5886 *Chem. Mater.* **2009,** *21,* 5886–5891
DOI:10.1021/cm902728p

CHEMISTRY OF
MATERIALS
Article

Crystallite Size Controls the Crystal Structure of $Cu_{60}Pd_{40}$ Nanoparticles

Matthias Friedrich and Marc Armbrüster*

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Strasse 40, 01187 Dresden, Germany

Received September 2, 2009. Revised Manuscript Received November 5, 2009

Structurally disordered (Cu type of structure) or ordered (CsCl type of structure) modifications of intermetallic $Cu_{60}Pd_{40}$ nanoparticles can be synthesized by co-reduction of Cu- and Pd-acetylacetonate using $LiBEt_3H$ in THF or annealing in tetradecane, respectively. It is shown by X-ray diffraction, transmission electron microscopy, selected area electron diffraction, differential centrifugal sedimentation, and thermal analysis that the formation of the ordered or the disordered modification depends on the crystallite size of the nanoparticles rather than on temperature. Crystallites smaller than ~20 nm form the disordered modification of $Cu_{60}Pd_{40}$, whereas crystallites larger than 20 nm prefer the ordered modification.

Introduction

Metallic nanoparticles are of great interest because of their special properties, e.g., as catalysts in industrial reactions, where they provide high activity because of their large specific surface,[1] or as material in data storage applications, wherein the nanoparticles reveal high data storage density.[2] The controlled synthesis of nanoparticles has been a challenge for many years. Common problems are the stability and monodispersity of the formed particles as well as the control of composition and morphology.[3]

Ordered intermetallic compounds have been shown to be excellent catalysts in the semi-hydrogenation of acetylene.[4] Thus, synthesizing nanoparticles of intermetallic compounds seems to be very promising but includes further challenges compared to elemental metal particles like complete reduction of the involved metal ions and the formation of the intermetallic compound instead of a mixture of the corresponding metals. Reduction of metal ions of groups 6−12 and 14 in solution using $LiBEt_3H$ to obtain finely dispersed elemental metal particles was first reported by Bönnemann et al.[5] Up to now, bimetallic Cu−Pd nanoparticles have been synthesized by thermal decomposition[6] or reduction by 2-ethoxyethanol,[7] NaH/t-BuOH,[8] or glycol[9] of the corresponding acetates or acetylacetonates. Despite preparations over the whole compositional range in the Cu−Pd system and synthesis temperatures between 63 and 198 °C, only the disordered face centered cubic structure has been reported.[8,9]

Looking at the thermodynamic properties of nanosized materials, it is widely known that they often differ from the corresponding bulk compounds.[10] Although the crystal structure may vary with the crystallite size, which has been demonstrated in the case of elemental Co,[11,12] reports on size-dependent crystal structures of intermetallic nanoparticles are rare. In 2005, Sra et al. synthesized nanoparticles of CuAu and Cu_3Au.[13] The authors suggested crystallite size dependent formation of Cu−Au modifications by referring to experimental and theoretical studies[14−16] but could not prove it experimentally because they observed a change of both the crystallite size and the structure with temperature.

Corresponding to the bulk phase diagram of copper−palladium, $Cu_{60}Pd_{40}$ occurs in two different modifications.[17] The partially ordered low-temperature modification ($Pm\bar{3}m$, CsCl-type, $a = 2.965$ Å) of $Cu_{60}Pd_{40}$ forms below 598 °C,[18] whereas above, the completely disordered high-temperature modification ($Fm\bar{3}m$, Cu-type,

---

*Corresponding author. E-mail:research@armbruester.net.

