BNL-114376-2017-JA

Shape-Specific Patterning of Polymer-Functionalized Nanoparticles

E. Galati, O. Gang

Submitted to ACS Nano

May 2017

Center for Functional Nanomaterials

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Shape-Specific Patterning of Polymer-Functionalized Nanoparticles

Elizabeth Galati,¹ Moritz Tebbe,¹ Ana Querejeta-Fernández,^{1†} Huolin L. Xin,² Oleg Gang,^{2,3,4} Ekaterina B. Zhulina,^{5,6} and Eugenia Kumacheva^{*,1,7,8}

¹Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada

²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA

³Department of Chemical Engineering, Columbia University, New York, NY, 10027, USA

⁴Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY, 10027, USA

⁵Institute of Macromolecular Compounds of the Russian Academy of Sciences, Saint Petersburg, 199004, Russia

⁶Saint Petersburg National University of Informational Technologies, Mechanics and Optics, Saint Petersburg, 197101, Russia

⁷Institute of Biomaterials and Biomedical Engineering, University of Toronto, 4 Taddle Creek Road, Toronto, Ontario M5S 3G9, Canada

⁸Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario M5S 3E5, Canada

KEYWORDS: Nanoparticles, nanocubes, surface patterning, surface curvature, pinned micelles, polymer patches

ABSTRACT: Chemically and topographically patterned nanoparticles (NPs) with dimensions on the order of tens of nanometers have a diverse range of applications and are a valuable system for fundamental research. Recently, thermodynamically controlled segregation of a smooth layer of polymer ligands into pinned micelles (patches) offered a new approach to nanopatterning of polymer-functionalized NPs. Control of the patch number, size and spatial distribution on the surface of spherical NPs has been achieved, however the role of NP shape remained elusive. In the present work, we report the role of NP shape, namely, the effect of the local surface curvature, on polymer segregation into surface patches. For polymer-functionalized metal nanocubes, we show experimentally and theoretically that the patches form preferentially on the high-curvature regions such as vertices and edges. An *in-situ* transformation of the nanocubes into nanospheres leads to the change in the number and distribution of patches in the process that is dominated by the balance between the surface energy and the stretching energy of the polymer ligands. The experimental and theoretical results presented in this work pave the way for the surface patterning of polymer-capped NPs with a variety of shapes, thus enabling the exploration of new self-assembly modes and use of NPs as colloidal surfactants and templates for the synthesis of hybrid nanomaterials.

Nanoparticles (NPs) patterned with chemically or topographically distinct surface regions (the so called "patchy" NPs) have promising applications as building blocks for the next generation of functional nanomaterials.¹ Carefully designed surface patches can render directionality in NP interactions, thus allowing for their self-assembly in nanostructures with desired orientation-dependent properties and functions.^{2,3} Other applications of surface-patterned NPs include their use as colloidal surfactants⁴ and templates for the synthesis of multicomponent particles.⁵ Substantial progress has been achieved in the generation of micrometer-size patchy particles.⁶⁻⁹ Surface patterning of NPs with dimensions on the order of tens of nanometers is less common in the colloidal domain, and is best developed for multicompartiment copolymer micelles.¹⁰⁻¹² Generally, surface patterning of inorganic nanoparticles is accomplished by phase separation of two different ligands,¹³⁻¹⁶ or site-specific surface functionalization *via* partial particle masking.¹⁷⁻¹⁹ These methods are limited to the generation of NPs with two distinct surface regions, surface ripples, or a 'raspberry' surface morphology.

