



Peapod-Type Nanocomposites through the In Situ Growth of Gold Nanoparticles within Preformed Hexaniobate Nanoscrolls**

Shiva Adireddy, Cecilia E. Carbo, Taha Rostamzadeh, Jose M. Vargas, Leonard Spinu, and John B. Wiley*

Abstract: A facile *in situ* method to grow Au nanoparticles (NPs) in hexaniobate nanoscrolls is applied to the formation of plasmonic Au@hexaniobate and bifunctional plasmonic-magnetic Au-Fe₃O₄@hexaniobate nanopeapods (NPPs). Utilizing a solvothermal treatment, rigid multiwalled hexaniobate nanoscrolls and partially filled Fe₃O₄@hexaniobate NPPs were first fabricated. These nanostructures were then used as templates for the controlled *in situ* growth of Au NPs. The resulting peapod structures exhibited high filling fractions and long-range uniformity. Optical measurements showed a progressive red shift in plasmonic behavior between Au NPs, Au NPPs, and Au-Fe₃O₄ NPPs; magnetic studies found that the addition of gold in the Fe₃O₄@hexaniobate NPPs reduced interparticle coupling effects. The development of this approach allows for the routine bulk preparation of noble-metal-containing bifunctional nanopeapod materials.

One of the critical aspects of nanomaterials development is the controlled assembly of nanoscale components in set geometries.^[1] The realization of targeted organization is essential for directing properties, especially those resulting from synergistic interactions between sets of nanocomponents.^[2] Differing geometries have been sought, including clusters, core-shell, nanowires, nanotubes, dendritics, and chain structures.^[3] Researchers have worked to combine various components for applications in drug delivery, catalysis, sensors, data storage, among others.^[4] Examples of tuned nanocomposites include cluster/shell Fe₃O₄/Au nanoparticles (NPs),^[5] multifunctional Fe₃O₄@Ag/SiO₂/Au core/shell microspheres,^[6] nanoplasmonic Au necklaces,^[7] and dendritic Au nanostructures.^[8] Among the 1D structures, those based on nanopeapods (NPPs) are especially interesting.^[9] The geometry-dependent physical properties of the NPPs make them attractive for various applications,^[10] and this arrangement can support both mechanical and chemical stability while allowing for interactions between adjacent nanoparticle

components. Many such NPP structures have been achieved, including Au@SiO₂,^[10] Pt@CoAl₂O₄,^[11] Au@Ga₂O₃,^[12] Au@MgO,^[13] Cu@Al₂O₃,^[14] Cu@TiO₂,^[14] Ag@TiO₂,^[15] Ni@TiO₂,^[16] Au@Te,^[17] Ag@SiO₂,^[18] and Ni@Ni₃S₂.^[19]

Recently, we developed a high-yield solvothermal method for forming magnetic NPPs by the capture of preformed ferrite NPs in scrolled nanosheets.^[20] Building on this effort, we sought to expand the approach to the fabrication of bifunctional NPPs. Whereas the simultaneous capture of dissimilar NPs is one possible strategy, the insertion of noble-metal species by chemical deposition after NPP fabrication is another viable approach. Au nanoarchitectures can function as catalysts, contrast agents, carriers for drug delivery, and transducers for the photothermal destruction of tumor cells.^[21] As a complement to gold, magnetic NPs (e.g. Fe₃O₄) also have varied applications, such as recycling of expensive catalysts, pharmaceuticals, magnetic resonance imaging, drug delivery, ferrofluids, data storage, and magnetics.^[22] The combination of Au and Fe₃O₄ brings together important technological properties while allowing for effective physical probes of nanomaterials in terms of plasmonic and magnetic behavior, respectively. Herein, we report methods for the growth of gold NPs within the empty regions of nanoscroll structures. Either Au@hexaniobate or Au-Fe₃O₄@hexaniobate nanostructures can be made by this approach, and in the case of the bifunctional Au-Fe₃O₄ nanostructures, changes in both plasmonic and magnetic responses can be realized.

