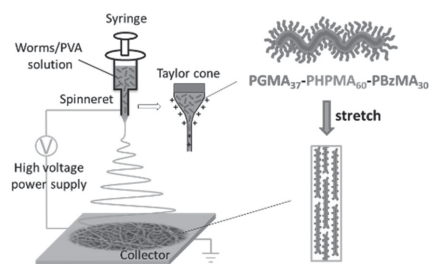


Directed Assembly of Soft Anisotropic Nanoparticles by Colloid Electrospinning

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Directed assembly of triblock copolymer worms to produce nanostructured fibers is achieved via colloid electrospinning. These copolymer worms are conveniently prepared by polymerization-induced self-assembly in concentrated aqueous dispersion. Addition of a second water-soluble component, poly(vinyl alcohol), is found to be critical for the production of well-defined fibers: trial experiments performed using the worms alone produce only spherical microparticles. Transmission electron microscopy studies confirm that the worm morphology survives electrospinning and the worms become orientated parallel to the main axis of the fibers during their generation. The average deviant angle (θ_{dev}) between the worm orientation and fiber axis decreases from 17° to 9° as the worm/PVA mass ratio increases from 1.15:1 to 5:1, indicating a greater degree of worm alignment within fibers with higher worm contents and smaller fiber diameters. Thus triblock copolymer fibers of $\approx 300 \pm 120$ nm diameter can be readily produced that comprise aligned worms on the nanoscale.



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1. Introduction

Controlled and directed assembly of nanoparticles has been used for the fabrication of metamaterials,^[1] information storage,^[2] and sensing devices.^[3] Examples of such assemblies include 1D structures fabricated under the influence of an electric field,^[4,5] a magnetic field,^[6] or by self-assembly.^[7,8] An attractive alternative is the orientation of microdomains induced by the shear and elongation of the polymer jet during the electrospinning process.^[9] Electrospinning allows fibers to be conveniently fabricated with mean diameters ranging from ≈ 10 nm to $10 \mu\text{m}$. Such fibers are formed by uniaxial stretching of a viscoelastic liquid, typically a polymer solution or melt.^[10–12] The polymer jet is charged in an external electrostatic field and accelerated and stretched to produce ultrafine nanofibers. The nanoparticles that are initially randomly oriented in suspensions begin to align along the streamlines of the jet. Continuous fibers comprising aligned nanoparticles can be collected to form a composite nonwoven membrane. Electrospun fibers have already found applications in tissue

engineering,^[13] water purification,^[14] as sensors,^[15] or as catalyst supports.^[16,17]

In principle, using block copolymers for electrospinning enables the production of nanostructured fibers.^[18–21] However, domain structures can be underdeveloped because of the intense stretching and concomitant rapid solvent evaporation that occurs during electrospinning.^[19] More uniform phase separation can be achieved by embedding block copolymer chains within a polymer matrix of a sufficiently high glass transition temperature (T_g).^[20] By annealing the fibers above the T_g of the block copolymer and below that of the matrix, periodic structures could be produced within the fibers. Alternatively, a thermally stable silica sheath can be used to enable fiber annealing at high temperature. Pure copolymer fibers with well-ordered, confined assembly could be obtained by removing the silica overlayer by exposure to NaOH.^[9,19,22] Another strategy to promote the structuring of electrospun fibers is based on the self-assembly of supramolecular comb-coil block copolymers with hydrogen-bonded amphiphiles.^[23,24] The amphiphiles can be cleaved from the annealed structure using selective solvents, which allows control over the pore size in the fibers. However, the strategies discussed above require either annealing to promote phase separation or deposition of a sheath to confine assembly.

Herein, we report a facile and efficient approach for directing the assembly of anisotropic objects by colloid-electrospinning. Our approach enables the combination of the well-known self-assembly of block copolymers with electrospinning in order to fabricate internally nanostructured fibers comprising oriented anisotropic copolymer nanoparticles.