Recently, our group has proposed a new approach to NP patterning with polymer patches.²⁰ The strategy utilizes ther-

modynamically controlled segregation of polymer ligands end-grafted to the NP surface. Following transfer of the polymer-capped NPs from a good solvent to a poor solvent, an originally smooth polymer layer segregates into surface-pinned micelles (acting as surface patches), in order to avoid unfavorable polymer-solvent interactions. The balance between the loss in energy due to the stretching of polymer ligands and the gain in energy due to polymer attraction in a poor solvent determines the number, dimensions and the distribution of the patches on the NP surface.²⁰⁻²²

For spherical metal NPs, a decreasing NP diameter, that is, an increasing surface curvature, favored polymer surface segregation into patches: the increase in the surface free energy per polymer chain destabilized the uniformly-thick polymer shell.²⁰ Preliminary results obtained for NPs with shape-specific surface curvatures such as nanorods, nanocubes and triangular prisms showed a trend for polymer segregation on high-curvature NP regions, however this effect has not been explored.

In the present work, we focused on polymer-functionalized metal nanocubes (NCs), which have planar facets with zero curvature and high-curvature edges and vertices. Metal NCs

have interesting properties and, potentially useful applications. For example, their assemblies exhibit NC orientation-dependent localized field effects and optical responses.^{23,24}

We explored experimentally and theoretically how the NP shape governs the segregation of polymer ligands into patches. We show that for the NCs, polymer patches form preferentially on the areas of high curvature, that is, on the edges and vertices. The transformation of patchy NCs into nanospheres (NSs) changed the number and the distribution of polymer patches on the NP surface. Following the NC-to-NS transition (achieved by etching NC edges and vertices), the patches that were originally localized at the high curvature regions transformed into three patches evenly distributed on the NS surface. The latter surface pattern is similar to the pattern generated on the surface of as-synthesized polymer-capped NSs equilibrated in a poor solvent.²⁰ The experimentally observed trends were supported by an asymptotic scaling theory.

The importance of these results is at least, three-fold. First, the distribution of polymer patches on the NP with different shapes underlines the importance of surface curvature in NP patterning, with implications for polymer surface segregation on rough surfaces. Second, it validates the nanopatterning approach for dynamically shape-transforming NPs.²⁵ Third, nanopatterning of NCs with site-specific polymer patches paves the way for the exploration of new self-assembly modalities.^{23,24}

RESULTS AND DISCUSSION

Figure 1, top row shows the approach to the surface patterning of NCs with polymer patches. The bottom row in Figure 1 shows the corresponding transmission electron microscopy (TEM) images of the NCs (two-dimensional projection or top view). Gold NCs with edge length of 59 ± 2 nm were synthesized *via* the procedure reported elsewhere²⁰ using cetyltrimethylammonium bromide (CTAB) as a surfactant (Figures 1a and a'). The CTAB ligands were replaced with thiol-terminated polystyrene molecules with a molecular weight of 53,000 g/mol (later in the text referred to as PS-50K) in tetrahydrofuran. Subsequently, the polymer-functionalized NCs were transferred to *N,N*-dimethylformamide (DMF), a good solvent for polystyrene (with a second virial coefficient, A_2 , of 3.5×10^{-4} mol cm³ g⁻², equivalent to a Flory-Huggins interaction parameter of 0.46).²⁶ In the DMF solution, the NC were capped with a uniform PS-50K layer (Figure 1b and b'). Polymer surface segregation into patches was achieved by reducing the quality of the solvent for the polymer ligands by adding water to the NC solution in DMF to a final water concentration of $C_w = 1$ vol%. To avoid kinetic trapping of the polymer surface structures, the water was introduced to the NC solution in a DMF/water mixture.²⁷ Importantly, to suppress NC self-assembly in a poor solvent, due to the association of polymer ligands of different NCs, a dilute (< 1 nM) solution of NCs was used. In the DMF/water mixture, polymer ligands capping NC surface underwent surface segregation into pinned micelles (patches) to minimize unfavorable interactions with a poor solvent. Figure 1c illustrates polymer segregation at the NC surface, while Figure 1c' shows the two-dimensional projection of the patchy NCs *via* TEM imaging, with four large patches localized at the NC vertices and four narrow patches capping NC edges.