Initially, gold NP chains were grown within empty nanoscrolls. Well-defined intercalated multiwalled hexaniobate nanoscrolls (INS) consisting of 2–6 layers with an average inner diameter of about 12 nm were first obtained through solvothermal treatment (Figure 1a).^[23] The nanoscrolls were then used as templates to grow Au NP chains (Figure 1b–d) by an *in situ* method involving the reduction of Au³⁺ with oleylamine (OAm). Nanoscroll samples, combined with HAuCl₄·4H₂O, OAm, and oleic acid (OAc) in toluene, were heated for 1 h at 50 °C and aged at room temperature for 24 h. This approach readily produces gold NPP structures in high yield. TEM images demonstrate that the product was dominated by uniform Au NP chains inside the hexaniobate nanoscrolls (Figure 1b–d). Typical particles were spherical in shape and averaged 8–11 nm in size. Interparticle distances were about 2.5 nm, slightly smaller than what is seen in other peapods made by scrolled encapsulation.^[20] However, in some instances nanoparticles had reduced interparticle distances, direct contact, or clear evidence of intergrowth between 2 or more adjacent particles. The latter could be enhanced by increasing reaction times; this produced occasional rod

[*] Dr. S. Adireddy, C. E. Carbo, T. Rostamzadeh, Prof. J. B. Wiley
Department of Chemistry and AMRI, University of New Orleans
New Orleans, LA 70148 (USA)
E-mail: jwiley@uno.edu

Dr. J. M. Vargas, Prof. L. Spinu
Department of Physics and AMRI, University of New Orleans
New Orleans, LA 70148 (USA)

[**] This work was supported in part by the Louisiana Board of Regents Post-Katrina Support Fund Initiative (PKSFI, LEQSF(2007-12)-ENH-PKSFI-PRS-04). C.E.C.'s REU summer support through NSF DMR-1262904 is gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201310834>.

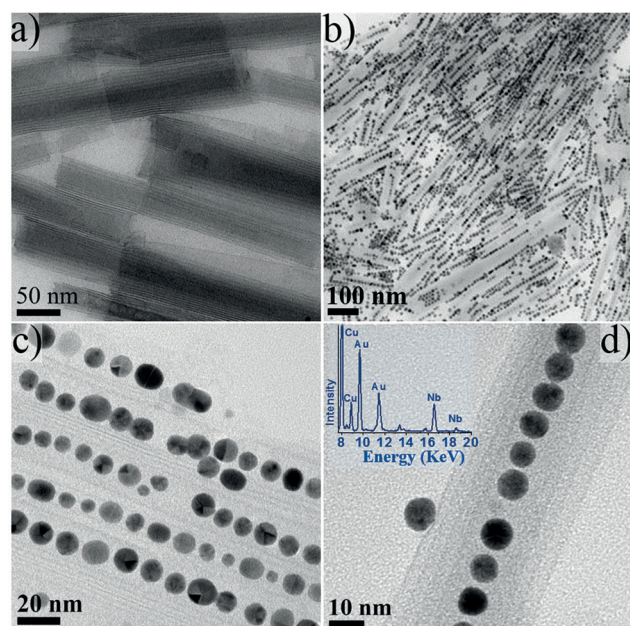


Figure 1. TEM images of a) nanoscrolls and b–d) Au@hexaniobate nanopeapods. The inset in (d) shows EDS data for sample (Cu peaks from the TEM grid).

shapes > 200 nm in length (Supporting information, Figure S1).

