Nanoparticle Synthesis

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Shape-Controlled Synthesis of Copper Nanocrystals in an Aqueous Solution with Glucose as a Reducing Agent and Hexadecylamine as a Capping Agent**

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In addition to Ag and Au, Cu is another metal known to exhibit localized surface plasmon resonance (LSPR) peaks in the visible region when it is prepared as nanostructures.[1] Copper nanostructures are also of great interest and importance for applications in microelectronics and catalysis. For example, Cu nanowires (polycrystalline, usually fabricated by lithographic techniques) are currently used as the interconnects in computer chips.[2] Copper nanoparticles have been widely used as catalysts for water–gas shift[3] and gas detoxification reactions.[4] All of these fundamental studies and applications would greatly benefit from the availability of Cu nanocrystals with well-defined and controllable shapes, as well as in large quantity and good uniformity. However, due to the difficulty in reducing Cu^{II} or Cu^{I} into Cu^{0} in an aqueous solution and the susceptibility to oxidation upon exposure to air, synthesis of Cu nanocrystals is still in a rudimentary state of development relative to what has been achieved for both Ag and Au.[5]

There were a few reports in literature on the synthesis of Cu nanocubes,[6] but later studies suggested that some of these disclosed nanocubes were likely made of Cu_2O rather than Cu. For penta-twinned Cu nanorods, two solution-phase methods have been reported. The first method involved the reduction of copper(II) bis(2-ethylhexyl)sulfosuccinate, $Cu(AOT)_2$, with hydrazine in a mixture of isooctane and water.[7] The second method is an oil-phase approach, in which 1,2-hexadecanediol was used as a reductant while oleic acid and oleylamine served as the capping agents.[8] Recently, penta-twinned Cu nanowires ca. 50 nm in diameter and ca. 10 μm in length have also been prepared by taking advantage of the disproportionation of Cu^{I} (used as a complex with oleylamine) into Cu^{II} and Cu^{0} in oleylamine at 200 °C.[9] Under a hydrothermal environment, single-crystal Cu nanowires thicker than 60 nm have also been prepared by reducing $CuCl_2$ with glucose.[10] As for Cu nanoplates, $Cu(CH_3COO)_2$ was reduced with hydrazine in acetonitrile at 80 °C under an inert atmosphere to generate hexagonal plates with broad lateral sizes that displayed an LSPR peak at 575 nm.[11] Among different methods reported so far for Cu nanocrystals, the one developed by Zeng and co-workers is worth mentioning due to its simplicity, versatility, and robustness.[12] This method involved the formation of $Cu(OH)_2$ precipitates upon mixing aqueous $Cu(NO_3)_2$ and NaOH solutions, followed by the introduction of ethylenediamine (EDA, a coordination ligand for Cu^{II}) and hydrazine (a reductant). After heating at 60 °C for 15 min, polycrystalline Cu nanowires with a circular cross section were obtained with sizes in the range of 90–120 nm. In a recent study, this method was further modified by Wiley and co-workers to produce single-crystal Cu nanowires with diameters around 90 nm.[13] Despite these reports, it remains a grand challenge to produce Cu nanocrystals with well-defined and controllable shapes, under ambient conditions, as well as with desirable quality and quantity for investigation of their optical/electrical properties and applications.

It is well-known that the growth habit of a nanocrystal is determined by the ratio between growth rates of different facets.[14] In recent studies, capping agents have been widely used to maneuver the surface energies and growth rates of different facets and therefore the shape taken by a nanocrystal.[5c] For example, we have shown that poly(vinyl pyrrolidone) (PVP) can serve as a capping agent that binds most strongly to the {100} facets of Ag or Pd.[15] This preferential capping favors the addition of atoms primarily to the poorly passivated {111} facets, leading to the formation of nanocubes, bipyramids, or penta-twinned nanowires enclosed by {100} facets, depending on the types of seeds. In addition to PVP, bromide was also found to selectively adsorb onto the {100} facets of Ag, Au, Pd, or Pt, and thereby induce the formation of nanocubes, nanobars, or penta-twinned nanowires (again, determined by the seeds).[16] These studies clearly demonstrate the power and versatility of a capping agent in controlling the shape of a noble-metal nanocrystal. However, no effective capping agent has been found for manipulating the shapes of Cu nanocrystals and, at the same

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time, preventing them from being oxidized by air. Here we demonstrate that hexadecylamine (HDA) is an effective capping agent for Cu, with a good selectivity toward the {100} facets. When used in conjunction with glucose (a reductant capable of reducing Cu^{II} into Cu^0), this new capping agent allowed us to produce Cu nanocrystals with controlled shapes in relatively large quantity, and with high purity and good uniformity.