2. Results and Discussion

ABC triblock copolymer nanoparticles were prepared by polymerization-induced self-assembly (PISA), as reported recently.^[25,26] A poly(glycerol monomethacrylate) (PGMA) macromolecular chain-transfer agent (macro-CTA) was synthesized via reversible addition-fragmentation chain transfer (RAFT) solution polymerization in ethanol. This PGMA macro-CTA was chain-extended using 60 units of 2-hydroxypropyl methacrylate (HPMA) via RAFT aqueous dispersion polymerization. Then this PGMA₃₇-PHPMA₆₀ diblock copolymer was subsequently chain-extended with benzyl methacrylate (BzMA) via RAFT seeded emulsion polymerization to obtain the final PGMA₃₇-PHPMA₆₀-PBzMA₃₀ triblock copolymer. ¹H NMR spectroscopy studies indicated that more than 99% BzMA conversion was achieved within 4 h at 70 °C (see Figure S1, Supporting Information). Gel permeation chromatography analysis (DMF eluent) against poly(methyl methacrylate) standards

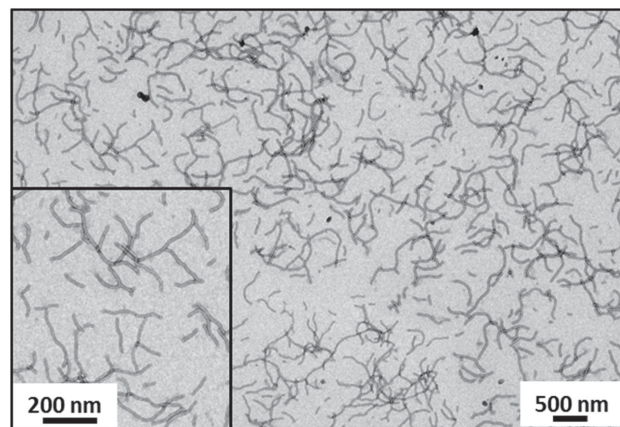


Figure 1. Transmission electron microscopy micrographs of the PGMA₃₇-PHPMA₆₀-PBzMA₃₀ triblock copolymer worms. A uranyl formate negative stain was used to improve the electron density contrast.

indicated that a near-monodisperse triblock copolymer was obtained with a relatively high blocking efficiency and minimal macro-CTA contamination ($M_n = 22\,100\text{ g mol}^{-1}$, $M_w/M_n = 1.12$). Transmission electron microscopy (TEM) studies (see Figure 1) confirm that the triblock copolymer chains undergo polymerization-induced self-assembly to form worm-like micelles (referred to hereafter as “worms”). The worms have a relatively well-defined mean width of $\approx 20\text{ nm}$, while the mean worm length is of the order of 600 nm (worm anisotropy = worm length/worm width ≈ 30). These worms are distributed randomly within the aqueous dispersion.

These copolymer worms were then processed into fibers using colloid-electrospinning, as shown in the graphical abstract. Various electrospinning parameters are summarized in Table 1. Empirically, it was found to be necessary to add a water-soluble polymer, poly(vinyl alcohol) (PVA; $M_n = 125\,000\text{ g mol}^{-1}$; mean degree of hydrolysis = 88%), to the aqueous copolymer worm dispersion in order to produce well-defined fibers. Indeed, in the classical solution-electrospinning process, soluble polymers of relatively high molecular weight are normally required at relatively high concentration in order to provide sufficient entanglements (and therefore viscoelastic forces) to counteract the effect of surface tension. Without such viscoelastic forces,

Table 1. Composition of the electrospinning feed.

Entry	Copolymer worm/ PVA mass ratio	Solids content [wt%]	PVA [wt%]
1	1:0	13.0	0
2	5:1	11.4	2.0
3	3:1	13.5	3.4
4	1.15:1	9.3	4.3

