Size Limitations for the Formation of Ordered Striped Nanoparticles

Randy P. Carney,[†] Gretchen A. DeVries,[†] Cedric Dubois,[†] Hyewon Kim,[†] Jin Young Kim,[†]
Chetana Singh,[||] Pradip K. Ghorai,[||] Joseph B. Tracy,[§] Rebecca L. Stiles,[§] Royce W. Murray,[§]
Sharon C. Glotzer,[‡,||] and Francesco Stellacci*,[†]

*Department of Materials Science & Engineering, MIT, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139,
Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109, Department of
Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, and Department of Materials Science
and Engineering, University of Michigan, Ann Arbor, Michigan 48109*

Received September 27, 2007; E-mail: frstella@mit.edu

Nanoparticles (NPs) are much-studied due to their electronic[1] and optical[2] properties and their potential for use in systems such as chemical or biological sensing[3] and catalysis.[4] A common type of NP consists of a gold core coated with a self-assembled monolayer (SAM) of thiolated molecules. The SAM, or ligand shell, imparts many properties to the NP, such as solubility[5] and assembly into complex structures.[6] A thorough understanding of the composition and morphology of the ligand shell is essential for controlling the properties and behavior of NPs.

In a SAM composed of two immiscible molecules on a flat surface, phase separation occurs and the molecules segregate into randomly shaped patterns.[7] We have previously demonstrated[5,8,9] that when a NP is coated with such a mixture, the ligands phase separate into ordered, striped domains, or "ripples" (see Figure 1). These stripes form because of a competition between enthalpic losses and entropic gains (when mixing molecules of different length) at phase boundaries.[10] The alignment of stripes is driven by topological constraints inherent in assembling what should be a 2D crystal (the SAM) onto a 3D surface.[11] Ripples impart unique properties.[5,8,9] For example, a series of NPs with an increasing ratio of hydrophobic to hydrophilic ligands shows anomalous nonmonotonic solubility in various solvents.[5] Rippled NPs also are highly resistant to protein nonspecific adsorption.[5]

We recently predicted the existence of a size range for ordered striped domains in simulations.[10] On small NPs, a binary mixture of surfactants separates into two "bulk" phases. On increasing the NP radius, phase separation into ordered ripples occurs. When the radius is further increased, disordered stripes and patchy domains form. The experimental size range where ordered ripples (and consequently structure-determined properties) are present was not determined. This is the goal of this Communication.

The potential for the introduction of divalency is a major consequence of ripples in NPs; that is, rippled NPs possess two highly reactive polar point defects.[11] Molecules in a SAM have a tilt angle relative to the surface normal to maximize interactions with their neighbors.[7,12] For NPs, this tilt angle remains consistent relative to an axis of the NP rather than changing on each facet of the crystalline core.[13,14] Arranging such a vectorial order (projections of the SAM molecules) onto a topological sphere (a NP core) is only possible if two defect points form in diametrically opposed positions on the sphere (Hairy Ball Theorem).[15,16] This implies that two defect sites exist in the ligand shell at which the molecules are not optimally stabilized by intermolecular interactions. We proved that these sites, or "poles", are highly reactive and can be selectively
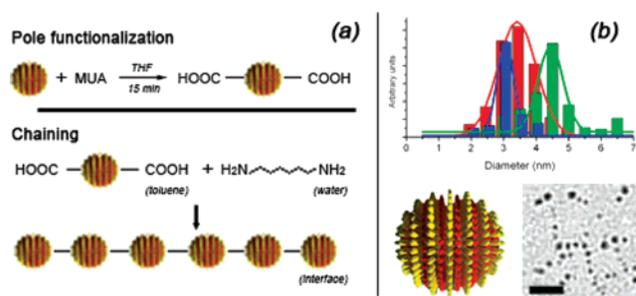

Figure 1. (a) Two steps of chain formation: pole functionalization of rippled NPs with MUA then interfacial polymerization. (b) NP size distributions measured from TEM images. Red is that of the starting NPs, green is that of chained NPs, and blue is that of unchained NPs. Bars represent the actual distribution; lines are Gaussian fits. The graphs are normalized for better visualization; the average NPs size after chaining is 2.7 nm. Below left is a cartoon of a rippled NP; below right is a representative TEM image of NP chains, scale bar 25 nm.

functionalized with a place-exchange reaction.[11] Specifically, we placed carboxylic acid-terminated molecules at the poles to generate divalent NPs; subsequent reaction of these NPs with diamine molecules generated chains of NPs. Notably, this chemical divalency cannot be introduced in homoligand NPs. Here we show that divalent NPs (and consequently rippled NPs) exist only in a certain size range; smaller and larger NPs cannot form chains.