(1) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025–1102.
(2) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989–1992.
(3) Bönnemann, H.; Richards, R. M. *Eur. J. Inorg. Chem.* **2001**, *10*, 2455–2480.
(4) (a) Osswald, J.; Giedigkeit, R.; Jentoft, R. E.; Armbrüster, M.; Girgsdies, F.; Kovnir, K.; Ressler, T.; Grin, Y.; Schlögl, R. *J. Catal.* **2008**, *258*, 210–218. (b) Osswald, J.; Kovnir, K.; Armbrüster, M.; Giedigkeit, R.; Jentoft, R. E.; Wild, U.; Grin, Y.; Schlögl, R. *J. Catal.* **2008**, *258*, 219–227.
(5) Bönnemann, H.; Brijoux, W.; Joussen, T. *Angew. Chem., Int. Ed.* **1990**, *29*, 273–275.
(6) Esumi, K.; Tano, T.; Torigoe, K.; Meguro, K. *Chem. Mater.* **1990**, *2*, 564–567.
(7) Bradley, J. S.; Hill, E. W.; Klein, C.; Chaudret, B.; Duteil, A. *Chem. Mater.* **1993**, *5*, 254–256.
(8) Illy-cherrey, S.; Tillement, O.; Massicot, F.; Fort, Y.; Ghanbaja, J.; Dubois, J. M. *Mater. Sci. Eng., A* **2000**, *283*, 11–16.
(9) Toshima, N.; Wang, Y. *Chem. Lett.* **1993**, *22*, 1611–1614.
(10) Roduner, E. *Chem. Soc. Rev.* **2006**, *35*, 583–592.
(11) Owen, E. A.; Jones, D. M. *Proc. Phys. Soc. B* **1954**, *67*, 456–466.
(12) Kitakami, O.; Sato, H.; Shimada, Y.; Sato, F.; Tanaka, M. *Phys. Rev. B* **1997**, *56*, 13849–13854.
(13) Sra, A. K.; Ewers, T. D.; Schaak, R. E. *Chem. Mater.* **2005**, *17*, 758–766.
(14) Schülli, T.; Trenkler, J.; Mönch, I.; Le Bolloc'h, D.; Dosch, H. *Europhys. Lett.* **2002**, *58*, 737–743.
(15) Tadaki, T.; Koreeda, A.; Nakata, Y.; Kinoshita, T. *Surf. Rev. Lett.* **1996**, *3*, 65–69.
(16) Tadaki, T.; Kinoshita, T.; Nakata, Y.; Ohkubo, T.; Hirotsu, Y. *Z. Phys. D* **1997**, *40*, 493–495.
(17) Subramanian, P. R.; Laughlin, D. E. *J. Phase Equilib.* **1991**, *12*, 231–243.
(18) Jones, F. W.; Sykes, C. *J. Inst. Met.* **1939**, *65*, 419–433.

a = 3.731 Å) is stable.[19] Here we report on the controlled synthesis of each of the respective structural modifications of $Cu_{60}Pd_{40}$ in nanoparticulate form. To the best of our knowledge, this is the first time that a structural dependence on crystallite diameter has been shown for intermetallic compounds.

Experimental Section

The following reagents were used: $Cu(acac)_2$ (acac = acetylacetonate, 99%, Acros), $Pd(acac)_2$ (purum, Fluka), $LiBEt_3H$ (Superhydride, 1 M in tetrahydrofurane (THF), Aldrich), THF (99.9%, Roth, distilled over CaH_2 under a protective argon atmosphere before use), and tetradecane (99%, Acros). All procedures were carried out under a protective argon atmosphere in a glove box with oxygen and water concentrations below 0.1 ppm.

For a typical synthesis of the disordered modification of $Cu_{60}Pd_{40}$, 0.2930 g (1.119 mmol) of $Cu(acac)_2$ (99%, Acros) and 0.2265 g (0.744 mmol) of $Pd(acac)_2$ are added to 15 mL of THF in a reflux apparatus and stirred until a grey-bluish suspension is obtained. The suspension is heated to 50 °C in 5 min, and then 3.72 mL (3.72 mmol) $LiBEt_3H$ are added via a syringe pump with a speed of 149.1 mL/h, leading to a black precipitate. Heating and stirring are switched off at once to prevent formation of solid by-products like Li(acac). The suspension is centrifuged (EBA 20, Hettich) at 6000 rpm to separate the solid products from the solution. The black precipitate is washed three times with 2 mL of THF and centrifuged each time before being dried in a vacuum (10 mbar).

To synthesize the ordered modification, we suspended dry powder of previously obtained disordered $Cu_{60}Pd_{40}$ in 15 mL of tetradecane and treated it at 230 °C for 85 h. Subsequently, the product was isolated and cleaned as described above.

The products were analyzed by transmission X-ray powder diffraction (XRD) performed on an image plate Guinier camera (G670, Huber, Cu $K_{\alpha 1}$ radiation, λ = 1.54056 Å, quartz monochromator, $3° \leq 2\theta \leq 100°$, internal standard LaB_6, a = 4.15692 Å). To prevent contact with air, we mounted the powders in a glove box between two Kapton foils for the measurements.