To explore the distribution of patches over the entire NC surface, we performed 3D imaging of the NCs using electron tomography. Tilt images were acquired from -70 degrees to +70 degrees with 2° increments. The reconstruction was computed using weighted back-projection. Figure 2 and Videos S1 and S2 show a 3D reconstructed image of the patchy NC. The polymer was concentrated on the NC vertices and edges, with a convex layer formed on the planar facets between the edges.

Figure 1. Schematic of gold NC patterning with polymer patches (top row) and corresponding TEM images of the NCs (bottom row). (a, a') CTAB-stabilized NCs in water. In (a) CTAB ligands are omitted. (b, b') NCs functionalized with PS-50K forming a uniform polymer ligand shell in good solvents, tetrahydrofuran and DMF (inset). (c, c') Patchy NCs in DMF/water mixture at $C_w = 1$ vol% (poor solvent conditions). Scale bars are 50 nm.

The vertex patches were higher than the edge patches (the latter showed a transient decrease in patch height from the vertex to the center of the edge). Limited accumulation of the polymer at the NC-substrate interface took place due to the partial wetting of the substrate with the polymer solution (Videos S1 and S2). Thus, polymer patches preferentially formed on the NC regions with higher curvature. Later in the text, we refer to the TEM images (top view) of patchy NCs, in which four large vertex patches corresponded to 20 patches (one for each vertex and edge) in a three-dimensional reconstruction.

Figure 2. Electron tomography reconstruction images of a 60-nm-size NC carrying PS-50K patches, taken at different observation angles.

Next, the patchy NCs were transformed into patchy NSs. To achieve the NC-to-NS shape transition, we adapted the methods developed for end-selective etching of gold nanorods by Au³⁺ in an aqueous solution of CTAB.^{28,29} Several adjustments were made to the reported procedures to account for the

presence of polymer ligands on the NC surface and for the change in solvent from water to the DMF/water mixture (since DMF is a mild reducing agent).³⁰ The change in the shape of the NCs was monitored by *in-situ* ultraviolet-visible (UV-vis) spectroscopy and TEM imaging.

To develop the etching process, we first, performed it for a 10 pM NC solution in DMF. In a good solvent, the NCs were coated with a uniform swollen polymer layer (Figure 1b and b'), which ensured access of Au^{3+} to the NC surface. The etching conditions were optimized to remove only NC edges and vertices, so that after etching, the diameter of the NSs was equal to the initial length of the NC edge (confirmed by TEM imaging of the NCs and NSs).

Following these experiments, etching was conducted in a DMF/water mixture, that is, for patchy NCs. Due to reduced colloidal stability of the NCs under these conditions, the concentration of the NCs was reduced to 1.8 pM. The optimized NC etching conditions, such as the HAuCl_4 concentration and the etching time, are provided in Supporting Information.

Figure 3. Variation in extinction spectra of polymer-coated NCs during the course of NC etching in DMF. (a) Extinction spectra of NCs acquired throughout the etching process. Peaks labeled 1-3 correspond to the Au^{3+} , Au^{3+} -CTAB complex, and the NP surface plasmon resonance peak respectively. (b) Variation in the spectral position (red circles) and intensity of plasmonic resonance (peak 3, blue triangles) with etching time.

Figures 3 and 4 show the variation in extinction spectra of the NCs in the course of the etching process carried out in DMF (Figure 3) and in the DMF/water mixture at $C_w = 1$ vol% (Figure 4). The time-dependent extinction spectra exhibit three distinct peaks: (1) the absorption peak centered at 320 nm, corresponding to Au^{3+} ,³¹ (2) the absorption peak centered at 393 nm, corresponding to the Au^{3+} -CTAB complex;³² and (3) the characteristic plasmonic resonance peak of NCs and NSs

in the spectral range of 500-600 nm. At the beginning of the etching process, peak 1 was prominent, however, it rapidly diminished with the formation of the Au^{3+} -CTAB complex. As a result, the intensity of peak 2, corresponding to the Au^{3+} -CTAB complex, initially increased but in the course of the redox reaction, this peak gradually diminished. This complex was responsible for the selective oxidation of the Au^0 atoms to soluble Au^{+1} ions at the NC vertices and edges.^{28,29} The evolution of the two absorption peaks (peak 1 and 2) throughout the NC etching process was consistent for both DMF and DMF/water mixture (Figures 3 and 4, respectively), indicating similar chemical processes occurring during the NC shape transformation.

