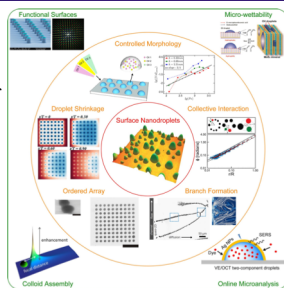- The optical properties of metal oxides based surface hollow nanolenses are tested.

Figure 1. Features and applications of surface nanodroplets. Reproduced from Ref. 1

Method

A ternary liquid mixture comprising oleic acid, ethanol and water serves as solution A. The ternary phase diagram is shown in Figure 2. Solvent exchange process took place in a fluid cell, as shown in Figure 3. Solution A was injected into the cell firstly, followed by injecting pure water (solution B). [3] After oleic acid nanodroplets formed on the substrate (Si wafer), 0.01 M $MnCl_2$ + 0.02 M $FeCl_3$ aqueous solution was injected to react with the oleic acid nanodroplets. The cell was then disassembled. The Si wafer with nanodroplets was annealed at 300°C in air for 30 min.
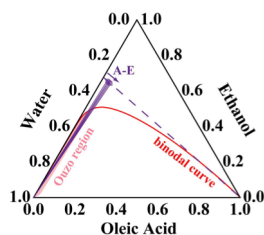

Figure 2. Ternary phase diagram of water, ethanol and oleic acid. The initial component ratio of Sample A-E in Table 1 are also marked here.
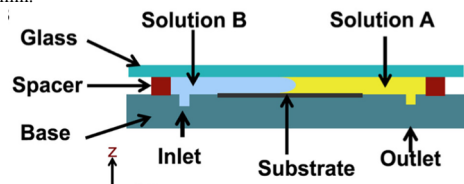

Figure 3. Sketch of the fluid cell set up for the formation of oleic acid nanodroplets on a Si wafer.
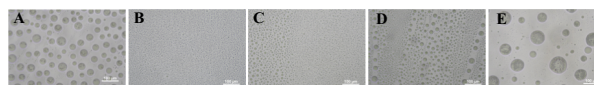
Results

Figure 4. Optical images of oleic acid nanodroplets formation in different concentrations.

The size of the nanodroplets that formed on the Si wafer depends on the concentration of oleic acid. The different concentrations, according to the purple points in Figure 2, cause the droplets to vary in volume, diameter and size distribution. The optical images are shown in Figure 4.

Table 1. The component ratios of solution A.

Sample	Solution A (Oleic acid/Deionized water/Ethanol)	Solution B (Deionized water)
A	4.1/30/70	100
B	4.25/30/70	100
C	4.4/30/70	100
D	4.6/30/70	100
E	4.8/30/70	100

The probability distribution function (PDF) profiles of droplet volume are shown in Figure 5. The droplet volume is calculated based on the assumption that the contact angle of nanodroplet is ~ 20°. Except sample B, the other four samples show similar trends with wider size distributions and two maximal values, which agrees with the results in Figure 4.
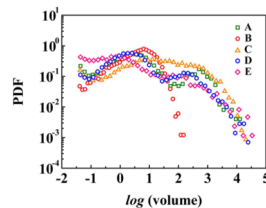

Figure 5. Corresponding PDF profiles of oleic acid nanodroplets formed in Figure 3.
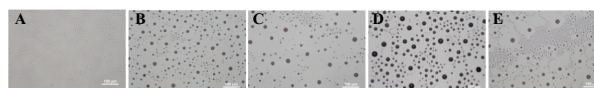

Figure 6. Optical images of metal oxides based surface hollow nanolenses produced from oleic acid with different diameters.

As shown in Figure 7, the Fe/Mn precursors reacted with oleic acid only at the liquid/liquid interface to form the shell structured Fe/Mn coordination compounds, which will be further converted into Fe/Mn oxides hollow nanolenses after annealing. As shown in Figure 6, the diameter of the nanolenses can be adjusted. Compared to the size of nanodroplets, the nanolenses always shrink ~20%.

Figure 7. Optical image of a typical broken metal oxides based surface hollow nanolens.

The nanolenses can also be formed on the glass slide, as shown in Figure 8A. The morphology is similar to the one on the Si wafer. As shown in Figure 8B, the diffraction patterns of the array were taken by projecting a beam of white light normal to the lens array through a pinhole. The pattern shows several rings from center to outer part with different color.
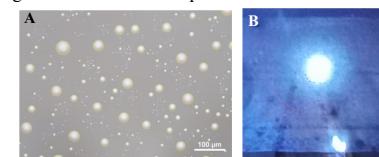

Figure 8. Optical image of nanolenses formation on glass slides and the corresponding light diffraction pattern.

Conclusions

- Oleic acid surface nanodroplets were produced *via* solvent exchange process. The droplet geometries can be adjusted by changing the initial oleic acid ratio.
- When the initial component ratio of oleic acid/water/ethanol is 4.25/30/70, the droplet formation can be homogeneous compared to other ratios.
- The metal (Fe and Mn) precursors can react with oleic acid at the droplet surface, further leading to the formation of surface hollow nanolenses after annealing in air.
- The preliminary results show that the surface hollow nanolenses can show a diffraction pattern with color changing.
- The surface hollow nanolenses show a potential for photocatalysis, plasmonics, lab-on-chip devices, and others.
- The experimental results are close to previous studies.

Acknowledgements

References:
[1] J. Qian, G. Arends, X. Zhang, *Langmuir* **2019**, DOI: 10.1021/acs.langmuir.9b01051.
[2] H. Yu, S. Peng, L. Lei, J. Zhang, T. L. Greaves, X. Zhang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 22679-22687.
[3] D. Lohse, X. Zhang, *Rev. Mod. Phys.* **2015**, *87*, 981-1035.