Transmission electron microscopy (TEM) in combination with selected area electron diffraction (SAED), both performed using a Tecnai 10 (100 kV, LaB_6 cathode), was also applied. High-resolution TEM was performed using a Tecnai F20 (200 kV, Schottky FEG, Cs-corrector). Samples were prepared from a methanol suspension on a carbon-coated copper grid (300 mesh, SPI Supplies).

Disc centrifuge (DC) measurements on a CPS DC24000 were used to determine the particle size distribution. The dried samples were suspended in cyclohexane and then injected into the rotating disc. The disc speed was set to 6000 rpm and the density gradient was built up from cyclohexane and halocarbon (density: 1.8 g/cm^3). A size range from 5 nm to 7 μm was analyzed.

Thermal analysis was carried out on a Netzsch STA 449 C Jupiter in argon atmosphere in Al_2O_3 crucibles with a heating rate of 10 K/min. Differential thermal analysis (DTA) and thermogravimetry (TG) signals were detected simultaneously.

Results and Discussion

Synthesis of Disordered (Cu Type of Structure) $Cu_{60}Pd_{40}$. According to the XRD analysis, the disordered modification of $Cu_{60}Pd_{40}$ was obtained in phase pure form after synthesis at 50 °C in THF (Fig. 1). The lattice parameter was determined as a = 3.75(1) Å. The broad reflections indicate a very small crystallite size, which was calculated as 2 nm by the Scherrer equation[20], using the (111) reflection (K = 0.93). Referring to the phase diagram of copper−palladium, the disordered Cu-type modification is thermodynamically stable only above 598 °C. Thus, the crystallographic structure of the nanosized crystallites does not correspond to the structure of low temperature bulk material.

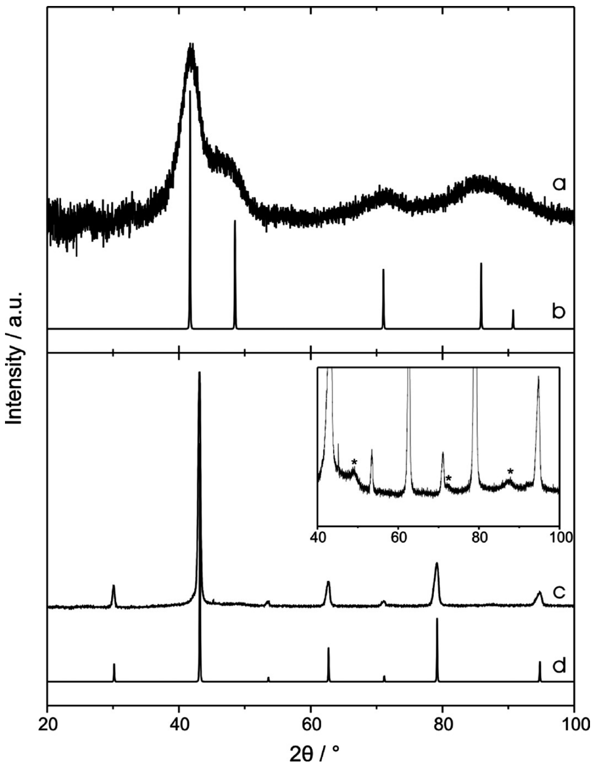

Figure 1. X-ray powder diffraction: (a) product after synthesis in THF at 50 °C (crystallite size = 2 nm), (b) disordered $Cu_{60}Pd_{40}$ (calculated with a = 3.75 Å), (c) product after annealing in tetradecane at 230 °C (crystallite size = 20 nm), (d) ordered $Cu_{60}Pd_{40}$ (calculated with a = 2.9601 Å). Inset, stars indicate reflections of disordered $Cu_{60}Pd_{40}$ (crystallite size = 5 nm).

Figure 2 shows TEM pictures of the particles after synthesis at 50 °C in THF. According to general agreement in the literature, agglomerates are formed by more than one particle. Particles themselves can consist of more than one crystallite. Agglomerates of some hundred nanometres were found. These agglomerates consist of small particles with diameters between 2 and 12 nm. The absence of sinter necks shows that the individual particles only stick together, but are not interconnected (Figure 2b). Selected area electron diffraction was applied on the agglomerate as shown in Figure 2a. The agreement with the calculated diffraction pattern of disordered $Cu_{60}Pd_{40}$ is good. The existence of closed Debye−Scherrer rings indicates a large number of very small crystallites, being in accordance with a crystallite size of 2 nm determined from XRD. Both XRD and SAED results show that the particles synthesized at 50 °C in THF

---

(19) Raub, E.; Loebich, O., Jr.; Plate, W.; Krill, H. *Z. Metallkd.* **1971**, *62*, 826–830.