This in situ Au NP growth process is not limited to empty nanoscrolls. Uniform Au-Fe₃O₄@hexaniobate NPPs were also fabricated by treating partially filled Fe₃O₄@hexaniobate NPPs by the same approach. Low loadings of Fe₃O₄ NPs in the synthesis of Fe₃O₄@hexaniobate NPPs led to nanoscrolls with significant open space along the length of the peapod structure (Figure 2a,b). Au treatment then produces NPPs that contain both Au and Fe₃O₄ NPs. These Au-Fe₃O₄@hexaniobate NPPs were examined with TEM, high-angle annular dark-field scanning TEM (HAADF-STEM), and EDS elemental mapping. TEM images (Figure 2c,d) show clear regions of Au and Fe₃O₄ NPs in the Au-Fe₃O₄@hexaniobate NPPs. HAADF-STEM with elemental mapping provides further illumination of gold, iron, and niobium regions (Figure 2e–i). High contrast between the Au and Fe₃O₄ NPs is especially apparent in Figure 2e,g,h. The niobium from the hexaniobate nanosheets is more evenly distributed throughout these regions (Figure 2i).

This approach to gold NP growth in the nanoscroll structures (Figure 3) readily occurs to produce both Au@hexaniobate and Au-Fe₃O₄@hexaniobate NPPs. The Au NPs grow both outside and inside the scrolls. While the free (outer) NPs are readily removed during centrifugation, the others are retained by the scrolls. The reduction of Au³⁺ to Au⁰ is known to occur in the presence of OAm, and researchers have shown that OAm can be used as both a surfactant and reducing agent to produce various sizes of gold and silver NPs on a large scale.^[24] The particle size, nucleation, and growth data can be interpreted in terms of a classical nucleation/diffusional growth model.^[25] It would appear that, within the hexaniobate nanoscroll, gold atoms self-nucleate to form a fixed number of seeds and gold NPs

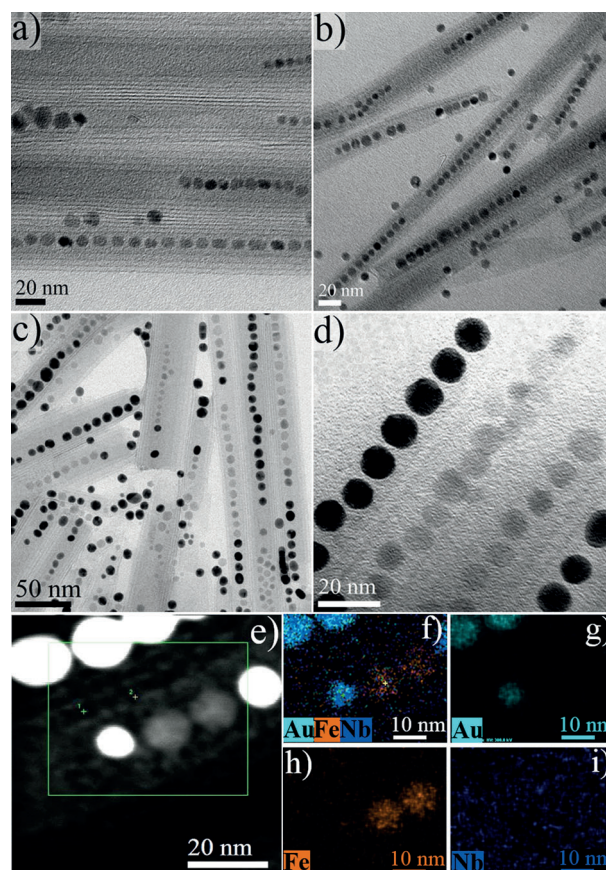


Figure 2. a–d) TEM images of the partially filled Fe₃O₄@hexaniobate NPPs showing the empty spaces in the hexaniobate nanoscrolls that were used as templates to grow Au NPs (a,b) and Au-Fe₃O₄@hexaniobate NPP structures (c,d). e) HAADF-STEM image. f–i) EDS elemental mapping analysis of bifunctional NPPs. f) Au, Fe, and Nb; g) Au (cyan); h) Fe (orange); i) Nb (purple).

