Single Phase Transition Leads to the Coffee Ring Deposition of Nanoparticles in an Evaporating Sessile Droplet

Sujay Paul, [†] and Arun Chattopadhyay^{*,†, ‡}

[†] Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India.

[‡] Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati - 781039, Assam, India.

ABSTRACT: The coffee-ring formation upon evaporation of a sessile droplet laden with dispersed particles occurs via capillary flow of the fluid towards the three-phase pinned contact line. In the process, the particles are carried towards the contact line followed by gradual deposition that accelerates towards the end of drying. However, we have observed using surface enhanced Raman spectroscopy (SERS) with gold nanoparticles that the deposition process at the contact line occurred in a short window of time that was akin to a phase transition and that was complete well before the drying of the droplet. Further, the concentration of nanoparticles at the time of deposition was the same irrespective of the initial concentrations studied, the value of which was calculated to have been on the order of 13 μ M.

INTRODUCTION:

Evaporation of a sessile droplet containing colloidal particles is scientifically intriguing and technologically important such as in inkjet printing,¹ device fabrication² and disease diagnosis³. The well-established knowledge in this regard is that faster evaporation of the fluid at the three-phase contact line sets up a capillary flow that helps carry the fluid from the bulk to the periphery. The dispersed particles that are carried towards the contact line are deposited gradually there with acceleration of the process towards the end of evaporation. The end result is a characteristic ring formation in the deposits. The phenomenon is popularly referred to as the "coffee ring effect" (CRE).⁴ Various modern experimental techniques have helped improve the understanding of the particle movement and deposition characteristics that depend on the

particle size,³ temperature,⁵ humidity,⁶ substrate morphology⁷ and viscosity of the solvent⁸. However, pursuing the deposition of nanoscale particles on substrate surface with time is also important, considering their impact in current progress in technology. For example, droplet evaporation driven plasmonic nanoparticle assembly have advantages in heterogenous plasmon catalysis,⁹ toxic analyte detection,¹⁰ accurate diagnosis of cancer¹¹ and biomolecule detection that are especially relevant in disease diagnosis¹². Surface enhanced Raman spectroscopy (SERS) is a well-established method that could be utilized in order to probe particle deposition at the pinned contact line owing to plasmonic 'hot-spot' generation at the junctions of plasmonic nanoparticles (Au or Ag).¹³ Thus, a question can be raised about the possibility of new findings in the evaporation process leading to coffee ring formation. In other words, could SERS based pursuit of the droplet evaporation at the pinned contact line reveal new information about the nanoscale particle deposition process?

Herein, we report, for the first time, the observation of phase transition leading to solid particle deposition, in the evaporation of water droplets containing sodium 4-mercaptobenzoate capped gold nanoparticles (NaMBA-AuNPs). The nanoparticles helped in pursuing SERS during the formation of ring pattern at the pinned three-phase contact line (TPCL). Droplet evaporation and ring pattern formation were simultaneously observed using Raman microscope and a digital camera. Before complete drying, there was a sudden increase in the Raman signal intensity due to 4-MBA molecules that were attached to the nanoparticles, and which remained nearly constant till the droplet was dry. The plot of Raman signal of a characteristic peak with time indicated a sharp change in the intensity at the point of deposition, analogous to a transition from dispersed to deposit phase of the particles.

RESULTS AND DISCUSSIONS:

A stable dispersion in water that consisted of 2.5 nM spherical NaMBA-AuNP having a diameter of 25.3 ± 4.2 nm was used in the 'coffee-ring' formation experiment. 5 µL of the NP dispersion was dropped on a glass substrate and taken to the sample holder of the Raman spectrometer. Typical diameter of the droplet was less than 2 mm. Raman spectra were recorded on a spot at the periphery and images of the entire droplet were captured after every 2.5 min while it was evaporating at 22 °C temperature and 65% relative humidity in an airconditioned room as shown in Figure 1a. With time as the droplet was evaporating there were changes in the height and contact angle; however, no signal due to NaMBA-AuNP could be observed for a significant amount of time. We observed photographically the starting of AuNP

deposition at the TPCL from 22.5 min (Figure 1b(ii)), which is also reflected in the appearance of Raman signal of MBA as presented in Figure 1c(ii). The maximum Raman signal intensity