We used gold NPs coated with a 2:1 molar mixture of 1-nonanethiol and 4-methylbenzenethiol, as previously studied.[11] To obtain a range of NP sizes, we synthesized NPs with different methods: a one-phase reaction in ethanol,[17] a two-phase reaction in toluene and water,[18] and a one-phase reaction in benzene.[19]

The synthesis of NP chains is a two-step reaction (Figure 1a). The first step, pole functionalization, is a place-exchange reaction at the polar defect sites, in which the NPs are stirred with a small excess (typically ~20-fold) of 11-mercaptoundecanoic acid (MUA), then filtered to remove unreacted MUA. The NPs are transferred into toluene for the second step: an interfacial polymerization in which the NPs in toluene react with a water solution of 1,6-diaminohexane. A precipitate appears at the interface, indicating the formation of insoluble chains. At equilibrium (as all the reactions presented are), up to 80% of the NPs precipitate from the two-phase polymerization (depending on the amount of MUA excess). Transmission electron microscopy (TEM) was used to characterize the precipitate (Figure 1b)[11] and the supernatant and to determine the NP size distribution.

To determine the effect of NP size on chain formation, we pole functionalized and made chains with a polydisperse sample of NPs and then measured the size distribution of the NPs within and outside the chains in both the precipitate and the supernatant.

[†] MIT.
[‡] Department of Materials Science and Engineering, University of Michigan.
[§] University of North Carolina.
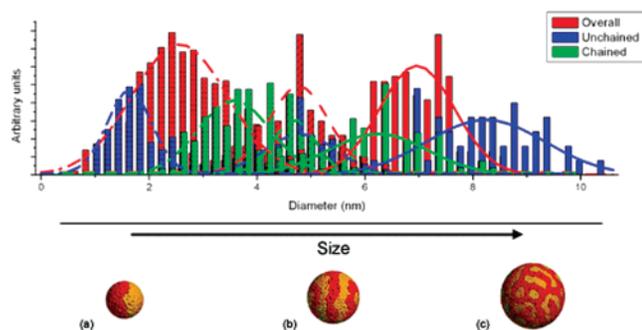[||] Department of Chemical Engineering, University of Michigan.

Figure 2. Size distributions before and after chaining for three different sets of NPs. Chains form only for NPs in a certain size range. Bars represent actual data; lines are Gaussian fits. Each type of line (solid, dashed, or dashed-dotted) represents one complete set of NPs (starting, unchained, and chained distributions). (a−c) Simulation snapshots of phase separation in mixtures of surfactants of unequal length on spheres of increasing diameter.

These NPs, synthesized with a one-phase synthesis, had an average diameter of 3.2 ± 0.7 nm (before the chaining reaction), close in size with those used in previous studies.[11] We observed a size selection after chaining: the average diameter of the NPs in chains was 4.2 ± 0.9 nm and that of isolated NPs was 2.8 ± 0.5 nm (Figure 1b). We twice obtained the same result. To strengthen this conclusion, we performed t-tests ($\alpha = 0.05$) on the data. A statistical difference between the sizes of the chained and the unchained NPs was found, but the results from the two experiments were statistically indistinguishable; that is, there was no significant difference between the sizes of the NPs in the chains (and similarly outside the chains) from the two experiments. Similarly, we used NPs from two different batches (this time synthesized with the two-phase reaction) and again found a statistical difference between the distributions of chained and unchained NPs but not between the results from the two batches. To show that the results were not influenced by size-selective precipitation, we compared the sizes of chained NPs (and similarly of unchained NPs) in the precipitate to those in the supernatant (dimers tend not to precipitate)[11] and found no difference. Similar results were obtained for batches of smaller NPs (2.5 nm - see Supporting Information). We analyzed the size of the NPs before and after chaining (including precipitate and supernatant) (3.5 ± 0.9 and 3.5 ± 0.3, respectively) and found no evidence for size changes during the process.