then grow by the diffusion-driven deposition of gold onto these seeds. Interparticle distances are then typically dictated by surface groups,^[20] such that spacing should be tunable by varying the capping agents.^[26] In the Au-Fe₃O₄@hexaniobate NPPs, Au NPs can be seen filling the void spaces of the partially filled Fe₃O₄-NPPs. Whereas many of the Au NPs fill open spaces at the end of the NPPs, the diffusion of gold ions around Fe₃O₄ NPs also allows the Au NPs to form between individual or sets of Fe₃O₄ NPs. (Figure S3)

The Au-Fe₃O₄ nanocomposites produced in this study have both optical and magnetic components, and the unusual collinear arrangement of NPs provides a unique means for probing interparticle interactions. Initially UV/Vis studies were carried out on samples dispersed in toluene. UV/Vis spectra of empty nanoscrolls show minimal absorption in the visible region (Figure 4a), as expected for the wide band-gap of hexaniobate.^[27] The spectra of free Au NPs (10 nm), Au@hexaniobate NPPs, and Au-Fe₃O₄@hexaniobate NPPs are shown in Figure 4b. Au NPs exhibit a surface plasmon resonance (SPR) peak at 524 nm, which is in good agreement with the literature.^[28] The energy of a plasmon resonance band is known to depend on the dielectric properties of the surrounding media and NP morphology.^[29] Au NPs inside hexaniobate nanoscrolls were anticipated to shift the SPR to

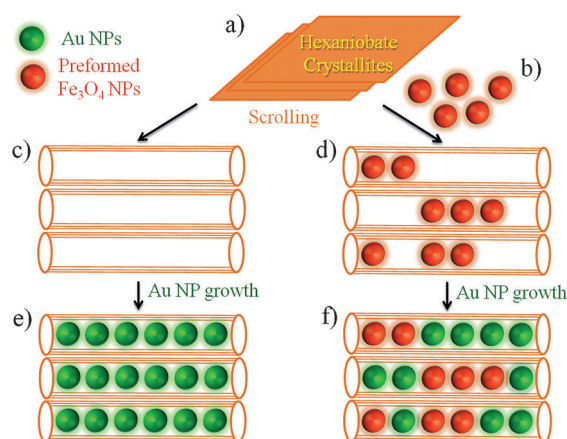


Figure 3. Au NP in situ growth in preformed nanoscrolls and partially filled Fe_3O_4 @hexaniobate NPPs. a) Hexaniobate crystallites. b) Preformed Fe_3O_4 NPs. c) Nanoscrolls. d) Partially filled Fe_3O_4 @hexaniobate NPPs. e) Au@hexaniobate NPPs. f) Au- Fe_3O_4 @hexaniobate bifunctional NPPs.

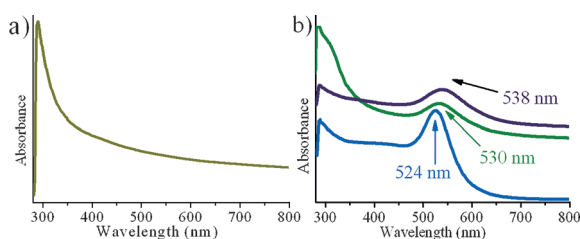


Figure 4. UV/Vis absorption spectrum of a) hexaniobate nanoscrolls and b) Au NPs (blue), Au@hexaniobate NPPs (green), and Au- Fe_3O_4 @hexaniobate NPPs (purple).

higher wavelengths due to interaction between NPs within the Au chains;^[30] a shift of about 6 nm was observed for the Au NPPs versus the free NPs. Interestingly, a further shift in SPR is seen for Au- Fe_3O_4 @hexaniobate NPPs. There have been several studies gold-iron oxide nanoparticles (heterodimers)^[31] where a red shift in the SPR is attributed to the iron oxide component, thus producing a charge transfer from gold at their interface. Whereas it is possible that similar influences are occurring here, the less intimate contact between Au and Fe_3O_4 nanoparticles in our studies, owing to OAm capping groups on the NP surfaces, should reduce the impact of the Fe_3O_4 on SPR.