In a standard synthesis, 21 mg $CuCl_2{\cdot}2H_2O$ (the precursor), 50 mg glucose (the reductant), 180 mg HDA (the capping agent), and 10 mL water (the solvent) were mixed in a glass vial, capped, and the final solution was magnetically stirred at room temperature overnight. The vial was then transferred into an oil bath and heated at 100 °C for 6 h under magnetic stirring. As the reaction proceeded, the solution gradually changed its color from blue to red-brown (see the photograph in Figure 1 a), implying the formation of Cu^0 species due to the reduction of Cu^{2+} by glucose. Figure 1 a also shows an X-ray diffraction (XRD) pattern of the product, where the three peaks at $2\theta = 43.5$, 50.7, and 74.4° correspond to diffractions from {111}, {200}, and {220} planes of face-centered cubic Cu (JCPDS #03-1018). No other phases such as Cu_2O and CuO were detected. We also measured the concentrations of Cu^{2+}/Cu^{+} ions left behind in the reaction solution using inductively-coupled plasma mass spectrometry (ICP-MS) and found that the precursor had been converted into atomic Cu at a percentage of 93 %. The SEM image shown in Figure 1 b demonstrates that the Cu nanowires could be prepared in high purity, typically approaching 95 %, without any post-synthesis separation when the standard procedure was used. If necessary, the small amount of Cu nanocubes co-existing with the Cu nanowires could be easily removed.[17] In addition, the nanowires were found to be highly flexible and some of them showed bending more than 360 degrees without being broken. Both the SEM image at a higher magnification (Figure 1 c) and TEM image (Figure 1 d) clearly reveal that the nanowires were uniform in diameter and tended to be aligned in parallel to form bundles during sample preparation. The nanowires had an average diameter of 24 ± 4 nm as calculated from 100 nanowires randomly selected from a number of TEM images (Figure S1 in the Supporting Information). The lengths of the Cu nanowires varied in the range of several tens to hundreds of micrometers; some of them were as long as several millimeters. The band-like contrast (see the box in Figure 1 d) observed on the TEM images can be attributed to strains caused by bending or twisting.

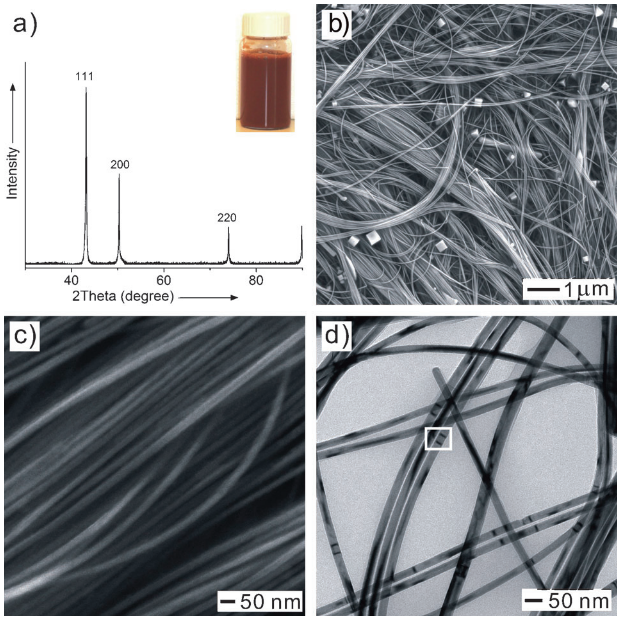

Figure 1. Structural and morphological characterizations of the Cu nanowires that were prepared using the standard procedure: a) XRD pattern; b, c) SEM images; and d) TEM image. The inset in (a) shows a photograph of the as-prepared suspension of Cu nanowires in water, and the box in (d) marks the band-like contrast caused by strains in the nanowires.