(20) Patterson, A. L. *Phys. Rev.* **1939**, *56*, 978–982.

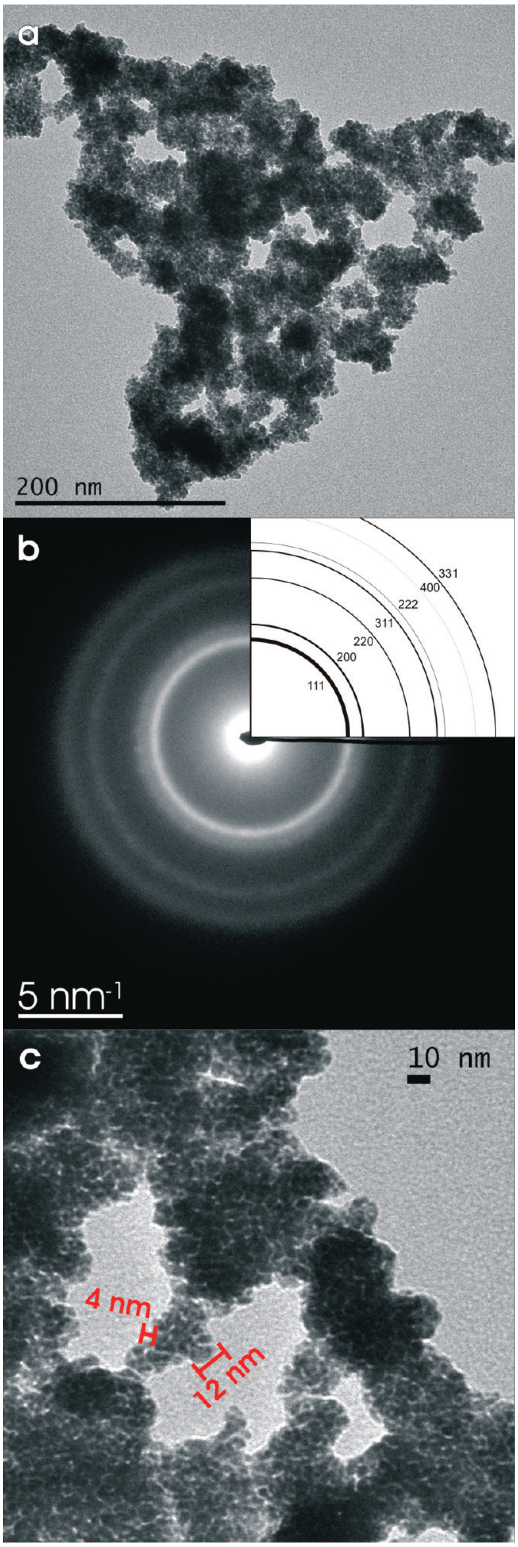

Figure 2. (a) Transmission electron micrograph of $Cu_{60}Pd_{40}$ particles obtained after synthesis at 50 °C in THF. (b) Selected area electron diffraction was applied to the whole area of the image 2a. The calculated diffraction pattern of disordered $Cu_{60}Pd_{40}$ (a = 3.731 Å) is shown in the upper right part and the thickness of the lines corresponds to the calculated intensity. (c) Transmission electron micrograph of $Cu_{60}Pd_{40}$ particles obtained after synthesis at 50 °C in THF. No sinter necks could be observed within the agglomerate.

exclusively form the disordered modification of $Cu_{60}Pd_{40}$. Disc centrifuge measurements of the particle size distribution of large amounts of the sample confirm the results obtained with TEM, as can be seen in Figure 3. The particles synthesized at 50 °C in THF have a weight maximum at about 280 nm, which indicates agglomerate formation in very good agreement with the TEM data. The particles are smaller than 10 nm, but stick together to form agglomerates of some hundred nanometres. Because differential centrifugal sedimentation detects the particles according to their mass, the method can not distinguish between agglomerates and primary particles of the same mass. Because of agglomeration, the primary particles (diameter 2–12 nm) in this sample were not detected.