Divalent NPs are an effect of the rippled ligand structure. The fact that smaller NPs do not form chains can be explained by postulating either that poles in small NPs are less reactive than those in large ones or that poles (and thus ripples) in small NPs do not exist.[20] The latter is consistent with our simulations.[10] To distinguish between these cases, we focused on three batches of polydisperse NPs with different average diameters (2.5, 4.5, and 6.9 nm). For the set with the smallest sizes, the chained NPs were larger than the unchained ones (3.5 and 1.7 nm); for the set with the largest sizes, the reverse was found (6.2 nm in chains versus 8.2 nm unchained); see Figure 2. In both cases, the sizes of the chained and unchained NPs were statistically different. For the middle set, there was no difference between the sizes of the chained and unchained NPs (4.6 nm). Chains form only in a specific size range, for our system[21] between ∼2.5 and ∼8.0 nm. Prompted by simulation results (Figure 2), we believe this implies that rippled domains form only on NPs in that size range; that is, mixed monolayers on NPs outside this range assume a different morphology than the ordered phase separation that leads to polar defects and chains. Experiments on 1.8 ± 0.6 nm NPs support this interpretation. These NPs did not form chains, and we found no domains in scanning tunneling microscopy images (see Supporting

Information). We recently developed[22] a method to calculate the equilibrium constant of pole functionalization by correlating the amount of precipitation from the interfacial reaction to the fraction of pole functionalized NPs. This method assumes that all NPs are available for pole functionalization and chain formation, that is, that all NPs have rippled ligand domains. This is reasonable for the sample of Figure 1 (3.2 nm average diameter), where most of the NPs are within the size range for ripple formation; for these types of samples, we obtained an average equilibrium constant of $1000 \pm 50 \text{ M}^{-1}$. For the smallest sample of Figure 2, when we do not account for the 40% of the NPs that are too small to be rippled, we obtain an equilibrium constant of $400 \pm 11 \text{ M}^{-1}$. Accounting for the unavailable NPs, we obtain $800 \pm 64 \text{ M}^{-1}$, in better agreement with the value for Figure 1. This reinforces the idea that only NPs in a certain size range are divalent.

In conclusion, this work demonstrates that chaining occurs only with NPs in a certain size range; this, by extension, implies that the aligned rippled organization of the ligand shell only exists in that specific size range as predicted by simulation. We believe that these size limitations will have implications for other properties of rippled NPs. Moreover, here we have presented a simple approach to determine whether NPs have "rippled" ligand shells.

Supporting Information Available: Experimental and simulation details; statistical data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R. *Science* **1996**, *272*, 1323−1325.
(2) Thomas, K. G.; Kamat, P. V. *Acc. Chem. Res.* **2003**, *36*, 888−898.
(3) Willets, K. A.; Van Duyne, R. P. *Ann. Rev. Phys. Chem.* **2007**, *58*, 267−297.
(4) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346.
(5) Jackson, A. M.; Myerson, J. W.; Stellacci, F. *Nat. Mater.* **2004**, *3*, 330−336.
(6) Zhang, Z. L.; Horsch, M. A.; Lamm, M. H.; Glotzer, S. C. *Nano Lett.* **2003**, *3*, 1341−1346.
(7) Schreiber, F. *Prog. Surf. Sci.* **2000**, *65*, 151−256.
(8) Jackson, A. M.; Hu, Y.; Silva, P. J.; Stellacci, F. *J. Am. Chem. Soc.* **2006**, *128*, 11135−11149.
(9) Centrone, A.; Hu, Y.; Jackson, A. M.; Zerbi, G.; Stellacci, F. *Small* **2007**, *3*, 814−817.
(10) Singh, C.; Ghorai, P. K.; Horsch, M. A.; Jackson, A. M.; Larson, R. G.; Stellacci, F.; Glotzer, S. C. *Phys. Rev. Lett.* **2007**, *99*, 226106.
(11) DeVries, G. A.; Brunnbauer, M.; Hu, Y.; Jackson, A. M.; Long, B.; Neltner, B. T.; Uzun, O.; Wunsch, B. H.; Stellacci, F. *Science* **2007**, *315*, 358−361.
(12) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1169.
(13) Luedtke, W. D.; Landman, U. *J. Phys. Chem. B* **1998**, *102*, 6566−6572.
(14) Ghorai, P. K.; Glotzer, S. C. *J. Phys. Chem. B* **2007**, in press.
(15) Nelson, D. R. *Nano Lett.* **2002**, *2*, 1125−1129.
(16) Poincare, H. *J. Math. Pure Appl.* **1885**, *1*, 167.
(17) Stellacci, F.; Bauer, C. A.; Meyer-Friedrichsen, T.; Wenseleers, W.; Marder, S. R.; Perry, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 328−329.
(18) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802.
(19) Zheng, N.; Fan, J.; Stucky, G. D. *J. Am. Chem. Soc.* **2006**, *128*, 6550−6551.
(20) The chaining reaction reaches equilibrium in our conditions.
(21) We expect that the size range for obtaining ordered ripples will depend on the nature and molecular ratio of the ligands.
(22) DeVries, G. A.; Talley, F. R.; Carney, R. P.; Stellacci, F. *Adv. Mat.* **2007**, accepted.

JA077383M