Metallic nanowires are expected to find widespread use in applications such as fabrication of transparent electrodes for flexible electronic and display devices. To this end, Cambrios, a startup in the Bay Area, is commercializing composites based on Ag nanowires for touch screen displays under the trade name of ClearOhm.[18] Other groups have also started to explore the use of penta-twinned Ag nanowires in preparation of flexible conducting films with conductivities and transmittances comparable to ITO.[19] Compared to Ag, Cu is 1000 times more abundant and 100 times less expensive. As such, conducting films fabricated from Cu nanowires hold great promise as transparent electrodes for various applications, including fabrication of low-cost flexible displays, light-emitting diodes, and thin film solar cells. Motivated by these advantages, Wiley and co-workers recently demonstrated the synthesis of Cu nanowires in aqueous solutions and evaluated their potential use in fabrication of flexible conducting films.[13] It was found that films made of Cu nanowires (ca. 90 nm in diameter) transmit 25 % less light in the visible region than ITO films with the same sheet resistance. It is reasonable to expect that the transmittance could be further increased by reducing the size of the nanowires and improving their uniformity. Our Cu nanowires with a uniform diameter of ca. 24 nm should provide a superb candidate for this type of application. The use of a small molecule rather than a big macromolecule like PVP (for Ag nanowires) as the capping agent may also greatly facilitate electron hopping between Cu nanowires. Figure S2 shows UV/Vis transmission spectra recorded from aqueous suspensions of the 24 nm Cu nanowires and penta-twinned Ag nanowires of 80 nm in diameter (Figure S3, prepared according to the literature[20]) at roughly the same metal concentration ($30\ \mu g\,mL^{-1}$), suggesting a slightly higher transmittance in the visible region for the Cu nanowires. This higher transmittance could be attributed to the smaller diameter of the Cu nanowires.

We further studied the structures of these Cu nanowires by high-resolution TEM. Figure 2 shows TEM and the corresponding high-resolution TEM images taken from the middle and end portions of two different Cu nanowires, respectively. The insets schematically illustrate the orientations of the Cu nanowires relative to the incident electron beam (indicated by arrows). The high-resolution TEM images

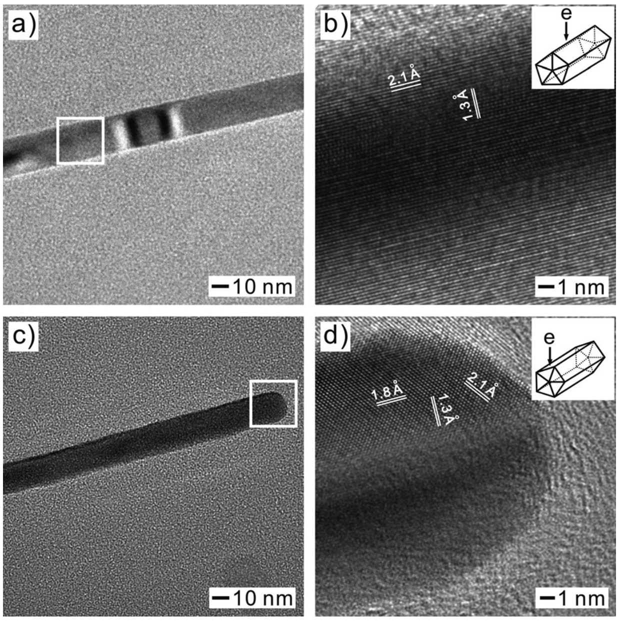

Figure 2. a, c) TEM images taken from two different Cu nanowires; b, d) high-resolution TEM images of the regions marked by two boxes in (a) and (c), respectively. The insets in (b) and (d) schematically depict the orientations of the two Cu nanowires relative to the incident electron beam.