Figure 4. Variation in extinction spectra of polymer-coated patchy NCs during the course of NC etching process in the DMF/water mixture at $C_w = 1$ vol%. (a) Extinction spectra of PS-50K-coated NCs. Peaks labeled 1-3 correspond to the Au^{3+} , Au^{3+} -CTAB complex, and the NP surface plasmon resonance peak respectively. (b) Variation in the spectral position (red circles) and intensity of the surface plasmon resonance (peak 3, blue triangles) with etching time.

The changes in the spectral position and the intensity of peak 3 with the NC-to-NS transformation are shown in Figures 3b and 4b, for the NCs etched in DMF and the DMF/water mixture, respectively. The spectral position of the peak shifted from 548 to 540 nm for the NCs etched in DMF and from 548 to 538 nm for the NCs etched in the DMF/water mixture. In addition, the peak width decreased by 10 nm. These changes occurred because of the transient increase in NP symmetry, following the NC-to-NS transition. During this transition, the anisotropy of the NCs decreased, thereby affecting their plasmonic modes.³³⁻³⁵ Notably, the spectral position of the plasmonic resonance at 540 nm was consistent with as-synthesized 60 nm-diameter NSs (Supporting Information,

Figure S2). Furthermore, during the etching process, as the Au^0 atoms were oxidized, the total volume of the NCs reduced, which resulted in the decrease of the intensity of peak 3 (Figure 3 and 4).

The change in the NC shape upon etching in the DMF/water mixture was characterized by analyzing their TEM images. Figure 5a shows the approach to the characterization of the change in the NC shape during the NC-to-NS transformation. We used the change in the edge rounding ratio, $R = (r/L) \times 100\%$, where r is the rounded vertex radius, and L is the NP size.³⁶ For the NCs, the value of L corresponds to the edge length, and for the NSs, L is the NS diameter. Thus, for a perfect cube and a perfect sphere, the values of R are 0 and 50%, respectively. Importantly, under optimized etching conditions, the value of L remained constant due to the selective removal of the vertices and edges of the NCs.

Figure 5b shows that in the course of etching, the average value of the rounding ratio R changed from $28 \pm 4\%$ (prior to NC etching) to $48 \pm 4\%$ (post-etching). The most significant change in R -values was observed in the first 60 min of the etching process. This rate of change was consistent with the time-dependent change in the spectral position of peak 3 and intensity in the extinction spectra (Figure 4b).

Figure 5. Variation in the size and shape of the NCs in the course of the etching process. (a) Definition of the edge rounding ratio, R , following the change in shape from a cube to a sphere. (b) Variation in the NC edge rounding ratio R (red circles), and edge length L (blue triangles), both plotted as a function of the NC etching time.

The number of patches per NC and NS prior to and following the etching process was determined by analyzing their TEM images. Both types of NPs showed no aggregation. For NCs ($R = 28 \pm 4\%$, $L = 59 \pm 2$ nm) we used their top-view images. Figure 6a shows that among the patchy NCs, a fraction of 0.15, 0.80, and 0.05 of patchy NCs had three, four and five polymer patches, respectively. We note that ideally, in 3D reconstruction four top vertex patches correspond to 20

