

# NANOPARTICLE HALO FORMATION AROUND COLLOIDAL MICROSPHERES IN BINARY SOLUTIONS

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## INTRODUCTION

Colloidal suspensions enjoy widespread use in applications ranging from food science to advanced materials.[1, 2] In most systems of practical importance, van der Waals forces must be balanced by Coulombic, steric or other repulsive interactions to provide control over suspension stability. Nanoparticle engineering[3] is a new paradigm by which these interactions may be regulated. It's been recently demonstrated that binary mixtures possessing high size and charge asymmetry, in which microspheres are negligibly charged and nanoparticles are highly charged, experience a rich phase behavior that transitions from a colloidal gel to a stable fluid and subsequently to a colloidal gel with increasing nanoparticle concentration. We attributed the stabilizing transition to nanoparticle "haloing" around the microspheres, which serves to mitigate their van der Waals attraction.

This novel stabilization route has been observed experimentally in many binary mixtures composed of microspheres and nanoparticles [3-5]. Due to the large size difference (~100-fold) between the microspheres and nanoparticles, resolving the spatial distribution of nanoparticles around the microspheres is difficult. In this study, we report ultra-small-angle X-ray scattering (USAXS) measurements of the structure of silica microsphere-zirconia nanoparticle mixtures that quantify the extent of nanoparticle halo formation in this system.

## EXPERIMENTAL

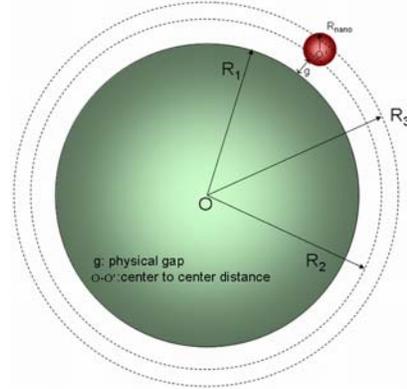
Details of synthesis can be found in [6]. The USAXS studies are conducted at beamline 33-ID at the Advanced Photon Source, Argonne National Laboratory. This instrument employs Bonse-Hart-type double-crystal optics to extend the scattering vector  $q$  range of small-angle X-ray scattering (SAXS) to a very small value, which is normally buried behind the beamstop for pinhole SAXS cameras. We measured the scattering intensity as a function of  $q$  using collimated and monochromatic X-rays in the standard transmission geometry. The wavelength is 1.20 Å.

We loaded the samples into a custom-made stainless steel cell with Kapton entrance and exit windows and a 1mm liquid scattering path. We collected two sets of USAXS measurements to determine the instrumental scattering profile: one with an empty cell, and the other with the cell filled with solvent (DI water or pH 1.5 water). In the data reduction process we eliminated the contributions of Kapton and solvent to the scattering signal of the microsphere, nanoparticle, or microsphere-nanoparticle suspensions.

We measured the USAXS intensity over a  $q$  range from  $1 \times 10^{-4} \text{ \AA}^{-1}$  to  $0.5 \text{ \AA}^{-1}$ . The  $q$  resolution is  $1.5 \times 10^{-4} \text{ \AA}^{-1}$ . The beam size is  $2.0 \times 0.6 \text{ mm}^2$ . The incident photon flux on the sample is  $10^{12}$  photons per second. No radiation damage was observed.

## RESULTS

We modeled the scattering form factor with a mean-field model illustrated in the figure below:



We studied the distribution of nanoparticles near the surface of silica microspheres in binary mixtures stabilized by nanoparticle haloing. We found that the nanoparticles self-organize into a halo that resides at a separation distance of  $\sim 2 \text{ nm}$  from the microsphere surface. This distance is nearly equivalent to the Debye length. We have further found that the nanoparticle concentration within this shell is significantly enriched relative to its bulk value in solution; yet, the lateral separation distance between nanoparticles within each halo greatly exceeds their characteristic size.

## REFERENCES

- [1] J.A. Lewis, Direct-write assembly of ceramics from colloidal inks, *Current Opinion in Solid State & Materials Science* 6 (2002) 245-250.
- [2] Y.N. Xia, B. Gates, Y.D. Yin, Y. Lu, Monodispersed colloidal spheres: Old materials with new applications, *Advanced Materials* 12 (2000) 693-713.
- [3] V. Tohver, J.E. Smay, A. Braem, P.V. Braun, J.A. Lewis, Nanoparticle halos: A new colloid stabilization mechanism, *PNAS* 98 (2001) 8950-8954.
- [4] A.T. Chan, J.A. Lewis, Electrostatically tuned interactions in silica microsphere-polystyrene nanoparticle mixtures, *Langmuir* 21 (2005) 8576-8579.
- [5] D.Y. Kong, H. Yang, Y. Yang, S. Wei, H.B. Wang, B.J. Cheng, Dispersion behavior and stabilization mechanism of alumina powders in silica sol, *Materials Letters* 58 (2004) 3503-3508.
- [6] V. Tohver, A. Chan, O. Sakurada, J.A. Lewis, Nanoparticle Engineering of Complex Fluid Behavior, *Langmuir* 17 (2001) 8414-8421.

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