We have also examined the magnetic behavior of the Au- Fe_3O_4 @hexaniobate NPPs relative to partially filled Fe_3O_4 @hexaniobate NPPs. Magnetic nanoparticle chains, including those within NPPs, have an increase in their zero-field-cooled (ZFC) maximum and coercivity (H_c) relative to free particles, owing to one-dimensional dipolar coupling of adjacent nanoparticles.^[20] Upon insertion of gold into the Fe_3O_4 @hexaniobate NPPs, a decrease in the ZFC (Figure 5) and coercivity are seen (Figure S4). It is apparent that the introduction of Au into the Fe_3O_4 @hexaniobate NPPs serves to disrupt magnetic coupling between adjacent NPs.

The method presented here demonstrates an effective approach to the growth of gold nanoparticles within niobate nanoscrolls and leads to new nanopeapod structures. Similar approaches should be effective in other materials that form

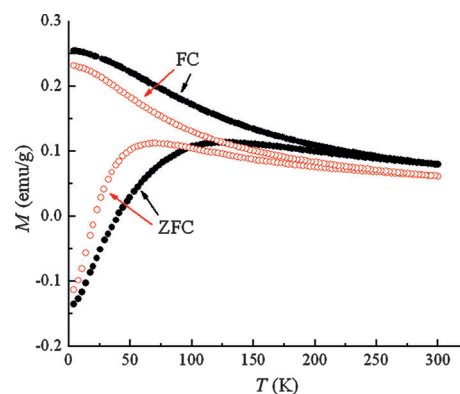


Figure 5. Field-cooled (FC) and zero-field-cooled (ZFC) variable-temperature magnetic data at 20 Oe of partially filled Fe_3O_4 @hexaniobate NPPs (filled circles) and bifunctional Au- Fe_3O_4 @hexaniobate NPPs (open circles).

scrolls (graphene, boron nitride, layered perovskites, transition metal dichalcogenides, and so on),^[32] as well as in preformed nanotubes.^[33] Further, this method will not be limited to gold—similar chemistries should be accessible with other easily reduced transition and main-group metals.^[34] Also, by controlling reaction conditions one should be able to move to structures beyond NPs to produce metal nanorods and nanowires by this approach.

Another important outcome of this method relates to bifunctional nanopeapod structures. In this example, we have formed partially filled nanopeapods with Fe_3O_4 NPs; a variety of other partially filled nanopeapods can also be formed, including different ferrites (MFe_2O_4), metal oxides (TiO_2 , CeO_2), metals (Co, Ag), quantum dots (CdS, CdSe), and others.^[9a,20,35] Such bifunctional materials, including the Au- Fe_3O_4 nanopeapods presented here, hold the promise of tuned properties.^[31a,d,36] Two or more magnetic, optical, electrical, or catalytic materials could be combined with gold to make multifunctional materials, or even to access metamaterials.^[37] For example, Au magnetic nanoarchitectures can perform as magnetically separable photocatalysts, in addition to several other promising magnetic, optical, and biomedical applications.^[38] Further, by immobilizing the Au NPs inside the Fe_3O_4 @hexaniobate NPPs, multifunctional nanocomposites can be readily prepared, possibly rendering them useful as transducers for the photothermal destruction of tumor cells.^[36a,38d]

In summary, we have demonstrated synthetic strategies for the preparation of novel nanocomposites by growing Au NPs in hexaniobate nanoscrolls by a facile non-aqueous method. The approach was successfully extended to the fabrication of novel bifunctional Au- Fe_3O_4 @hexaniobate NPPs. This study highlights the extensive potential of NPP systems, where it is possible to direct nanocomponents within the nanoscrolls so that a variety of technologically significant magnetic, optical, catalytic, and electronic nanocomposites can be developed.