patches (8 for the vertices and 12 for the edges). Following the NC-to-NS transition ($R = 48 \pm 4\%$, $L = 59 \pm 2$ nm), a fraction of 0.05, 0.60, 0.27, and 0.08 of patchy NSs had two, three, four, and five patches, respectively. As a control system, we used as-synthesized gold NSs ($R = 51 \pm 4\%$, $L = 60 \pm 2$ nm) that were functionalized with PS-50K and equilibrated in the DMF/water mixture for 24 h. Among patchy NSs, a fraction of 0.12, 0.65, 0.20, and 0.03 carried two, three, four, and five patches, respectively, that is, the distribution of the number of patches was similar to that on the NSs obtained by NC etching (Figure 6b). Under particular solvent quality, the number and the distribution of patches on the NS surface was governed by the ratio between the NS diameter and the size of polymer ligands.²⁰

We note that upon etching, the average polymer grafting density may change, however, as we showed in our earlier work,²⁰ an approximately ten-fold variation in polymer grafting density did not change the number or the distribution of PS-50K patches on the surface of 60 nm-diameter NSs.

Figure 6. Distribution of the populations of NCs and NSs carrying a different number of patches per NP. (a) Fractions of NCs ($R = 28 \pm 4\%$, $L = 59 \pm 2$ nm) with a different number of PS-50K patches. (b) Fractions of NSs with a different number of PS-50K patches. Solid blue bars: NC-to-NS transformation after 80 min of etching of the patchy NCs ($R = 48 \pm 4\%$, $L = 59 \pm 2$ nm). Striped blue bars: as-synthesized 60 nm-diameter patchy NSs ($R = 51 \pm 4\%$, $L = 60 \pm 2$ nm), in the DMF/water mixture at $C_w = 4$ vol%.

The location of the NC surface patches, as well as the change in the patch number with the NC-to-NS transformation were modeled using an asymptotic scaling theory (see Supporting Information for details). The model predicted the

relationship between the free energies of patches (or pinned micelles) formed on the NC faces, edges and vertices. Figure 7 shows the variation in the reduced free energies per polymer molecule, F_i/F_1 , in the facet, edge, and vertex patches, plotted as a function of the reduced number of polymer molecules per patch P/P_1 . Here, $F_i(P)$ is the free energy per molecule in a patch with P molecules, specific to the patch location on the facet ($i = 1$), edge ($i = 2$) and vertex ($i = 3$), and F_1 is the free energy per molecule in a facet micelle with the aggregation number P_1 (corresponding to the lowest F_1).

Figure 7. Reduced free energies $F_i(P)/F_1(P_1)$ per molecule in the facet (red color), edge (blue color) and vertex (green color) micelles (patches), plotted as a function of the relative aggregation number P/P_1 of pinned micelles (patches) for the NC size larger or comparable with the patch radius and the ratios of polymer grafting densities on the faces, edges and vertices exceeding the threshold values of $(\sigma_3/\sigma_1) = 7/3$ and $(\sigma_2/\sigma_1) = 3/2$. The dotted black line shows the variation in the reduced free energy per molecule, $F_s(P)/F_1(P_1)$ for patches formed on the NS. Arrows show the reduced free energies corresponding to the equilibrium aggregation numbers. F_1 is the equilibrium free energy per molecule in a facet micelle with the optimized aggregation number P_1 .

Figure 7 shows that the vertex and edge patches had a lower reduced free energy than the facet patches (and were thus thermodynamically preferred) upon two conditions (i) the NC size L was larger or comparable with the patch radius and (ii) the ratios of polymer grafting densities on the faces, edges and vertices exceeded the threshold values of $(\sigma_3/\sigma_1) = 7/3$ and $(\sigma_2/\sigma_1) = 3/2$. Here σ_1 , σ_2 and σ_3 are the average polymer grafting densities in the NC facet, edge and vertex micelles, respectively. The first condition was satisfied in the experiments. The second condition, that is, a higher grafting density on the NC vertices and edges of NCs was expected, due to the reduction in steric repulsion between polymer chains on high curvature regions.^{37–39} Figure 7 can be considered as a state diagram, in which at $F_i(P)/F_1(P_1) < 1$ (the bottom part of the figure) the formation of the NCs with vertex and edge micelles was expected, while at $F_i(P)/F_1(P_1) > 1$, the NCs with facet micelles were predicted (the top part of the figure). Notably, for $\sigma_1 = \sigma_2 = \sigma_3$ the facet patches had the lowest free energy per