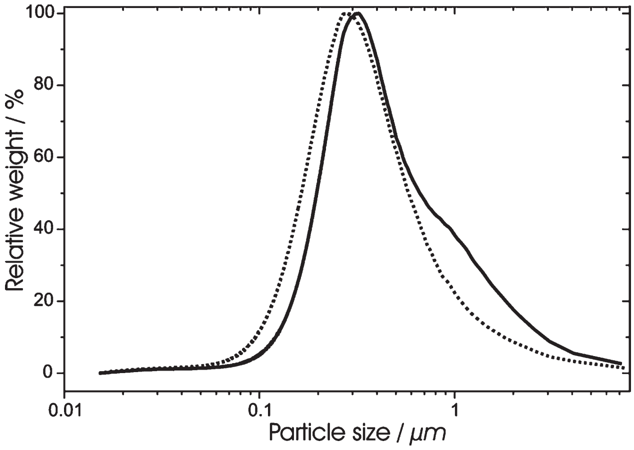

Figure 3. Differential centrifugal sedimentation: Disc centrifuge measurements of particle suspensions in cyclohexane at 6000 rpm. Dashed line, synthesis at 50 °C in THF; solid line, annealing at 230 °C in tetradecane.

Crystallite Growth and Transformation to Ordered (CsCl Type of Structure) $Cu_{60}Pd_{40}$. X-ray diffraction (Figure 1) proves the formation of the ordered modification of $Cu_{60}Pd_{40}$ from a disordered sample when the product obtained at 50 °C in THF is annealed at 230 °C in tetradecane. The lattice parameter of the product is a = 2.9601(5) Å. The reflections possess a much smaller full width at half maximum (FWHM) than the sample synthesized at 50 °C, indicating larger crystallites. Calculation of the crystallite diameter by the Scherrer equation resulted in 20 nm, using the (100) reflection. TEM images and SAED patterns of particles synthesized at 230 °C (Figure 4) support the data obtained from XRD. The SAED pattern (Figure 4b) is in excellent agreement with the calculated diffraction pattern of ordered $Cu_{60}Pd_{40}$. Single reflections in the pattern indicate a small number of large crystallites. In addition, TEM reveals that the formerly small particles are grown together during the temperature treatment and form irregular netlike agglomerates on the scale of some hundred nanometers. In contrast to the product obtained at 50 °C, sinter necks and smoothing of the particle shape is frequently observed between the formerly significantly smaller primary particles (Figure 4b). The results of differential sedimentation (Figure 3) fit well to the information obtained by the TEM studies. The weight maximum is at 320 nm which is close to the agglomerate size of the particles synthesized at 50 °C. A shoulder in this peak at about 1 μm indicates the formation of even larger agglomerates due to sintering.