Received: December 13, 2013

Published online: March 12, 2014

Keywords: layered inorganics · magnetic nanochains ·
nanopeapods · plasmonic nanochains

- [1] a) A. Scheffel, M. Gruska, D. Faivre, A. Linaroudis, J. M. Plitzko, D. Schuler, *Nature* **2006**, *440*, 110; b) S. R. Whaley, D. S. English, E. L. Hu, P. F. Barbara, A. M. Belcher, *Nature* **2000**, *405*, 665; c) S. Adireddy, C. K. Lin, B. B. Cao, W. L. Zhou, G. Caruntu, *Chem. Mater.* **2010**, *22*, 1946; d) N. J. Halas, *Nano Lett.* **2010**, *10*, 3816.
- [2] a) A. Verma, F. Stellacci, *Small* **2010**, *6*, 12; b) A. E. Nel, L. Madler, D. Velegol, T. Xia, E. M. V. Hoek, P. Somasundaran, F. Klaessig, V. Castranova, M. Thompson, *Nat. Mater.* **2009**, *8*, 543.
- [3] a) A. Nel, T. Xia, L. Madler, N. Li, *Science* **2006**, *311*, 622; b) C. Sanchez, B. Julian, P. Belleville, M. Popall, *J. Mater. Chem.* **2005**, *15*, 3559; c) M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, C. M. Lieber, *Nature* **2002**, *415*, 617.
- [4] a) A. H. Lu, E. L. Salabas, F. Schuth, *Angew. Chem.* **2007**, *119*, 1242; *Angew. Chem. Int. Ed.* **2007**, *46*, 1222; b) J. L. Lyon, D. A. Fleming, M. B. Stone, P. Schiffer, M. E. Williams, *Nano Lett.* **2004**, *4*, 719.
- [5] X. Zhou, W. L. Xu, Y. Wang, Q. Kuang, Y. F. Shi, L. B. Zhong, Q. Q. Zhang, *J. Phys. Chem. C* **2010**, *114*, 19607.
- [6] J. H. Shen, Y. H. Zhu, X. L. Yang, J. Zong, C. Z. Li, *Langmuir* **2013**, *29*, 690.
- [7] A. J. Pasquale, B. M. Reinhard, L. Dal Negro, *ACS Nano* **2011**, *5*, 6578.
- [8] D. P. Huang, X. T. Bai, L. Q. Zheng, *J. Phys. Chem. C* **2011**, *115*, 14641.
- [9] a) Y. Yao, G. S. Chaubey, J. B. Wiley, *J. Am. Chem. Soc.* **2012**, *134*, 2450; b) B. W. Smith, D. E. Luzzi, *Chem. Phys. Lett.* **2000**, *321*, 169.
- [10] M. S. Hu, H. L. Chen, C. H. Shen, L. S. Hong, B. R. Huang, K. H. Chen, L. C. Chen, *Nat. Mater.* **2006**, *5*, 102.
- [11] L. F. Liu, W. Lee, R. Scholz, E. Pippel, U. Gosele, *Angew. Chem.* **2008**, *120*, 7112; *Angew. Chem. Int. Ed.* **2008**, *47*, 7004.
- [12] a) C. H. Hsieh, L. J. Chou, G. R. Lin, Y. Bando, D. Golberg, *Nano Lett.* **2008**, *8*, 3081; b) P. H. Chen, C. H. Hsieh, S. Y. Chen, C. H. Wu, Y. J. Wu, L. J. Chou, L. J. Chen, *Nano Lett.* **2010**, *10*, 3267.
- [13] a) Y. F. Lai, P. Chaudouet, F. Charlot, I. Matko, C. Dubourdieu, *Appl. Phys. Lett.* **2009**, *94*, 022904; b) W. W. Zhou, L. Sun, T. Yu, J. X. Zhang, H. Gong, H. J. Fan, *Nanotechnology* **2009**, *20*, 455603.