molecule and thus were thermodynamically most favorable, as predicted earlier by Olvera de la Cruz et al.⁴⁰ For the NSs with the radius $L/2$ and polymer grafting density, σ_s , and, the approximation $\sigma_s \approx \sigma_1$ enabled the estimation of the equilibrium aggregation number, P_s , of polymer molecules in the NS patches, and the free energy $F_s(P_s)$ per molecule in the patches (pinned micelles) with the core radius $R_s \ll L/2$, since $P_s \approx P_1$ and $F_s(P_s) \approx F_1$. The variation in the reduced free energy $F_s(P)/F_1(P_1)$ on the normalized aggregation number for the NS patch is shown in Figure 7 with a dotted black line.

The theoretical model captured the experimental trends observed for the number of patches and their spatial distribution on the NCs. It also predicted the aggregation number for the NS patches and thus the number of NS patches governed by the balance between the interfacial polymer energy in a poor solvent and the energy of polymer chain stretching.¹⁹ Interestingly, at the threshold grafting density ratios, the vertex patches were predicted to be larger (taller) than the edge micelles by $\sim 20\%$ (Supporting Information), which was consistent with experimental observations (Figure 2).

Thus, we conclude that the NP shape governed the polymer pattern on its surface, as is shown for the NC transforming into a NS in Figure 8. More specifically, with elimination of the high curvature, i.e. high polymer grafting density regions of the NCs, the number of patches on the NSs is reduced to three and was governed by the balance between the interfacial energy and the stretching energy of the polymer chains that formed patches.

Figure 8. Schematic of the NC-to-NS transformation with the corresponding change in the polymer surface pattern.

CONCLUSIONS

The experimental and theoretical results presented in the present work show the capability to surface pattern NPs with high surface curvature regions. The nanopatterning approach utilizes the segregation of a smooth layer of end-grafted polymer ligands into pinned micelles (polymer patches) when the solvent quality for the polymer is reduced.²⁰ For metal NCs, we show that the patches preferentially form on the regions with a high surface curvature, that is, on 12 edges and 8 vertices. This localization was predicted for NCs with dimensions larger or comparable with the patch size and for polymer grafting densities being higher on the edges and vertices than on the NC facets.

The second important implication of our work is the governing role of NP shape in patch number and distribution. Using gradual NC-to-NS transformation, we show that when the surface curvature is uniform, as in the case of NSs, the location and distribution of the patches is a result of the balance between the reduction of surface free energy due to polymer-polymer interaction in a poor solvent and the increase in the stretching energy of polymer ligands upon patch formation. For the 60 nm-diameter NSs and PS-50K ligands, the polymer layer segregated into 3 patches.

This work provides more complete fundamental understanding of the role of NP shape (surface curvature or surface roughness) on the structure of polymer-functionalized substrates. Control over the location and the number of patches on NPs enables the exploration of their new self-assembly modes. More specifically, patchy NCs are interesting building blocks for self-assembled nanostructures, owing to the large hotspot volumes in linear NC assemblies and orientation-dependent plasmonic properties.^{23,41} Furthermore, NCs with a controllable number and position of patches can be used as templates for the synthesis and assembly of hybrid NPs with complex architectures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Supplementary methods, further discussion on the grafting density of the NCs, optimization of etching conditions, and theoretical models, UV-vis characterization of as-synthesized NSs (PDF) and movies of 3D reconstruction of the gold NC coated with polymer patches, visualized by volume rendition.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ekumache@chem.utoronto.ca

Present Addresses

[†]Department of Physical Chemistry, Biomedical Research Center (CINBIO), and Southern Galicia Institute of Health Research (IISGS), University of Vigo, 36310 Vigo, Spain.