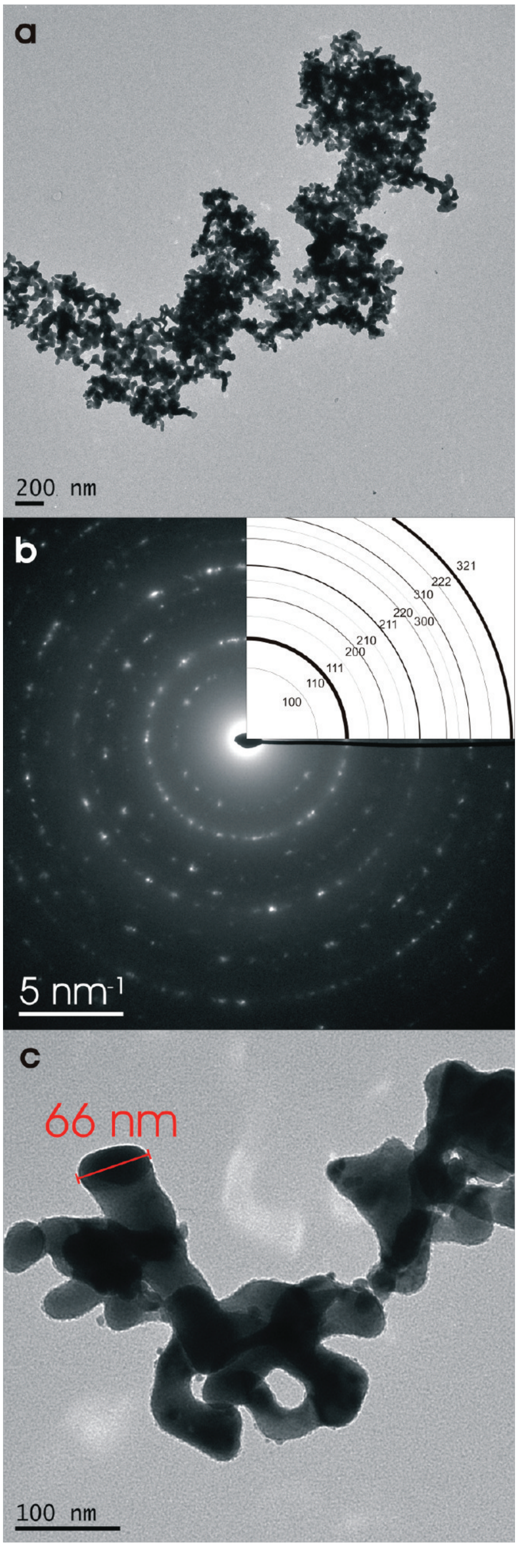

Figure 4. (a) Transmission electron micrograph of $Cu_{60}Pd_{40}$ particles obtained after annealing at 230 °C in tetradecane. (b) Selected area electron diffraction was applied to the whole area of image a. The calculated diffraction pattern of ordered $Cu_{60}Pd_{40}$ is shown in the upper right part (a = 2.965 Å). (c) Transmission electron micrograph of $Cu_{60}Pd_{40}$ particles obtained after annealing at 230 °C in tetradecane. The sinter necks formed during the temperature treatment are clearly visible.