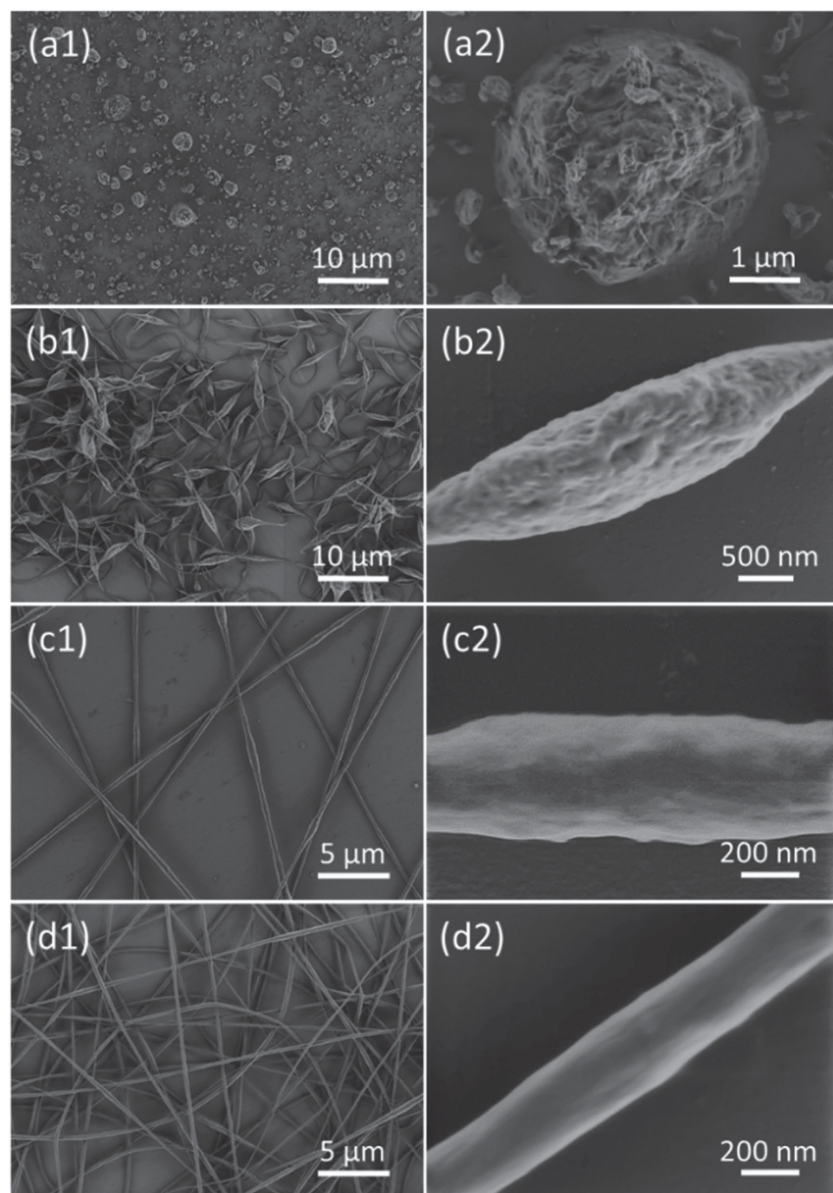


Figure 2. Scanning electron microscopy images obtained for the copolymer worm/PVA composite fibers prepared using copolymer worm/PVA mass ratios of a1-a2) 1:0, b1-b2) 5:1, c1-c2) 3:1, and d1-d2) 1.15:1.

the polymer jet simply forms spherical droplets rather than fibers, because the former morphology minimizes the interfacial energy. Indeed, scanning electron microscopy studies of the products revealed only polydisperse micrometer-sized spherical microparticles when worm electrospinning was attempted in the absence of any PVA (see entry 1 in Table 1 and Figure 2a1-a2). Thus various amounts of PVA were added to the aqueous copolymer worm dispersion for a second series of experiments (see Table 1 and Figure 2b-d).

The copolymer worm/PVA mass ratio has a significant influence on the fiber morphology. As discussed above, fibers are not obtained in the absence of PVA. Moreover,

using a copolymer worm/PVA mass ratio of 5:1 (see entry 2 in Table 1) merely led to the formation of beads (Figure 2b1-b2). Bead formation is associated with capillary breakup of the jet by surface tension.^[27] The surface energy is minimized when the jet forms spherical droplets. The formation of beads suggests that there were insufficient chain entanglements during electrospinning because of the low concentration of PVA. When a copolymer worm/PVA mass ratio of 3:1 was utilized, the fibers had a relatively rough surface morphology (see entry 3 in Table 1 and Figure 2c1-c2). Finally, smooth uniform fibers with a mean fiber diameter of $\approx 300 \pm 120$ nm were obtained when using a copolymer worm/PVA mass ratio of 1.15:1 (Figure 2d1-d2).

The composite fibers were examined at higher magnification using TEM. In order to visualize the directed assembly of the individual worms within the fibers, uranyl formate was used as an electron-dense negative stain in order to improve contrast.^[28] TEM studies revealed that the fibers were composed of bundles of worms oriented parallel to the main fiber axis (see Figure 3). The original morphology of the linear triblock copolymer worms is conserved during electrospinning, since this process does not require any solvent^[18] or thermal annealing.^[20] Moreover, fibers prepared using higher copolymer worm/PVA mass ratios exhibited greater structural order, as shown in Figure 3.