Funding Sources

National Science and Engineering Research Council of Canada (Discovery and Canada Research Chair programs); Russian Foundation for Basic Research (grant 14-03-00372a), Government of Russian Federation (grant 074-U01). Research was in part carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory supported by the US Department of Energy, Office of Basic Energy Sciences (under contract number DE-SC0012704), Alexander von Humboldt-Foundation (Feodor Lynen Research Fellowship)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors thank Prof. Gilbert Walker (University of Toronto) for helpful discussions.

REFERENCES

- Pawar, A. B.; Kretzschmar, I. *Macromol. Rapid Commun.* **2010**, *31*, 150–168.
- Lattuada, M.; Hatton, T. A. *Nano Today* **2011**, *6*, 286–308.
- Nie, Z.; Petukhova, A.; Kumacheva, E. *Nat. Nanotechnol.* **2010**, *5*, 15–25.
- Binks, B. P. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21–41.
- Chen, T.; Chen, G.; Xing, S.; Wu, T.; Chen, H. *Chem. Mater* **2010**, *22*, 3826–3828.
- Du, J.; O'Reilly, R. K. *Chem. Soc. Rev.* **2011**, *40*, 2402–2416.
- Pawar, A. B.; Kretzschmar, I. *Langmuir* **2009**, *25*, 9057–9063.
- Nie, Z.; Li, W.; Seo, M.; Xu, S.; Kumacheva, E. *J. Am. Chem. Soc.* **2006**, *128*, 9408–9412.
- Wang, Y.; Wang, Y.; Breed, D. R.; Manoharan, V. N.; Feng, L.; Hollingsworth, A. D.; Weck, M.; Pine, D. J.; Figure, S.; Wang, Y.; Breed, D. R.; Manoharan, V. N.; Feng, L.; Hollingsworth, A. D.; Weck, M.; Pine, D. J. *Nature* **2012**, *491*, 51–55.
- Gröschel, A. H.; Schacher, F. H.; Schmalz, H.; Borisov, O. V.; Zhulina, E. B.; Walther, A.; Müller, A. H. E. *Nat. Commun.* **2012**, *3*, 710–719.
- Löbbling, T. I.; Borisov, O.; Haataja, J. S.; Ikkala, O.; Gröschel, A. H.; Müller, A. H. E. *Nat. Commun.* **2016**, *7*, 12097.
- Ye, X.; Li, Z. W.; Sun, Z. Y.; Khomami, B. *ACS Nano* **2016**, *10*, 5199–5203.
- Andala, D. M.; Shin, H. S. R.; Lee, H.-Y.; Bishop, K. J. M. *ACS Nano* **2012**, *6*, 1044–1050.
- Vilain, C.; Goettmann, F.; Moores, A.; Le Floch, P.; Sanchez, C. J. *Mater. Chem.* **2007**, *17*, 3509.
- Jackson, A. M.; Myerson, J. W.; Stellacci, F. *Nat. Mater.* **2004**, *3*, 330–336.
- Bao, C.; Tang, S.; Wright, R. A. E.; Tang, P.; Qiu, F.; Zhu, L.; Zhao, B. *Macromolecules* **2014**, *47*, 6824–6835.
- Lattuada, M.; Hatton, T. A. *J. Am. Chem. Soc.* **2007**, *129*, 12878–12889.
- Wang, B.; Li, B.; Zhao, B.; Li, C. Y. *J. Am. Chem. Soc.* **2008**, *130*, 11594–11595.
- Maye, M. M.; Nykypanchuk, D.; Cuisinier, M.; van der Lelie, D.; Gang, O. *Nat. Mater.* **2009**, *8*, 388–391.
- Choueiri, R. M.; Galati, E.; Thérien-Aubin, H.; Klinkova, A.; Larin, E. M.; Querejeta-Fernández, A.; Han, L.; Xin, H. L.; Gang, O.; Zhulina, E. B.; Rubinstein, M.; Kumacheva, E. *Nature* **2016**, *538*, 79–83.
- Zhulina, E. B.; Birshtein, T. M.; Priamitsyn, V. a;