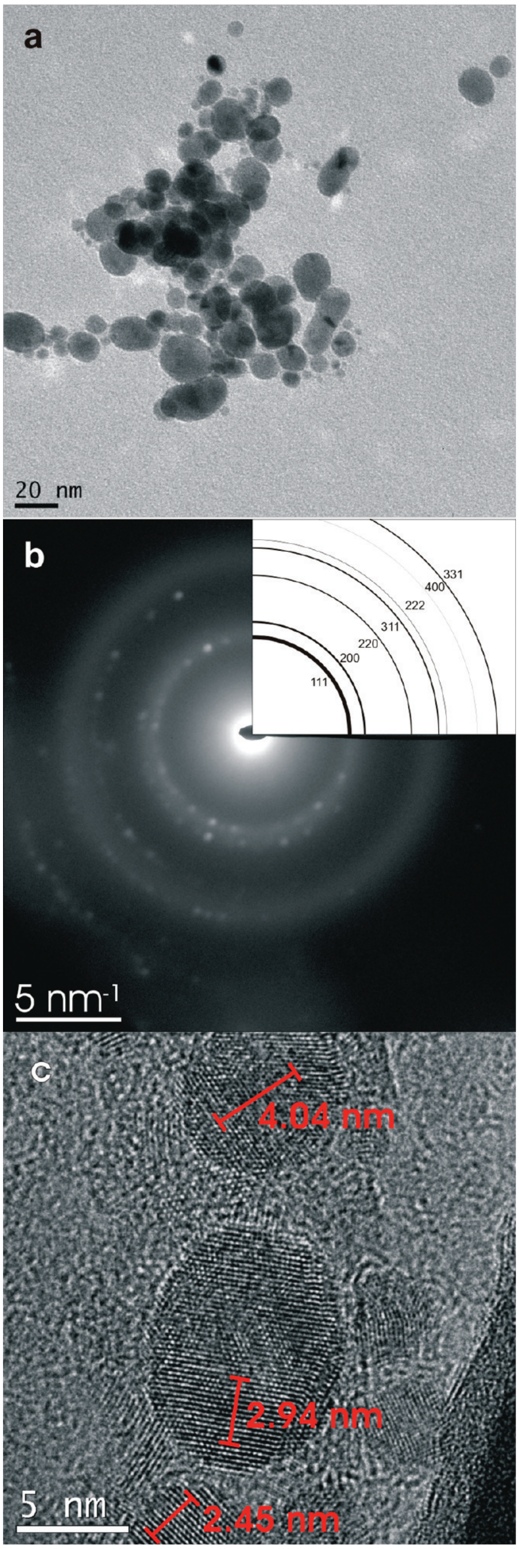

Figure 5. (a) Transmission electron micrograph of small $Cu_{60}Pd_{40}$ particles remaining after annealing at 230 °C in tetradecane. (b) Selected area electron diffraction was applied to the whole area of image a. The calculated diffraction pattern of disordered $Cu_{60}Pd_{40}$ is shown in the upper right part (a = 3.731 Å). (c) High-resolution transmission electron micrograph of single $Cu_{60}Pd_{40}$ particles after annealing at 230 °C in tetradecane. Upper particle: 4.04 nm represent the size of 21 lattice planes. The resulting lattice vector of 1.93 Å fits well to the (200) plane of disordered $Cu_{60}Pd_{40}$. Central particle: 2.94 nm represent the size of 13 lattice planes. The resulting lattice vector of 2.26 Å fits well to the (111) plane of disordered $Cu_{60}Pd_{40}$. Lower particle: 2.45 nm represent the size of 11 lattice planes. The resulting lattice vector of 2.23 Å fits well to the (111) plane of disordered $Cu_{60}Pd_{40}$.

Surprisingly, a careful examination of the XRD pattern after annealing at 230 °C also revealed some broad reflections (see embedded pattern in Figure 1) of the

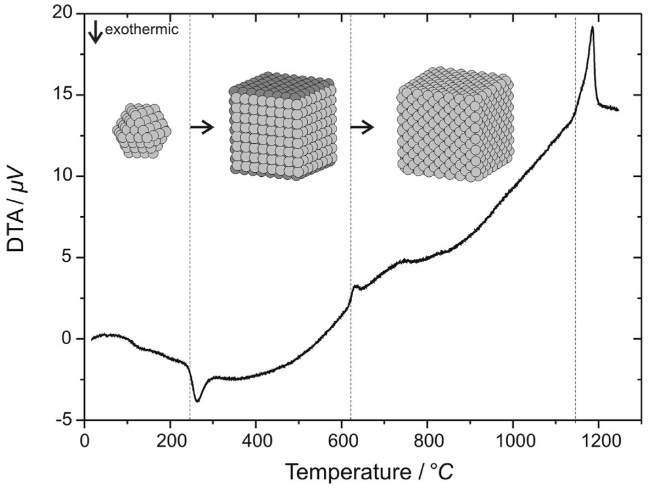

Figure 6. Differential thermal analysis: Transformation of nano-$Cu_{60}Pd_{40}$ (disordered) into bulk-$Cu_{60}Pd_{40}$ (ordered) at 243 °C, following the transition into bulk-$Cu_{60}Pd_{40}$ (disordered) at 621 °C and melting at 1140 °C. Grey balls represent mixed positions, either occupied by Cu or Pd, whereas black balls display atom sites occupied only by Cu. Dashed lines indicate onset temperatures.

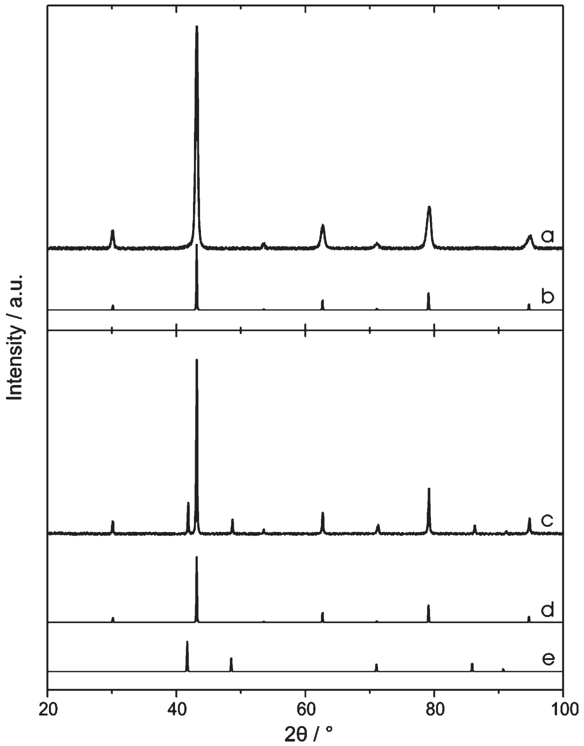

Figure 7. X-ray powder diffraction: (a) Product after DTA aborted at 300 °C, (b) ordered $Cu_{60}Pd_{40}$ (calculated with a = 2.9601 Å), (c) product after DTA aborted at 700 °C, (d) ordered $Cu_{60}Pd_{40}$ (calculated with a = 2.9601 Å), (e) disordered $Cu_{60}Pd_{40}$ (calculated with a = 3.75 Å).

disordered modification of $Cu_{60}Pd_{40}$. The crystallite size was 5 nm as determined by the Scherrer equation using the (111) reflection. Subsequent TEM and SAED confirmed the existence of small disordered $Cu_{60}Pd_{40}$ particles among the majority of large $Cu_{60}Pd_{40}$ agglomerates with the ordered structure. Figure 5 shows particles within the sample annealed at 230 °C that are between 4 and 25 nm in diameter. According to the SAED pattern these small particles only realize the disordered modification (Figure 5a). High-resolution images of single particles reveal the disordered structure, proving that no transformation into the ordered modification has occurred during the annealing (Figure 5b).