Figure 1: (a) Schematic of the experimental setup of the Raman measurement using 633 nm laser while the droplet of NaMBA-AuNP dispersion was evaporating. (b) Raman microscopic images recorded from above the droplet and at the three-phase contact line. (c) Raman spectra recorded at the contact line and (d) side-view of the droplet captured using a camera at (i) 0 min, (ii) 22.5 min, (iii) 25.0 min and (iv) 45.0 min of evaporation, respectively.

was observed at 25.0 min (Figure 1c(iii)). At that moment, AuNP deposition was pronounced as can be seen in Figure 1b(iii) and water was still present as shown in Figure 1d(iii). We obtained a ring pattern consisting of the deposit that hinted of the presence of NaMBA-AuNP after complete drying (Figure 1b(iv). It took took around 40 min for complete drying of the droplet. The time-dependent Raman spectra observed in a typical experiment are plotted in Figure 2a. As can be observed from the figure, the Raman intensities were negligible till about 20.0 min. Then there was sudden increase in the peak intensities. From the plot of the intensity of 1078.0 cm⁻¹ Raman peak - corresponding to combined C=C stretching and C–S stretching vibrations¹⁴ - with time, we observed significant change in the intensity within a short window of time from 20.0 min to 25.0 min, as shown in Figure 2b. The intensity was further reduced after complete drying of the droplet at 40.0 min. This was due to complete loss of water, which acts as a better dielectric environment for NaMBA-AuNP in order to give intense SERS signal.¹⁵ Here, the intensity of the Raman signal was dependent only on molecule-laden particle concentration (in the form of the deposit) as laser power was kept constant. As is clear from the graphs, the signal intensity was negligible when the particles were in dispersed phase. On the other hand, when the particles were deposited as solid SERS and plasmonic 'hot-spot' generation at the junctions of nanoparticles would have significantly increased Raman signal intensity. Further, a continuous deposition at the point of probe (contact line) would have



Figure 2: (a) Raman spectra, measured at the three-phase contact line and at different times, of the evaporating droplet containing 2.5 nM NaMBA-AuNP. (b) Plot of intensity of the 1078 cm^{-1} Raman peak versus time and the red curve is Boltzmann fitting of sigmoidal growth.

resulted in a monotonous increase in the Raman signal intensity. However, our observation of a sudden jump in the intensity represents a phase transition of the dispersed NaMBA-AuNPs into solid deposit as shown in Figure 2b with the fitted plot. The inflection-point at 23.0 min of the fitted plot implied the moment of phase transition when water was still present. The concentration of the particle of the particular size at the TPCL during phase transition was calculated using the formula,

$$C(\mathbf{r},t) = \frac{N(t) \times 10^{15}}{N_A \times v(\mathbf{r},t)} \,\mu \mathbf{M} \tag{1}$$

where N(t) is number of particles that reached the coffee ring at time t obtained using expression reported earlier,¹⁶ N_A is the Avogadro's number and v(r,t) is the volume in nL of the liquid at the TPCL, which was calculated by approximating the TPCL region as right triangular prism of height that was equal to the periphery of the droplet. The concentration of the NaMBA-AuNPs at the TPCL during phase transition of this experiment was calculated to be 11.5 μ M. It may be mentioned here that the experiments performed with different initial NaMBA-AuNP concentrations revealed that higher concentrations resulted in faster phase transition time and the concentration of the particles at the TPCL during phase transition was nearly the same. In summary, for the first time, we have observed a phase transition during the evaporation of water droplet containing Raman active molecule attached to AuNPs, based on SERS. NaMBA-AuNPs were deposited as solid at the contact line in a window of short period of time much before the complete evaporation of the solvent. Average concentration of the nanoparticles at the TPCL during phase transition - that was based on three independent experiments - was found to be on the order of $13 \mu M$.

ACKNOWLEDGEMENT:

This work was supported by Ministry of Electronics and Information Technology, Government of India (MEITY grant no. 5(1)/2022- NANO). AC thanks the Science and Engineering Research Board of the Department of Science and Technology, Government of India, for a J. C. Bose Fellowship (JCB/2019/000039). Instrument facility from Central Instruments Facility (CIF), and Centre for Nanotechnology at IIT Guwahati are acknowledged. Sujay Paul thanks Council of Scientific & Industrial Research (CSIR) for fellowship [File number: 09/731(0165)/2018-EMR-I].

AUTHOR INFORMATION:

Corresponding Author

Arun Chattopadhyay – Professor, Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam- 781039; Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati, Assam- 781039; orcid.org/ 0000-0001-5095-6463; Email: arun@iitg.ac.in

Author

Sujay Paul – Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam- 781039; orcid.org/0009-0002-1306-8947; Email: <u>sujaypaul@iitg.ac.in</u>

Keywords: Coffee-ring effect, gold nanoparticles, phase transition, surface enhanced Raman spectroscopy.