- Klushin, L. I. *Macromolecules* **1995**, *28*, 8612–8620.
- (22) Williams, D. R. M. *J. Phys. II* **1993**, *3*, 1313–1318.
- (23) Klinkova, A.; Thérien-Aubin, H.; Ahmed, A.; Nykypanchuk, D.; Choueiri, R. M.; Gagnon, B.; Muntyanu, A.; Gang, O.; Walker, G. C.; Kumacheva, E. *Nano Lett.* **2014**, *14*, 6314–6321.
- (24) Gao, B.; Arya, G.; Tao, A. R. *Nat. Nanotechnol.* **2012**, *7*, 433–437.
- (25) Rodríguez-Lorenzo, L.; Romo-Herrera, J. M.; Pérez-Juste, J.; Alvarez-Puebla, R. a.; Liz-Marzán, L. M. *J. Mater. Chem.* **2011**, *21*, 11544.
- (26) Wolf, B. A.; Willms, M. M. *Makromol. Chem* **1978**, *179*, 2265–2277.
- (27) Nie, Z.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. *Nat. Mater.* **2007**, *6*, 609–614.
- (28) Rodríguez-Fernández, J.; Pérez-Juste, J.; Mulvaney, P.; Liz-Marzán, L. M. *J. Phys. Chem. B* **2005**, *109*, 14257–14261.
- (29) Khanadeev, V. A.; Khlebtsov, N. G.; Burov, A. M.; Khlebtsov, B. N. *Colloid J.* **2015**, *77*, 652–660.
- (30) Pastoriza-Santos, I.; Liz-Marzán, L. M. *Adv Funct Mater* **2009**, *19*, 679–688.
- (31) Gaikwad, A. V.; Verschuren, P.; Kinge, S.; Rothenberg, G.; Eiserz, E. *Phys. Chem. Chem. Phys.* **2008**, *10*, 951–956.
- (32) Kundu, S. *J. Mater. Chem. C* **2013**, *1*, 831.
- (33) Fuchs, R. *Phys. Rev. B* **1975**, *11*, 1732–1740.
- (34) Cortie, M. B.; Liu, F.; Arnold, M. D.; Niidome, Y. *Langmuir* **2012**, *28*, 9103–9112.
- (35) Raziman, T. V.; Martin, O. J. F. *Opt. Express* **2013**, *21*, 21500–21507.
- (36) Grillet, N.; Manchon, D.; Bertorelle, F.; Bonnet, C.; Broyer, M.; Cottancin, E.; Lermé, J.; Hillenkamp, M.; Pellarin, M. *ACS Nano* **2011**, *5*, 9450–9462.
- (37) Walkey, C. D.; Olsen, J. B.; Guo, H.; Emili, A.; Chan, W. C. W. *J. Am. Chem. Soc.* **2012**, *134*, 2139–2147.
- (38) Hill, H. D.; Millstone, J. E.; Banholzer, M. J.; Mirkin, C. A. *ACS Nano* **2009**, *3*, 418–424.
- (39) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Eur. Phys. J. E* **2006**, *20*, 243–256.
- (40) Guo, P.; Sknepnek, R.; Olvera De La Cruz, M. *J. Phys. Chem. C* **2011**, *115*, 6484–6490.
- (41) Chen, T.; Yang, M.; Wang, X.; Li, H. T.; Chen, H. *J. Am. Chem. Soc.* **2008**, *130*, 11858–11859.

Table of Contents Graphic