clearly show the existence of {111} twin planes parallel to the long axis of the nanowire. When the direction of the e-beam was perpendicular to the bottom side of the pentagonal nanowire (Figure 2 b), two sets of fringes with lattice spacing of 2.1 nm and 1.3 nm were observed, corresponding to the {111} and {220} planes of Cu, respectively. Figure 2 d shows the high-resolution TEM image taken from a Cu nanowire oriented with one of its side faces parallel to the e-beam. The fringes with lattice spacing of 2.1, 1.8, and 1.3 Å could be indexed to the {111}, {200}, and {220} planes of Cu, respectively. Based on the results of both SEM and high-resolution TEM analyses, we can conclude that the Cu nanowires had a penta-twinned structure bound by ten {111} facets at the two ends and five {100} side faces, which are consistent with the results previously reported for other metals including Ag, Au, and Pd.[21]

By simply increasing the concentration of glucose in the standard procedure from 5 to 10 $\mathrm{mg\,mL^{-1}}$, we also obtained tadpole-like Cu nanowires (Figure 3). In an effort to uncover the growth mechanism, we analyzed the products obtained at different reaction times. In the initial stage ($t = 30$ min), the solution changed its color from blue to red-brown due to the formation of tapered Cu nanocrystals whose diameter gradually changed from 200 to 25 nm over a length of 0.5–1 μm (Figure 3 a). The tapered Cu nanocrystals exhibited a UV/Vis absorption peak around 591 nm (Figure S4), and they represent a novel class of pentagonal bipyramids (Figure S5) formed by stretching apart the five-fold apices of a decahedron. After the reaction had proceeded to $t = 1$ h (Figure 3 b), thin Cu nanowire of ca. 24 nm in diameter started to appear from the thinner end of a tapered nanocrystal. As the reaction was continued to $t = 3$ h (Figure 3 c and d), the Cu nanowires further grew along the long axes with almost no change to their diameters. These results indicate that the tadpole-like Cu nanowires originated from the tapered nanocrystals, through a mechanism similar to what was proposed by Wiley and co-workers.[13] The SEM image in the inset of Figure 3 d indicates that the tadpole-like Cu nanowires also had a pentagonal cross-section. The TEM and high-resolution TEM images shown in Figure 3 e and f, further confirm a tadpole-like morphology and a penta-twinned structure for the Cu nanowires.

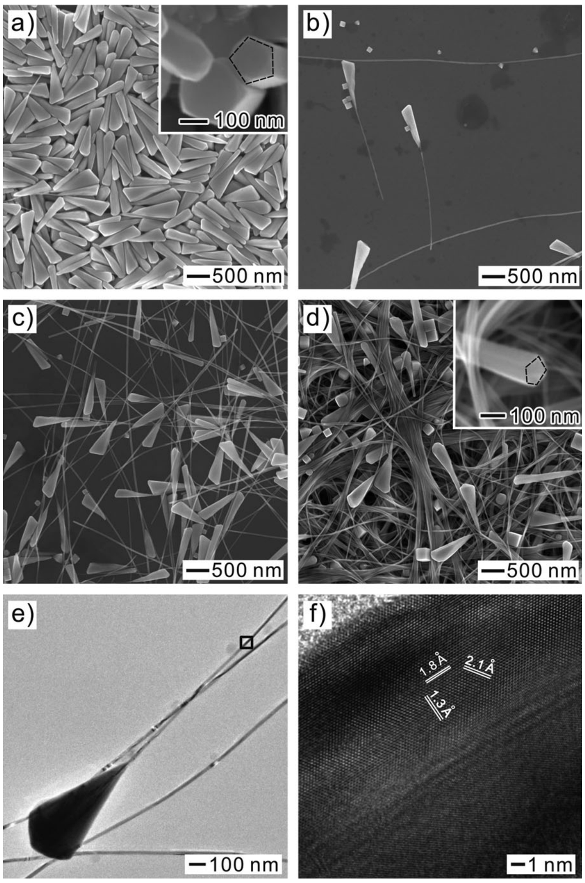

Figure 3. SEM images of tadpole-like Cu nanowires prepared at different time points using the standard procedure except that the glucose concentration was increased from 5 to 10 $\mathrm{mg\,mL^{-1}}$: a) 0.5, b) 1, c) 3, and d) 6 h. The insets in (a) and (d) show SEM images taken from tilted samples, revealing pentagonal cross-sections of the nanocrystals. e) TEM image of the tadpole-like Cu nanowires shown in (d). f) High-resolution TEM image taken from the region marked by a box in (e).