- [14] Y. Qin, S. M. Lee, A. Pan, U. Gosele, M. Knez, *Nano Lett.* **2008**, *8*, 114.
- [15] J. A. Sioss, C. D. Keating, *Nano Lett.* **2005**, *5*, 1779.
- [16] W. Zhu, G. Z. Wang, X. Hong, X. S. Shen, D. P. Li, X. Xie, *Electrochim. Acta* **2009**, *55*, 480.
- [17] C. M. Hangarter, Y. I. Lee, S. C. Hernandez, Y. H. Choa, N. V. Myung, *Angew. Chem.* **2010**, *122*, 7235; *Angew. Chem. Int. Ed.* **2010**, *49*, 7081.
- [18] S. E. Hunyadi, C. J. Murphy, *J. Phys. Chem. B* **2006**, *110*, 7226.
- [19] W. Zhou, W. M. Chen, J. W. Nai, P. G. Yin, C. P. Chen, L. Guo, *Adv. Funct. Mater.* **2010**, *20*, 3678.
- [20] S. Adireddy, C. E. Carbo, Y. Yao, J. M. Vargas, L. Spinu, J. B. Wiley, *Chem. Mater.* **2013**, *25*, 3902.
- [21] a) N. L. Rosi, C. A. Mirkin, *Chem. Rev.* **2005**, *105*, 1547; b) J. Homola, S. S. Yee, G. Gauglitz, *Sens. Actuators B* **1999**, *54*, 3.
- [22] a) S. Adireddy, C. K. Lin, V. Palshin, Y. M. Dong, R. Cole, G. Caruntu, *J. Phys. Chem. C* **2009**, *113*, 20800; b) Q. A. Pankhurst, N. T. K. Thanh, S. K. Jones, J. Dobson, *J. Phys. D* **2009**, *42*, 224001; c) A. K. Gupta, M. Gupta, *Biomaterials* **2005**, *26*, 3995.
- [23] S. Adireddy, Y. Yao, J. He, J. B. Wiley, *Mater. Res. Bull.* **2013**, *48*, 3236.
- [24] a) M. Saruyama, M. Kanehara, T. Teranishi, *J. Am. Chem. Soc.* **2010**, *132*, 3280; b) H. Hiramatsu, F. E. Osterloh, *Chem. Mater.* **2004**, *16*, 2509.
- [25] a) J. T. G. Overbeek, *Adv. Colloid Interface Sci.* **1982**, *15*, 251; b) V. Privman, D. V. Goia, J. Park, E. Matijevic, *J. Colloid Interface Sci.* **1999**, *213*, 36; c) V. K. LaMer, R. H. Dinegar, *J. Am. Chem. Soc.* **1950**, *72*, 4847.
- [26] a) R. C. Wadams, L. Fabris, R. A. Vaia, K. Park, *Chem. Mater.* **2013**, *25*, 4772; b) A. M. Alkilany, C. J. Murphy, *Langmuir* **2009**, *25*, 13874.
- [27] F. E. Sarac, C. Yilmaz, F. Y. Acar, U. Unal, *RSC Adv.* **2012**, *2*, 10182.
- [28] a) K. C. Grabar, R. G. Freeman, M. B. Hommer, M. J. Natan, *Anal. Chem.* **1995**, *67*, 735; b) L. Rivas, S. Sanchez-Cortes, J. V. Garcia-Ramos, G. Morcillo, *Langmuir* **2000**, *16*, 9722.
- [29] a) M. Q. Zhao, R. M. Crooks, *Chem. Mater.* **1999**, *11*, 3379; b) S. K. Pillalamarri, F. D. Blum, A. T. Tokunishi, M. F. Bertino, *Chem. Mater.* **2005**, *17*, 5941; c) O. M. Wilson, R. W. J. Scott, J. C. Garcia-Martinez, R. M. Crooks, *J. Am. Chem. Soc.* **2005**, *127*, 1015.