To quantify the degree of worm alignment along the fiber axis direction, the average deviant angle (θ_{dev}), or angular difference between the worm orientation and fiber axis, was measured.^[28] Twenty yellow-highlighted worms in red boxes were randomly selected for the calculation of θ_{dev} (see Figure 3). The degree of worm alignment increased for higher worm/PVA mass ratios. For example, θ_{dev} was reduced from 17° at a worm/PVA mass ratio of 1.15:1 to 11° at a mass ratio of 3:1, and 9° at a mass ratio of 5:1. This greater degree of worm alignment also correlated with a reduction in mean fiber diameter, from 365 to 210 nm as the worm/PVA mass ratio was increased from 1.15:1 to 5:1. The degree of worm orientation mainly depends on the shear-induced elongation of the polymer

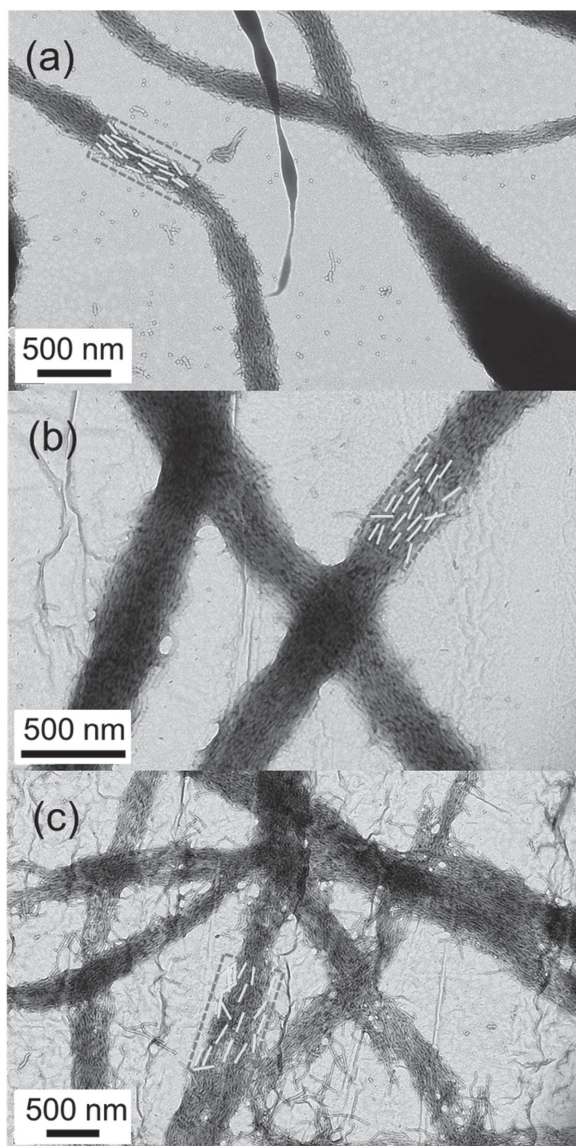


Figure 3. Transmission electron microscopy micrographs obtained for the copolymer worm/PVA fibers prepared using copolymer worm/PVA mass ratios of a) 5:1, b) 3:1, and c) 1.15:1.

jet during the electrospinning process.^[9] This observation is consistent with a recent report of the alignment of rigid gold nanorods within electrospun poly(ethylene oxide) nanofibers.^[29] The fiber diameter played an important role in determining the extent of nanorod alignment, whereas the nanorod concentration could be varied with no discernible influence on the net degree of alignment.

Remarkably, using purely PVA (i.e., in the absence of any copolymer worms) did not produce uniform fibers under the same electrospinning conditions, i.e., using the same distance between syringe and electrode, voltage, and feed rate (see Figure S2, Supporting Information). This suggests that the hydrophobic interactions present within the amphiphilic copolymer worms most likely

contribute to the cohesive energy required to counteract surface tension effects. This remarkable feature observed during the preparation of electrospun fibers has also been reported for other types of supramolecular interactions, such as in polyurethanes with tunable extents of hydrogen bonding,^[30] as well as with peptide amphiphiles,^[31] diphenylalanine,^[32] phospholipids,^[33] cyclodextrins,^[34] and a self-complementary host-guest supramolecular polymer.^[35]