The amount of HDA was also found to play an important role in controlling the final morphology of Cu nanocrystals. Interestingly, the products were dominated by Cu nanocubes when the concentration of HDA was reduced from 18 to 9 $\mathrm{mg\,mL^{-1}}$ in the standard procedure. Figure 4 a–c, shows SEM images of the products obtained at $t = 0.5$ h, 1 h, and 6 h and Figure 4 d shows an XRD pattern of the nanocubes obtained at $t = 6$ h. For bulk Cu, the strongest XRD diffraction is the (111) peak, followed by the (200), (220), and (311) peaks. In contrast, the Cu nanocubes tend to give (200) diffraction as the strongest peak because of their preferential orientation with {100} planes parallel to the substrate. The

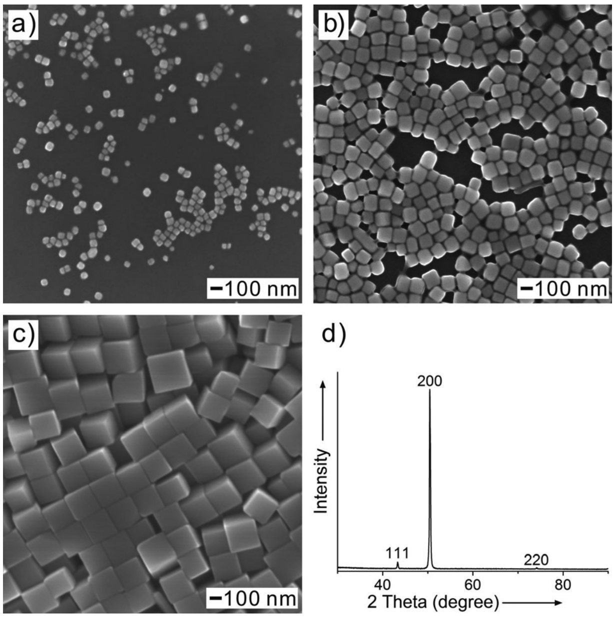

Figure 4. a–c) SEM images of Cu nanocubes prepared at different time points using the standard procedure except that the HDA concentration was reduced from 18 to 9 mg mL^{-1}: a) 0.5, b) 1, and c) 6 h. The edge lengths of the nanocubes increased from 50 to 200 nm as the reaction time increased from 0.5 to 6 h. d) XRD pattern of the Cu nanocubes obtained at 6 h.

high-resolution TEM image of an individual Cu nanocube viewed along the ⟨100⟩ zone axis (Figure S6) clearly shows well-resolved, continuous fringes with lattice spacing of 1.8 Å, corresponding to the {100} planes, indicating that the nanocube was a single crystal bound by {100} facets. Figure S7 shows UV/Vis absorption spectra taken from the Cu nanocubes dispersed in water. The Cu nanocubes exhibited a major LSPR peak in the visible region, whose position was red-shifted from 565 to 625 nm as the edge length of the nanocubes was increased from 50 to 200 nm. Compared to Ag nanocubes with a similar size, the LSPR peak of the Cu nanocubes was positioned at a much longer wavelength. These results agreed with the theoretical calculations and observations by other groups.[22]