- [30] a) S. Lin, M. Li, E. Dujardin, C. Girard, S. Mann, *Adv. Mater.* **2005**, *17*, 2553; b) S. A. Maier, P. G. Kik, H. A. Atwater, *Appl. Phys. Lett.* **2002**, *81*, 1714; c) B. Q. Ding, Z. T. Deng, H. Yan, S. Cabrini, R. N. Zuckermann, J. Bokor, *J. Am. Chem. Soc.* **2010**, *132*, 3248; d) Q. H. Wei, K. H. Su, S. Durant, X. Zhang, *Nano Lett.* **2004**, *4*, 1067.
- [31] a) Z. C. Xu, Y. L. Hou, S. H. Sun, *J. Am. Chem. Soc.* **2007**, *129*, 8698; b) D. S. Wang, Y. D. Li, *J. Am. Chem. Soc.* **2010**, *132*, 6280; c) F. H. Lin, R. A. Doong, *J. Phys. Chem. C* **2011**, *115*, 6591; d) C. Xu, J. Xie, D. Ho, C. Wang, N. Kohler, E. G. Walsh, J. R. Morgan, Y. E. Chin, S. Sun, *Angew. Chem.* **2008**, *120*, 179; *Angew. Chem. Int. Ed.* **2008**, *47*, 173.
- [32] a) U. Maitra, H. Matte, P. Kumar, C. N. R. Rao, *Chimia* **2012**, *66*, 941; b) E. Perim, D. S. Galvao, *Nanotechnology* **2009**, *20*, 335702; c) D. Xia, Q. Z. Xue, J. Xie, H. J. Chen, C. Lv, F. Besenbacher, M. D. Dong, *Small* **2010**, *6*, 2010.
- [33] a) R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787; b) J. T. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435.
- [34] a) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.* **2000**, *30*, 545; b) A. R. Tao, S. Habas, P. D. Yang, *Small* **2008**, *4*, 310; c) Y. N. Xia, Y. J. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2009**, *121*, 62; *Angew. Chem. Int. Ed.* **2009**, *48*, 60.
- [35] S. Adireddy, T. Rostamzadeh, J. B. Wiley, unpublished results.
- [36] a) L. Y. Wang, J. Luo, Q. Fan, M. Suzuki, I. S. Suzuki, M. H. Engelhard, Y. H. Lin, N. Kim, J. Q. Wang, C. J. Zhong, *J. Phys. Chem. B* **2005**, *109*, 21593; b) H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White, S. H. Sun, *Nano Lett.* **2005**, *5*, 379.
- [37] a) W. S. Cai, U. K. Chettiar, A. V. Kildishev, V. M. Shalae, *Nat. Photonics* **2007**, *1*, 224; b) E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia, V. Laukhin, *Nature* **2000**, *408*, 447; c) C. B. Murray, S. H. Sun, W. Gaschler, H. Doyle, T. A. Betley, C. R. Kagan, *IBM J. Res. Dev.* **2001**, *45*, 47; d) F. X. Redl, K. S. Cho, C. B. Murray, S. O'Brien, *Nature* **2003**, *423*, 968.
- [38] a) X. Q. Chi, D. T. Huang, Z. H. Zhao, Z. J. Zhou, Z. Y. Yin, J. H. Gao, *Biomaterials* **2012**, *33*, 189; b) E. Cubukcu, E. A. Kort, K. B. Crozier, F. Capasso, *Appl. Phys. Lett.* **2006**, *89*, 093120; c) E. Cubukcu, N. F. Yu, E. J. Smythe, L. Diehl, K. B. Crozier, F. Capasso, *IEEE J. Sel. Top. Quantum Electron.* **2008**, *14*, 1448; d) X. H. Huang, P. K. Jain, I. H. El-Sayed, M. A. El-Sayed, *Nanomedicine* **2007**, *2*, 681; e) H. Zeng, S. H. Sun, *Adv. Funct. Mater.* **2008**, *18*, 391.