REFERENCES:

 Torrisi, F.; Hasan, T.; Wu, W.; Sun, Z.; Lombardo, A.; Kulmala, T. S.; Haieh, G.-W.; Jung, S.; Bonaccorso, F.; Paul, P. J.; Chu, D.; Ferrari, A. C. Inkjet-Printed Graphene Electronics. *ACS Nano* 2012, *6*, 2992-3006.

- Sliz, R.; Czajkowski, J.; Fabritius, T. Taming the Coffee Ring Effect: Enhanced Thermal Control as a Method for Thin-Film Nanopatterning. *Langmuir* 2020, *36*, 9562-9570.
- Wong, T.-S.; Chen, T.-H.; Shen, X.; Ho, C.-M. Nanochromatography Driven by the Coffee Ring Effect. *Anal. Chem.* 2011, *83*, 1871-1873.
- Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Contact line deposits in an evaporating drop. *Phys. Rev. E* 2000, *62*, 756-765.
- 5. Zhang, W.; Yu, T.; Liao, L.; Cao, Z. Ring formation from a drying sessile colloidal droplet. *AIP Advances* **2013**, *3*, 102109.
- 6. Brutin, D. Influence of relative humidity and nano-particle concentration on pattern formation and evaporation rate of pinned drying drops of nanofluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013**, *429*, 112-120.
- Lohani, D.; Basavaraj, M. G.; Satapathy, D. K.; Sarkar, S. Coupled effect of concentration, particle size and substrate morphology on the formation of coffee rings. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2020, 589 124387.
- Wilkinson, J.; Tam, C.; Askounis, A.; Qi, S. Suppression of the coffee-ring effect by tailoring the viscosity of pharmaceutical sessile drops. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2021, 614, 126144.
- Pal, S.; Paul, S.; Chattopadhyay, A. Enhanced Solid-State Plasmon Catalyzed Oxidation and SERS Signal in the Presence of Transition Metal Cations at the Surface of Gold Nanostructures. *Phys. Chem. Chem. Phys.* **2021**, *23*, 21808-21816.
- Bhakat, A.; Paul, S.; Chattopadhyay, A. Molecular Specificity in the Intense Surface-Enhanced Raman Scattering on Copper(II) 8-Hydroxyquinoline Microcrystals. *J. Phys. Chem. C* 2023, *127*, 5169-5177.
- 11. Gao, S.; Lin, Y.; Zhao, X.; Gao, J.; Xie, S.; Gong, W.; Yu, Y.; Lin, J. Label-free surface enhanced Raman spectroscopy analysis of blood serum via coffee ring effect for accurate diagnosis of cancers. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2022, 267, 120605.
- 12. Tahir, M. A.; Dina, N. E.; Cheng, H.; Valev, V. K.; Zhang, L. Surface-enhanced Raman spectroscopy for bioanalysis and diagnosis. *Nanoscale*, **2021**, *13*, 11593-11634.

- Langer, J.; Jimenez de Aberasturi, D.; Aizpurua, J.; Alvarez-Puebla, R. A.; Auguié, B.; Baumberg, J. J.; Bazan, G. C.; Bell, S. E. J.; Boisen, A.; Brolo, A. G., et al. Present and Future of Surface-Enhanced Raman Scattering. *ACS Nano* 2020, *14*, 28-117.
- Marques, F. C.; Alves, R. S.; dos Santos, D. P.; Andrade, G. F. S. Surface-enhanced Raman spectroscopy of one and a few molecules of acid 4-mercaptobenzoic in AgNP enabled by hot spots generated by hydrogen bonding. *Phys. Chem. Chem. Phys.* 2022, 24, 27449-27458.
- 15. de Barros, A.; Shimizu, F. M.; de Oliveira, C. S.; Sigoli, F. A.; dos Santos, D. P.; Mazali, I. O. Dynamic Behavior of Surface-Enhanced Raman Spectra for Rhodamine 6G Interacting with Gold Nanorods: Implication for Analyses under Wet versus Dry Conditions. ACS Appl. Nano Mater. 2020, 3, 8138-8147.
- 16. Boulonge, F.; Ingremeau, F.; Stone, H. A. Coffee-stain growth dynamics on dry and wet surfaces. *J. Phys.: Condens. Matter* **2017**, *29*, 074001.