As it has been demonstrated for a number of metals,[5c] there is a correlation between the internal structure of a seed and the shape taken by a nanocrystal: for example, a nanocube must grow from a single-crystal seed while a pentagonal nanowire must grow from a decahedral seed with a multiply twinned structure. The distribution of single-crystal versus multiply twinned seeds can be manipulated through the introduction of oxidative etching, which have been successfully demonstrated for a number of noble metals including Ag, Au, Pd, and Rh.[15b,23] We believe oxidative etching was also involved in the formation of the Cu nanocubes because Cu is more reactive than Ag and can be more easily oxidized and etched by the Cl^{-}/O$_2$ pair (Figure S8). When the concentration of HDA was high (18 mg mL^{-1}), this capping agent could prevent the twinned seeds from being oxidized and etched. As such, the multiply twinned seeds prevailed due to a relatively lower surface energy for the {111} facets than the {100} facets. When the concentration of this capping agent was reduced to 9 mg mL^{-1}, the multiply twinned seeds could not survive the oxidative etching, leaving behind the single-crystal seeds in the system to grow into nanocubes. Besides the concentration of the capping agent, the reduction kinetics is also important in this synthesis. As demonstrated in previous studies, highly anisotropic structures tended to become favorable in a slow reduction process.[24] The concentration of glucose was thus found to have an important impact on the morphology of the final product. With a relatively low concentration of glucose (5 mg mL^{-1}), the decahedral seeds tended to form penta-twinned nanowires with uniform diameter due to the anisotropic growth. When the concentration of glucose was increased from 5 to 10 mg mL^{-1}, the reaction rate increased remarkably. The decahedral seeds still favored isotropic growth in the early stage, and formed the decahedra with larger sizes (typically around 200 nm). As the reaction proceeded, glucose would be consumed, resulting in lower reduction rates. Meanwhile, the isotropic growth was switched to an anisotropic mode, leading to the formation of the pentagonal bipyramids. Finally, these pentagonal bipyramids could further grow into tadpole-like nanowires.

In summary, Cu nanocrystals with controllable shapes have been synthesized by reducing a Cu^{II} salt with glucose in water with HDA serving as a capping agent. The distribution of single-crystal versus multiply twinned seeds could be manipulated at the nucleation stage by adjusting the concentration of HDA. Four different types of Cu nanocrystals bound mainly by {100} facets, including pentagonal nanowires, tadpole-like nanowires, pentagonal bipyramids, and nanocubes, have been successfully produced with purity approaching 100% thanks to the selective adsorption of HDA on the {100} facets. We believe that these Cu nanocrystals will find widespread use in applications related to plasmonics, SERS detection, microelectronics, and catalysis.

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[1] M. Rycenga, C. Cobley, J. Zeng, W. Li, C. Moran, Q. Zhang, D. Qin, Y. Xia, *Chem. Rev.* **2011**, *111*, 3669.

[2] J. Perelaer, P. Smith, D. Mager, D. Soltman, S. Volkman, V. Subramanian, J. Korvink, U. Schubert, *J. Mater. Chem.* **2010**, *20*, 8446.

[3] a) R. Keiski, O. Desponds, Y. Chang, G. Somorjai, *Appl. Catal. A* **1993**, *101*, 317; b) T. Ressler, B. Kniep, I. Kasatkin, R. Schlögl, *Angew. Chem.* **2005**, *117*, 4782; *Angew. Chem. Int. Ed.* **2005**, *44*, 4704; c) A. Gokhale, J. Dumesic, M. Mavrikakis, *J. Am. Chem. Soc.* **2008**, *130*, 1402.

[4] S. Vukojević, O. Trapp, J. Grunwaldt, C. Kiener, F. Schüth, *Angew. Chem.* **2005**, *117*, 8192; *Angew. Chem. Int. Ed.* **2005**, *44*, 7978.

[5] a) C. Murphy, T. Sau, A. Gole, C. Orendorff, *MRS Bull.* **2005**, *30*, 349; b) B. Wiley, Y. Sun, Y. Xia, *Acc. Chem. Res.* **2007**, *40*, 1067; c) Y. Xia, Y. Xiong, B. Lim, S. Skrabalak, *Angew. Chem.* **2009**, *121*, 62; *Angew. Chem. Int. Ed.* **2009**, *48*, 60.

[6] a) T. Pal, N. Jana, Z. Wang, T. Sau, *Curr. Sci.* **2000**, *79*, 1367; b) K. Ziegler, R. Doty, K. Johnston, B. Korgel, *J. Am. Chem. Soc.* **2001**, *123*, 7797; c) Y. Wang, P. Chen, M. Liu, *Nanotechnology* **2006**, *17*, 6000; d) M. Lu, G. Zhou, Z. Yang, *Langmuir* **2006**, *22*, 5900.