3. Conclusions

In conclusion, triblock copolymer worms could be readily processed in the presence of poly(vinyl alcohol) via electrospinning to produce uniform smooth fibers, thereby substantially increasing the persistence length of the original building block. Transmission electron microscopy studies confirm that the worm morphology survives electrospinning. The fibers comprise bundles of worms oriented along the main fiber axis. Increasing the worm content within the PVA fibers reduced the fiber diameter and promoted greater worm alignment, as verified by the smaller mean deviant angle between the oriented worms and the fiber axis. No fibers could be obtained in the absence of the PVA additive and electrospinning PVA alone did not produce fibers either. Thus a strongly synergistic effect is obtained by combining the copolymer worms with an appropriate amount of PVA. The aligned triblock copolymer worms impose a unique fingerprint on the fibers, which in principle could be used as barcodes for labeling and authenticating goods.^[36] According to the literature, either metallic stripes,^[37,38] the photoluminescence properties of polymer wires,^[39] or encapsulated DNA sequences^[40] have already been examined for such applications. However, for the present system a more convenient means of reading the encoded information than TEM analysis of selectively stained fibers would be desirable.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: S.J. and C.J.M. contributed equally to this work. The authors thank Dr. Vincent Ladmiral for the synthesis of the G₃₇ macro-CTA. The authors also thank Christopher Hill and Svetomir Tzokov at the University of Sheffield Biomedical Science Electron Microscopy Suite for their TEM assistance. S.P.A. thanks the European Research Council for an ERC Advanced Investigator grant (PISA 320372) to support C.J.M. and also acknowledges an EPSRC Platform grant (EP/J007846/1). D.C. acknowledges financial support from “MPG-CAS Joint Doctoral Promotion Program (DPP).”

Received: May 9, 2016; Revised: June 2, 2016; Published online: ;
DOI: 10.1002/marc.201600270

Keywords: alignment; copolymer worms; directed assembly;
electrospinning; nanoparticles