At this point, the question arises why after synthesis at 230 °C there are particles left that did not transform into the ordered modification of $Cu_{60}Pd_{40}$. The results show, that the transition temperatures as well as the enthalpy of formation of the synthesized nanoparticles differ significantly from the bulk Cu−Pd compounds. Furthermore, the obtained data suggest that the structural transformation can occur only after particle growth. Because only small crystallites with the disordered modification and exclusively large crystallites with the ordered modification are observed, the thermodynamically stable structure for crystallites smaller than ~20 nm is the higher symmetric structurally disordered modification, whereas crystallites larger than 20 nm favor the lower symmetric structurally ordered modification. The existence of small disordered particles in the annealed sample is due to local isolation from other particles which made sintering impossible. Thus, the formation of ordered and disordered modifications of $Cu_{60}Pd_{40}$ seems to depend on the crystallite size rather than on temperature.

This conclusion is further supported by differential thermal analysis (Fig. 6) in combination with XRD. For this purpose, disordered samples were measured by DTA (10 K/min), aborted at 300, 700, or 1250 °C and subsequently analyzed by powder X-ray diffraction (Figure 7). Particles of disordered $Cu_{60}Pd_{40}$ synthesized at 50 °C underwent three significant changes during heating up to 1250 °C. A first exothermic transition occurred at 243 °C and corresponds well to sintering and subsequent transformation to the ordered modification, which was also observed in XRD after annealing of the disordered sample at 230 °C in tetradecane. Applying the Scherrer equation to the (100) reflection results in a crystallite size of 20 nm, which is significantly larger than at the beginning (Figure 1). The second signal is endothermic and results from the transformation of ordered $Cu_{60}Pd_{40}$ to disordered bulk $Cu_{60}Pd_{40}$. The transition temperature of 621 °C is in good agreement with the literature value of 598 °C for the bulk compound.[15] Figure 7c shows a two-phase sample after aborting the DTA measurement at 700 °C because the cooling rate was too slow, resulting in partially back transformation to the ordered modification. With a crystallite size of 56 nm by using the (111) reflection of the disordered phase, the sample thus clearly shows bulk behavior. The area of the DTA signal of the exothermic peak at 243 °C is three times larger than the area of the endothermic peak at 621 °C. This is an indication for the presence of additional exothermic processes at 243 °C like sintering resulting in the release of surface energy. Finally, the compound melts at 1140 °C. Simultaneous thermogravimetry showed a continuous mass loss of 3 wt %, which can be assigned to desorption of solvent molecules from the particle surface.

Conclusions

Synthesis of disordered (Cu type of structure) and ordered (CsCl type of structure) modifications of

$Cu_{60}Pd_{40}$ nanoparticles from solution in a one-pot reaction by first reduction using $LiBEt_3H$ in THF and subsequent annealing in tetradecane is described. The resulting particles behave differently to the bulk regarding the structural stability of the ordered and disordered modification. In difference to the bulk, the crystal structure seems to be driven by crystallite size rather than by temperature. Synthesis at 50 °C in THF yielded particles consisting of 2 nm crystallites, which exclusively formed the disordered modification. Annealing this sample in tetradecane at higher temperature (230 °C) led to an increase in crystallite size accompanied by a structural transition into the partially ordered modification. A small number of particles consisting of crystallites 5−20 nm in size with the disordered structure are still present after annealing at 230 °C in tetradecane. The results indicate a critical crystallite size for the transformation into the ordered structure of ~20 nm. DTA measurements support the phase transformation and sintering processes, respectively. Theoretical calculations on this phenomenon are in progress.

Acknowledgment. We thank F. Röder and H. Lichte from the Triebenberg Laboratory for High-Resolution Electron Microscopy and Holography for the possibility to record high-resolution TEM images and W. Carrillo-Cabrera for helpful discussions.