[7] J. Tanori, M. Pileni, *Langmuir* **1997**, *13*, 639.

[8] D. Mott, J. Galkowski, L. Wang, J. Luo, C. Zhong, *Langmuir* **2007**, *23*, 5740.

[9] E. Ye, S. Zhang, S. Liu, M. Han, *Chem. Eur. J.* **2011**, *17*, 3074.

[10] M. Mohl, P. Pusztai, A. Kukovecz, Z. Konya, *Langmuir* **2010**, *26*, 16496.

[11] A. Curtis, D. Duff, P. Edwards, D. Jefferson, B. G. Johnson, A. Kirkland, A. Wallace, *Angew. Chem.* **1988**, *100*, 1588; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1530.

[12] Y. Chang, M. Lye, H. Zeng, *Langmuir* **2005**, *21*, 3746.

[13] A. Rathmell, S. Bergin, Y. Hua, Z. Li, B. Wiley, *Adv. Mater.* **2010**, *22*, 3558.

[14] Z. Wang, *J. Phys. Chem. B* **2000**, *104*, 1153.

[15] a) Y. Xiong, J. Chen, B. Wiley, Y. Xia, Y. Yin, Z. Li, *Nano Lett.* **2005**, *5*, 1237; b) B. Wiley, Y. Xiong, Z. Li, Y. Yin, Y. Xia, *Nano Lett.* **2006**, *6*, 765.

[16] a) D. Yu, V. Yam, *J. Am. Chem. Soc.* **2004**, *126*, 13200; b) Y. Xiong, H. Cai, B. Wiley, J. Wang, M. Kim, Y. Xia, *J. Am. Chem. Soc.* **2007**, *129*, 3665; c) Y. Xiong, Y. Xia, *Adv. Mater.* **2007**, *19*, 3385; d) M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu, Y. Xia, *Nano Res.* **2011**, *4*, 83.

[17] K. Pradel, K. Sohn, J. Huang, *Angew. Chem.* **2011**, *123*, 3474; *Angew. Chem. Int. Ed.* **2011**, *50*, 3412.

[18] "Cambrios ClearOhm Film Used in Smart Phone", can be found under http://www.cambrios.com/207/Smart_Phone_Release.htm, **2011**.

[19] a) S. De, T. Higgins, P. Lyons, E. Doherty, P. Nirmalraj, W. Blau, J. Boland, J. Coleman, *ACS Nano* **2009**, *3*, 1767; b) Y. Cui, L. Hu, H. Kim, J. Lee, P. Peumans, *ACS Nano* **2010**, *4*, 2955.

[20] K. Korte, S. Skrabalak, Y. Xia, *J. Mater. Chem.* **2008**, *18*, 437.

[21] a) C. Johnson, E. Dujardin, S. Davis, C. Murphy, S. Mann, *J. Mater. Chem.* **2002**, *12*, 1765; b) Y. Sun, B. Mayers, T. Herricks, Y. Xia, *Nano Lett.* **2003**, *3*, 955; c) S. Zhang, Z. Jiang, Z. Xie, X. Xu, R. Huang, L. Zheng, *J. Phys. Chem. B* **2005**, *109*, 9416; d) X. Huang, N. Zheng, *J. Am. Chem. Soc.* **2009**, *131*, 4602.

[22] *Topics in Applied Physics, Vol. 103* (Eds.: K. Kneipp, M. Moskovits, H. Kneipp), Springer, Berlin, **2006**.

[23] a) B. Wiley, T. Herricks, Y. Sun, Y. Xia, *Nano Lett.* **2004**, *4*, 2057; b) Y. Xiong, J. Chen, B. Wiley, Y. Xia, *J. Am. Chem. Soc.* **2005**, *127*, 7332.

[24] J. Chen, T. Herricks, M. Geissler, Y. Xia, *J. Am. Chem. Soc.* **2004**, *126*, 10854.