- [1] V. M. Shalaev, *Nat. Photonics* **2007**, *1*, 41.
 [2] P. Zijlstra, J. W. Chon, M. Gu, *Nature* **2009**, *459*, 410.
 [3] L. Wang, Y. Zhu, L. Xu, W. Chen, H. Kuang, L. Liu, A. Agarwal, C. Xu, N. A. Kotov, *Angew. Chem. Int. Ed.* **2010**, *49*, 5472.
 [4] D. Crespy, K. Friedemann, A. M. Popa, *Macromol. Rapid Commun.* **2012**, *33*, 1978.
 [5] A. Demortière, A. Snezhko, M. V. Sapozhnikov, N. Becker, T. Proslie, I. S. Aranson, *Nat. Commun.* **2014**, *5*, 335.
 [6] M. B. Bannwarth, S. W. Kazer, S. Ulrich, G. Glasser, D. Crespy, K. Landfester, *Angew. Chem. Int. Ed.* **2013**, *52*, 10107.
 [7] K. Liu, Z. Nie, N. Zhao, W. Li, M. Rubinstein, E. Kumacheva, *Science* **2010**, *329*, 197.
 [8] K. S. Khalil, A. Sagastegui, Y. Li, M. A. Tahir, J. E. Socolar, B. J. Wiley, B. B. Yellen, *Nat. Commun.* **2012**, *3*, 794.
 [9] V. Kalra, S. Mendez, J. H. Lee, H. Nguyen, M. Marquez, Y. L. Joo, *Adv. Mater.* **2006**, *18*, 3299.
 [10] D. Li, Y. N. Xia, *Adv. Mater.* **2004**, *16*, 1151.
 [11] A. Greiner, J. H. Wendorff, *Angew. Chem. Int. Ed.* **2007**, *46*, 5670.
 [12] D. H. Reneker, A. L. Yarin, *Polymer* **2008**, *49*, 2387.
 [13] C. Xu, R. Inai, M. Kotaki, S. Ramakrishna, *Biomaterials* **2004**, *25*, 877.
 [14] X. Wang, X. Chen, K. Yoon, D. Fang, B. S. Hsiao, B. Chu, *Environ. Sci. Technol.* **2005**, *39*, 7684.
 [15] B. Ding, M. Wang, X. Wang, J. Yu, G. Sun, *Mater. Today* **2010**, *13*, 16.
 [16] N. Horzum, R. Muñoz-Espí, G. Glasser, M. M. Demir, K. Landfester, D. Crespy, *ACS Appl. Mater. Interfaces* **2012**, *4*, 6338.
 [17] D. Joe, F. E. Golling, K. Friedemann, D. Crespy, M. Klapper, K. Müllen, *Macromol. Mater. Eng.* **2014**, *299*, 1155.
 [18] T. Ruotsalainen, J. Turku, P. Hiekkataipale, U. Vainio, R. Serimaa, G. ten Brinke, A. Harlin, J. Ruokolainen, O. Ikkala, *Soft Matter* **2007**, *3*, 978.
 [19] V. Kalra, P. A. Kakad, S. Mendez, T. Ivannikov, M. Kamperman, Y. L. Joo, *Macromolecules* **2006**, *39*, 5453.
 [20] M. Ma, V. Krikorian, J. H. Yu, E. L. Thomas, G. C. Rutledge, *Nano Lett.* **2006**, *6*, 2969.
 [21] Y. Luu, K. Kim, B. Hsiao, B. Chu, M. Hadjiargyrou, *J. Controlled Release* **2003**, *89*, 341.
 [22] V. Kalra, J. H. Lee, J. H. Park, M. Marquez, Y. L. Joo, *Small* **2009**, *5*, 2323.
 [23] T. Ruotsalainen, J. Turku, P. Heikkilä, J. Ruokolainen, A. Nykänen, T. Laitinen, M. Torckeli, R. Serimaa, G. ten Brinke, A. Harlin, O. Ikkala, *Adv. Mater.* **2005**, *17*, 1048.
 [24] T. Ruotsalainen, J. Turku, P. Hiekkataipale, U. Vainio, R. Serimaa, G. T. Brinke, A. Harlin, J. Ruokolainen, O. Ikkala, *Soft Matter* **2007**, *3*, 978.
 [25] K. Thompson, C. Mable, A. Cockram, N. Warren, V. Cunningham, E. Jones, R. Verber, S. Armes, *Soft Matter* **2014**, *10*, 8615.
 [26] K. L. Thompson, C. J. Mable, J. A. Lane, M. J. Derry, L. A. Fielding, S. P. Armes, *Langmuir* **2015**, *31*, 4137.
 [27] H. Fong, I. Chun, D. Reneker, *Polymer* **1999**, *40*, 4585.
 [28] R. Leberman, *J. Mol. Biol.* **1965**, *13*, 606.
 [29] K. E. Roskov, K. A. Kozek, W.-C. Wu, R. K. Chhetri, A. L. Oldenburg, R. J. Spontak, J. B. Tracy, *Langmuir* **2011**, *27*, 13965.
 [30] D. Hermida-Merino, M. Belal, B. W. Greenland, P. Woodward, A. Slark, F. J. Davis, G. R. Mitchell, I. Hamley, W. Hayes, *Eur. Polym. J.* **2012**, *48*, 1249.
 [31] A. S. Tayi, E. T. Pashuck, C. J. Newcomb, M. T. McClendon, S. I. Stupp, *Biomacromolecules* **2014**, *15*, 1323.
 [32] G. Singh, A. M. Bittner, S. Loscher, N. Malinowski, K. Kern, *Adv. Mater.* **2008**, *20*, 2332.
 [33] M. G. McKee, J. M. Layman, M. P. Cashion, T. E. Long, *Science* **2006**, *311*, 353.
 [34] A. Celebioglu, T. Uyar, *Langmuir* **2011**, *27*, 6218.
 [35] X. Yan, M. Zhou, J. Chen, X. Chi, S. Dong, M. Zhang, X. Ding, Y. Yu, S. Shao, F. Huang, *Chem. Commun.* **2011**, *47*, 7086.
 [36] M. Wang, B. Duong, H. Fenniri, M. Su, *Nanoscale* **2015**, *7*, 11240.
 [37] S. R. Nicewarner-Peña, R. G. Freeman, B. D. Reiss, L. He, D. J. Peña, I. D. Walton, R. Cromer, C. D. Keating, M. J. Natan, *Science* **2001**, *294*, 137.
 [38] J. B. H. Tok, F. Chuang, M. C. Kao, K. A. Rose, S. S. Pannu, M. Y. Sha, G. Chakarova, S. G. Penn, G. M. Dougherty, *Angew. Chem. Int. Ed.* **2006**, *45*, 6900.
 [39] D. H. Park, Y. K. Hong, E. H. Cho, M. S. Kim, D.-C. Kim, J. Bang, J. Kim, J. Joo, *ACS Nano* **2010**, *4*, 5155.
 [40] M. Puddu, D. Paunescu, W. J. Stark, R. N. Grass, *ACS Nano* **2014**, *8*, 2677.